

PERGAMON INTERNATIONAL LIBRARY
of Science, Technology, Engineering and Social Studies

*The 1000-volume original paperback library in aid of education,
industrial training and the enjoyment of leisure*

Publisher: Robert Maxwell, M.C.



The Chemistry of
**CHROMIUM, MOLYBDENUM AND
TUNGSTEN**

Publisher's Notice to Educators

**THE PERGAMON TEXTBOOK
INSPECTION COPY SERVICE**

An inspection copy of any book suitable for use as a course text for undergraduate or graduate students will gladly be sent for consideration for adoption without obligation. Copies may be retained for a period of 30 days from receipt and returned if not suitable. When a particular title is adopted or recommended for adoption for class use and the recommendation results in a sale of 12 or more copies, the inspection copy may be retained with our compliments. If after examination the lecturer decides that the book is not suitable for adoption but would like to retain it for his personal library, then our Educators' Discount of 10% is allowed on the invoiced price.

Comprehensive Inorganic Chemistry

EDITORIAL BOARD

J. C. BAILAR JR., *Urbana*

H. J. EMELÉUS, F.R.S., *Cambridge*

† SIR RONALD NYHOLM, F.R.S., *London*

A. F. TROTMAN-DICKENSON, *Cardiff*
(*Executive Editor*)

The Chemistry of

CHROMIUM, MOLYBDENUM AND TUNGSTEN

Carl L. Rollinson

Chapter 36 of
Comprehensive Inorganic Chemistry



PERGAMON PRESS

OXFORD . NEW YORK . TORONTO
SYDNEY . PARIS . BRAUNSCHWEIG

Pergamon Press Offices:

U.K.	Pergamon Press Ltd., Headington Hill Hall, Oxford, OX3 0BW, England
U.S.A.	Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.
CANADA	Pergamon of Canada Ltd., 207 Queen's Quay West, Toronto 1, Canada
AUSTRALIA	Pergamon Press (Aust.) Pty. Ltd., 19a Boundary Street, Rushcutters Bay, N.S.W. 2011, Australia
FRANCE	Pergamon Press SARL, 24 rue des Ecoles, 75240 Paris, Cedex 05, France
WEST GERMANY	Pergamon Press GmbH, D-3300 Braunschweig, Postfach 2923, Burgplatz 1, West Germany

Copyright © Pergamon Press 1973

All Rights Reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means: electronic, electrostatic, magnetic tape, mechanical, photocopying, recording or otherwise, without permission in writing from the publishers

First edition 1973

Reprinted, with corrections, from Comprehensive Inorganic Chemistry. 1975

Library of Congress Catalog Card No. 77-189736

Printed in Great Britain by A. Wheaton & Co, Exeter

ISBN 0 08 018868 0 (Hard cover)

ISBN 0 08 018867 2 (Flexicover)

PREFACE

The excellent reception that has been accorded to *Comprehensive Inorganic Chemistry* since the simultaneous publication of the five volumes of the complete work has been accompanied by the plea that sections should be made available in a form that would enable specialists to purchase copies for their own use. To meet this demand the publishers have decided to issue selected chapters and groups of chapters as separate editions. These chapters will, apart from the corrections of misprints and the addition of prefatory material and individual indices, appear just as they did in the main work. Extensive revision would delay publication and greatly raise the cost, so limiting the circulation of these definitive reviews.

A. F. TROTMAN-DICKENSON
Executive Editor

36. CHROMIUM, MOLYBDENUM AND TUNGSTEN

CARL L. ROLLINSON

University of Maryland

INTRODUCTION

Chromium, molybdenum and tungsten, *d*-block transition metals of periodic group VIB, have the following configurations of their outermost electron shells: Cr, $3d^5 4s^1$; Mo, $4d^5 5s^1$; W, $5d^4 6s^2$. They have oxidation states ranging from 2- to 6+. With many characteristics in common as members of the same periodic group, they differ markedly in certain properties dependent on their atomic and ionic radii. With increasing number of electron shells, the trend in properties is such that the chemistry of molybdenum and tungsten (which are quite similar chemically) differs in many respects from that of chromium. Thus chromium forms many compounds of types unknown or rare in molybdenum and tungsten chemistry (and conversely).

The three elements are refractory metals of high melting points and boiling points. They are stable against attack by numerous chemicals including oxidizing acids, particularly at low temperatures. On the other hand, at elevated temperatures, they react with many substances. With the nonmetallic elements they form numerous binary compounds and with the metals, intermediate phases of various types including intermetallic compounds.

In their lowest oxidation states, stabilized by π -bonding ligands, chromium, molybdenum and tungsten show their greatest chemical similarity. Each forms innumerable organometallic compounds, a stable hexacarbonyl, and many substituted carbonyls. In these categories, many analogous compounds of the three elements resemble each other closely.

To a smaller degree, the three metals in their highest oxidation state (6+) show similarities in chemical behavior. Each has an acidic oxide MO_3 from which salts of the ion MO_4^{2-} are derived; in these respects Cr^{6+} , Mo^{6+} , and W^{6+} resemble S^{6+} . On the other hand, although the chromate-dichromate equilibrium is well known, and trichromates and tetrachromates can be prepared, apparently Cr^{6+} does not undergo extensive polymerization in acidic aqueous solution, a reaction characteristic of Mo^{6+} and W^{6+} leading to formation of the iso- and heteropoly molybdates and tungstates; nor does chromium form compounds analogous to the molybdenum and tungsten bronzes. Even greater differences exist between the chemistry of chromium and that of molybdenum and tungsten in oxidation states 2+, 3+, 4+ and 5+.

Chromium has a well-defined 2+ state and many chromium(II) salts and complexes are readily prepared. Exclusive of compounds in which low oxidation states are stabilized by π -bonding ligands, Mo^{2+} and W^{2+} compounds are generally not at all analogous to those of Cr^{2+} although corresponding molybdenum and tungsten compounds are quite similar. What is characteristic of Mo^{2+} and W^{2+} compounds is the metal-atom cluster,

an octahedral array of six metal atoms exhibiting metal-metal bonding, a type of structure apparently unknown for chromium.

The most stable oxidation state of chromium is $3+$, and a major area of chromium chemistry is the chemistry of chromium(III) coordination compounds of which thousands are known. In contrast, little coordination chemistry of Mo^{3+} and W^{3+} has been reported to the present and relatively few Mo^{3+} and W^{3+} compounds have been described.

Finally, while there is very little chromium(IV) and chromium(V) aqueous solution chemistry and only a few compounds of chromium in these oxidation states exist, numerous compounds of molybdenum and tungsten of oxidation states $4+$ and $5+$ have been described and a quite extensive solution chemistry has been developed for the two metals in these oxidation states. It is in these oxidation states that molybdenum and tungsten form Werner-type complexes, mainly complex anions quite analogous to those of chromium(III), but nowhere near as many. In some of these complexes, the metal has coordination number 8, which is unknown with chromium.

I. Chromium

1. THE ELEMENT

1.1. DISCOVERY AND HISTORY¹⁻³

Chromium was discovered by Nicolas-Louis Vauquelin in 1797 in Siberian red lead, the mineral *crocoite*, PbCrO_4 . In 1798, he isolated the new metal by reduction of CrO_3 with charcoal at high temperature. In the same year he analyzed a Peruvian emerald and found that its green color is due to the new element. Fourcroy and Haüy suggested the name chromium (from the Greek *chroma*, color) for the new element because of its many colored compounds.

In 1798, Tobias Lowitz and Martin Heinrich Klaproth independently found chromium in chromite samples from Russia, and in the following year Tassaert, a German chemist at the Paris School of Mines, found it in French chromite. This ore, a spinel, $\text{Fe}(\text{CrO}_2)_2$, is the only commercial source of chromium.

Chromite was discovered near Baltimore, Maryland (USA), by Isaac Tyson about 1810⁴. His observations led him to the recognition of the association of chromite with serpentines. He located the serpentine terrain by its comparative barrenness of vegetation; this is an early example of "biogeochemical prospecting"⁵. Tyson discovered additional chromite deposits in Maryland and others in Virginia and Pennsylvania. He established a chromium chemical plant in Baltimore in 1845 which was sold to the Mutual Chemical Company in 1908. From about 1828 to 1850, most of the world's supply of chromite came from the mines near Baltimore, but these deposits rapidly lost their importance

¹ M. E. Weeks and H. M. Leicester, *Discovery of the Elements*, Journal of Chemical Education, Easton, Penna., 7th edn. (1968), p. 271.

² F. E. Bacon, "Chromium and Chromium Alloys", p. 451; W. H. Hartford and R. L. Copson, "Chromium Compounds", p. 473, in *Encyclopedia of Chemical Technology*, 5, Interscience, New York, 2nd edn. (1964).

³ M. J. Udy, "History of Chromium", in *Chromium*, 2, Reinhold, New York (1956).

⁴ J. T. Singewald, *The Chrome Industry in Maryland*, Maryland Geological Survey Reports, 12 (1928) 158.

⁵ D. P. Malyuga, *Biogeochemical Methods of Prospecting*, Consultants Bureau, New York (1964); H. L. Cannon, *Science*, 132 (1960) 591.

an octahedral array of six metal atoms exhibiting metal-metal bonding, a type of structure apparently unknown for chromium.

The most stable oxidation state of chromium is $3+$, and a major area of chromium chemistry is the chemistry of chromium(III) coordination compounds of which thousands are known. In contrast, little coordination chemistry of Mo^{3+} and W^{3+} has been reported to the present and relatively few Mo^{3+} and W^{3+} compounds have been described.

Finally, while there is very little chromium(IV) and chromium(V) aqueous solution chemistry and only a few compounds of chromium in these oxidation states exist, numerous compounds of molybdenum and tungsten of oxidation states $4+$ and $5+$ have been described and a quite extensive solution chemistry has been developed for the two metals in these oxidation states. It is in these oxidation states that molybdenum and tungsten form Werner-type complexes, mainly complex anions quite analogous to those of chromium(III), but nowhere near as many. In some of these complexes, the metal has coordination number 8, which is unknown with chromium.

I. Chromium

1. THE ELEMENT

1.1. DISCOVERY AND HISTORY¹⁻³

Chromium was discovered by Nicolas-Louis Vauquelin in 1797 in Siberian red lead, the mineral *crocoite*, PbCrO_4 . In 1798, he isolated the new metal by reduction of CrO_3 with charcoal at high temperature. In the same year he analyzed a Peruvian emerald and found that its green color is due to the new element. Fourcroy and Haüy suggested the name chromium (from the Greek *chroma*, color) for the new element because of its many colored compounds.

In 1798, Tobias Lowitz and Martin Heinrich Klaproth independently found chromium in chromite samples from Russia, and in the following year Tassaert, a German chemist at the Paris School of Mines, found it in French chromite. This ore, a spinel, $\text{Fe}(\text{CrO}_2)_2$, is the only commercial source of chromium.

Chromite was discovered near Baltimore, Maryland (USA), by Isaac Tyson about 1810⁴. His observations led him to the recognition of the association of chromite with serpentines. He located the serpentine terrain by its comparative barrenness of vegetation; this is an early example of "biogeochemical prospecting"⁵. Tyson discovered additional chromite deposits in Maryland and others in Virginia and Pennsylvania. He established a chromium chemical plant in Baltimore in 1845 which was sold to the Mutual Chemical Company in 1908. From about 1828 to 1850, most of the world's supply of chromite came from the mines near Baltimore, but these deposits rapidly lost their importance

¹ M. E. Weeks and H. M. Leicester, *Discovery of the Elements*, Journal of Chemical Education, Easton, Penna., 7th edn. (1968), p. 271.

² F. E. Bacon, "Chromium and Chromium Alloys", p. 451; W. H. Hartford and R. L. Copson, "Chromium Compounds", p. 473, in *Encyclopedia of Chemical Technology*, 5, Interscience, New York, 2nd edn. (1964).

³ M. J. Udy, "History of Chromium", in *Chromium*, 2, Reinhold, New York (1956).

⁴ J. T. Singewald, *The Chrome Industry in Maryland*, Maryland Geological Survey Reports, 12 (1928) 158.

⁵ D. P. Malyuga, *Biogeochemical Methods of Prospecting*, Consultants Bureau, New York (1964); H. L. Cannon, *Science*, 132 (1960) 591.

after the large and rich Turkish chromite deposits were discovered in 1848 by the American geologist, J. Lawrence Smith.

A few years after the discovery of chromium, the commercial process of manufacturing chromates was developed (roasting chromite with lime and soda ash). Andreas Kurtz, a pupil of Vauquelin, started manufacturing chromium chemicals in London in 1816. In 1822 he moved his operations to Manchester where he produced bichromates and chromium pigments such as lead chromate, which is still an important yellow pigment (in the United States, the color of school buses). Mordant dyeing with chromium compounds was started in 1820. Chrome tanning was invented by Friedrich Knapp in 1858; it was commercialized in 1884 after the patenting of the chrome-tanning process of Augustus Schultz. Utilization of chromite as a refractory started in 1879; its use in metallurgy started to become important about 1910. Chrome plating in its modern form dates from about 1926.

Chromium metal was obtained by Moissan in 1893 by reduction of chromic oxide with carbon in the electric furnace. In 1894 Goldschmidt developed the aluminothermic ("thermit") process for producing chromium by reduction of the oxide with aluminum powder and extended it to other metals^{6a}.

The first deliberate attempts to make chromium alloy steels were those of Michael Faraday who began experimenting in 1819 at the Royal Institution and also at a steel works^{6b}. Commercial interest in chrome steels began in 1865 when Julius Bauer in New York obtained a patent; such steel was first produced at Unieux (France) by Jacob Holtzer^{6b} in 1877.

Chromyl compounds were discovered in 1824 and chromous compounds in 1844. The first organochromium compound was isolated by Hein in 1919 and chromium carbonyl was synthesized for the first time in 1927 by Job and Cassal. Currently the carbonyls and organochromium compounds constitute one of the most active areas of research in chromium chemistry.

Chromium is the most recently recognized biologically essential trace metal. The first conclusive evidence demonstrating a metabolic role of chromium was obtained by Mertz and Schwarz in a series of investigations of which the first report appeared in 1955⁷.

1.2. OCCURRENCE AND DISTRIBUTION

The only important chromium ore is chromite, a spinel⁸. Chromite of ideal composition, $\text{Fe}(\text{CrO}_2)_2$, would contain 68% Cr_2O_3 and 32% FeO ; the higher grades of ore contain 42–56% Cr_2O_3 , 10–26% Fe , and varying amounts of other substances such as magnesia, alumina and silica.

The chief producers of chromite have been the USSR, Union of South Africa, the Philippines, Turkey and Rhodesia. Chromite deposits are also found in many other countries, including the United States, Albania, Cuba, Brazil, Japan, India, New Caledonia, Pakistan, Iran and the Malagasy Republic⁸.

Crocoite, PbCrO_4 , has been found in small quantities in, for example, Russia, Brazil,

⁶ (a) R. Chadwick, "New Extraction Processes for Metals", p. 97; (b) H. R. Schubert, "The Steel Industry", p. 64, in *A History of Technology*, 5, Oxford University Press, London (1958).

⁷ W. Mertz and K. Schwarz, *Arch. Biochem. Biophys.* **58** (1955) 504; W. Mertz, *Physiol. Reviews*, **49** (1969) 163.

⁸ F. E. Bacon, "Chromium and Chromium Alloys", in *Encyclopedia of Chemical Technology*, 5, Interscience, New York, 2nd edn. (1964), p. 452.

Hungary, the Philippine Islands, Arizona and Tasmania. Chromium occurs in minor amounts in many minerals, in which (as Cr^{3+}) it replaces Fe^{3+} or Al^{3+} , e.g. in the chromium tourmalines, chromium garnets, chromium micas and chromium chlorites⁹. The true emerald is a form of beryl (beryllium aluminum silicate) colored green by incorporation of a small amount of chromium in place of aluminum¹⁰. The color of the ruby is also due to a trace of chromic oxide which distinguishes the gem from the common crystalline corundum (alumina).

Chromium ranks twenty-first in order of abundance of the elements in the earth's crust (100 ppm)¹¹. Chondrites, the commonest meteorites, contain 3000 ppm Cr¹².

TABLE 1. DISTRIBUTION OF CHROMIUM

Material	Cr (ppm) ^a	Ref. 13
Soils	5-3000 ^b (median, 100)	(page) 39, 181
Igneous rocks	100	16, 181
Shales	90	16, 181
Sandstones	35	16, 181
Coal	60	16
Fresh water	0.0001-0.08 (median, 0.00018)	31, 181
Sea water	0.00005	19, 181
Land plants	0.23	181
Marine plants	1	181
Land animals	0.075	181
Marine animals	0.2-1	181
Plant tissues	0.8-3.5	68
Mammalian tissues	0.025-0.85	76
Hard tissues (marine organisms)	0.2-0.85	72
Mammalian blood	0.26	81
Plasma	0.24	81
Red cells	0.0015 ^c	81

^a Results for soils and biological materials reported on oven-dried basis.

^b Highest in soils derived from basalt and serpentine.

^c 120 Cr atoms per red cell.

The distribution of chromium in various substances (according to Bowen¹³) is shown in Table 1. Mertz¹⁴ has discussed in detail the distribution of chromium in soils, water, animals and man, and its relation to the biological role of chromium.

1.3. PRODUCTION AND INDUSTRIAL USE

Chromium and chromium compounds are produced from chromite which is also useful as a refractory. Better grades of chromite contain 62-82% $\text{Fe}(\text{CrO}_2)_2$. In 1967

⁹ H. Remy, *Treatise on Inorganic Chemistry*, 2, Elsevier, Amsterdam (1956), p. 125.

¹⁰ M. E. Weeks and H. M. Leicester, *Discovery of the Elements*, Journal of Chemical Education, Easton, Penna., 7th edn. (1968), p. 279.

¹¹ K. B. Krauskopf, *Introduction to Geochemistry*, McGraw-Hill, New York (1967), p. 639.

¹² L. H. Ahrens, *Distribution of the Elements in Our Planet*, McGraw-Hill, New York (1965), p. 97.

¹³ H. J. M. Bowen, *Trace Elements in Biochemistry*, Academic Press, London (1966).

¹⁴ W. Mertz, *Physiol. Reviews* 49 (1969) 163.

the United States used about 1,400,000 tons of chromite¹⁵ for refractories, chemicals and metallurgical applications; 539,000 tons of metallurgical chromite was imported of which more than half came from the USSR¹⁶. The estimated US consumption of chromite for 1969 is 1,513,000–1,568,00 tons¹⁵.

Chromium metal is produced commercially by reduction of Cr_2O_3 by aluminum, silicon or carbon, or by electrolysis of either CrO_3 or chrome alum solutions^{17, 18}. The electrolyte for the chrome alum electrolysis process is obtained by dissolving ferrochrome. This alloy, which is used extensively in the manufacture of alloy steels, is produced by reducing chromite ore with carbon in an electric furnace.

Chromium produced by the aluminothermic process is 97–99% pure and contains aluminum and silicon as the major impurities. Silicon-reduced chromium has a lower aluminum content but, of course, contains more silicon (up to 0.8%).

Chromium obtained by the chrome alum process is 99.8% pure; the major impurity is iron¹⁸. The product made by electrolysis of CrO_3 solutions contains less gas (0.02% O_2 , 0.0025% N_2 , 0.009% H_2) than that obtained from chrome alum.

Powder metallurgy or arc melting in an inert atmosphere can be used to consolidate the electrolytic chromium. The deposited metal, $\frac{1}{8}$ – $\frac{1}{4}$ in. thick, is stripped from the electrodes, crushed, washed, ground, compressed and sintered (1450–1500°) in hydrogen, helium, or argon; simultaneous purification is possible when hydrogen is used (removal of oxygen).

Chromium is electroplated onto other surfaces either for decoration or to provide extremely hardwear-resistant surfaces (as in bearings). Since the decorative plate is extremely thin and porous, steel is first plated with copper or nickel onto which the chromium is deposited. Hard chromium deposits also contain cracks, but these are sealed over as the deposit becomes thicker. The electrolyte used in chrome plating is a solution containing CrO_3 (250 or 400 g/l) and H_2SO_4 with a ratio of $\text{H}_2\text{SO}_4:\text{CrO}_3$ about 1:100.

The two most important functions of chromium in steels are improving the mechanical properties (particularly hardenability) and increasing the corrosion resistance¹⁹. The magnitude of the effect in each case is roughly proportional to the per cent chromium in the steel.

Low-chromium steels (< 3% Cr), produced in all structural shapes such as bars, tubes, sheets, plates, etc., are used extensively as engineering materials in every branch of industry. Together with molybdenum, nickel, manganese and vanadium, chromium is used in steels designed for applications requiring high strength (e.g. in springs, rails, and roller and ball bearings). Chromium steels are used for making tools suitable for the entire range of operating conditions, from light to heavy duty. For all but the heaviest duty applications, Cr content is generally less than 6%. The tool steels of highest chromium content are outstanding in their resistance to wear. These steels also contain some combination of the other alloying elements (manganese, vanadium, cobalt, nickel, molybdenum, tungsten, silicon).

¹⁵ J. H. Krieger, *Chem. Engng. News*, September 2, 1968, 74A.

¹⁶ *Chem. Engng. News*, August 12, 1968, 31.

¹⁷ M. J. Udy, "Recovery of Chromium from its Ores"; "Electrowinning of Chromium: Chromic Acid Electrolyte"; R. R. Lloyd, "Electrowinning of Chromium from Chromium-Alum Electrolytes"; J. M. Hosdevich, "Electroplating of Chromium", in *Chromium*, 2, Reinhold, New York (1956).

¹⁸ F. E. Bacon, "Chromium and Chromium Alloys", in *Encyclopedia of Chemical Technology*, 5, Interscience, New York, 2nd edn. (1964), p. 453.

¹⁹ M. C. Udy *et al.*, "Physical Properties of Chromium, Its Alloys and Metallurgical Use", in *Chromium*, 2, Reinhold, New York (1956).

Steels containing more than 10% chromium are designated stainless because of their resistance to corrosion and oxidation. Nonhardenable grades contain 0.08–0.20% carbon and 11.5–27.0% chromium. Type 430 (AISI) is used in large quantities for trim on buildings, automobiles, etc., and for nitric acid manufacturing equipment. The austenitic stainless steels (nonhardenable) contain 16–26% chromium and 3.5–22.0% nickel. Typical hardenable stainless steels contain 11.5–18.0% chromium and 0.15–1.25% carbon.

Many nonferrous alloys contain chromium, whose function is to impart, in particular, high-temperature strength and resistance to abrasion, corrosion, and oxidation¹⁹. Chromel and Nichrome are heat- and oxidation-resistant alloys of Cr and Ni or Cr, Ni and Fe. Alloys of this type are particularly useful for heating elements and other components of high-temperature equipment (and a commonly used thermocouple combination is Chromel-Alumel). Another Cr–Fe–Ni alloy is Inconel, used in heat-treating equipment and corrosion-resistant equipment for petroleum and chemical processing operations. Hastelloy C is an alloy of Cr, Mo, W, Fe and Ni useful in equipment for handling HCl, oxidizing acids, hypochlorite, etc. The Stellites are alloys of Cr, Co, Ni, C and W (or Mo) designed for applications requiring retention of hardness and abrasion resistance at high temperatures, as in lathe tools for high-speed cutting and hard-facings of engine valves, for which resistance to corrosion is also necessary.

Sodium chromate and dichromate are the chromium chemicals from which all the others are produced²⁰. A solution of sodium chromate is obtained by leaching the reaction mixture produced by roasting chromite ore with Na_2CO_3 and CaCO_3 . Chromates can be obtained by crystallization from this solution, or it can be acidified to produce dichromates. Chromic acid is produced by heating $\text{Na}_2\text{Cr}_2\text{O}_7$ with H_2SO_4 . Trivalent chromium chemicals are produced from solutions obtained by reducing dichromate solutions with, for example, SO_2 or glucose.

The following are some uses of chromium chemicals²⁰: *tanning agent*: basic Cr(III) sulfate; *dye-metallizing agent*: Cr(III) in solution; *pigments*: Cr_2O_3 (chrome oxide green); $\text{Cr}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ (Guignet's green); $\text{K}_2\text{O} \cdot 4\text{ZnO} \cdot 4\text{CrO}_3 \cdot 3\text{H}_2\text{O}$ (zinc yellow); $4\text{ZnO} \cdot \text{CrO}_3 \cdot \text{XH}_2\text{O}$ (corrosion inhibiting); $\text{Na}_2\text{O} \cdot 4\text{CuO} \cdot 4\text{CrO}_3 \cdot 3\text{H}_2\text{O}$ (anti-fouling); BaCrO_4 , CaCrO_4 (primers); PbCrO_4 (orange yellow); PbCrO_4 with PbSO_4 ("lemon" or "primrose" yellow pigments); PbCrO_4 in tetragonal solid solution with PbSO_4 and PbMoO_4 (molybdate orange); basic lead chromate (chrome orange); *catalysts*: Cr_2O_3 with other oxides, e.g. Al_2O_3 (dehydrogenation); $\text{Zn}(\text{CrO}_2)_2$ (synthetic methanol); *corrosion inhibitors*: soluble chromates (in recirculating water systems); BaCrO_4 ; $\text{Li}_2\text{Cr}_2\text{O}_7$; *fungicide*: $4\text{CuO} \cdot \text{CrO}_3 \cdot \text{XH}_2\text{O}$; *wood preservatives*: soluble chromates; *metal anodizing agent*: CrO_3 ; *flares*: BaCrO_4 .

Only a few Cr(IV) compounds have been reported and until recently none was commercially important. Chromium(IV) oxide, CrO_2 (ferromagnetic; rutile structure, $a = 4.41 \text{ \AA}$, $c = 2.91 \text{ \AA}$), is now in production as a recording tape material. Such tapes (Crolyn) are claimed to have better high frequency response than iron oxide tapes and better resolution at any given output level. The oxide is made, for example, by heating higher oxides such as CrO_3 at about 500°C in water vapor at 500–3000 atm²¹.

²⁰ W. H. Hartford and R. L. Copson, "Chromium Compounds", in *Encyclopedia of Chemical Technology*, 5, Interscience, New York, 2nd edn. (1964), p. 473.

²¹ *Chem. Engng. News*, June 26, 1967, 12; P. Arthur, Jr., and J. N. Ingraham, US Patent 3,117,093, January 7, 1964 (to duPont).

1.4. PREPARATION OF PURE CHROMIUM^{22, 23}

To make ductile chromium from electrolytic chromium, oxygen must be removed, which can be accomplished by reduction at 1500° with pure dry hydrogen. Although other impurities are not removed, the oxygen content may be decreased from 0.12% to less than 0.005%.

Chromium may also be purified by the formation and decomposition of chromium iodide. The iodide is produced by reaction of the elements at about 900°C; the chromium iodide vapor is decomposed on a hotter surface (i.e. a filament) at 1000–1300°. Impurities in the chromium produced in this way are very low; e.g. oxygen, 0.0008%; nitrogen, 0.003%; hydrogen, 0.00008%; carbon, 0.001%.

In the calcium-refining process, chromium is heated with calcium vapor (1000°) in a titanium-lined bomb (evacuated before the start of heating). Levels of impurities in the product are: oxygen, 0.027%; nitrogen, 0.018%; carbon, 0.008%; sulfur, 0.012%; iron, 0.015%.

Pure chromium is ductile and can be rolled, forged or extruded at high temperatures (800–1250°). Generally, ductility is adequate if the impurities are below the following levels: oxygen, 0.2%; nitrogen, 0.01%; carbon, 0.01%; silicon, 0.15%. The hydrogen content should not be more than 4–18 ppm.

Methods suitable for preparing chromium metal in the laboratory are²⁴: aluminothermic reduction of Cr_2O_3 ; reduction of potassium chromium chloride with Mg; electrolysis of a solution of CrO_3 and $\text{Cr}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$; and heating the metal obtained at 600° (*in vacuo*) to remove hydrogen. Ductile chromium can be obtained by reducing CrCl_3 with Ca in a bomb.

1.5. ALLOTROPES

The ordinary form of chromium (20°) is body-centred cubic^{23, 25} ($a = 2.8844\text{--}2.8848 \text{ \AA}$, space group O_h^2). There is a transition to a face-centred cubic structure²⁶ at about 1840° ($a \approx$ approximately $3.8 \text{ \AA}$, space group O_h^5). Some compendia^{26, 27} list other forms supposedly produced by electrodeposition, i.e. a close-packed hexagonal form produced below 20°C and an α -manganese form produced above 26°. These results appear in the older literature. More recent reports indicate that these allotropes do not exist; the substances presumed to be allotropes are actually hydrides²⁸.

1.6. NUCLEAR PROPERTIES

Chromium as found in nature is a mixture of four stable isotopes of mass numbers (A) 50, 52, 53 and 54. Their abundances, mass excesses ($\Delta = M - A$, M = isotopic weight) and thermal neutron capture cross sections (σ_c) are listed in Table 2.

²² H. L. Gilbert and R. G. Nelson, "Ductile Chromium", in *Chromium*, 2, Reinhold, New York (1956), p. 148.

²³ F. E. Bacon, "Chromium and Chromium Alloys", in *Encyclopedia of Chemical Technology*, 5, Interscience, New York, 2nd edn. (1964), p. 459.

²⁴ F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, 2, Academic Press, New York, 2nd edn. (1965), pp. 1161, 1334.

²⁵ C. J. Smithells, *Metals Reference Book*, 1, Plenum Press, New York, 4th edn. (1967), p. 157.

²⁶ E. N. Simons, "Chromium", in *Guide to Uncommon Metals*, Hart, New York (1967), p. 49.

²⁷ F. E. Bacon, "Chromium", in *Metals Handbook*, 1, *Properties and Selection of Metals*, American Society for Metals, Metals Park, Ohio, 5th edn (1961), p. 1200.

²⁸ K. M. Mackay, *Hydrogen Compounds of the Metallic Elements*, Spon, London (1966), pp. 45, 52, 85.

Five radioactive chromium isotopes are known whose characteristics are summarized in Table 3. Two additional radioisotopes ($A = 46, 47$) have been reported, but their existence

TABLE 2. STABLE CHROMIUM ISOTOPES²⁹

A^a	%	Δ (meV) ^b	σ_c^c
50	4.31	-50.249	17
52	83.76	-55.411	0.8
53	9.55	-55.281	18
54	2.38	-56.931	0.38

^a Mass number.

^b Mass excess = $M - A$ (M = isotopic weight), $^{12}\text{C} = 0$.

^c Thermal neutron capture cross-section (barns).

TABLE 3. RADIOACTIVE CHROMIUM ISOTOPES²⁹

A^a	Half-life ^b	Δ (meV) ^c	Mode of decay	Radiations, energies (meV) ^d	Mode of production ^e
48	23-24 h	-43.1	EC	γ , 0.116, 0.31, V X-rays; e^- , 0.111, 0.31; daughter radiations from ^{48}V	^{46}Ti (α , 2 n)
49	41.7-41.9 m	-45.39	β^+	1.54 max; e^- , 0.058, 0.084, 0.148; γ , 0.063, 0.091, 0.153, 0.511, V X-rays	^{48}Ti (α , 3 n) ^{47}Ti (α , 2 n) ^{46}Ti (α , n)
51	27.5-27.9 d	-51.447	EC	γ , 0.320 (9%), V X-rays; e^- , 0.315	^{50}Cr (n, γ)
55	3.52-3.6 m	-55.11	β^-	2.59 max.	^{54}Cr (n, γ)
56	5.9 m	-55.3	β^-	1.5 max; e^- (0.020, 0.077) ^f ; γ , 0.026, 0.083, Mn X-rays; daughter radiations from ^{56}Mn	^{54}Cr (t, p)

^a Mass number.

^b h, hours; m, minutes; d, days.

^c $\Delta = M - A$ (M = isotopic weight), $^{12}\text{C} = 0$.

^d EC, electron capture; β^+ , positron emission; β^- , electron emission; γ , gamma radiation; max., maximum; e^- , Auger or conversion electrons.

^e α , $^4\text{He}^{2+}$; n, neutron; t, $^3\text{H}^+$; p, $^1\text{H}^+$.

^f Calculated.

is uncertain. The radioisotope commonly used in tracer work is ^{51}Cr . Commercially available chemical forms include Cr(III) in dilute acid, usually HCl, and chromate.

²⁹ C. M. Lederer, J. M. Hollender and I. Perlman, *Table of Isotopes*, John Wiley, New York, 6th edn. (1967), p. 18.

1.7. PHYSICAL PROPERTIES

In Table 4 are listed some of the physical properties of chromium. There is disagreement in the literature with regard to the numerical values of some of these properties. In fact, sometimes different values for the same property can be found in different places in the same treatise. It is, of course, difficult to obtain reliable and reproducible results in measurements of high-temperature properties (such as melting point, boiling point, heat of sublimation,

TABLE 4. SOME PHYSICAL PROPERTIES OF CHROMIUM

Property	Value	Reference																								
Color	Gray	30																								
Atomic number (<i>Z</i>)	24	30																								
Atomic weight	51.996	30																								
Density	7.14 g/cm ³ (20°C)	30, 31																								
Atomic volume	7.29 cm ³ /mole	31																								
Crystal structure	< 1840°C: body-centred cubic, type <i>A2</i> , space group <i>O</i> _h ² <i>a</i> , 2.88 Å	32																								
	Closest approach of atoms, 2.498 Å	31																								
	Lattice energy, 80.6 kcal/mole	33																								
	> 1840°C: cubic, type <i>A1</i> , space group <i>O</i> _h ⁵ , <i>a</i> = ~ 3.8 Å	34																								
	1903 ± 10°C	32																								
Melting point (m.p.)	1903 ± 10°C	30																								
Heat of fusion (ΔH_f)	3.5 kcal/mole	30																								
Boiling point (b.p.)	2642°C	30																								
Heat of vaporization (ΔH_v)	81.7 kcal/mole (at b.p.)	32																								
Heat of sublimation (ΔH_s)	94.8 kcal/mole (25°C)	32																								
Heat capacity (<i>C</i> _p ; cal/mole/°C)	Cr(s) 5.58 (25°C)	30																								
	<i>C</i> _p = 5.84 + 2.36 × 10 ⁻³ <i>T</i> - 0.88 × 10 ⁵ <i>T</i> ⁻² (<i>T</i> = °K)	32																								
	Cr (l) 9.4 (at m.p.)	32																								
	Cr (g) 4.97 (25°C)	30																								
Entropy (cal/mole/°C)	<table><tr><th>Cr(s)</th><th>°C</th><th>Cr(g)</th></tr><tr><td>5.7</td><td>25</td><td>41.6</td></tr><tr><td>8.8</td><td>227</td><td>44.2</td></tr><tr><td>13.5</td><td>727</td><td>47.6</td></tr><tr><td>16.9</td><td>1237</td><td>49.7</td></tr><tr><td>19.7</td><td>1727</td><td>51.3</td></tr><tr><td></td><td>2227</td><td>52.6</td></tr><tr><td></td><td>2727</td><td>53.5</td></tr></table>	Cr(s)	°C	Cr(g)	5.7	25	41.6	8.8	227	44.2	13.5	727	47.6	16.9	1237	49.7	19.7	1727	51.3		2227	52.6		2727	53.5	34
Cr(s)	°C	Cr(g)																								
5.7	25	41.6																								
8.8	227	44.2																								
13.5	727	47.6																								
16.9	1237	49.7																								
19.7	1727	51.3																								
	2227	52.6																								
	2727	53.5																								
Vapor pressure	<table><tr><th>°C</th><th>mm Hg</th></tr><tr><td>965</td><td>2.4 × 10⁻⁶</td></tr><tr><td>1093</td><td>2.1 × 10⁻⁵</td></tr><tr><td>1197</td><td>2.0 × 10⁻⁴</td></tr><tr><td>1288</td><td>1.8 × 10⁻³</td></tr><tr><td>(m.p.)</td><td>7.4</td></tr></table>	°C	mm Hg	965	2.4 × 10 ⁻⁶	1093	2.1 × 10 ⁻⁵	1197	2.0 × 10 ⁻⁴	1288	1.8 × 10 ⁻³	(m.p.)	7.4	34												
°C	mm Hg																									
965	2.4 × 10 ⁻⁶																									
1093	2.1 × 10 ⁻⁵																									
1197	2.0 × 10 ⁻⁴																									
1288	1.8 × 10 ⁻³																									
(m.p.)	7.4																									
Configuration and ground state: un-ionized atom	<table><tr><td></td><td>3<i>d</i>⁵</td><td>4<i>s</i>;</td><td>⁷<i>S</i>₃</td></tr><tr><td>Cr¹⁺</td><td>3<i>d</i>⁵;</td><td></td><td>⁶<i>S</i>_{5/2}</td></tr><tr><td>Cr²⁺</td><td>3<i>d</i>⁴;</td><td></td><td>⁵<i>D</i>₀</td></tr><tr><td>Cr³⁺</td><td>3<i>d</i>³;</td><td></td><td>⁴<i>F</i>_{3/2}</td></tr></table>		3 <i>d</i> ⁵	4 <i>s</i> ;	⁷ <i>S</i> ₃	Cr ¹⁺	3 <i>d</i> ⁵ ;		⁶ <i>S</i> _{5/2}	Cr ²⁺	3 <i>d</i> ⁴ ;		⁵ <i>D</i> ₀	Cr ³⁺	3 <i>d</i> ³ ;		⁴ <i>F</i> _{3/2}	34								
	3 <i>d</i> ⁵	4 <i>s</i> ;	⁷ <i>S</i> ₃																							
Cr ¹⁺	3 <i>d</i> ⁵ ;		⁶ <i>S</i> _{5/2}																							
Cr ²⁺	3 <i>d</i> ⁴ ;		⁵ <i>D</i> ₀																							
Cr ³⁺	3 <i>d</i> ³ ;		⁴ <i>F</i> _{3/2}																							
Atomic radius	1.27–1.28 Å	34																								
Ionic radii	Cr ⁶⁺ 0.52–0.53 Å	34																								
	Cr ³⁺ 0.64 Å																									
	Cr ²⁺ 0.83 Å																									

TABLE 4—(cont.)

Property	Value					Reference
Radii of 3 <i>p</i> orbitals	Cr ²⁺	0.414 Å			34	
	Cr ³⁺	0.411 Å				
Radii of 3 <i>d</i> orbitals	Cr ²⁺	0.424 Å			34	
	Cr ³⁺	0.401 Å				
Ionization potentials (eV)	1st:	6.764	6th:	90.6	34	
	2nd:	16.49	7th:	161.1		
	3rd:	31	8th:	185		
	4th:	(51)	9th:	290±1		
	5th:	73	10th:	246±2		
Bond energies of inner electrons (keV)	<i>K</i> 6.000	<i>L</i> _{II} 0.585	<i>L</i> _{III} 0.575	<i>M</i> _{II, III} 0.042	<i>M</i> _{IV, V} 0.002	34
<i>K</i> X-ray emission spectra (Å)	α' 2.29353	α 2.28965	β 2.08479	γ 2.07089		34
Electron affinity	1.6 eV					34
Work function (ϕ)	4.58 eV					34
Reflectivity	%		Wavelength (Å)			33
	67		3,000			
	70		5,000			
	63		10,000			
	88		40,000			
Emission coefficient (ε_λ)	0.34					34
(Cr(s) unoxidized, smooth surface)	$(\lambda = 6500 \text{ Å, room temperature})$					
Magnetic susceptibility	3.49×10^{-6} cgs units					33
Resistivity (ρ , microhm cm)	ρ	°C	ρ	C°		33, 34
	0.5	-260	31	407		
	13	20	40	600		
	18	152	47	652		
	20	200	66	1000		
Temperature coefficient of electrical resistivity	0.003 per °C (0°C)					33
Contact potential (Cr vs. constantin)	51.1 μ V/°C					33
Thermal conductivity, cal/cm ² /cm/sec/°C						32
	0.16	20°C				
	0.182	426°C				
	0.161	760°C				
Linear coefficient of thermal expansion (fractional change in length/°C, α)	α		°C			30
	8.2×10^{-6}		20			
	6.25×10^{-6}		-100 to +200			
	10.60×10^{-6}		270-730			
	14.90×10^{-6}		730-1100			
Hardness: Vickers	19.4×10^{-6}		1100-1590			34
Brinell	110 (99.96% extruded, annealed at 1100°C)					32
	160 (99.96%, extruded, annealed, rolled at 400°C)					32
	125 (~20°C, as cast)					33
	70 (700°C, as cast)					33
	500-1250 (electrolytic)					31
	70-90 (electrodeposited, annealed)					33

TABLE 4—(cont.)

Property	Value				Reference
Tensile strength (kg/cm ²) (recrystallized, swaged arc-cast electrolytic Cr)	°C		°C		35
	846	20	2862	500	
	2390	200	2475	600	
	2579	300	2080	700	
	2016	350	1833	800	
	2298	400			
Compressibility ($\frac{\Delta V}{V_0}$)	0.8 × 10 ⁻⁶ (20°; 100–510 kg/cm ²)				31
Modulus of elasticity in tension	253,700 kg/cm ²				33

etc.) of chromium and similar metals which are not only refractory but also react with many substances at elevated temperatures. Furthermore, many of the properties vary with the purity of the metal, which is frequently not known or at least not stated, and some are dependent on the way in which the metal has been mechanically worked.

The excellent compilation of Goldsmith *et al.*³⁶ is easy to use because of graphical presentation of data for several important properties. The following properties of chromium are summarized: specific heat, thermal conductivity, linear thermal expansion, vapour pressure, electrical resistivity, emissivity (as a function of temperature), spectral emissivity, reflectivity (as a function of wave length).

1.8. CHEMISTRY AND CHEMICAL PROPERTIES

Chromium is resistant to the attack of a wide variety of chemicals at normal temperature but reacts with many of these at elevated temperatures (Table 5). Rates of corrosion of chromium by O₂, H₂O, SO₂ and CO₂ as a function of temperature are shown in Table 6.

During electrodeposition, chromium absorbs considerable quantities of H₂. According to some authorities, two unstable hydrides (which may be insertion compounds) are formed^{37a, 38a, b}.

Chromium reacts with several of the common acids with evolution of H₂. It reacts slowly with dilute H₂SO₄^{38a}. It dissolves in aqueous HX (X = F, Cl, Br, I) with formation of Cr²⁺ (in the absence of air); if pure Cr is used, very little Cr³⁺ is formed^{39, 40}. It is not attacked by

³⁰ R. Keller, *Basic Tables in Chemistry*, McGraw-Hill, New York (1967).

³¹ J. Amiel, in *Nouveau Traité de Chimie Minérale*, 14, Masson et Cie, Paris (1959).

³² C. J. Smithells, *Metals Reference Book*, Plenum Press, New York, 4th edn. (1967).

³³ E. N. Simons, "Chromium", in *Guide to Uncommon Metals*, Hart, New York (1967).

³⁴ G. V. Samsonov (ed.), *Handbook of the Physicochemical Properties of the Elements*, Plenum Press, New York (1968).

³⁵ F. E. Bacon, "Chromium", in *Metals Handbook*, 1, *Properties and Selection of Metals*, American Society for Metals, Metals Park, Ohio, 5th edn. (1961), p. 1200.

³⁶ A. Goldsmith, T. E. Waterman and H. K. Hirschhorn, *Handbook of Thermophysical Properties of Solid Materials*, 1, Macmillan, New York, revised edn. (1961), pp. 215–219.

³⁷ Ref. 34: (a) p. 733; (b) p. 585.

³⁸ Ref. 31: (a) p. 62; (b) p. 125.

³⁹ J. Koppel, *Z. anorg. u. allgem. Chem.* **45** (1905) 359.

⁴⁰ H. Lux, L. Eberle and D. Sarre, *Chem. Ber.* **97** (1964) 503.

phosphoric acid^{37b} and is resistant to attack by many organic acids including formic, citric and tartaric, but is attacked slowly by acetic acid^{37b, 38a}.

Chromium is insoluble in nitric acid, fuming nitric acid and aqua regia^{37b, 38a}. It is made passive by these acids and by other oxidizing agents such as chlorine, bromine and solutions

TABLE 5. REACTIONS OF CHROMIUM WITH ELEMENTS AND COMPOUNDS AT ELEVATED TEMPERATURES

Reactant	Products	Reference
H ₂ ^a	(Absorbed)	31, 34
B	Borides	31, 34
C	Carbides	31, 34
Si	Silicides (~ 1300°C)	31, 34
N ₂	Nitrides (900–1200°C)	31, 34
P	Phosphides	34
O ₂	Oxide coating (600–900°C); Burns to Cr ₂ O ₃ (2000°C)	31, 34
S	Sulfides (700°C)	31, 34
Se	Selenides	34
Te	Tellurides	34
F ₂ ^b	CrF ₄ , CrF ₅ (red heat)	31, 34
Cl ₂	CrCl ₃ (~ 600°C)	31, 34
Br ₂	Bromides (red heat)	31, 34
I ₂	CrI ₂ , CrI ₃ (750–800°C)	31, 34
NH ₃	Nitrides (850°C)	31, 34
NO	Nitride, oxide	31
H ₂ O	Cr ₂ O ₃ , H ₂ (red heat)	31
H ₂ S	Sulfides (~ 1200°C)	31, 34
CS ₂	Cr ₂ S ₃	31
HF	CrF ₂ (red heat)	31
HCl	CrCl ₂ (red heat)	31
HBr	CrBr ₂ (red heat)	31
HI	CrI ₂ (750–850°C)	31

^a An insignificant amount of H₂ is absorbed; the amount increases with increasing temperature.

^b Superficial reaction at room temperature³⁵; reacts to form CrF₃ at room temperature³⁴.

TABLE 6. RATES OF CORROSION OF CHROMIUM^a

Temperature (°C)	mg/cm ² /hr			
	O ₂	H ₂ O	SO ₂	CO
700	0.019	0.002	0.007	0.011
800	0.040	0.015	0.016	0.014
900	0.093	0.048	0.135	0.056
1000	0.265	0.09	0.149	0.128

^a Duration of test, 24 h³⁴.

of chloric acid and CrO₃; it is also slowly passivated by superficial oxidation in air, although this is far less effective in causing passivation than the other agents mentioned^{38a}. Passive chromium can be made active by a reduction process, e.g. treatment with hydrogen, or by immersing the chromium in dilute H₂SO₄ and touching it with Zn below the surface of the acid^{38a}.

While passive chromium acts somewhat like a noble metal and is not attacked by mineral

acids, in the nonpassive state it is quite an active metal (note redox potentials⁴¹, Table 7); in aqueous solution it can displace copper, tin and nickel ions from their salts^{42a}. Passivation has been attributed to surface absorption of oxygen or formation of an oxide coat on the chromium, but it must be concluded that no adequate explanation has been proposed^{42a}.

Chromium reacts with fused hydroxides at red heat but not with alkali carbonates; it is rapidly oxidized to chromates by nitrates and chlorates^{38a}.

Chromium has the ground state electronic configuration $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$. This distribution of the outermost electrons is favored over $3d^4 4s^2$ because of the increased

TABLE 7. SOME CHROMIUM ELECTRODE POTENTIALS⁴¹

Reaction	μ^a	$\log k$	E V	$^{\circ}\text{C}$
$\text{Cr}^{3+} + 3e \rightleftharpoons \text{Cr}(s)$	0	-37.7	-0.74	25
$\text{Cr}^{2+} + 2e \rightleftharpoons \text{Cr}(s)$	0 (c)	-30.9	-0.91	19
$\text{Cr}^{3+} + e \rightleftharpoons \text{Cr}^{2+}$	dil.	-6.9 to -7.9	-0.398 to -0.454	18
	0	-6.9	-0.41	25
$[\text{Cr}(\text{CN})_6]^{3-} + e \rightleftharpoons [\text{Cr}(\text{CN})_6]^{4-}$	1 M KCN	-19.3	-1.14	25
	0 (c)	-21.6	-1.28	
$\frac{1}{2}\text{Cr}_2\text{O}_7^{2-} + 7\text{H}^+ + 3e \rightleftharpoons \text{Cr}^{3+} + 3\frac{1}{2}\text{H}_2\text{O}$	0	67.6	1.33	25
$\text{HCrO}_2^- + 7\text{H}^+ + 3e \rightleftharpoons \text{Cr}^{3+} + 4\text{H}_2\text{O}$	dil.	60.6	1.195	25
$\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3e \rightleftharpoons \text{Cr}(\text{OH})_3(s) + 5\text{OH}^-$	0	-6.9	-0.13	25

^a Ionic strength: 0 (c), results corrected to 0; dil., not > 0.01 M; 1 M KCN, KCN kept constant at 1 M.

stability of the half-filled $3d$ shell with one electron in each of the orbitals. The half-filled shell leads to S states ($L = 0$) which are especially stable, supposedly because of the large amount of exchange energy^{42b}. The d orbitals project close enough to the surfaces of the ions that the electrons in them interact with the chemical environment^{42c}.

A typical transition element, chromium forms many compounds that are colored and paramagnetic. Chromium has oxidation states as follows: $2-$, $1-$, 0 , $1+$, $2+$, $3+$, $4+$, $5+$, $6+$; the highest oxidation state, $6+$, corresponds to the sum of the numbers of $3d$ and $4s$ electrons (as with Ti and V). The most common and stable oxidation states are $2+$, $3+$ and $6+$. The lowest, $2-$, $1-$, 0 and $1+$, are formal oxidation states displayed by chromium in compounds such as carbonyls, nitrosyls and organometallic complexes.

Chromium in these lowest oxidation states is strongly reducing. The lowest oxidation state known in aqueous solution is $2+$. The most stable and important oxidation state is $3+$. Chromium(III) forms some binary compounds such as Cr_2O_3 , Cr_2S_3 and the halides CrX_3 ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$). However, the aqueous chemistry of $\text{Cr}(\text{III})$ is almost entirely the chemistry of coordinate and chelate compounds of which thousands are known. Only a few compounds of Cr^{4+} and Cr^{5+} have been isolated^{42a}. Compounds of these oxidation states occur as transient intermediates in reduction of Cr^{6+} compounds. Otherwise there is no aqueous chemistry of Cr^{4+} and Cr^{5+} because they rapidly disproportionate to Cr^{3+} and Cr^{6+} . All $\text{Cr}(\text{VI})$ compounds except CrF_6 are oxo compounds^{42d}. Compounds of $\text{Cr}(\text{VI})$ are quite effective oxidizing agents (note redox potentials, Table 7). Chromium forms several peroxides, which are compounds of Cr^{6+} , Cr^{5+} and Cr^{4+} .

⁴¹ L. G. Sillén and A. E. Martell, *Stability Constants*, Special Publication No. 17, Chemical Society, London (1964), p. 4.

⁴² F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 2nd edn. (1966): (a) p. 820; (b) p. 632; (c) p. 627; (d) p. 828.

1.9. BIOLOGICAL ACTIVITY

Chromium(VI) compounds such as chromates, dichromates and particularly chromic acid act as irritants of the skin and mucous membranes^{43, 44}. Dermatitis results in the cases of some individuals who have become sensitized and allergic to Cr(VI) compounds. In plants where such compounds are produced or used, many precautions are taken to prevent exposure to their dusts and mists. There is no evidence that Cr(III) compounds have any toxic effects.

On the contrary, chromium, as Cr(III), appears to be an essential trace metal in mammalian metabolism. The first demonstration of a metabolic effect of chromium was reported by Mertz and Schwarz in 1955⁴⁵. In the meantime, a great deal of evidence pointing to the essentiality of chromium has been obtained, much of it by Mertz and his associates and by Schroeder's group. The following summary is based principally on a fine critical review compiled by Mertz⁴⁴, in which all the pertinent references will be found.

When analytical methods of sufficient sensitivity (e.g. atomic absorption, activation analysis) are used, essentially all biological materials are found to contain chromium. A brief summary of its distribution in water, soils and biological tissues is given in Section 1.2.

Chromium is not well absorbed in the intestinal tract; Cr⁶⁺ is absorbed better than the biologically active Cr³⁺. It is presumably transported by the blood protein siderophilin, which is also the carrier of iron. Chromium is excreted mainly in the urine and to a smaller extent in feces.

Testes, bones, liver and spleen have a high affinity for chromium while the affinity of muscle and brain is low. Chromium(III) coordinates with proteins. Since chromates penetrate walls of red cells ⁵¹CrO₄²⁻ is used to label erythrocytes. Wacker and Vallee found high concentrations of several metals, including chromium, in beef liver RNA.

There is a close dependence of the biological effect of chromium (as Cr(III)) on the presence of insulin, the apparent effect of chromium supplementation in diets depends on the existence of a deficiency state, and there is a narrow dose range for optimum effect. The effects of chromium deficiency in rats and monkeys include impaired glucose tolerance, decreased glycogen reserve, increased incidence of aortic lesions, disturbance in utilization of amino acids in protein synthesis and a syndrome resembling diabetes. The effects of chromium supplementation are manifested in numerous ways including the following: increased survival of rats and mice; prolonging of survival of old animals; increase in growth rate of rats and mice raised in a controlled environment.

Roginski and Mertz found that in 10–15% of the rats fed a diet deficient in both protein and chromium (100 ppb), a visible eye lesion develops which results in opacity of the cornea in one or both eyes; although this is prevented by sufficient chromium in the diet, the fully developed defect is not reversed by feeding chromium, high protein, or both.

Considerable work has been done directly relevant to the metabolic role of chromium in human beings (e.g. investigations of Mertz, Doisy, Hopkins and Schroeder). It has been found that chromium supplementation improves or normalizes impaired glucose tolerance of some diabetics, old people, and malnourished children, but not of others. It has become evident that, although low chromium states exist, they are not the sole cause of impaired glucose tolerance. Schroeder's group have shown that offspring deplete breeder rats of

⁴³ W. H. Hartford and R. L. Copson, "Chromium Compounds", in *Encyclopedia of Chemical Technology*, 5, Interscience, New York, 2nd edn. (1955), p. 505.

⁴⁴ W. Mertz, *Physiol. Rev.* **49** (1969) 163.

⁴⁵ W. Mertz and K. Schwarz, *Arch. Biochem. Biophys.* **58** (1955) 504.

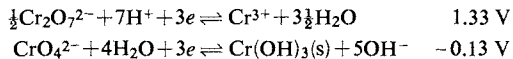
chromium. The known worsening of glucose tolerance among women who have had several children may be related to chromium depletion. Hambidge has shown that the chromium content of hair of mothers is less than a third of that of nulliparae.

Mertz and associates have utilized *in vitro* techniques for evaluating chromium compounds with respect to the relation between chemical composition of chromium compounds and their biological effects. These comprise comparing the rates of utilization of ^{14}C -tagged glucose by epididymal tissue from diabetic rats in the presence of insulin with and without added chromium. The most stable complexes such as $\text{Cr}(\text{acac})_3$ (acac = acetylacetonate) are relatively ineffective while less stable complexes (such as those of ethylenediamine, methionine, etc.) enhance the action of insulin. Outstanding activity is manifested by the glucose tolerance factor (GTF), a chromium complex extracted from brewer's yeast and pork kidney powder (both *in vitro* and *in vivo*).

An ultimate objective in this area is to write a series of equations for all reactions that $\text{Cr}(\text{III})$ undergoes from absorption to excretion. It is assumed that the final biologically effective form of chromium is produced as a result of a sequence of reactions of $\text{Cr}(\text{III})$ with ligands present in the biological system. Specifically it is essential to determine which of the many biological substances are most likely to maintain $\text{Cr}(\text{III})$ in transportable (and presumably available) form⁴⁶. This question is discussed further under Section 2.6.4(e).

1.10. ANALYTICAL CHEMISTRY

Numerous satisfactory procedures for determining chromium in macroscopic amounts are available^{47, 48}. In most of these, chromium is oxidized to Cr^{6+} which is determined by titration with a standard reducing agent such as ferrous sulfate. The reactions and electrode potentials are:



Other methods include procedures based on precipitation of chromium hydroxide, barium chromate or lead chromate, polarography and chromatographic adsorption.

Of numerous oxidants that have been used successfully, perchloric acid, sodium peroxide and persulfate in presence of silver ion are preferred. Excess oxidizing agent is not a problem with HClO_4 which acts only as a strong nonoxidizing acid in the cooled analytical solution. Excess sodium peroxide, silver peroxide and persulfate can be destroyed by boiling the solution several minutes. Ferric ion is sometimes added to catalyze the decomposition of sodium peroxide. Permanganate, sometimes used to complete the oxidation after use of some other oxidant, can be destroyed by sodium azide, sodium nitrite or HCl .

The perchloric acid method gives slightly low results presumably because of reduction of Cr^{6+} that occurs as the hot oxidized solution is cooled. Also, a little chromium may be lost as chromyl compounds if such chloride or fluoride is present. Thus although the method is satisfactory with samples containing considerable chromium, it is not sufficiently accurate for micro quantities.

⁴⁶ C. L. Rollinson and E. W. Rosenbloom, "Coordination in Biochemistry: Reactions of Chromium(III)", in *Coordination Chemistry: Papers Presented in Honor of Professor John C. Bailar, Jr.*, Plenum Press, New York (1969).

⁴⁷ W. H. Hartford, "Chromium", in *Treatise on Analytical Chemistry*, II, 8, Interscience, New York (1963).

⁴⁸ R. A. Chalmers, "Chromium", in *Comprehensive Analytical Chemistry*, IC, Elsevier, Amsterdam (1962).

After removal of excess oxidant if necessary, Cr^{6+} is titrated with ferrous sulfate or ferrous ammonium sulfate solution, or an excess is added and back-titration is performed with dichromate, permanganate, or a Ce^{4+} solution. The end-point can be determined potentiometrically or with an indicator such as barium diphenylamine sulfonate or *o*-phenanthroline ferrous complex. Iodometrically Cr^{6+} is reduced with KI and the I_2 produced is titrated with thiosulfate (starch indicator).

About the only interferences are permanganate and vanadate. Manganese in the sample will be oxidized by $\text{S}_2\text{O}_8^{2-}-\text{Ag}^+$ (but not by HClO_4) to MnO_4^- which is removed as described above. Vanadium(V) will be titrated with Cr^{6+} ; correction is made by a second titration for vanadium alone.

Ore samples and ash of organic materials can be processed for analysis by sodium peroxide fusion or by digestion with $\text{HClO}_4\text{--H}_2\text{SO}_4$ or $\text{HClO}_4\text{--H}_3\text{PO}_4$ mixtures, which can also be used to dissolve and oxidize stainless steel and other chromium alloys. Organic samples such as plant and animal tissue can be "wet-ashed" with $\text{HClO}_4\text{--H}_2\text{SO}_4\text{--HNO}_3$. It is essential to destroy all the organic matter before the oxidizing temperature is reached ($\sim 180^\circ$), and this is accomplished by the nitric acid; violent explosions occur when hot perchloric acid comes into contact with organic matter. In an alternative wet-ashing procedure, a mixture of nitric acid and hydrogen peroxide is used which leaves the chromium as Cr^{3+} .

A direct complexometric titration of Cr^{3+} with, for example, EDTA is not feasible because of the inert nature of Cr(III) complexes which makes the chelating reaction too slow. However, when the Cr(III)–EDTA solution is heated, all the chromium is chelated and the excess EDTA can be back-titrated with solutions of ions that are chelated rapidly (e.g. Fe^{3+} , Mn^{2+} , Zn^{2+}).

A spectrophotometric method is based on the color of the $[\text{Cr}(\text{C}_2\text{O}_4)]^{3-}$ ion⁴⁹. Oxalate is a powerful chelating agent that can convert many Cr(III) compounds to the oxalato complex; it can even extract chromium from chrome-tanned leather. The per cent transmission of the oxalato complex solution is determined at the absorption maximum (490 $\text{m}\mu$) and concentration of chromium is read off a curve established with solutions of known concentration. This method, which is rapid and convenient, is satisfactory if results of the highest accuracy are not required.

Other approaches are required for trace and ultratrace quantities of chromium⁴⁷. Analysis in this range has become increasingly important in recent years during which evidence has been accumulating to indicate that chromium is an essential element in mammalian metabolism (see Section 1.9).

Qualitatively, the yellow color of chromate permits detection down to 1 ppm of chromium (absorption maximum of chromate, 370 $\text{m}\mu$). Bichromate reacts with *s*-diphenyl carbazide to produce a red-violet color (presumably due to a Cr(III) complex of diphenyl carbazone, absorption maximum 540 $\text{m}\mu$). This test is sensitive to 0.01 ppm Cr and can be made quantitative.

By means of atomic absorption, chromium can be determined down to 10 ppb⁵⁰. Biological samples are digested with $\text{HClO}_4\text{--H}_2\text{SO}_4\text{--HNO}_3$. The oxidized chromium is extracted with methyl isobutyl ketone and the extract is aspirated into a fuel-rich hydrogen–air flame of the spectrometer.

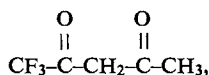
By means of X-ray fluorescence with focusing optics, it has been possible to determine

⁴⁹ E. R. Theis, E. J. Serfass and A. J. Clark, *J. Am. Leather Chem. Assoc.* **41** (1946) 449.

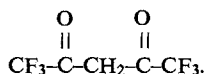
⁵⁰ F. J. Feldman, E. C. Knoblock and W. C. Purdy, *Anal. Chim. Acta* **38** (1967) 489.

chromium in urine down to 0.16 ppb (4 nanograms in 25 ml)⁵¹. Chromium is extracted with chloroform as the 8-hydroxyquinoline complex. The chromium target is formed by evaporating drops of the extract on the end of a $\frac{1}{8}$ in. brass rod.

It has been known for a long time that the nonionic 1,3-diketone metal chelate compounds such as those of acetylacetone (acac) can be sublimed. In an exciting development having great potentialities for ultratrace analysis, Sievers, Moshier and their colleagues have exploited the volatility of such chelates in gas-chromatographic procedures^{52, 53}. The volatility of the chelates is increased by fluorine substitution; the most thoroughly studied fluorinated diketones are trifluoroacetylacetone (tfa),



and hexafluoroacetylacetone (hfa),



Chelates of these compounds can be eluted from columns at much lower temperatures than those of acetylacetone. The temperatures required to produce a vapor pressure of 1 mm of the chromium chelates [Cr(dk)₃] (dk = diketonate) are: acac, 179°; tfa, 128°; hfa, 67°. Procedures for converting several metals in biological materials to the F-substituted acetylacetones have been described, e.g. for determination of beryllium in blood, urine and tissue (procedures which can probably be applied to other metals), and chromium in serum. Detection limits as low as 3×10^{-12} g of chromium (3 picograms) have been attained with the hfa complex and even lower limits are probably attainable. Results in this range are made possible by the sensitivity of the electron capture detector.

Beyermann⁵⁴ has critically examined many procedures for chromium trace analysis. Winchester⁵⁵ has compared the sensitivities of several methods with that of neutron activation analysis. Mertz⁵⁶ has reviewed the utilization of various methods in biochemical investigations.

2. CHROMIUM COMPOUNDS

2.1. INTERMETALLIC PHASES IN BINARY CHROMIUM ALLOYS^{57-59*}

No general theory is available to account for the complex behavior of metals in alloy systems. The most important factors governing the interactions of metals with each other

* These basic references include information pertaining to all systems discussed in this section. The page numbers refer to their excellent indices listing all systems and compounds covered.

⁵¹ K. Beyermann, H. J. Rose, Jr., and G. Christian, *Anal. Chim. Acta* **45** (1969) 51.

⁵² R. E. Sievers, "Gas Chromatographic and Related Studies of Metal Chelates", in *Coordination Chemistry: Papers Presented in Honor of Professor John C. Bailar, Jr.*, Plenum Press, New York (1969).

⁵³ R. W. Moshier and R. E. Sievers, *Gas Chromatography of Metal Chelates*, Pergamon Press, Oxford (1965).

⁵⁴ K. Beyermann, *Z. anal. Chem.* **190** (1962) 4; **191** (1962) 346.

⁵⁵ J. W. Winchester, "Radioactivation Analysis in Inorganic Geochemistry", in *Progress in Inorganic Chemistry*, **2**, Interscience, New York (1960).

⁵⁶ W. Mertz, *Physiol. Rev.* **49** (1969) 163.

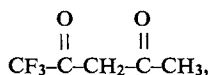
⁵⁷ M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York (1958), pp. ix-xvi.

⁵⁸ R. P. Elliott, *Constitution of Binary Alloys, First Supplement*, McGraw-Hill, New York (1965), pp. ix-xxx (cumulative).

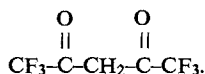
⁵⁹ J. H. Westbrook (ed.), *Intermetallic Compounds*, John Wiley, New York (1967), pp. 639-663.

chromium in urine down to 0.16 ppb (4 nanograms in 25 ml)⁵¹. Chromium is extracted with chloroform as the 8-hydroxyquinoline complex. The chromium target is formed by evaporating drops of the extract on the end of a $\frac{1}{8}$ in. brass rod.

It has been known for a long time that the nonionic 1,3-diketone metal chelate compounds such as those of acetylacetone (acac) can be sublimed. In an exciting development having great potentialities for ultratrace analysis, Sievers, Moshier and their colleagues have exploited the volatility of such chelates in gas-chromatographic procedures^{52, 53}. The volatility of the chelates is increased by fluorine substitution; the most thoroughly studied fluorinated diketones are trifluoroacetylacetone (tfa),



and hexafluoroacetylacetone (hfa),



Chelates of these compounds can be eluted from columns at much lower temperatures than those of acetylacetone. The temperatures required to produce a vapor pressure of 1 mm of the chromium chelates [Cr(dk)₃] (dk = diketonate) are: acac, 179°; tfa, 128°; hfa, 67°. Procedures for converting several metals in biological materials to the F-substituted acetylacetones have been described, e.g. for determination of beryllium in blood, urine and tissue (procedures which can probably be applied to other metals), and chromium in serum. Detection limits as low as 3×10^{-12} g of chromium (3 picograms) have been attained with the hfa complex and even lower limits are probably attainable. Results in this range are made possible by the sensitivity of the electron capture detector.

Beyermann⁵⁴ has critically examined many procedures for chromium trace analysis. Winchester⁵⁵ has compared the sensitivities of several methods with that of neutron activation analysis. Mertz⁵⁶ has reviewed the utilization of various methods in biochemical investigations.

2. CHROMIUM COMPOUNDS

2.1. INTERMETALLIC PHASES IN BINARY CHROMIUM ALLOYS^{57-59*}

No general theory is available to account for the complex behavior of metals in alloy systems. The most important factors governing the interactions of metals with each other

* These basic references include information pertaining to all systems discussed in this section. The page numbers refer to their excellent indices listing all systems and compounds covered.

⁵¹ K. Beyermann, H. J. Rose, Jr., and G. Christian, *Anal. Chim. Acta* **45** (1969) 51.

⁵² R. E. Sievers, "Gas Chromatographic and Related Studies of Metal Chelates", in *Coordination Chemistry: Papers Presented in Honor of Professor John C. Bailar, Jr.*, Plenum Press, New York (1969).

⁵³ R. W. Moshier and R. E. Sievers, *Gas Chromatography of Metal Chelates*, Pergamon Press, Oxford (1965).

⁵⁴ K. Beyermann, *Z. anal. Chem.* **190** (1962) 4; **191** (1962) 346.

⁵⁵ J. W. Winchester, "Radioactivation Analysis in Inorganic Geochemistry", in *Progress in Inorganic Chemistry*, **2**, Interscience, New York (1960).

⁵⁶ W. Mertz, *Physiol. Rev.* **49** (1969) 163.

⁵⁷ M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York (1958), pp. ix-xvi.

⁵⁸ R. P. Elliott, *Constitution of Binary Alloys, First Supplement*, McGraw-Hill, New York (1965), pp. ix-xxx (cumulative).

⁵⁹ J. H. Westbrook (ed.), *Intermetallic Compounds*, John Wiley, New York (1967), pp. 639-663.

(and with nonmetals) are the atomic radii of the elements, their valences, ionization potentials and relative electronegativities^{60a, 61}. All of these depend on their positions in the periodic chart.

The ionization potentials of the transition elements do not vary widely, nor do their electronegativities⁶². Hence the tendency of these metals is to form solid solutions rather than compounds with each other. In contrast, with increasing difference in "metallo-chemical" properties, as measured by electronegativity and ionization potential, the type of bonding between two elements becomes increasingly ionic.

The term *compound*, as applied to many intermetallic substances, has a broader meaning than it usually does outside the domain of alloy chemistry. In the first place, metals often appear to have unusual oxidation states, e.g. in stoichiometric compounds such as those of the Cr₃Si type. Secondly, many intermetallic phases (e.g. σ phases) have variable composition; such a phase retains its identity as a substance of fixed crystal structure (although the crystal dimensions may vary somewhat) over a range of composition.

Thus the usual ideas of compound formation have to be modified in this area of chemistry⁶³. Covalency and electrovalency, respectively electron-pair sharing and electron transfer, are not very relevant. Instead, compositions have to be interpreted on the basis of radius ratios, electron : atom ratios, etc.

TABLE 8. SIGMA PHASES IN BINARY CHROMIUM ALLOYS^{61, 64a}:
STRUKTURBERICHT TYPE D8_b (TETRAGONAL)

<i>B</i>	<i>B</i> (atom %)	r_A/r_B	Electron : atom ratio	<i>T</i> (°C)
Mn ^{a, b}	76–84	0.98	6.76–6.84	1000
Tc	55–75	0.94	6.55–6.75	700
Re ^{a, b}	~ 63	0.93	~ 6.63	1200
Fe ^{a, b}	50–56	1.01	7.02–7.14	600
Ru ^b	32–35.5	0.96	~ 6.68	1200
Os	~ 40	0.95	~ 6.75	1000–1300
Co ^a	37–42	1.02	7.11–7.26	1200

^a Phase diagram in ref. 57.

^b Phase diagram in ref. 58.

There appears to be no one unifying principle correlating the compositions and structures of the great number of intermetallic phases formed in binary alloy systems. However, a large fraction of the total number belong to a quite limited number of types. When the intermetallic phases are grouped according to composition and structure some factors operative in determining their formation become apparent. Three important families are considered in the following: the σ phases (berthollides), the Laves phases (daltonides) and compounds of the Cr₃Si type (daltonides) (Tables 8–10).

⁶⁰ I. I. Kornilov, *The Chemistry of the Metallides*, Consultants Bureau, New York (1966): (a) p. 2; (b) p. 20.

⁶¹ J. H. Wernick, "Topologically Close-packed Structures", in ref. 59, p. 197.

⁶² F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 2nd edn. (1966), pp. 31, 100.

⁶³ W. Hume-Rothery, *Electrons, Atoms, Metals and Alloys*, Dover, New York, 3rd edn. (1963), chaps. 36–39.

⁶⁴ M. V. Nevitt, "Alloy Chemistry of Transition Elements", in *Electronic Structure and Alloy Chemistry of the Transition Elements*, Interscience, New York (1963): (a) p. 105; (b) p. 146; (c) p. 123.

Electronic factors are operative in formation of several types of phases of variable composition such as the σ phases^{61, 64a} (σ , Strukturbericht type $D8_8$, tetragonal)⁶⁵. This evidence includes their systematic absence from certain systems, i.e., in the first, second and

TABLE 9. BINARY LAVES PHASES CONTAINING CHROMIUM^{60b, 61, 64b}

Compound	c (Å)	a (Å)	c/a	Electron : atom ratio	r_A/r_B	Type ^a
CrBe ₂ ^{b, c}	6.975	4.285	1.638	3.33	1.136	C14
NbCr ₂ ^c		6.990		5.67	1.145	C15
TaCr ₂ ^{b, c}		6.979		5.67	1.144	C15 ^d
TaCr ₂	8.062	4.925	1.637	5.67	1.144	C14
TiCr ₂ ^b		6.943		5.33	1.140	C15 ^d
ZrCr ₂ ^b	8.279	5.089	1.627	5.33	1.250	C14 ^d
ZrCr ₂		7.193		5.33	1.250	C15
HfCr ₂	8.237	5.067	1.625	5.33	1.232	C14
HfCr ₂		7.011		5.33	1.232	C15

^a C14, MgZn₂ type (hexagonal); C15, MgCu₂ type (cubic).

^b Phase diagram in ref. 57.

^c Phase diagram in ref. 58.

^d Low temperature modification.

third transition series, (Cr,Ni) σ , (Mo,Pd) σ and (W,Pt) σ respectively are missing, and no σ phase is formed by any combination of a chromium group and a nickel group metal.

Although there seems to be little doubt of the dependence of formation of σ phases on electronic factors, there is only a rough correlation with the electron concentration (ratio of electrons outside filled shells to number of atoms). For forty-five binary sigma phases^{64a}, the ratio is 5.6 to 7.6 with two exceptions for which it is about 4.5. In the chromium σ phases, the electron : atom ratio varies within narrower limits (Table 8). The ratios of the radii of the atoms (r_A/r_B) are close to 1 for the chromium compounds; in general, large differences in atomic sizes of the A and B components are not conducive to σ phase formation.

The Laves phases include three crystal types⁶¹: C15, MgCu₂ type (cubic); C14, MgZn₂ type (hexagonal); C36, MgNi₂ type (hexagonal). These phases are structure types that appear to depend on both packing considerations and electronic properties^{60b, 61, 64a, 66}. The structures are related by stacking of double layers in different sequences.

A determining factor in formation of Laves phases is the relative sizes of the constituent atoms⁶¹. The ideal ratio of atomic radii is 1.224; this is based on a hard-sphere model, A atoms touching A atoms and B atoms touching B atoms. The value of r_A/r_B calculated from the atomic radii of the pure metals forming Laves phases ranges from 1.05 to 1.68. However, the *effective* radius ratio is close to 1.225 since the A and B atoms, which have a wide range of Goldschmidt radii, contract or expand to achieve the effective ratio; the A atom must be larger than the B atom and the radius ratio must be close to 1.225.

⁶⁵ C. J. Smithells, "Crystal Chemistry", in *Metals Reference Book*, 1, Plenum Press, New York, 4th edn. (1967), p. 181.

⁶⁶ B. W. Roberts, "Superconductive Properties", in ref. 59, p. 598.

TABLE 10. Cr₃Si TYPE PHASES IN BINARY
CHROMIUM ALLOYS^{64c, 67};
STRUKTURBERICHT TYPE A15 (CUBIC)

Compound	<i>a</i> (Å)	<i>r</i> _A / <i>r</i> _B
Cr ₃ Si ^{a, b}	4.550	0.972
Cr ₃ Ru ^b	4.683	0.957
Cr ₃ Os	4.677	0.948
Cr ₃ Rh	4.656	0.953
Cr ₃ Ir	4.668	0.945
Cr ₃ Pt ^a	4.706	0.924
Cr ₃ Ga	4.645	0.909
Cr ₃ Ge	4.623	0.936

^a Phase diagram in ref. 57.

^b Phase diagram in ref. 58.

A considerable number of compounds belong to the Cr₃Si type (cubic, type A15)^{64c, 67}. This is the principle type for composition A₃B in which A is a metal of the titanium, vanadium, or chromium group, and B is an element of the manganese, iron, cobalt, nickel, copper, aluminum, silicon, or phosphorus group. Atomic size is an important factor in formation of these phases. The radius ratio *r*_A/*r*_B for fifty-four Cr₃Si type compounds peaks at 1 and all but eight of the ratios are within 10 per cent of unity⁶⁷. For compounds in which A is an element from the vanadium or chromium group and B is a metal from the iron, cobalt, nickel, or copper group, the Cr₃Si structure is almost as efficient in space filling as the structures of the pure metals and the atoms of these elements have about the same effective volumes in the Cr₃Si type phases as in the structures of the pure metals.

In addition to the binary intermetallic compounds of chromium listed herein, there are of course numerous others. Compound formation apparently has not been observed in the systems Cr–X in which X is one of the following^{57–59}: Li, Sc, Y, lanthanides (La–Lu), Th, U, Pu, V, W, Cu, Ag, Cd, Hg, Sn, Pb, Bi.

2.2. BINARY COMPOUNDS OF CHROMIUM WITH NONMETALS^{68–70*}

In this section compounds of chromium with hydrogen and with the nonmetallic elements of periodic groups IIIA, IVA, VA and VIA (except oxygen) are considered (Table 11). Compounds of chromium with these nonmetallic elements often contain chromium in what appear to be anomalous oxidation states and have properties which set

* These are basic references containing data pertaining to all systems discussed in this section. The page numbers refer to their excellent indexing of all compounds and systems covered.

⁶⁷ M. V. Nevitt, "Miscellaneous Phases of Fixed Stoichiometry", in ref. 59, p. 217.

⁶⁸ M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York (1958), pp. ix–xvi.

⁶⁹ R. P. Elliott, *Constitution of Binary Alloys, First Supplement*, McGraw-Hill, New York (1965), pp. ix–xxx.

⁷⁰ J. H. Westbrook (ed.), *Intermetallic Compounds*, John Wiley, New York (1967), pp. 639–663.

TABLE 11. BINARY COMPOUNDS OF CHROMIUM WITH NONMETALLIC ELEMENTS⁶⁸⁻⁷⁰

Compound	Structure	Crystal parameters (Å)			Melting point (°C)	References
		<i>a</i>	<i>b</i>	<i>c</i>		
CrH	hcp	2.727		3.441		71
CrH ₂	fcc	3.861				
Cr ₄ B ^a	Orthorhombic	4.26	7.38	14.71	1750	72(a), 73, 74, 75(a)
Cr ₂ B ^b	Tetragonal	5.18		4.31	1890	
Cr ₃ B ₃	Tetragonal	5.46		10.64	2000	
CrB	Orthorhombic	2.96	7.81	2.94	2050	
Cr ₃ B ₄	Orthorhombic	2.99	13.02	2.95	1950	
CrB ₂	Hexagonal	2.97		3.07	~ 2200	
Cr ₂₃ C ₆ ^c	Cubic	10.638			1550 (dec.)	72(a), 73, 74, 75(b), 76
Cr ₇ C ₃ ^d	Hexagonal	13.98		4.52	1665	
Cr ₃ C ₂	Orthorhombic	2.821	5.52	11.46	1895	
Cr ₃ Si ^{a, e}	Cubic	4.56			~ 1710	72(c), 73, 75(c)
Cr ₅ Si ₃	Tetragonal				~ 1600	
CrSi	Cubic	4.62			~ 1600	
CrSi ₂	Hexagonal	4.422		6.351	~ 1550	
Cr ₃ Si ₂ ^e	Tetragonal	9.16		4.64		
Cr ₂ N ^a	Hexagonal	2.74		4.45	1650	72(d), 73, 75(d), 77, 78
CrN	Cubic	4.14			dissociates, 1500	
Cr ₃ P ^{e, f}	Tetragonal	9.13		4.56		72(e), 74, 75(e)
Cr ₂ P						
CrP	Orthorhombic	5.36	3.11	6.02		
CrP ₂						
Cr ₂ As	Tetragonal	3.61		6.33		74, 75(f)
Cr ₃ As ₂ ^g	Tetragonal					
CrAs	Orthorhombic	3.49	6.22	5.74		
CrS ^h	Monoclinic	3.83	5.91	6.09	~ 1550	72(f), 75(g)
Cr ₇ S ₈	Hexagonal	3.46		5.76		
Cr ₅ S ₆	Hexagonal	5.98		11.51		
Cr ₃ S ₄ ⁱ	Monoclinic	~ 5.97	~ 3.43	~ 11.36		
Cr ₂ S ₃ ^j	Hexagonal	5.94		11.19		
Cr ₂ S ₃	Rhombohedral	5.94		16.79		
CrSe	Hexagonal	3.71		6.03		72(g), 75(h)
Cr ₇ Se ₈						
Cr ₃ Se ₄ ^k	Monoclinic	6.32	3.62	11.77		
Cr ₂ Se ₃						
CrTe						72(g), 75(i)

^a Phase diagram in ref. 69.^b Isomorphous with Fe₂B.^c Phase diagram in ref. 68.^d Isomorphous with Mn₇C₃.^e Isomorphous with Cr₃Ge₂.^f Isomorphous with M₃P (M = V, Mn, Ni, Fe).^g Ferromagnetic.^h $\beta = 101^\circ 36'$, paramagnetic.ⁱ $\beta = 91^\circ 9'$ to $91^\circ 38'$.^j Paramagnetic.^k $\beta = 91^\circ 28'$.

them off as a group quite analogous to the intermetallic compounds. In fact, some authorities consider compounds of these two types examples of one class^{68-70, 73}, sometimes given the name "metallides"⁷³. In the chemistry of these compounds, Hagg's rule is very useful, i.e. if the ratio of the radius of the nonmetal (r_n) to the radius of the metal (r_m) does not exceed 0.59, interstitial phases with simple crystal structures are formed^{72a}.

Transition metal hydrides generally have conductivities and magnetic and other properties typical of metals⁷¹. During electrodeposition of Cr from CrO_3 solutions, CrH (hcp) and CrH_2 (fcc) may be formed. The composition CrH_2 is not certain.

Unusual physicochemical properties of transition metal borides arise from the presence of the unfilled electron shells. The ratios r_n/r_m for borides of transition metals are always greater than 0.59 and so such borides are intermediate between interstitial phases and intermetallic compounds (Hagg's rule). Of the five types of borides^{72a}, four include chromium borides, as follows: those with isolated boron atoms (Cr_2B , Cr_4B); those with chains of boron atoms ($\delta\text{-CrB}$); those with double chains of boron atoms (Cr_3B_4); those with networks of boron atoms in a hexagonal two-dimensional lattice and metal atoms in an hcp lattice (Cr_2B_5). Chromium borides may be prepared by, for example, reduction of chromium oxide with boron carbide, reaction of boron with Cr_2O_3 , and electrolysis of fused mixtures of borate and chromium oxide. They are solid refractory compounds with metallic conductivity.

The *d*-transition metal carbides⁷⁶ are metallic in nature. Most simple carbides are interstitial phases^{72b}. They are characterized by high hardness, refractoriness, heat resistance and chemical resistance. Chromium carbides may be made by reaction of chromium with carbon or of Cr_2O_3 with C *in vacuo* or in a hydrogen atmosphere. They are oxidized in air at about 600°C.

Transition metals form metal-like silicides which are characterized by metallic metal-silicon bonds and covalent silicon-silicon bonds^{72c}. As the number of silicon atoms increases there is a change from structures characterized by isolated silicon atoms (e.g. in M_3Si phases, M = metal) to those having isolated pairs, chains, layers (e.g. in CrSi_2) and three-dimensional silicon atom frameworks. The chromium silicides are prepared by reaction of the elements at high temperatures or by reduction of $\text{Cr}_2\text{O}_3\text{-SiO}_2$ mixture with aluminum in the presence of copper. They are quite inert chemically.

Transition metal nitrides⁷⁷ are refractory substances with metallic properties such as high thermal conductivity and electrical conductivity. Most of them satisfy the requirement of Hagg's rule, i.e. $r_n/r_m \leq 0.59$. They are thus interstitial phases (products resulting from insertion of nitrogen atoms into the metal crystal lattices). Nitrides of this type have broad

⁷¹ K. M. Mackay, *Hydrogen Compounds of the Metallic Elements*, Spon, London (1966), pp. 45, 52, 85.

⁷² G. V. Samsonov (ed.), *Handbook of the Physicochemical Properties of the Elements*, Plenum Press, New York (1968): (a) pp. 738, 743; (b) pp. 746, 752; (c) pp. 754, 760; (d) pp. 764, 775; (e) pp. 778, 786; (f) pp. 810, 822; (g) pp. 828, 834.

⁷³ I. I. Kornilov, *The Chemistry of the Metallides*, Consultants Bureau, New York (1966), pp. 23-27.

⁷⁴ C. J. Smithells, "Crystal Chemistry", in *Metals Reference Book*, 1, Plenum Press, New York, 4th edn. (1967), p. 155.

⁷⁵ J. Amiel, in *Nouveau Traité de Chimie Minérale*, 14, Masson et Cie, Paris (1959); (a) p. 387; (b) p. 361; (c) p. 380; (d) p. 338; (e) p. 347; (f) p. 356; (g) p. 311; (h) p. 332; (i) p. 335.

⁷⁶ E. K. Storms, "The Chromium-Chromium Carbide System", in *The Refractory Carbides*, Academic Press, New York (1967), pp. 102-121.

⁷⁷ J. Juza, "Nitrides of Metals of the First Transition Series", in *Advances in Inorganic Chemistry and Radiochemistry*, 9, Academic Press, New York (1966), p. 81.

⁷⁸ F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, 2, Academic Press, New York, 2nd edn. (1965), p. 1347.

regions of homogeneity (i.e. they are berthollides). Methods for preparing chromium nitrides include: reaction of chromium borides with ammonia; heating chromium in N_2 or NH_3 ⁷⁸; Cr_2N can also be obtained by heating $CrCl_3$ in gaseous NH_3 . While CrN is stable toward water, acids and alkalis, Cr_2N is not so chemically stable.

Chromium belongs to the group of transition metals having a considerable degree of completeness and high energy state of the d -shell, and its phosphides have a high value of Hagg's ratio^{72e}. They are characterized by pairs, chains, etc., of phosphorus atoms. The chromium phosphides can be made by heating chromium with phosphorus *in vacuo* in quartz ampoules, electrolyzing melts of phosphates and chromium oxide and by reaction of chromium halogen compounds with phosphorus compounds or phosphorus vapor.

Chromium arsenides are formed when chromium is heated with arsenic in an inert atmosphere. Reports of these compounds are not numerous, and what little information exists is not very recent.

Many transition-metal sulfides, including the chromium sulfides, are berthollides^{72f}. They can be synthesized by heating chromium powder with sulfur in evacuated ampoules or by reaction of $CrCl_3$, Cr_2O_3 , or Cr with H_2S . The lower sulfides are made by thermally decomposing the higher sulfides. The sulfide CrS is found in nature (Mexico) as *daubrelite*; it is presumably of meteoritic origin.

Related to the sulfides are the thiochromites^{75g}, e.g. sodium thiochromite, $NaCrS_2$. Several thiochromites of the formula MCr_2S_4 have been described ($M = Cu, Hg, Fe, Sn, Co, Zn, Pb, Ni, Cd, Mn$).

Transition metal selenides and tellurides are isomorphous with the corresponding sulfides. Like the sulfides, they are berthollides. They have high melting points ($> 2200^\circ$) and are relatively stable chemically. They are made by reaction of chromium with selenium or tellurium at high temperature.

2.3. CHROMIUM COMPOUNDS OF π -ACCEPTOR LIGANDS⁷⁹⁻⁸³

A remarkable property of the d -group transition elements is their capacity for forming complexes with many neutral compounds that stabilize low oxidation states of the metal, which may be zero or even negative. Low oxidation states imply high electron density on the metal which, in the compounds under discussion, can be delocalized into the vacant orbitals of the ligands (" π acidity"). Among the π -acceptor ligands are carbon monoxide, nitric oxide, isocyanides, substituted phosphines, arsines and stibines, ligands containing 1,2-dithioketone or 1,2-dithiolene groups and some aromatic amines.

The structure of complexes of π -acceptor ligands differs basically from that of the organometallic complexes of transition metals (discussed in the following section) in which low oxidation states are also stabilized. The π -acceptors bond to metals via σ orbitals and

⁷⁹ F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 2nd edn. (1966), chap. 27; (a) pp. 750-751; (b) p. 756.

⁸⁰ H. A. Skinner, "The Strengths of Metal-to-Carbon Bonds", in *Advances in Organometallic Chemistry*, 2, Academic Press, New York (1964): (a) p. 86; (b) p. 95.

⁸¹ R. B. King, "Reactions of Alkali Metal Derivatives of Metal Carbonyls and Related Compounds", in *Advances in Organometallic Chemistry*, 2, Academic Press, New York (1964), p. 182.

⁸² T. A. Manuel, "Lewis Base-Metal Carbonyl Complexes", in *Advances in Organometallic Chemistry*, 3, Academic Press, New York (1965): (a) p. 182; (b) p. 191.

⁸³ F. Calderazzo, R. Ercoli and G. Natta, "Metal Carbonyls: Preparation, Structure and Properties", in *Organic Syntheses via Metal Carbonyls*, 1, Interscience, New York (1968); (a) p. 28; (b) p. 38; (c) p. 45; (d) p. 147.

manifest their π acidity by means of π orbitals whose nodal planes include the axis of the σ bond; in the organometallic complexes, however, π orbitals are utilized for both donation and back-acceptance of electron density from the metal. In these complexes, therefore, the metal is not in the molecular plane of the ligands (see Fig. 1); in the carbonyls and related complexes, the metal is situated on the axis of a linear ligand and in the plane of a planar ligand.

What distinguishes the complexes of π -acceptor ligands from the Werner complexes is the low oxidation state of the metal which reflects the nature of the bonding. Although σ -bonding is involved in both types of compound, the ligands in many Werner complexes

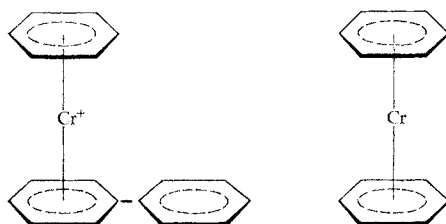


FIG. 1. π -Bonded organochromium compounds.

(Reprinted from ref. 79, p. 770, © 1966, by permission of John Wiley & Sons Inc.)

lack the necessary orbitals for the back-donation of electron density characteristic of the π -acceptor ligands, and so the metals in these complexes display their "normal" oxidation state (2+ and 3+ for chromium).

It should be emphasized, however, that in some Werner complexes there may be considerable π bonding. The cyanide ion, for example, produces a larger ligand field splitting Δ than any other ligand. This is certainly not due to any unusual bonding capability of the particular lone pair of electrons of this ligand; what gives it its exceptional high coordinating tendency is additional bonding resulting from a pair of normally unoccupied anti-bonding π orbitals of the right symmetry to combine with t_{2g} orbitals in octahedral complexes. Thus CN^- forms not only the complex anion $[\text{Cr}(\text{CN})_6]^{3-}$, in which Cr has one of its "normal" oxidation states, 3+, but also the complex $\text{K}_3[\text{Cr}(\text{CN})_4]$ in which the π -acceptor characteristic of CN^- makes possible the low oxidation state 1+ for Cr.

Some molecules characterized by delocalized π orbitals also have acceptor capacity. These include the heterocyclic aromatic amines such as pyridine, 2,2'-dipyridyl and 1,10-phenanthroline. The complete series of complexes $[\text{Cr}^x(\text{dipy})_3]^x$, x having the values 3+, 2+, 1+ and 0, is known (dipy=2,2'-dipyridyl). The extremes of the series, $[\text{Cr}^{3+}(\text{dipy})_3]^{3+}$ and $[\text{Cr}^0(\text{dipy})_3]^0$, are quite typical examples of Werner complexes and π -acceptor type complexes, respectively.

There are also compounds that are mixtures of these types, e.g. $[\text{Cr}(\text{CO})_a(\text{NH}_3)_b]$ ($a=5, 4, 3$; $b=1, 2, 3$). As NH_3 ligands are substituted for CO molecules, a smaller number of the latter have to accomplish the function of withdrawing electron density from the metal, since the NH_3 has no orbitals for this.

In the development of this field of chemistry, the "effective atomic number rule" or "rare gas rule" has been extremely useful; according to this rule, the number of electrons of the metal plus the number contributed by the ligands will equal the number of electrons of the succeeding rare gas. This reflects the tendency of the metal atom to use its nd , $(n+1)s$ and $(n+1)p$ valence orbitals to the maximum extent in forming bonds with the ligands. The formulas of many compounds have been predicted by this rule, which has

been most useful in connection with metal carbonyls, nitrosyls and isonitriles and their substitution products. There are, of course, numerous exceptions, such as the dipyriddy and dithio-olefin complexes.

For the carbonyls the rule works as follows. Each terminal CO contributes two electrons; each bridging CO contributes one electron to each of the bridged atoms; if there is a metal-metal bond, one electron of the pair is considered as belonging to each atom. Thus the electron count is 36 (krypton configuration) for $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ (Fe 26 electrons; Cr 24 electrons).

The rule at least formally accounts for the facts that transition metals of even atomic number such as Fe, Cr, Mo and W form monomeric hexacarbonyls, while those of odd atomic number (Co, Mn) do not. For a monomeric carbonyl of Co (27 electrons) the numbers of electrons associated with a Co atom would be 35 for a tetracarbonyl and 37 for a pentacarbonyl. What is formed is the dimer $\text{Co}_2(\text{CO})_8$ with a Co-Co bond group; the number of electrons associated with each Co atom is 36.

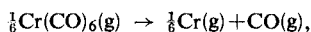
The numbers of electrons contributed by various ligands are as follows^{82a}: *one electron*: $\cdot\text{H}$, $\cdot\text{Cl}$, $\cdot\text{I}$, $\cdot\text{CH}_2\text{R}$, $\cdot\text{COR}$, $\cdot\text{CF}_2\text{R}$, $\cdot\text{SnR}_3$; *two electrons*: CO, NR_3 , PR_3 , SbR_3 , OR_2 , SR_2 , Cl^- , Br^- , I^- , CN^- , H^- ; *three electrons*: NO, $\cdot\text{PR}_2$, $\cdot\text{AsR}_2$, $\cdot\text{SR}$ (R = organic radical).

2.3.1. Chromium Carbonyls

Chromium hexacarbonyl, $\text{Cr}(\text{CO})_6$, was first prepared in 1926^{83a} by the reaction of CrCl_3 with phenylmagnesium bromide and CO in ether (4° and 1 atm pressure), followed by hydrolysis of the product⁸⁴. Although many attempts to improve the procedure were made, results with this method have been erratic. The course of the reaction is strongly solvent-dependent; labile solvated phenyl chromium compounds are intermediates in the formation of $\text{Cr}(\text{CO})_6$.

Acceptable procedures comprise reaction of CO (100–300 atm pressure) with a chromium halide in suspension in a solvent such as benzene ether at 140 – 150° ; various reducing agents have been used including aluminum powder^{83a} (in the presence of AlCl_3) and lithium aluminum hydride. Another procedure^{83a} reported to give good yields comprises reducing chromium compounds (e.g. anhydrous Cr(III) acetate, Cr(III) acetylacetonate) with Mg in anhydrous pyridine containing small amounts of iodine or organic halogen compounds (130 – 180° , 100–200 atm). The essential feature is the metal-pyridine combination; no chromium carbonyl was formed in the absence of pyridine.

Chromium hexacarbonyl is a colorless hydrophobic solid with low solubility in organic solvents such as hydrocarbons and tetrahydrofuran. It melts at 130° (with decomposition)^{80a}, ^{83b}. Some of its thermodynamic properties are as follows (kilocalories per mole): heat of combustion^{80a}, ^{83b}, -443.1 ; heat of formation^{80a}, ^{83b}, -257.6 (c), -240.4 (g); heat of vaporization^{80a}, ^{83b}, 16.57 – 18.2 ; heat of atomization^{80b}, 1718.2 . The mean dissociation energy, Cr-C bond,



is 27.1 – 29.5 kcal^{80b}, ^{83b}. Chromium carbonyl is octahedral. The interatomic distances (Å) are: Cr-C, 1.92; C-O, 1.16, 1.15^{83c}.

Chromium carbonyl is not attacked by concentrated HCl, reacts slowly with H_2SO_4 and is rapidly decomposed by HNO_3 ^{83d}. It is quite resistant to attack by I_2 and Br_2 but

⁸⁴ B. B. Owen, J. English, Jr., H. G. Cassidy and C. V. Dundon, *Inorg. Syn.* 3, McGraw-Hill, New York (1950), p. 156.

is oxidized to CrCl_3 by Cl_2 . In comparison with molybdenum hexacarbonyl, chromium carbonyl is exceptionally unreactive; suspended in liquid SO_3 , $\text{Cr}(\text{CO})_6$ is unaffected even at 160° while $\text{Mo}(\text{CO})_6$ is oxidized at -10° to $\text{MoO}(\text{CO})_4(\text{SO}_3)_2$. Chromium carbonyl is oxidized by carboxylic acids and β -diketones. Conversion of $\text{Cr}(\text{CO})_6$ to the β -diketonate requires a temperature of about 120° .

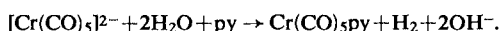
The anion $[\text{Cr}(\text{CO})_5]^{2-}$ is produced by reduction of $\text{Cr}(\text{CO})_6$ with Na, Li, Ca or Ba in liquid ammonia^{81, 83d}, or by sodium amalgam in tetrahydrofuran or diglyme. It has been directly prepared by reduction of CrCl_3 with Na in diglyme or tetrahydrofuran under CO pressure⁸¹. Other anions obtained by reduction of $\text{Cr}(\text{CO})_6$ are $[\text{Cr}(\text{CO})_5]^{2-}$, $[\text{CrH}(\text{CO})_5]^-$, $[\text{Cr}_2\text{H}(\text{CO})_{10}]^-$ and $[\text{Cr}_3(\text{CO})_{14}]^{2-}$; when NaBH_4 is used as the reducing agent, $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ is the product^{83d}.

2.3.2. Derivatives of Chromium Carbonyl^{82, 85, 86}

Thousands of compounds are known that can be made by displacing CO molecules from metal carbonyls by other ligands, or can be regarded formally as in this class even though prepared by indirect methods. Most of the ligands have, like CO, both σ -donor and π -acceptor properties. Some ligands, such as ethers and amines, can act only as donors since they bond through atoms (N, O, etc.) lacking low-lying empty orbitals. Phosphines and arsines have acceptor abilities due to empty d orbitals in the phosphorus and arsenic atoms. The ring systems in such unsaturated heterocyclic compounds as 2,2'-dipyridyl have acceptor properties.

If the CO molecules are displaced by ligands that are less capable as acceptors, more and more of the function of withdrawing electron density from the metal atom will be imposed on the remaining ligands and this limits the number of molecules of such ligands that can be incorporated into the substituted carbonyl. In $\text{Cr}(\text{CO})_6$, the electrons are distributed among the six identical ligands for a maximum metal-carbon bond order of 1.5. If the CO molecules are replaced by ligand L having no acceptor properties the limiting composition is $\text{Cr}(\text{CO})_3\text{L}_3$ in which the hypothetical maximum bond order of 2.0 is attained^{82b}.

The halogeno metal carbonyls may be prepared by reaction of the metal halides with CO at high pressure or oxidation of the metal carbonyl with halogens. Other substituted carbonyls are prepared by the following methods^{86a}: direct displacement of CO from the metal carbonyl (ultraviolet radiation sometimes promotes the displacement); displacement of CO by some ligand L_1 to form an intermediate mixed complex followed by displacement of L_1 by the desired ligand L_2 (useful particularly when direct displacement of CO by L_2 would require excessively drastic conditions); reaction of carbonyl metallate ion with ligand, e.g.:



A "spectrochemical series" for π -bonding ligands has been established on the basis of infrared studies⁸⁷. When two of the CO groups in $\text{Co}(\text{CO})_3\text{NO}$ are replaced by other ligands, the remaining CO and NO compete for the electron density back-donated from the filled metal orbitals into the vacant antibonding ligand π orbitals. When the charge

⁸⁵ F. Calderazzo, "Halogeno Metal Carbonyls and Related Compounds", in *Halogen Chemistry*, 3, Academic Press, New York (1967), p. 383.

⁸⁶ G. R. Dobson, I. W. Stolz and R. K. Sheline, "Substitution Products of the Group VIB Metal Carbonyls", in *Advances in Inorganic Chemistry and Radiochemistry*, 8, Academic Press, New York (1965): (a) p. 22; (b) p. 24; (c) pp. 28, 34, 36.

⁸⁷ W. D. Horrocks, Jr., and R. C. Taylor, *Inorg. Chem.* 2 (1963) 723; ref. 82(b).

density on the metal atom is increased by replacing CO by other ligands, the IR frequency of the bands corresponding to the remaining CO and NO groups is decreased. Thus the IR absorption frequencies are sensitive indicators of the back-donation of electron density—the greater the back-donation, the lower the C–O or N–O frequency. In the spectrochemical series (of twenty-seven ligands), NO and CO have the greatest ability to withdraw charge from the central metal atom and diethylenetriamine the least⁸⁷.

TABLE 12. SOME SUBSTITUTED CHROMIUM CARBONYLS WITH SINGLY COORDINATING LIGANDS

Ligand	Formula ^a	<i>a</i>	<i>b</i>
Halogen ^b	Cr(CO) ₅ X (X = I, CN, NCS)	—	—
	Cr(CO) ₅ X [−] (X = Cl, Br, I, NCS)	—	—
	Cr ₂ (CO) ₁₀ X (X = I, NCS)	—	—
	Cr ₂ (CO) ₁₀ I [−]	—	—
Isonitrile ^c	Cr(CO) _a (CNR) _b (R = Me, ϕ)	5, 4, 3	1, 2, 3
	Cr(CO) ₃ (<i>p</i> -CN ϕ CH ₃) ₃	—	—
	Cr(CO) _a (<i>p</i> -CN ϕ OCH ₃) _b	5, 3	1, 3
Nitrile ^c	Cr(CO) _a (CH ₃ CN) _b	5, 4, 3	1, 2, 3
	Cr(CO) ₅ ϕ CN	—	—
Amine ^c	Cr(CO) _a (py) _b	5, 4, 3	1, 2, 3
	Cr(CO) ₅ ϕ NH ₂	—	—
	Cr(CO) _a (NH ₃) _b	5, 4, 3	1, 2, 3
Phosphine ^c	Cr(CO) _a (PR ₃) _b (R = Et, ϕ)	5, 4, 3	1, 2, 3
	Cr(CO) _a (P ϕ Et ₂) _b	4, 3	2, 3
	Cr(CO) _a (PCl ₃) _b	5, 4, 3, 2	1, 2, 3, 4
PCl ₃ ^c	Cr(CO) _a (PCl ₃) _b	5, 3	1, 3
Arsine ^d	Cr(CO) _a (As ϕ 3) _b	—	—
Stibine ^d	Cr(CO) ₅ Sb ϕ 3	—	—
SbCl ₃ ^c	Cr(CO) _a (SbCl ₃) _b	5, 3	1, 3
THF ^c	Cr(CO) ₅ THF	—	—

^a Me = CH₃; ϕ = C₆H₅; py = C₆H₅N; Et = C₂H₅; THF = tetrahydrofuran.

^b Ref. 85, p. 388.

^c Ref. 86, p. 24.

^d Ref. 82, p. 204.

TABLE 13. SOME SUBSTITUTED CHROMIUM CARBONYLS OF VARIOUS TYPES^a

Type	Formula ^b	Structural details
With polydentate ligands	Cr(CO) ₄ (aa)	aa = phen, dipy, en, 8-aminoquinoline, chd, C ₂ H ₄ (PEt ₂) ₂ , <i>o</i> - ϕ (PEt ₂) ₂ , diars, DTH
	Cr(CO) ₃ (aaa)	aaa = dien, triars, TTU
Heptacoordinated	Cr(CO) ₃ phenL ₃	L = NH ₃ , py
	[Cr(CO) ₂ (diars) ₂ X]X	X = Br, I
Polynuclear	[Cr(CO) ₂ (diars) ₂ X]X ₃	X = Br, I
	(CO) ₅ CrBCr(CO) ₅	B = <i>m</i> - ϕ (NH ₂) ₂ , <i>p</i> - ϕ (NH ₂) ₂ , 1,3,5- ϕ (NH ₂) ₃ , P ₂ Me ₄ , As ₂ Me ₄ , I
	(CO) ₄ Cr(PR ₂) ₂ Cr(CO) ₄	R = Me, Et
	(CO) ₃ Cren ₃ Cr(CO) ₃	

^a Phen, 1,10-phenanthroline; dipy, 2,2'-dipyridyl; en, ethylenediamine; chd, cyclohexane-1,2-diamine; Et, C₂H₅; ϕ , C₆H₅; diars, *o*-phenylenebis(dimethylarsine); DTH, 2,5-dithiahexane; dien, diethylenetriamine; triars, methylbis(3-propyldimethylarsine)arsine; py, pyridine; Me, CH₃; TTU, 3,6,9-trithiaundecane.

^b Ref. 86, pp. 28, 31, 34, 36.

Some typical substituted chromium carbonyls are listed in Tables 12 and 13. Although the compounds listed represent only a tiny fraction of the number that have been described,

they illustrate the wide range of composition possible in such compounds. Many more are listed in the reference cited and similar reviews.

2.3.3. Nitrosyl^{79a} and Cyano Complexes^{79a, 88}

Nitric oxide is isoelectronic with CO. The NO complexes may be regarded as containing the nitrosonium ion, NO^+ , resulting from loss of an electron from the neutral molecule NO to the metal (reducing its valence by one), with back-bonding to the NO analogous to the situation with CO. Thus NO in the nitrosyl complexes can be regarded as a 3-electron donor in applying the rare gas rule. Except for this difference, it resembles CO more closely than any other π -acceptor ligand. Many nitrosyl complexes have been reported, particularly those of Co, Ni, Fe, V, Mn and Pt. Reports of chromium nitrosyl complexes are nowhere near as numerous as those of other π -acceptor ligands⁸⁹. Apparently no simple chromium nitrosyl compound, such as a halide, has been prepared. Although CrNO reacts readily with $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ with formation of $\text{Mo}(\text{NO})_2\text{Cl}_2$ and $\text{W}(\text{NO})_2\text{Cl}_2$, no reaction with $\text{Cr}(\text{CO})_6$ occurs under similar conditions⁸⁹.

The nitrosyl cyano complex $\text{K}_3[\text{Cr}^{\text{I}}(\text{CN})_5\text{NO}] \cdot \text{H}_2\text{O}$ can be made by reduction of K_2CrO_4 with NH_2OH in a basic KCN solution⁸⁸. It has a magnetic moment of 1.9 B. It can be electrolytically reduced, in a solution of KCN and KOH, to $\text{K}_4[\text{Cr}^0(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$, which is weakly paramagnetic. In the complexes $[\text{Cr}(\text{NO})\text{L}_5]^x$ ($\text{L} = \text{CN}, \text{NH}_3, \text{H}_2\text{O}$) NO is present as NO^+ , as shown by e.s.r. data, and there is considerable back-donation. Some nitrosyl organometallic chromium compounds are listed in Section 2.4.

The complex $\text{trans}[\text{CrCINO}(\text{das})_2]^+$ is obtained by reaction of *o*-phenylene-bis(dimethylarsine)(das) and NO with anhydrous CrCl_2 ⁹⁰. The three compounds $\text{trans}[\text{MCINO}(\text{das})_2]\text{ClO}_4$ ($\text{M} = \text{Fe}, \text{Co}, \text{Cr}$) are isomorphous. The magnetic susceptibility of the chromium compound is 1.70 B (room temperature), which is close to the calculated value (1.73) for one unpaired electron with no orbital contribution. This complex is reduced by dithionite to the neutral compound $[\text{CrNOCl}(\text{das})_2]$, which is diamagnetic.

When $\text{K}_3[\text{Cr}^{\text{III}}(\text{CN})_6]$ or $\text{K}_3[\text{Cr}^{\text{I}}(\text{CN})_5\text{NO}]$ is heated in H_2 at 400° , $\text{K}_3[\text{Cr}(\text{CN})_4]$ is obtained⁹¹. Its effective magnetic moment is 2.52 B, which lies between the spin-only value for one unpaired electron and the high-spin value for five unpaired electrons for Cr(I) compounds; it is consistent with a structure involving bridging cyanide groups. The dark green diamagnetic compound $\text{K}_6[\text{Cr}^0(\text{CN})_6]$ is obtained by reducing $\text{K}_3[\text{Cr}(\text{CN})_6]$ with potassium in liquid ammonia. It reacts with CO to form $\text{K}_3[\text{Cr}(\text{CO})_3(\text{CN})_3]$. Reaction of $\text{Na}_2[\text{Cr}(\text{CO})_5]$ with NaCN forms the diamagnetic compounds $\text{Na}[\text{Cr}(\text{CO})_5\text{CN}]$ and $\text{Na}_2[\text{Cr}(\text{CO})_4(\text{CN})_2]$ ⁸⁸.

2.3.4. Dipyridyl and Isonitrile Complexes⁹²

Resembling 1,2-diamines such as ethylenediamine as a bidentate ligand, 2,2'-dipyridyl forms many Werner-type complexes with transition metal ions, including chromium, in their normal oxidation states. These compounds contain strong σ bonds, although there may be some π bonding. What distinguishes the dipyridyl complexes is that they can be

⁸⁸ B. M. Chadwick and A. G. Sharpe, "Transition Metal Cyanides and their Complexes", in *Advances in Inorganic Chemistry and Radiochemistry*, **8**, Academic Press, New York (1965), p. 94.

⁸⁹ F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.* **3** (1964) 1609.

⁹⁰ R. D. Feltham, W. Silverthorn and G. McPherson, *Inorg. Chem.* **8** (1969) 344.

⁹¹ S. F. Banks and J. Kleinberg, *Inorg. Chem.* **6** (1967) 1849.

⁹² F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965), p. 1361.

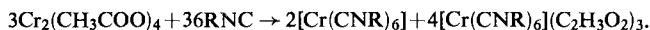
reduced to stable compounds with the metal in oxidation state 1, 0 or 1-. In connection with compounds of the types under discussion (carbonyls, etc.), formal oxidation states of the metals are not too significant and in fact sometimes more than one oxidation state can be arrived at depending on what assumptions are made.

With the dipyriddy transition metal complexes, some authorities have adapted the formalism of assuming that the dipyriddy is always neutral so that the oxidation state of the metal is equal to the charge of the complex. If this is so, π acidity of the dipyriddy results from absorption of electron density from the filled metal orbitals by the π^* anti-bonding orbitals of the aromatic rings.

The series of compounds containing Cr^{2+} , Cr^{1+} and Cr^0 can be obtained as follows⁹². All operations are conducted in a nitrogen atmosphere with deaerated liquids. The complex $[\text{Cr}^{\text{II}}(\text{dipy})_3](\text{ClO}_4)_2$ is obtained from a reaction mixture of $\text{Cr}(\text{II})$ and 2,2'-dipyriddy. A solution of this compound is reduced to $[\text{Cr}^{\text{I}}(\text{dipy})_3]\text{ClO}_4$ with Mg . Reduction of $[\text{Cr}^{\text{II}}(\text{dipy})_3]\text{ClO}_4$ (in tetrahydrofuran) with sodium produces $[\text{Cr}^0(\text{dipy})_3]$. Alternatively, this compound can be made by reaction of dipyriddy with $\text{Cr}_2(\text{CH}_3\text{COO})_4$; this is a disproportionation producing also $\text{Cr}(\text{II})$ and $\text{Cr}(\text{III})$ complexes.

A solution of the $\text{Cr}(\text{II})$ complex is oxidized by air to $[\text{Cr}(\text{dipy})_3]^{3+}$, which can be crystallized as the perchlorate (yellow crystals). The $\text{Cr}(\text{I})$ complex is indigo-blue. It is soluble in methanol, ethanol, acetone, and pyridine, but insoluble in water, benzene and ether. The solutions oxidize rapidly in air. The dry compound is spontaneously oxidized in air with evolution of heat and loss of dipyriddy. The $\text{Cr}(\text{O})$ compound is soluble in benzene, tetrahydrofuran, pyridine and dimethylformamide. The dry compound ignites in air to Cr_2O_3 .

The oxidation state zero for chromium can also be stabilized by isonitriles⁹³. Chromium-(II) acetate may be used as the starting material; the reaction is conducted in a nitrogen atmosphere:



The hexaphenylisonitrile compound⁹² is obtained as diamagnetic garnet red crystals, m.p. 178.5° , soluble in chloroform and benzene.

If CrX_2 ($\text{X} = \text{Cl}$ or Br) is used, the product is a $\text{Cr}(\text{II})$ complex, $[\text{Cr}(\text{CNR})_4\text{X}_2]$ ($\text{X} = \text{Cl}$, orange red; $\text{X} = \text{Br}$, olive brown)⁹². These compounds are paramagnetic (2.84 B, corresponding to Cr^{2+}). They are stable in air, insoluble in ether, alcohol and benzene, but soluble in methylene chloride and chloroform.

The difficulty of formation of the isonitrile complexes $[\text{M}^0(\text{CNR})_6]$ increases in the order $\text{Cr} < \text{Mo} < \text{W}$. This is the opposite of the order of ease of preparing the carbonyls, of which $\text{Cr}(\text{CO})_6$ is the most difficult to prepare.⁹³

2.3.5. Olefin Dithiol Complexes^{79b}

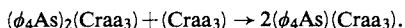
Numerous complexes of the ligands $\text{R}_2\text{C}_2\text{S}_2$ have been prepared⁹⁴. The chromium, molybdenum and tungsten complexes have the formulas $(\text{MS}_2\text{C}_2\text{R}_2)_z$. R may be, for example, CN , CF_3 or C_6H_5 ; z may be 3-, 2-, or 1- ($\text{R} = \text{CN}$) and 2-, 1- and 0 ($\text{R} = \text{CF}_3$, C_6H_5).

The complex $(\text{Craa}_3)^0$ (m.p. $210-215^\circ$, with decomposition, $\text{aa} = (\text{CF}_3)_2\text{C}_2\text{S}_2$) is prepared by reaction of the ligand with $\text{Cr}(\text{CO})_6$ in dry methyl cyclohexane. This is reduced to

⁹³ L. Malatesta, "Isonitrile Complexes of Metals", in *Progress in Inorganic Chemistry*, **1**, Interscience, New York (1959), p. 304.

⁹⁴ A. Davison and R. H. Holm, *Inorg. Syn.* **10**, McGraw-Hill, New York (1967), p. 8.

(Craa₃)²⁻ by hydrazine in ethanol; the complex is separated as ($\phi_4\text{As}$)₂(Craa₃) ($\phi = \text{C}_6\text{H}_5$; black needles; m.p. 193–194°, with decomposition). By reaction of these two complexes, the univalent anion is obtained:



The arsonium salt (black crystals) melts at 127.5–129°⁹⁴.

There is some controversy about the nature of these compounds. At one extreme is the idea that the oxidation state of the metal remains 3+ and the redox reactions involve only the ligands. At the other extreme is the assumption that the ligands remain unchanged while only the oxidation state of the metal changes. Some of the complexes (e.g. those of Ni) of the same ligand but different *z* are easily interconvertible by 1-electron changes that can be brought about either chemically or electrochemically.

2.4. ORGANOMETALLIC COMPLEXES OF CHROMIUM^{95–100}

In 1919, Hein isolated polyphenyl chromium complexes from the products of reaction of anhydrous CrCl₃ with phenylmagnesium bromide in ether^{96b}. The structure of these compounds was not known until 1954, when Zeiss and his colleagues showed that they are "sandwich" compounds with π -benzene ligands^{96b}. Similar compounds of chromium are formed with many other unsaturated compounds, including other aromatic compounds such as diphenyl and radicals such as cyclopentadienyl. Formation of such compounds is characteristic of all the *d*-group transition metals. In contrast with the complexes of π -acceptor ligands which form σ bonds with the metals and accept electron density into low-lying empty π orbitals, the π complexes utilize ligand π orbitals for both donation and back-acceptance.

Of the ligand and metal orbitals, only those having the same symmetry properties can combine to form molecular orbitals, and it is thus often possible to ascertain which combinations can result in bond formation^{96a}. Conventionally, the vertical axis (Fig. 1) is drawn coincident with the axis of symmetry and is designated the *z*-axis. With respect to rotation about this axis, the symmetry classification of the metal orbitals is as follows: σ , *s*, *d*_{z²}, *p*_z; π , *d*_{xy}, *d*_{yz}, *p*_y; δ , *d*_{x²-y²}, *d*_{xy}. The wave functions of the orbitals change sign as follows in rotation through 180° about the axis of symmetry: σ , none; π , once; δ , twice. The bonding of unsaturated hydrocarbon ligands to transition metals consists principally of two effects: (1) σ -donation from filled bonding molecular orbitals of the ligand into empty metal orbitals having σ -symmetry; (2) π interaction; the ligands may have donor or acceptor properties depending on whether the ligand orbitals are filled, or only partly filled.

The energies of the orbitals derived from the metal and ligand orbitals are not known from symmetry considerations alone, but must be experimentally determined (e.g. by

⁹⁵ F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 2nd edn. (1966), chap. 28.

⁹⁶ G. E. Coates, M. L. H. Green, P. Powell and K. Wade, *Principles of Organometallic Chemistry*, Methuen, London (1968): (a) chap. 5; (b) chap. 6.

⁹⁷ E. O. Fischer and H. Werner, *Metal π -Complexes*, 1, Elsevier, Amsterdam (1966).

⁹⁸ M. L. H. Green and P. L. I. Nagy, "Allyl Metal Complexes", in *Advances in Organometallic Chemistry*, 2, Academic Press, New York (1964).

⁹⁹ J. Birmingham, "Synthesis of Cyclopentadienyl Metal Compounds", in *Advances in Organometallic Chemistry*, 2, Academic Press, New York (1964).

¹⁰⁰ G. R. Dobson, I. W. Stolz and R. K. Sheline, "Substitution Products of Group VIB Metal Carbonyls", in *Advances in Inorganic Chemistry and Radiochemistry*, 8, Academic Press, New York (1965).

spectroscopic or magnetic measurements). Strong bonding results from a large overlap between orbitals of nearly the same energy. Ligand π -molecular orbitals and their possible interactions with metal orbitals are shown in detailed diagrams by Coates *et al.*^{96a}.

The "effective atomic number rule" or "rare gas rule" applies generally to these complexes as it does to the π -acceptor complexes previously discussed. It is sometimes stated as the "eighteen electron rule" since only the valence shell needs to be considered. The rule is applied as follows. The number of electrons in the valence shell of the uncomplexed metal atom is increased or decreased in accordance with the total charge on the metal complex, e.g.: Cr in a 1+ cation, $(6-1)=5$; in a neutral compound, $(6-0)=6$; in a 1- anion, $(6+1)=7$. To this is added the number of electrons formally contributed by the ligands.

The numbers of electrons contributed per molecule for some of these groups are as follows^{96a}: alkyl and aryl groups, one (as with $\cdot\text{Cl}$, $\cdot\text{CN}$, $\cdot\text{H}$, etc.); ethylene, two (as with CO); π -allyl, three (as with NO); cyclobutadiene, butadiene, four; π -cyclopentadienyl, five; benzene, cycloheptatriene, six; π -cycloheptadienyl, seven; cyclooctatetraene, eight.

Some applications of the rule are as follows. In dibenzenechromium, each benzene ring contributes six electrons and the number in the valence shell of the uncomplexed chromium atom is six, giving a total of eighteen. In $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_4]^+$, the chromium atom furnishes five $(6-1)$ electrons, four carbonyl groups contribute eight, and the cyclopentadienyl ligand contributes five, so the total is again eighteen. There are exceptions to the rule, of course, but it has been extremely useful in this area of chemistry.

The thermal stability of many organometallic compounds of the transition metals is rather low and it is thus desirable to use as mild reaction conditions as possible in preparing these compounds. Furthermore, organometallic compounds are unstable to attack by oxygen and many of them are oxidized at significant rates even at room temperature. It is consequently mandatory to carry out manipulations with these compounds *in vacuo* or in an inert atmosphere.

A general preparative method for metal carbonyls, olefin and arene complexes, etc. (complexes of metals in low oxidation states), comprises reducing an anhydrous metal halide in the presence of the ligand^{96a}. Thus $\text{Cr}(\text{CO})_6$ may be produced by reducing CrCl_3 with zinc amalgam under CO pressure; and reduction of CrCl_3 with Al in benzene in the presence of AlCl_3 produces $[(\pi\text{-C}_6\text{H}_6)_2\text{Cr}]^+(\text{AlCl}_4)^-$, which can be reduced to bis- π -benzenechromium by sodium dithionite in aqueous solution^{101, 102a}. The corresponding diphenyl and mixed phenyl-diphenyl complexes can be prepared similarly¹⁰¹. The neutral complexes can also be obtained by disproportionation of the cationic complexes in aqueous solution, but the reaction is incomplete and half the chromium is lost in the formation of oxidation products^{102a}.

Bisbenzenechromium(O), which is somewhat unstable exposed to the atmosphere, sublimates at 150° *in vacuo*, melts (under N_2) at $284\text{--}285^\circ$, and decomposes at 300° . It is insoluble in water, but somewhat soluble in benzene and similar solvents. The crystals are cubic (space group $Pa\bar{3}\text{--}T_h^6$). The compound is diamagnetic. Its heat of combustion (20°) is 1724 kcal/mole; its heat of formation (in the gas phase) from benzene and chromium is -58.3 kcal/mole (298°K)^{101a, 102a}.

Bisbenzenechromium(I) hydroxide is produced when air is bubbled through a reaction

¹⁰¹ F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, 2, Academic Press, New York, 2nd edn. (1965): (a) p. 1395; (b) p. 1375.

¹⁰² E. O. Fischer, *Inorg. Syn.*, McGraw-Hill, New York: (a) 6 (1960), p. 132; (b) 7 (1963), p. 136.

mixture of finely ground $(C_6H_6)_2Cr$ suspended in benzene and water^{102a}. From the aqueous phase, sparingly soluble salts of $[Cr(C_6H_6)_2]^+$ can be crystallized. The iodide (yellow crystals), for example, is paramagnetic, stable in air and somewhat soluble in water and alcohol. Analogous diphenyl and benzene-diphenyl complexes can be prepared^{101a}. Other salts readily prepared from the aqueous solution of the I^+ cations are the picrate, reineckate, perchlorate, and tetraphenylborate^{102a}.

TABLE 14. SOME π -BONDED ORGANOCHROMIUM COMPOUNDS

Type	Compound ^a	M.P. (°C)	Color
Allyl ^b	$Cr(C_3H_5)_3$	—	Deep red
	$CH_3(C_3H_4)CrCp(CO)_2$	118–121	Orange
	$CpICrCp(CO)_2$	74–75	Yellow
Cyclopentadienyl ^c	Cp_2Cr	173	Scarlet
	$CpCrX_2$ (X = Cl, Br, I)		Green or blue
	$CpCrBracac$	190 (dec.)	Green
	$CpCr(CO)_3H$	dec. 57–58	Yellow
	$CpCr(CO)_2(NO)$	67–68	Orange red
	$CpCr(NO)_2X$ (X = F, Cl, Br, I, CN, SCN)		
	$CpCr(NO)_2R$		
	(R = CH_3 , CH_2Cl , C_5H_5 , C_2H_5 , C_6H_5)		
	$[CpCr(CO)_4]BF_3$	—	Olive
	$[CpCr(NO)_2CO]PF_6$	—	Orange
Arene ^c	$CpCrC_6H_6$	227–229	Red
Arene carbonyl ^d	$C_6H_6Cr(CO)_2py$	—	Yellow
	$p-F_2\phi Cr(CO)_3$	111	Yellow
	$p-Cl_2\phi Cr(CO)_3$	88	Red
	$MtICr(CO)_2py$	—	Red
	$MtICr(CO)_2C_2H_4$	—	Red
	Naphthalene $Cr(CO)_3$	150–160 (dec.)	Yellow
	Anthracene $Cr(CO)_3$	189–192 (dec.)	Black
	Phenanthrene $Cr(CO)_3$	157–160	Red
	Chrysene $Cr(CO)_3$	129–130 (dec.)	Dark red
	Pyrene $Cr(CO)_3$	—	Red
Binuclear ^c	$[CpCr(CO)_3]_2$	163–168 (dec.)	Colorless
	$[Cp_2Cr][CpCr(CO)_3]$	190–193 (dec.)	Brown
	$[Cp_2Cr][CpCrCl_3]$	—	—
	$[Cp_2Cr(CO)_3]_2Hg$	—	—

^a Cp, cyclopentadienyl; Cpl, cyclopentenyl; acac, acetylacetonate; ϕ , phenyl; py, pyridine; Mtl mesitylene.

^b Ref. 98, p. 336.

^c Ref. 99, p. 391.

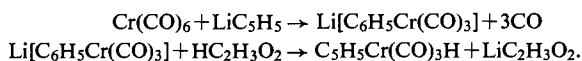
^d Ref. 100, pp. 47, 62.

Contrasting with these chromium compounds of the neutral aromatic molecules is the complex $Li_3[Cr(C_6H_5)_6] \cdot 2.5(C_2H_5)_2O$, containing the phenyl radical bonded to Cr(III). This complex is prepared by reaction of $Li(C_6H_5)$ with anhydrous $CrCl_3$. The yellow–orange crystals are soluble in ether, benzene and tetrahydrofuran. The compound is unstable in moist air and is completely hydrolyzed by water and alcohol^{101b}.

The π -cyclopentadienyl complexes constitute an important class of organochromium compounds. They may be prepared by a variety of methods, including the following^{98–100}: reaction of the cyclopentadiene ligand with the hexacarbonyl; reaction of an alkali metal cyclopentadienide with a chromium salt such as $CrCl_3$; reaction of the cyclopentadienyl Grignard reagent with a chromium salt; oxidation or reduction of a π -cyclopentadienyl

chromium complex prepared by one of the foregoing methods to put the metal in the desired oxidation state; displacement of cyclopentadienyl ligand with another ligand (anionic or neutral).

Frequently a π -bonded ligand such as the cyclopentadienyl group will stabilize a type of compound difficult or impossible to obtain otherwise. Examples of such compounds are the complex chromium hydrides¹⁰³. The cyclopentadienyl tricarbonyl hydride of chromium may be prepared, for example, by the following sequence of reactions in anhydrous dimethylformamide:



Another method comprises reaction of bis(cyclopentadienyl)chromium, $\text{Cr(C}_5\text{H}_5)_2$, with H_2 and CO at high pressure at 70° .

The bright yellow complex hydride is volatile, sensitive to oxidation, diamagnetic and soluble in organic solvents such as benzene and ether. At the melting point ($57\text{--}58^\circ$), hydrogen is evolved and $\text{C}_5\text{H}_5\text{Cr(CO)}_3$ is formed; this can be converted to the hydride by reduction with H_2 (150 atm, 70°).

Currently the chemistry of organometallic compounds is one of the most active fields of investigation; the rate at which new compounds are reported continually increases. In Table 14 are listed a few organometallic chromium compounds as an indication of the great variety of structures and composition that are possible.

2.5. OXIDATION STATE II

2.5.1. Anhydrous Chromium(II) Halides¹⁰⁴⁻¹⁰⁷

All four of the anhydrous Cr(II) halides are known. Some of their properties, as summarized by J. E. Fergusson¹⁰⁷ in a critical review, are listed in Table 15.

TABLE 15. CHROMIUM(II) HALIDES¹⁰⁷

Halide	Color	Thermal data, formation from elements, 298°K			Melting point ($^\circ\text{C}$)	Cr-X bond length ($\text{\AA}$)	Magnetic moment (B) at room temperature
		$-\Delta H^\circ$ (kcal/mole)	$-\Delta G^\circ$ (kcal/mole)	$-\Delta S^\circ$ (e.u.)			
CrF_2	Green	181, 182	170, 172	34	894	2 at 2.43 2 at 2.01 2 at 1.98	4.3
CrCl_2	White	92-97	84, 85	31-32	820-824	2 at 2.91 4 at 2.40	5.13
CrBr_2	White	81, 86		34	844	2 at 3.00 4 at 2.54	
CrI_2	Red-brown	38		37	868	2 at 3.24 4 at 2.74	

¹⁰³ B. L. Shaw, *Inorganic Hydrides*, Pergamon Press (1967), chap. 10.

¹⁰⁴ R. D. Peacock, "Some Fluorine Compounds of the Transition Metals", in *Progress in Inorganic Chemistry*, **2**, Interscience, New York (1960), p. 195.

¹⁰⁵ E. L. Muetterties and C. W. Tullock, "Binary Fluorides", in *Preparative Inorganic Reactions*, **2**, Interscience, New York (1965), pp. 241, 250, 268.

¹⁰⁶ J. D. Corbett, "Metal Halides in Low Oxidation States", in *Preparative Inorganic Reactions*, **3**, Interscience, New York (1966), pp. 7, 19, 27.

¹⁰⁷ J. E. Fergusson, "Halide Chemistry of Chromium, Molybdenum and Tungsten", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 228.

It is difficult to obtain CrF_2 in a pure form. With the older synthetic methods (reduction of CrF_3 with H_2 or reaction of HF with Cr , CrCl_2 , or CrS), the product is contaminated with starting materials or oxidation products. A product of satisfactory purity can be obtained in good yield with more recent methods¹⁰⁸, i.e. pyrolysis of $(\text{NH}_4)_3\text{CrF}_6$; disproportionation of CrF_3 (1100°); reduction of CrCl_3 with molten SnF_2 ; reduction of CrF_3 with Cr (1100°); oxidation of Cr with SnF_2 , BiF_3 , PbF_2 , CuF_2 or CdF_2 .

In the pyrolysis of $(\text{NH}_4)_3\text{CrF}_6$, CrF_3 is formed, part of which is reduced by H_2 , a product of the pyrolysis. At the high temperature (1100°) used, this disproportionates:



The investigations¹⁰⁸ leading to these methods uncovered a new compound, Cr(II, III) fluoride, of the approximate composition $\text{CrF}_{2.4}$. This can be made by heating ($800\text{--}900^\circ$) a mixture of CrF_2 and CrF_3 in a sealed platinum tube or by oxidizing CrF_2 with molten SnF_2 . Like CrF_2 , this double fluoride is so inert that it is difficult to analyze.

Chromium(II) chloride may be prepared by reduction of CrCl_3 with a stream of H_2 (containing HCl) at 500° , reaction of Cr with HCl at $1150\text{--}1200^\circ$, or reaction of dry HCl with an anhydrous Cr(II) compound such as $\text{Cr}_2(\text{CH}_3\text{COO})_4$ ^{109a, 110a}. It has also been prepared by reducing CrCl_3 with the stoichiometric quantity of Cr . In contrast with the unreactive CrF_2 , CrCl_2 is very hygroscopic, is easily oxidized, and dissolves in water to give a sky-blue solution. Anhydrous CrCl_2 can be sublimed *in vacuo*. Chromium(II) chloride absorbs gaseous NH_3 to form $\text{CrCl}_2 \cdot n\text{NH}_3$ ($n = 1\text{--}6$).

Anhydrous CrBr_2 is prepared by analogous methods^{109a}, i.e. reduction of CrBr_3 with H_2 in the presence of HBr and conversion of Cr(II) acetate to CrBr_2 by anhydrous HBr or acetyl bromide. It may also be made by oxidation of Cr in a $\text{Br}_2\text{--H}_2$ stream at $800\text{--}900^\circ$. Chromium(II) bromide is a white crystalline powder, rapidly oxidized in air. It is soluble in water. It is dimeric in the vapor state.

The iodide is generally prepared from the elements^{109a}. The product of the reaction between I_2 and Cr contains some CrI_3 ; the CrI_2 is purified by sublimation as it is formed; CrI_3 dissociates to CrI_2 at 500° . The leaflets of CrI_2 are brown-red. This compound is soluble in water and very sensitive to air and moisture. Pure chromium metal can be prepared by the dissociation of CrI_2 at $1100\text{--}1400^\circ$.

The chromium(II) halides have a distorted octahedral structure. There is a high degree of ionic character in the Cr--F bonds in contrast to the Cr--X bonds in the other dihalides, which are more covalent. The difluoride is isostructural with CuF_2 . In the double fluoride¹⁰⁸ the structure of each of the two components is the same as in the individual fluorides; the octahedra are joined through corners and edges.

These compounds illustrate one of the sharp contrasts between the chemistry of chromium and that of molybdenum and tungsten. Very few chromium compounds appear to have metal-metal bonding¹¹¹, which is common in the compounds of Mo and W in their

¹⁰⁸ B. J. Sturm, *Inorg. Chem.* **1** (1962) 665.

¹⁰⁹ F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965): (a) pp. 1336–1341; (b) pp. 1361–1370.

¹¹⁰ *Inorganic Syntheses*, McGraw-Hill, New York: (a) A. Burg, **3** (1950), p. 150; (b) J. H. Balthis, Jr. and J. C. Bailar, Jr., **1** (1939), p. 122; (c) M. R. Hatfield, **3** (1950), p. 148; (d) L. R. Ocone and B. P. Black, **8** (1966), p. 125; (e) M. Kranz and A. Witkowska, **6** (1960), p. 144; (f) D. G. Holah and J. P. Fackler, Jr., **10** (1967), p. 26; (g) D. Berman, G. Bokerman and R. W. Parry, **10** (1967), p. 35; (h) G. Schlessinger, **6** (1960), p. 18.

¹¹¹ M. C. Baird, "Metal-Metal Bonds in Transition Metal Compounds", in *Progress in Inorganic Chemistry*, **9**, Interscience, New York (1968), pp. 2, 23.

lower oxidation states. This gives rise to the characteristic "cluster" type compounds of Mo and W which are not formed by chromium. Probably the best criterion for the existence of metal-metal bonding is very short metal-metal interatomic distances approaching the values for the metals themselves as shown by X-ray investigation. Bonding interactions frequently cause the cations to distort the crystal structure with a resulting closer approach of the cations; non-bonding interactions, on the other hand, distort the structure so that the cations are as far apart as possible.

Chromium(II) fluoride and Cr(II) chloride have a distorted rutile-type structure and both are antiferromagnetic, but the closest metal-metal approach is about 3.5 Å (in the metal, it is 2.498 Å). Thus the magnetic properties are due to a superexchange mechanism. The dichloride has a chain structure; the octahedral units in the chain are linked by the short Cr-Cl bonds and the chains are held together by the long Cr-Cl bonds. The dibromide and diiodide also have the structure of long ribbons.

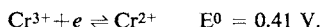
Molybdenum(II) chloride, which is diamagnetic, contains Mo_6 clusters in which the shortest Mo-Mo distance is 2.62 Å; in Mo metal it is 2.725 Å¹¹¹. In contrast to the behavior of CrCl_2 , MoCl_2 (although insoluble in water and resistant to oxidation) dissolves in concentrated HCl to give $[\text{Mo}_6\text{Cl}_8]^{4+}$ which acts as an entity in many reactions. Other molybdenum and tungsten compounds are isostructural with MoCl_2 (see also Part II, Section 2, Molybdenum Compounds and Part III, Section 2, Tungsten Compounds).

2.5.2. Chromium(II) Halide Complexes^{104, 107, 112}

The fluoride complexes $\text{Na}_2[\text{CrF}_4]$, $\text{NH}_4[\text{CrF}_3 \cdot 2\text{H}_2\text{O}]$ and $\text{K}[\text{CrF}_3]$ have been prepared. The last can be synthesized by the reaction of KHF_2 with anhydrous chromium(II) acetate under petroleum ether. Three types of compound have been found in phase studies of the systems $\text{CrCl}_2\text{-MCl}$, i.e.: $\text{Na}_3[\text{CrCl}_5]$, $\text{M}[\text{CrCl}_3]$, and $\text{M}_2[\text{CrCl}_4]$ ($\text{M}=\text{K}, \text{Cs}, \text{Rb}$). The complexes $\text{Cs}[\text{CrCl}_3]$ and $\text{Rb}[\text{CrCl}_3]$ have the hexagonal $\text{Cs}[\text{NiCl}_3]$ type structure.

2.5.3. Chromium(II) Salts and Complexes

The outstanding characteristic of the Cr(II) ion (sky blue in aqueous solution) is its strength as a reducing agent:



Since it is thus easily oxidized by oxygen, preservation of solutions requires exclusion of air. Even under such conditions, the Cr(II) ion is oxidized by water with formation of hydrogen. The rate of oxidation depends on several factors, including the acidity and the anions present.

The mechanism of oxidation of Cr(II) by O_2 may occur via a complex containing a Cr-O₂-Cr bridge¹¹³. The product of the reaction is the doubly bridged complex $[(\text{H}_2\text{O})_4\text{Cr}(\text{OH})_2\text{Cr}(\text{H}_2\text{O})_4]^{4+}$, which could be produced by protonation of the peroxy-bridged complex. The proposed mechanism is also consistent with the facts that all the oxygen atoms of the O_2 used up are found in the substitution-inert product and the rate of reaction is second order with respect to $[\text{Cr}^{2+}]$.

Chromium(II) can be obtained by reducing an acidic Cr(III) solution (such as a solution of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) with zinc^{109b, 110b, c, g} or with zinc amalgam^{109b, 110c, d, h}. In one variant

¹¹² G. W. A. Fowles, "Halide and Oxyhalide Complexes of Elements of the Titanium, Vanadium and Chromium Subgroups", in *Preparative Inorganic Reactions*, 1, Interscience, New York (1964), p. 128.

¹¹³ R. W. Kolaczowski and R. A. Plane, *Inorg. Chem.* 3 (1964) 323.

of the Zn-reduction method, the zinc (or zinc amalgam) is put into the reaction vessel containing the acidic Cr(III) solution and the reduced solution is filtered away from the excess zinc; in the other variant, the Cr(III) solution is poured through a Jones reductor arranged so that the reduced solution runs into a solution of the desired reagent. Chromous solutions so obtained, of course, contain Zn^{2+} ion. Whether this is a disadvantage or not depends on what the Cr(II) solution will be used for. At any rate, a separation can be made by precipitating the quite insoluble and inert chromous acetate.

It has been known for a long time that pure chromium (usually obtained by electrolysis) dissolves in acids to form Cr(II)¹¹⁴ with no (or very little) Cr(III) (if the solution is protected from air, of course); impurities apparently catalyze formation of Cr(III). Recently this method of preparing Cr(II) solutions has been exploited in synthetic procedures^{109b, 110f, 115, 116}. Chromium(II) solutions may also be obtained by electrolytic reduction of Cr(III)^{109b, 110f}.

Because of the sensitivity of Cr(II) to oxidation, it is necessary to protect chromous salts and solutions from air during preparative manipulations. One way of accomplishing this is to use an all-glass system, through which N_2 or CO_2 is circulated, designed to make possible all required manipulations such as filtering. Another is to perform the various operations inside a glove box filled with N_2 or CO_2 . Some investigators have even used a combination of the all-glass system inside the glove box.

All the variants mentioned are illustrated by the preparative procedures for the following: $\text{CrX}_2 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Br}, \text{I}, \text{ClO}_4$)^{109b, 110f}; $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$ ^{110b, f}; $[\text{Cr}(\text{dipy})_2](\text{ClO}_4)_2$ ($\text{dipy} = 2,2'$ -dipyridyl)^{109b}; $\text{CrC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ^{109b}; $\text{CrSO}_4 \cdot 5\text{H}_2\text{O}$ ^{109b, 110f}; CrSO_4 solution^{109b}; and Cr(II) solution for preparing Cr(III) complexes^{110g, h}.

Because it is one of the least soluble and most stable of the Cr(II) compounds, Cr(II) acetate^{109b, 110a-c, e} is an excellent starting material for preparing other Cr(II) compounds. Balthis and Bailar^{110b} converted it to the chloride by reaction with HCl. Reaction of acetylacetone (acac) with Cr(II) acetate produces the chelate $\text{Cr}(\text{acac})_2$ ^{110f}. This compound reacts slowly with water with production of hydrogen. It decomposes without melting at $218\text{--}219^\circ$. When it is anhydrous, it is pyrophoric, like the anhydrous acetate, which can be obtained by heating the hydrate *in vacuo* at 100° .

Crystalline Cr(II) acetate is apparently dimeric, with the composition $\text{Cr}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$. The binuclear complex has a carboxylato-bridged structure which has also been established for the acetates of Cu(II), Mo(II) and Rh(II); in all of these except the Mo(II) complex, neutral ligands (L) are present¹¹⁷. The structure consists of two metal octahedra with four bridging acetate groups, which leaves one coordination position on each chromium atom for coordination with water (Fig. 2).

The interatomic distances (Å) are^{118a}: Cr–O (acetate), 1.97; Cr–O (H_2O), 2.20; Cr–Cr, 2.46. The short Cr–Cr distance indicates strong interaction; since the four *d* electrons of each metal ion become paired, the compound is diamagnetic at room temperature. The metal–metal interaction, however, is not as great as it is in the analogous Mo compound (see p. 717) in which the metal–metal distance is only 2.13 Å. Other nearly diamagnetic

¹¹⁴ J. Koppel, *Z. anorg. u. allgem. Chem.* **45** (1905) 359.

¹¹⁵ H. Lux and G. Illman, *Chem. Ber.* **91** (1958) 2143.

¹¹⁶ H. Lux, L. Eberle and D. Sarre, *Chem. Ber.* **97** (1964) 503.

¹¹⁷ M. J. Bennett, K. G. Caulton and F. A. Cotton, *Inorg. Chem.* **8** (1969) 1.

¹¹⁸ F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 2nd edn. (1966): (a) p. 820; (b) p. 181.

Cr(II) carboxylates have been reported which are assumed to have structures like that of the acetate.

Numerous adducts of Cr(II) salts have been reported, among them acetonitrile complexes of the composition $\text{CrX}_2 \cdot 2\text{CH}_3\text{CN}$ ^{110f, 119}. By reaction of anhydrous or hydrated CrCl_2 with hot acetonitrile in hot ethanol solution, $\text{CrCl}_2 \cdot 2\text{CH}_3\text{CN}$ is obtained. The corresponding bromo compound can be prepared by reaction of acetonitrile with CrBr_2 (obtained by dehydrating $[\text{Cr}(\text{H}_2\text{O})_6]\text{Br}_2$ at 150° *in vacuo*). The iodide is prepared by reaction of acetonitrile with a solution of Cr(II) iodide obtained by reducing an aqueous solution of Cr(III) iodide with zinc amalgam. All manipulations are conducted in an inert atmosphere.

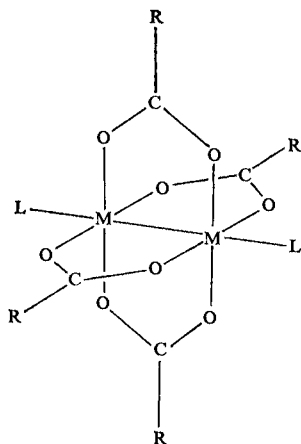


FIG. 2. Structure of dimeric Cr(II), Mo(II), Cu(II), and Rh(II) carboxylates¹¹⁷. (Reprinted from Ref. 117, © 1969, by permission of the American Chemical Society.)

Pyridine (py) complexes have also been prepared, e.g. $\text{CrX}_2 \cdot 2\text{py}$ ($\text{X} = \text{Cl}, \text{Br}$), $\text{CrI}_2 \cdot 4\text{py}$, $\text{CrX}_2 \cdot 6\text{py}$ ($\text{X} = \text{Br}, \text{I}$) and $[\text{Crpy}_3](\text{ClO}_4)_2$ ^{110f}. The last compound is stable for a long time in dry air but oxidizes slowly when it is wet. Powder patterns show that $\text{CrCl}_2 \cdot 2\text{CH}_3\text{CN}$ and $\text{CrBr}_2 \cdot 2\text{CH}_3\text{CN}$ are not isomorphous and do not have the same structure as the two isomorphous polymeric $\text{CrX}_2 \cdot 2\text{py}$ complexes¹¹⁹.

Hydrated or anhydrous Cr(II) halides dissolve in dimethylsulfoxide (DMSO) to give dark green solutions. When most of the DMSO has been removed *in vacuo*, pale blue crystals of DMSO adducts form which can be recrystallized from ethanol. These compounds have the composition $\text{CrCl}_2 \cdot 2\text{DMSO}$, $\text{CrBr}_2 \cdot 3\text{DMSO}$ and $\text{CrI}_2 \cdot 4\text{DMSO}$ ¹²⁰. The last two are particularly susceptible to decomposition during preparative manipulations. The Cr(II) in these compounds has a 6-coordinate distorted octahedral structure. They were studied by means of infrared and reflectance spectra in the visible region.

The hydrazine complexes $\text{CrX}_2 \cdot 2\text{N}_2\text{H}_4$ ($\text{X} = \text{Cl}, \text{I}$) are quite insoluble in water and stable toward oxidation^{118a}. The 2,2'-dipyridyl (dipy) complex^{109b} $[\text{Cr}(\text{dipy})_3]^{2+}$, on the other hand, is easily oxidized to $[\text{Cr}(\text{dipy})_3]^{3+}$ and reduced to $[\text{Cr}(\text{dipy})_3]^{1+}$; $[\text{Cr}(\text{dipy})_3]$, in which the oxidation state of Cr is zero, can also be prepared (see Section 2.3.4).

Reaction of Cr(II) acetate with excess KCN in aqueous solution (in an inert atmosphere) produces a red solution from which a blue cyanide complex is precipitated by addition of

¹¹⁹ D. G. Holah and J. P. Fackler, Jr., *Inorg. Chem.* **5** (1966) 479.

¹²⁰ D. G. Holah and J. P. Fackler, Jr., *Inorg. Chem.* **4** (1965) 1721.

ethanol. This compound is presumably $K_4[Cr(CN)_6] \cdot 3H_2O$, although there is some question as to its composition¹²¹. Solutions of the complex are also obtained by reaction of KCN with $CrCl_2$ in aqueous solution or by electrolytic reduction of a solution of $K_3[Cr(CN)_6]$. The Cr(II) complex is stable in neutral solution if protected from air but is oxidized to $K_3[Cr(CN)_6]$ (with reduction of H_2O) in acidic solution and in the presence of a platinum catalyst. Exchange of labeled cyanide with the complex Cr(II) cyanide is very fast. The magnetic moment of the complex is 3.2 B at room temperature. Apparently the complex ion is octahedral and the electronic configuration of the chromium atom is t_{2g}^4 .

2.5.4. Chromium(II) Oxide and Hydroxide¹²²

In early reports, Cr(II) oxide is described as a black pyrophoric powder that burns in air to Cr_2O_3 . It may be prepared by the action of HNO_3 or air on chromium amalgam.

The crystalline oxide (hexagonal, brown-red) has been prepared in small quantities by heating Cr_2O_3 in a melt of sodium fluoride in a reducing atmosphere, $H_2 + N_2$. The X-ray pattern of this oxide resembles those of BeO and ZnO.

This oxide is metastable at all temperatures. It is insoluble in water and some dilute acids but dissolves in dilute HCl to form a solution containing both Cr(II) and Cr(III).

If the preparation is accomplished in the absence of air, Cr(II) hydroxide (yellow) can be precipitated by alkalis from Cr(II) salt solutions. It is insoluble in dilute acids and water but dissolves slowly in concentrated acids. Heated strongly in air, it is converted to Cr_2O_3 . It can be dehydrated in a hydrogen atmosphere over H_2SO_4 . It is a powerful reducing agent.

2.5.5. Electron-transfer Reactions¹²³⁻¹²⁵

Numerous polynuclear complexes bridged by various ligands are known and in some of these electron interchange occurs through the bridge between two atoms in different oxidation states. In a somewhat analogous situation, oxidation-reduction reactions can occur readily if the reducing ion and oxidizing ion can be bridged by some ligand during the electron-transfer reaction. Reactions of this type, occurring via bridged intermediates, are called *inner sphere* reactions.

This is one of the two general mechanisms that have been established for electron-transfer reactions. In reactions occurring by the *outer sphere* mechanism, each of the two complexes retains its complete coordination sphere in the activated intermediate and electron transfer occurs by *tunneling* through both coordination spheres.

Chromium(II) has been a most useful reagent in investigations of mechanisms of inner sphere reactions¹²⁶. Chromium(II) is labile while the product of its oxidation, Cr(III), is inert. It follows, therefore, that ligands found in the Cr(III) product must be captured from the solution or the oxidizing agent by Cr(II), since the slowness of ligand displacement reactions of Cr(III) precludes the possibility that the ligands are acquired after the oxidation.

¹²¹ B. M. Chadwick and A. G. Sharpe, "Transition Metal Cyanides and their Complexes", in *Advances in Inorganic Chemistry and Radiochemistry*, **8**, Academic Press, New York (1965), p. 94.

¹²² J. Amiel, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959), p. 167.

¹²³ H. Taube, "Mechanisms of Redox Reactions of Simple Chemistry", in *Advances in Inorganic Chemistry and Radiochemistry*, **1**, Academic Press, New York (1959), p. 1.

¹²⁴ A. G. Sykes, "Further Advances in the Study of Mechanisms of Redox Reactions", in *Advances in Inorganic Chemistry and Radiochemistry*, **10**, Academic Press, New York (1967), p. 153.

¹²⁵ J. O. Edwards, *Inorganic Reaction Mechanisms*, Benjamin, New York (1964), chap. 7.

¹²⁶ B. A. Zabin and H. Taube, *Inorg. Chem.* **3** (1964) 963.

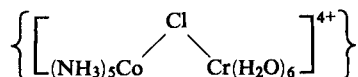
Many reactions of the following type have been studied^{118b}:



it is understood that each metal ion has its full complement of ligands. A particular reaction of this type (in acid solution) is



It is to be noted that Co(III) is inert, like Cr(III), and the coordinated chloride of the Co(III) reactant is found coordinated to Cr(III) in the product $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$. The bridged activated intermediate is presumably



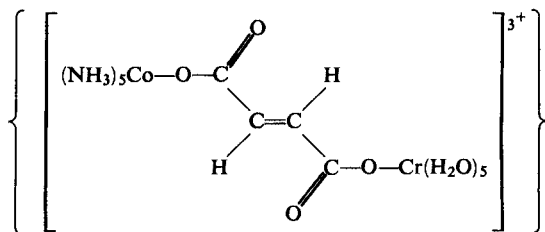
Investigation of Cr(II) reduction of other members of the series $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ shows that all of the following act as bridging ligands in the activated intermediate since they are transferred, like chloride, to the Cr(III) product: F^- , Br^- , I^- , SO_4^- , N_3^- , NCS^- , PO_4^{3-} , $\text{P}_2\text{O}_7^{4-}$, OH^- , monocarboxylate ions, oxalate succinate, maleate, fumarate, crotonate. In reactions that unquestionably occur via bridging mechanisms, the order of effectiveness of some ligands that often act as bridges is: $\text{N}_3^- \gg \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$.

The rate of reduction of $[\text{Co}(\text{NH}_3)_6]^{3+}$ is much lower than that of the complexes $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ because NH_3 does not act as a bridging ligand. This reaction thus occurs via an outer sphere mechanism¹²⁷.

Conjugated systems are particularly effective as electron-transfer paths as demonstrated by a comparison of rates of reduction of compounds of the type $[\text{Co}(\text{NH}_3)_5\text{L}]^{2+}$ in which L may be a monocarboxylate ion such as acetate or benzoate or a dicarboxylate ion acting as a singly coordinating ligand, such as succinate and maleate^{118b}. The rate law is¹²⁸

$$v = k[\text{Co}^{2+}][\text{Cr}^{2+}]$$

in which $\text{Co}^{2+} = [\text{Co}(\text{NH}_3)_5\text{L}]^{2+}$. When L is one of the monocarboxylates (acetate, chloroacetate benzoate, *p*-chlorobenzoate, etc.), the rates of reduction of Co(III) do not vary much. For a series of thirteen such ligands, the highest k is only about three times the lowest¹²⁸. When L is oxalate, maleate, fumarate or terephthalate, the rate is increased by a large factor. Evidently the Cr(II) combines with the carboxyl group remote from the Co(III) to form a bridged activated intermediate exemplified by the following (L = fumarate):

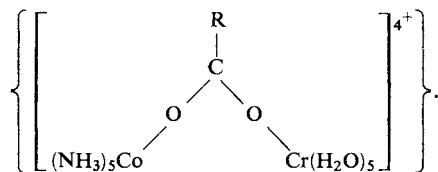


Thus the bridging ligand provides a continuous pathway of conjugated bonds between the metal atoms for the electrons. With the monocarboxylates, the reaction is slower because

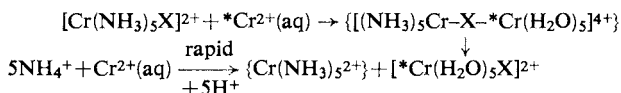
¹²⁷ D. . Pennington and A. Haim, *Inorg. Chem.* 6 (1967) 2138.

¹²⁸ Ref. 125, pp. 42, 120.

the Cr(II) has to attack the second oxygen of the carboxyl group attached to Co(III), which is sterically hindered; the structure of the activated intermediate presumably is



The aquation of many Cr(III) complexes is catalyzed by traces of Cr(II) and these reactions also occur via bridged intermediates; the bridging ligand is retained by Cr(III) while the other ligands are lost^{118b, 125}:

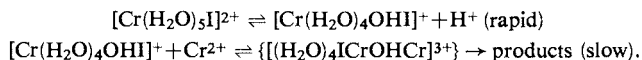


(* identifies the Cr that was originally Cr²⁺; X = F⁻, Cl⁻, Br⁻, I⁻).

Chromium(II) also catalyzes the aquation of *cis*- and *trans*-[Cren₂XCl]ⁿ⁺ (X = Cl, H₂O) by electron transfer via chloride-bridged transition states in acid solution¹²⁹. The spontaneous aquation of the *trans* isomers is too slow under the experimental conditions to affect the measurement of the Cr(II)-catalyzed reactions; with the *cis* isomers spontaneous aquation is fast enough that it has to be taken into account. For this series of compounds, the observed order of the rates is: *cis*-[Cren₂H₂OCl]²⁺ < *cis*-[Cren₂Cl₂]⁺ ≪ *trans*-[Cren₂H₂OCl]²⁺ < *trans*-[Cren₂Cl₂]⁺. The geometrical position of the non-bridging ligand (Cl⁻ or H₂O) has a greater effect than its nature (en = ethylenediamine).

Electron-transfer reactions between Cr(II) and [Cr(H₂O)₅X]⁺ in which X is a ligand such as F⁻, Cl⁻, Br⁻, NCS⁻ and N₃⁻, also proceed predominantly through bridged intermediates {[Cr-X-Cr]⁴⁺}. Ligand transfer accompanies electron transfer. In the investigations establishing these conclusions, the reaction conditions have generally been characterized by relatively low [Cr²⁺] and relatively high [H⁺].

With relatively high [Cr²⁺] and relatively low [H⁺], evidently another pathway is available¹²⁷. In the Cr(II)-catalyzed aquation of [Cr(H₂O)₅I]²⁺ under such conditions, it is postulated that the intermediate state may be {[Cr₂IOH]³⁺}. Since there is net loss of iodide from the coordination sphere, it is concluded that it is not acting as a bridging group. The mechanism may comprise hydrolysis followed by a rate-determining reaction via a hydroxy-bridged complex:



Multiple bridges may also be formed in electron-transfer reactions^{118b}. Examples of such reactions include the reduction of *cis*-[Cr(H₂O)₄(NH₃)₂]³⁺ with Cr(II) and reactions such as



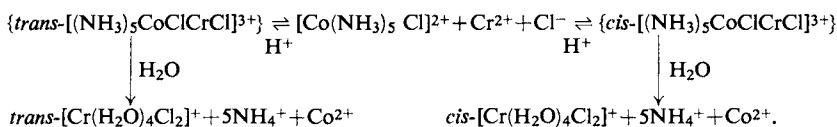
In this reaction, evidently EDTA (ethylenediaminetetraacetate) bridges through three oxygen atoms.

Added halide ion affects the rates of electron-transfer reactions between inert oxidants

¹²⁹ D. E. Pennington and A. Haim, *Inorg. Chem.* **5** (1966) 1887.

and labile reductants¹³⁰. Reactions whose rates are affected by added chloride ion include the outer sphere reduction of $[\text{Co}(\text{NH}_3)_6]^{3+}$ by Cr^{2+} (for which the rate increase is considerable), the inner sphere reductions of $[\text{Co}(\text{NH}_3)_5\text{L}]^x$ by Cr^{2+} ($\text{L} = \text{H}_2\text{O}$, $x = 3+$; $\text{L} = \text{chloride}$, acetate, acid fumarate, $x = 2+$), and the $\text{Cr}(\text{II})$ -catalyzed exchange of Cl^- between $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ and Cl^- . Fluoride, chloride and bromide increase the rate of substitution of iodide¹²⁷ in $[\text{Cr}(\text{H}_2\text{O})_5\text{I}]^{2+}$.

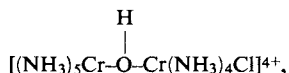
In some reactions, not only the rate but also the stoichiometry is changed. For example, in the reduction of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ by Cr^{2+} , if the reaction mixture contains no added Cl^- , the only $\text{Cr}(\text{III})$ product is $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ (*a*). In the presence of added Cl^- , $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ (*b*) is also produced and the ratio *b* : *a* increases with increased Cl^- ; *b* is a mixture of the *cis* and *trans* isomers¹²⁹. Presumably the added chloride enters the activated intermediate as a nonbridging ligand:



The non bridging Cl^- is more effective from the *trans* than from the *cis* position in promoting the electron transfer to $\text{Co}(\text{III})$.

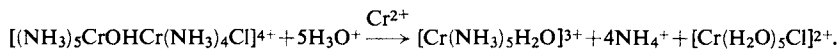
Non bridging ligands also affect the course of the chromium(II)-catalyzed aquation of $[\text{Cr}(\text{H}_2\text{O})_5\text{I}]^{2+}$. Fluoride, chloride and bromide ions increase markedly the rate of disappearance of $[\text{Cr}(\text{H}_2\text{O})_5\text{I}]^{2+}$ and change the stoichiometry¹²⁷. In the presence of one of these ions, $[\text{Cr}(\text{H}_2\text{O})_5\text{X}]^{2+}$ ($\text{X} = \text{F}^-$, Cl^- or Br^-) is produced. The yields of the chloro and bromo compounds are nearly quantitative; the yield of the fluoro compound is probably also quantitative initially, but it is reduced by subsequent $\text{Cr}(\text{II})$ -catalyzed aquation, which apparently is negligible with the other two halides. The formation of $[\text{Cr}(\text{H}_2\text{O})_5\text{X}]^{2+}$ ($\text{X} = \text{Cl}^-$, Br^- , F^-) indicates that the added halide ion forms a bond with a $\text{Cr}(\text{II})$ ion in the process of losing an electron. The transition state is thus formulated $\{[\text{CrL}]^{2+} \cdot [\text{CrX}]^+\}$.

In the reduction of the chloroerythro ion,



by $\text{Cr}(\text{II})$, either chromium atom could accept an electron, but the attack might be expected on the chloride, which is known to be an effective bridging group in electron-transfer reactions. However, the OH group is also an electron mediator and it might therefore permit transfer of an electron, accepted by the chloride, through the tetrammine chromium to the pentammine chromium¹³¹.

In the $\text{Cr}(\text{II})$ -catalyzed loss of NH_3 from the complex in aqueous acid solution, the rate-determining step appears to be an electron-transfer reaction with the chloride acting as a bridging ligand as expected; this conclusion is suggested by the form of the rate law and the formation of $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ in the reaction, which appears to be



Since tetrammine complexes are not formed, apparently the electron entering the chloroerythro ion does not reach the pentammine chromium, even though this must be connected

¹³⁰ D. E. Pennington and A. Haim, *Inorg. Chem.* **7** (1968) 1659.

¹³¹ D. W. Hoppenjans, J. B. Hunt and L. Penzhorn, *Inorg. Chem.* **7** (1968) 1467.

via the OH bridge to a Cr(II) (namely, the reduced chlorotetrammine fragment) for the lifetime of a ligand in the first coordination sphere of Cr(II).

There is considerable evidence that the chloride in the chloroerythro ion is *trans* to the bridging oxygen atom and so the ion is formally derived from *trans*-[Cr(NH₃)₄(H₂O)Cl]²⁺ by replacement of an H atom of the water molecule by [Cr(NH₃)₅]. This drastic alteration of structure leads to a large increase in rate of reaction; the second order rate constants for reaction of the chloroaquo compound and the dimer are respectively 3.0 and 1.1 M⁻¹ sec⁻¹ (25°, 1 M HClO₄).

2.6. OXIDATION STATE III

2.6.1. Anhydrous Chromium(III) Halides¹³²⁻¹³⁴

The following are some of the properties of the chromium halides CrX₃ (color; melting point, °C; Cr-X bond length, Å)¹³⁴:

CrF₃, green, 1100°, 1.90.

CrCl₃, red-violet, 1152°, 2.38.

CrBr₃, green, 1130° (estimated), 2.57.

CrI₃, black.

Their magnetic moments are in the range 3.69–4.1 B.

The geometry of the metal in the anhydrous Cr(III) halides is octahedral. These compounds have a layer structure; the bonding is predominantly covalent. In the chloride, the Cr-Cr distance between layers is 5.76 Å, while the Cr-Cr distance within layers is 3.46 Å; the structure contains ribbon-like dislocations. These distances indicate that no metal-metal bonding exists; the Cr-Cr distance in metallic Cr is 2.498 Å. Chromium(III) iodide is isomorphous with CrCl₃; the bromide is not, but has a quite similar structure.

A general method for preparing these halides is halogenation of the metal, although several other procedures are available¹³⁵⁻¹⁴⁰. Anhydrous CrCl₃ may be prepared in good yield by heating CrCl₃·6H₂O to 650° in a stream of CCl₄ vapor¹³⁶⁻¹³⁸; this reacts with intermediate hydrolysis products and prevents formation of CrOCl.

The anhydrous Cr(III) halides are insoluble in water but dissolve slowly in the presence of Cr(II) or a reducing agent (e.g. Zn), possibly because of the formation of a charge transfer complex, [Cr²⁺ - -X-Cr³⁺ - -X]¹⁴¹. Chromium(III) chloride reacts with tetrahydrofuran (THF) in the presence of Zn to form a stable adduct, CrCl₃·3THF; presumably the reaction proceeds via an intermediate Cr(II) compound¹⁴². It also reacts with anhydrous NH₃ and diamines to form ammine complexes (see Section 2.6.4). The Cr(III) halides are useful as

¹³² R. D. Peacock, "Some Fluorine Compounds of the Transition Metals", in *Progress in Inorganic Chemistry*, **2**, Interscience, New York (1960), p. 193.

¹³³ E. L. Muetterties and C. W. Tullock, "Binary Fluorides", in *Preparative Inorganic Reactions*, **2**, Interscience, New York (1965), p. 237.

¹³⁴ J. E. Fergusson, "Halide Chemistry of Chromium, Molybdenum and Tungsten", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 227.

¹³⁵ B. J. Sturm, *Inorg. Chem.* **1** (1962) 665.

¹³⁶ G. B. Heisig, B. Fowkes and R. Hedin, *Inorg. Syn.* **2**, McGraw-Hill, New York (1946), p. 193.

¹³⁷ F. Hein and S. Herzog, Section 24 in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965).

¹³⁸ A. Vavoulis, T. E. Austin and S. Y. Tyree, Jr., *Inorg. Syn.* **6**, McGraw-Hill, New York (1960), p. 129.

¹³⁹ G. W. Watt, P. S. Gentile and E. P. Helvenstan, *J. Am. Chem. Soc.* **77** (1955) 2752.

¹⁴⁰ N. W. Gregory and L. L. Handy, *Inorg. Syn.* **5**, McGraw-Hill, New York (1957), p. 128.

¹⁴¹ L. L. Handy and N. W. Gregory, *J. Am. Chem. Soc.* **72** (1950) 5049.

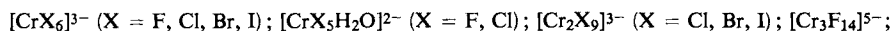
¹⁴² W. Herwig and H. H. Zeiss, *J. Am. Chem. Soc.* **79** (1957) 5959.

starting materials in the synthesis of organometallic compounds (see Sections 2.3 and 2.4).

Although the trihalides are quite stable to heat, at sufficiently high temperatures they dissociate into the dihalides and halogen. The iodide is least stable; at about 500°, it begins to decompose to CrI_2 , which finally dissociates to form the elements. The vapor pressure of CrCl_3 at 1000° is 278.2 mm; the molecules in the vapor state are monomeric. It dissociates to CrCl_2 and Cl_2 at 1300°. In the synthesis of fluorides, CrF_3 or CrF_2 (or a mixture) is useful as a catalyst in vapor phase fluoride-halogen exchange reactions; there is an equilibrium among the species CrF_2 , CrF_3 and CrF_5 .

2.6.2. Complex Chromium(III) Halides; Oxychloride^{132, 134, 143}

The following complex Cr(III)-halide anions are known^{134, 144}:



there appears to be no recent work on bromide and iodide complexes of the type $[\text{CrX}_6]^{3-}$. These compounds are usually obtained as alkali metal salts. They are water soluble. The mononuclear fluoro complexes are green; the chloro complexes are green or red-violet. Generally these compounds are prepared by fusing a mixture of Cr(III) halide and an alkali metal halide, although some (including K_3CrF_6) can be obtained from an aqueous solution of the chromium halide¹⁴⁵.

Fenske and associates¹⁴⁶ have discussed the energy levels, spin densities and nephelauxetic effect in the hexafluorides $[\text{MF}_6]^{3-}$ ($\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Fe}, \text{Co}$). The calculated value of Δ (10 Dq) for $[\text{CrF}_6]^{3-}$ agrees with the observed value (2.05 eV).

Anions of the type $[\text{Cr}_2\text{X}_9]^{3-}$ are of particular interest because of the possibility of metal-metal bonding¹⁴⁴ as in analogous tungsten ions such as $[\text{W}_2\text{Cl}_9]^{3-}$, which is diamagnetic. The magnetic properties of $[\text{Cr}_2\text{Cl}_9]^{3-}$ indicate, however, that there is no metal-metal bonding; another contraindication is the Cr-Cr distance, 3.12 Å, which is considerably larger than that in the metal (2.5 Å).

In $[\text{Cr}_2\text{Cl}_9]^{3-}$, each of the two chromium atoms is surrounded by six chloride ions in octahedral configuration, but the chromium atom is not exactly in the center of the octahedron; there are two different Cr-Cl bond lengths, i.e. 2.52 and 2.34 Å. The two octahedra share a common trigonal face; the two Cr atoms are displaced away from each other along the trigonal axis. This is the reverse of the situation with $[\text{W}_2\text{Cl}_9]^{3-}$, which has the same kind of structure except that the two metal atoms are displaced toward each other (bond distance, 2.6 Å), an indication of considerable W-W interaction.

The oxychloride, CrOCl , is produced as an intermediate in the preparation of CrCl_3 from $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, as previously described. It can also be prepared by reaction of Cr_2O_3 and CrCl_3 at high temperature, and by the reaction of other metal oxides with CrCl_3 . The magnetic moment of the compound is 3.9 B (295°) and the Cr-Cr distance is 3.04 Å; thus no metal-metal bonding is involved.

2.6.3. Chromium(III) Oxide and Hydroxide

Chromium(III) oxide, Cr_2O_3 , is the final product of calcination of numerous chromium compounds, e.g. hydrated Cr(III) oxide; Cr(III) nitrate; $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$ and many other

¹⁴³ G. W. A. Fowles, "Halide and Oxyhalide Complexes of Elements of the Titanium, Vanadium and Chromium Subgroups", in *Preparative Inorganic Reactions*, 1, Interscience, New York (1964), p. 126.

¹⁴⁴ R. Saillant and R. A. D. Wentworth, *Inorg. Chem.* 7 (1968) 1606.

¹⁴⁵ H. L. Schläfer, H. Gaussman and H. Zander, *Inorg. Chem.* 6 (1967) 1528.

¹⁴⁶ R. E. Fenske, K. G. Caulton, D. D. Radtke and C. C. Sweeney, *Inorg. Chem.* 5 (1966) 960.

complex compounds; HgCrO_4 ; $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$. It is also formed by ignition of compounds such as metal chromates and bichromates with reducing agents¹⁴⁷. Chromium(III) oxide and $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (Guignet's green) are important green pigments¹⁴⁸.

The chromites are obtained by fusing Cr_2O_3 with bivalent oxides¹⁴⁷. These crystalline double oxides are spinels, $\text{M}^{\text{II}}\text{O} \cdot \text{Cr}_2\text{O}_3$. The spinel structure is a close-packed cubic array of oxygen ions containing tetrahedral holes (two per anion) and octahedral holes (one per anion). The bivalent and trivalent cations occupy the tetrahedral and octahedral holes respectively. The only important commercial chromium mineral is the spinel chromite, $\text{Fe}(\text{CrO}_2)_2$.

Chromium(III) oxide starts to dissociate below its melting point (about 2275°)¹⁴⁹. The standard enthalpy and free energy of formation are respectively -269.7 and -250.2 kcal/mole¹⁵⁰. Crystalline Cr_2O_3 has the Al_2O_3 structure ($D5_1$)¹⁴⁹ with the following hexagonal lattice parameters: a , $4.950 \text{ \AA}$; c , $13.665 \text{ \AA}$; $c/a = 2.761$. Its density¹⁴⁷, varying with the method of preparation, is about 5.22 g/cm^3 .

Chromium hydroxide may be considered the ultimate product of a continued process of olation, i.e. polymerization via bridging OH^- groups (see Section 2.6.4(e)). The degree of hydration varies with the method of preparation. There is still a question whether chromium hydroxide is a definite compound or a mixture of hydrates¹⁴⁷. It is quite certain that products of widely different properties are obtained by varying the preparative conditions. For example, two forms of $\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ are said to be obtained by precipitating the hydroxide with NH_4OH from solutions of different Cr(III) chlorides¹³⁷. The *A*-hydroxide, obtained from a solution of $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, dissolves in dilute acids to form salts of the $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ series; the *B*-hydroxide, obtained from $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$, dissolves to produce $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ salts, but is insoluble in acetic acid, in contrast to the behavior of the *A*-type. Another hydroxide, $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$, is produced by reducing CrO_3 with ethanol¹³⁷.

Chromium hydroxide dissolves (or disperses) in concentrated alkali¹⁴⁷. It is not certain what species are present in solutions so prepared. There is strong probability that the so-called chromite solutions often contain colloiddally dispersed hydrous Cr(III) oxide which may thus not be truly amphoteric.

2.6.4. Coordination Chemistry of Chromium(III)^{151a}

One of the most characteristic features of the chemistry of chromium is the great ability of Cr(III) to form coordination compounds. It rivals Co(III) in this respect, and many analogous Co(III) and Cr(III) complexes are known. The solution of chemistry Cr(III) is exclusively coordination chemistry. The Cr(III) complexes, like those of Co(III), are inert, i.e. the rates of ligand interchange with these complexes are generally low. The complexes of Cr(III), however, are more susceptible to hydrolysis and formation of polynuclear complexes by olation than those of Co(III).

(a) Types of Chromium(III) Complexes^{151b}

The number of conceivable Cr(III) complex compounds is enormous since any ion or molecule capable of donating a pair of electrons, i.e. acting as a Lewis base, is potentially

¹⁴⁷ J. Amiel, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959), p. 170.

¹⁴⁸ W. H. Hartford and R. L. Copson, "Chromium Compounds", in *Encyclopedia of Chemical Technology*, **5**, Interscience, New York, 2nd edn. (1964), p. 507.

¹⁴⁹ M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York (1958), p. 546.

¹⁵⁰ R. Keller, *Basic Tables in Chemistry*, McGraw-Hill, New York (1967), p. 311.

¹⁵¹ M. M. Jones, *Elementary Coordination Chemistry*, Prentice-Hall, Englewood Cliffs, NJ (1964): (a) p. 86; (b) p. 17; (c) p. 48.

TABLE 16. SOME MONONUCLEAR CHROMIUM(III) COMPLEXES OF SINGLY COORDINATING AND BIDENTATE CHELATING LIGANDS

Type ^a	Ligands ^b
[CrA ₆] ³⁺	A = H ₂ O ^{137, 153, 154} ; NH ₃ ^{137, 156, 156a-c, 157} ; NH ₂ CONH ₂ ¹³⁷ ; $\frac{1}{2}$ en ^{137, 155, 156b, d, 158} ; $\frac{1}{2}$ pn ^{155, 156b, d} ; $\frac{1}{2}$ dipy ¹³⁷ ; $\frac{1}{2}$ phen ¹⁵⁹ ; $\frac{1}{2}$ biguanide ^{156e}
[CrA ₅ B] ³⁺	A, B = NH ₃ , H ₂ O ^{156a}
[CrA ₅ X] ²⁺	A, X = H ₂ O, Cl ¹³⁷ ; H ₂ O, NO ₃ ¹⁶⁰ ; NH ₃ , Cl ^{137, 156g} ; NH ₃ , Br ^{156f} ; NH ₃ , NO ₃ ^{156f} ; NH ₃ , NO ₂ ^{156f}
[CrA ₃ B ₂ X] ²⁺	A, B, X = NH ₃ , H ₂ O, Cl ¹⁶¹ ; NH ₃ , H ₂ O, Br ¹⁶¹
[CrA ₄ X ₂] ⁺	A, X = $\frac{1}{2}$ en, ONO ¹⁶² ; $\frac{1}{2}$ en, Cl (<i>cis</i>) ^{137, 156h, 163} ; $\frac{1}{2}$ en, SCN (<i>trans</i>) ^{137, 156h, 163} ; $\frac{1}{2}$ dipy, Cl ¹⁶⁴ ; $\frac{1}{2}$ phen, Cl ¹⁶⁴ ; $\frac{1}{2}$ dipy, $\frac{1}{2}$ ox ¹⁶⁵ ; $\frac{1}{2}$ phen, $\frac{1}{2}$ ox ¹⁶⁵
[CrA ₃ BX ₂] ⁺	A, B, X = NH ₃ , H ₂ O, Cl ¹⁶¹ ; NH ₃ , H ₂ O, Br ¹⁶¹
[CrA ₃ X ₃] ⁰	A, X = H ₂ O, Cl ¹³⁷ ; C ₂ H ₅ OH, Cl ¹³⁷ ; NH ₃ , Cl ^{137, 161} ; THF, Cl ^{156i, j} ; py, Cl ^{137, 156k} ; <i>N</i> -substituted amide, Cl ¹⁶⁶
[Cr(AX) ₃] ⁰	AX = acac ^{137, 156l} ; hfa ¹⁶⁷ ; 3-bromoacetylacetone ^{156m} ; formylacetone ¹⁵⁶ⁿ ; malonaldehyde ^{156o} ; CH ₃ COCH = (NHC ₆ H ₄ CH ₃)CH ₃ ^{156l} ; dibenzoyl-methane ^{156p} ; glycine ¹³⁷ ; alanine ¹³⁷ ; methionine ¹⁶⁸ ; diacetamide ¹⁶⁹ ; dibenzamide ¹⁶⁹
[CrA ₂ X ₄] ⁻	A, X = NH ₃ , SCN ¹³⁷ ; C ₂ H ₅ NH ₂ , SCN ¹³⁷ ; py, SCN ¹³⁷ ; H ₂ O, $\frac{1}{2}$ ox (<i>cis</i>) ^{170, 171} ; NH ₃ , $\frac{1}{2}$ ox (<i>cis</i>) ¹⁷¹ ; $\frac{1}{2}$ dipy, $\frac{1}{2}$ ox ¹⁷² ; $\frac{1}{2}$ phen, $\frac{1}{2}$ ox ¹⁷²
[CrAX ₅] ²⁻	A, X = H ₂ O, Br ¹⁷³
[CrX ₆] ³⁻	X = CN ^{137, 156q} ; SCN ¹³⁷ ; $\frac{1}{2}$ ox ^{137, 156r, 174}

^a A, B = singly coordinating neutral molecule or $\frac{1}{2}$ bidentate chelating neutral molecule; X = singly charged coordinated negative ion or $\frac{1}{2}$ bidentate doubly charged chelating ion; AX = bidentate chelating ligand coordinating via one neutral and one negative group.

^b en = ethylenediamine; pn = propylenediamine; dipy-2,2' = dipyridyl; phen = 1,10-phenanthroline; py = pyridine; acac = acetylacetone; hfa = hexafluoroacetylacetone; THF = tetrahydrofuran; ox = oxalate.

¹⁵² R. Duval and C. Duval, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959), p. 420.

¹⁵³ E. Birk, *Z. anorg. u. allgem. Chem.* **166** (1927) 284.

¹⁵⁴ K. R. Ashley, R. E. Hamm and R. H. Magnuson, *Inorg. Chem.* **6** (1967) 413.

¹⁵⁵ C. L. Rollinson and J. C. Bailar, Jr., *J. Am. Chem. Soc.* **65** (1943) 250.

¹⁵⁶ *Inorg. Syn.*, McGraw-Hill, New York: (a) A. L. Oppegard and J. C. Bailar, Jr., **3** (1950), p. 153; (b) D. Berman, G. Bokerman and R. W. Parry, **10** (1967), p. 35; (c) W. E. Hatfield, R. Whyman, R. C. Fay, K. N. Raymond and F. Basolo, **11** (1968), p. 47; (d) C. L. Rollinson and J. C. Bailar, Jr., **2** (1946), p. 196; (e) R. Rây, **6** (1960), p. 68; (f) M. Mori, **5** (1957), p. 13; (g) G. Shlessinger, **6** (1960), p. 138; (h) ref. (d), p. 200; (i) J. P. Collman and E. J. Kittleman, **8** (1966), p. 149; (j) F. Galsbøl and C. E. Schäffer, **10** (1967), p. 42; (k) J. C. Taft and M. M. Jones, **7** (1963), p. 132; (l) W. C. Fernelius and J. E. Blanch, **5** (1957), p. 130; (m) J. P. Collman, **7** (1963), p. 134; (n) J. P. Collman, E. T. Kittleman, W. S. Hurt and N. A. Moore, **8** (1966), p. 144; (o) ref. (h), p. 141; (p) R. G. Charles, **8** (1966), p. 135; (q) J. H. Bigelow, **2** (1946), p. 203; (r) J. C. Bailar, Jr. and E. M. Jones, **1** (1939), p. 35.

¹⁵⁷ K. N. Raymond, D. W. Meek and J. A. Ibers, *Inorg. Chem.* **7** (1968) 1111.

¹⁵⁸ K. N. Raymond, P. W. R. Corfield and J. A. Ibers, *Inorg. Chem.* **7** (1968) 1363.

¹⁵⁹ C. S. Lee, E. M. Gorton, A. M. Neumann and H. R. Hunt, Jr., *Inorg. Chem.* **5** (1966) 1397.

¹⁶⁰ M. Ardon and N. Sutin, *Inorg. Chem.* **6** (1967) 2268.

¹⁶¹ S. H. Caldwell and D. A. House, *Inorg. Chem.* **8** (1969) 151.

¹⁶² W. W. Fee, C. S. Garner and J. M. Harrowfield, *Inorg. Chem.* **6** (1967) 87.

¹⁶³ C. L. Rollinson and J. C. Bailar, Jr., *J. Am. Chem. Soc.* **66** (1944) 641.

¹⁶⁴ F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.* (1952) 3570.

¹⁶⁵ J. A. Broomhead, M. Dwyer and N. Kane-Maguire, *Inorg. Chem.* **7** (1968) 1388.

¹⁶⁶ C. L. Rollinson and R. C. White, *Inorg. Chem.* **1** (1962) 281.

¹⁶⁷ M. L. Morris, R. W. Moshier and R. E. Sievers, *Inorg. Chem.* **2** (1963) 411.

¹⁶⁸ C. A. McAuliffe, J. V. Quagliano and L. M. Vallarino, *Inorg. Chem.* **5** (1966) 1996.

¹⁶⁹ C. S. Kraihanzel and O. N. Stehly, *Inorg. Chem.* **6** (1967) 277.

¹⁷⁰ G. L. Welch and R. E. Hamm, *Inorg. Chem.* **2** (1963) 295.

¹⁷¹ A. Werner, *Ann.* **406** (1914) 261.

¹⁷² J. A. Broomhead: (a) *Australian J. Chem.* **15** (1962) 228; (b) *J. Inorg. Nuclear Chem.* **27** (1965) 2049.

¹⁷³ A. Werner and A. Gubser, *Ber.* **34** (1901) 1579.

¹⁷⁴ K. V. Krishnamurty and G. M. Harris, *Chem. Rev.* **61** (1961) 213.

TABLE 17. SOME CHROMIUM(III) COMPLEXES OF POLYDENTATE LIGANDS

Ligand	Formula	Type	Complexes
Iminodiacetate (IDA) ¹⁷⁵	$ \begin{array}{c} \text{O} \\ \\ \text{C}-\text{O}^- \\ \\ \text{HN} \\ \\ \text{C}-\text{O}^- \\ \\ \text{O} \end{array} $	Tridentate	$[\text{Cr}(\text{IDA})_2]^-$ (<i>cis</i>) $[\text{Cr}(\text{IDA})(\text{H}_2\text{O})_3]^+$
Methyliminodiacetate (MIDA) ¹⁷⁵	$ \begin{array}{c} \text{O} \\ \\ \text{C}-\text{O}^- \\ \\ \text{CH}_3\text{N} \\ \\ \text{C}-\text{O}^- \\ \\ \text{O} \end{array} $	Tridentate	$[\text{Cr}(\text{MIDA})_2]^-$ (<i>trans</i> , <i>facial</i>) $[\text{Cr}(\text{MIDA})(\text{H}_2\text{O})_3]^+$
IDA, MIDA ¹⁷⁵	$ \begin{array}{c} \text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2 \\ \text{O} \qquad \qquad \qquad \text{O} \\ \qquad \qquad \qquad \\ -\text{O}-\text{C} \qquad \qquad \qquad \text{C}-\text{O}^- \\ \qquad \qquad \qquad \\ \text{N}(\text{CH}_2)_2\text{N} \\ \qquad \qquad \qquad \\ -\text{O}-\text{C} \qquad \qquad \qquad \text{C}-\text{O}^- \\ \qquad \qquad \qquad \\ \text{O} \qquad \qquad \qquad \text{O} \end{array} $	Tridentate	$[\text{Cr}(\text{IDA})(\text{MIDA})]^-$ (<i>cis</i>) $[\text{Cr}(\text{trien})\text{Cl}_2]^+$ (<i>cis</i>)
Triethylenetetramine (trien) ¹⁷⁶		Tetradentate	
Ethylenediaminetetraacetate (EDTA) ¹⁷⁵	$ \begin{array}{c} \text{O} \qquad \qquad \qquad \text{O} \\ \qquad \qquad \qquad \\ -\text{O}-\text{C} \qquad \qquad \qquad \text{C}-\text{O}^- \\ \qquad \qquad \qquad \\ \text{N}(\text{CH}_2)_2\text{N} \\ \qquad \qquad \qquad \\ -\text{O}-\text{C} \qquad \qquad \qquad \text{C}-\text{O}^- \\ \qquad \qquad \qquad \\ \text{O} \qquad \qquad \qquad \text{O} \end{array} $	Pentadentate ^a	$[\text{Cr}(\text{EDTA})(\text{H}_2\text{O})]^-$
Tetraethylenepentamine (tetren) ^{177, 178}	$ \begin{array}{c} \text{O} \qquad \qquad \qquad \text{O} \\ \qquad \qquad \qquad \\ -\text{O}-\text{C} \qquad \qquad \qquad \text{C}-\text{O}^- \\ \qquad \qquad \qquad \\ \text{N}(\text{CH}_2)_3\text{N} \\ \qquad \qquad \qquad \\ -\text{O}-\text{C} \qquad \qquad \qquad \text{C}-\text{O}^- \\ \qquad \qquad \qquad \\ \text{O} \qquad \qquad \qquad \text{O} \end{array} $	Pentadentate	$[\text{Cr}(\text{tetren})\text{Cl}]^{2+}$ $[\text{Cr}(\text{tetren})\text{SCN}]^{2+}$
1,3-Propanediaminetetraacetate (PDTA) ¹⁷⁵	$ \begin{array}{c} \text{O} \qquad \qquad \qquad \text{O} \\ \qquad \qquad \qquad \\ -\text{O}-\text{C} \qquad \qquad \qquad \text{C}-\text{O}^- \\ \qquad \qquad \qquad \\ \text{N}(\text{CH}_2)_3\text{N} \\ \qquad \qquad \qquad \\ -\text{O}-\text{C} \qquad \qquad \qquad \text{C}-\text{O}^- \\ \qquad \qquad \qquad \\ \text{O} \qquad \qquad \qquad \text{O} \end{array} $	Hexadentate ^a	$[\text{Cr}(\text{PDTA})]^-$

^a Although EDTA is potentially hexadentate, it behaves as a pentadentate ligand here apparently because the last group is prevented from bonding because of strain in the rings which is removed by increase in ring size due to the additional $-\text{CH}_2-$ of PDTA.

capable of combining with the metal ion in the role of a Lewis base. Such ions and molecules (ligands) may be singly coordinating or chelating (ring forming). Chromium(III) complex compounds may be salts of complex cations, salts of complex anions, or neutral molecules.

Although the number of chromium complexes known is very large, fortunately they can be classified into a relatively small number of types. In Table 16 representative mononuclear Cr(III) complexes (of singly coordinating and bidentate chelating ligands) have been listed in accordance with a classification scheme based on that of the Pascal treatise¹⁵². Some complexes of polydentate ligands are listed in Table 17.

Numerous compounds are known that contain two or more chromium atoms per molecule linked by bridging groups such as OH⁻ (Table 18). The marked ability of Cr(III) to polymerize in this way is an unusual and important aspect of its chemistry which is dealt with in Section 2.6.4(e).

TABLE 18. SOME BRIDGED CHROMIUM(III) COMPLEXES¹⁵²

Compound	Bridging groups	Notes
[(NH ₃) ₅ Cr(OH)Cr(NH ₃) ₅] ⁵⁺	1 OH ⁻	"Rhodochromium(III)" ion ^{137, 179a}
[(NH ₃) ₅ Cr(OH)Cr(NH ₃) ₄ (H ₂ O)] ⁵⁺	1 OH ⁻	"Erythrochromium(III)" ion ^{137, 179a}
[(NH ₃) ₅ CrOCr(NH ₃) ₅] ⁴⁺	1 O ²⁻	"Basic rhodochromium(III)" ion ^{179a}
[(NH ₃) ₅ Cr(OH)Cr(NH ₃) ₄ (OH)] ⁴⁺	1 OH ⁻	"Basic erythrochromium(III)" ion ^{179a}
[(NH ₃) ₅ Cr(OH)Cr(NH ₃) ₄ Cl] ⁴⁺	1 OH ⁻	"Chloroerythrochromium(III)" ion ¹⁸⁰
[en ₂ Cr(OH) ₂ Cren ₂]·Br ₄ ·2.5H ₂ O	2 OH ⁻	en = ethylenediamine, NH ₂ CH ₂ CH ₂ NH ₂ ¹⁸¹
[(C ₂ O ₄) ₂ Cr(OH) ₂ Cr(C ₂ O ₄) ₂] ⁴⁻	2 OH ⁻	— ^{182a}
[(gly) ₂ Cr(OH) ₂ Cr(gly) ₂]	2 OH ⁻	gly = glycinate ^{137, 183}
[(ala) ₂ Cr(OH) ₂ Cr(ala) ₂]	2 OH ⁻	ala = alaninate ¹³⁷
[(phe) ₂ Cr(OH) ₂ Cr(phe) ₂]	2 OH ⁻	phe = phenylalaninate ¹⁸³
[(phen) ₂ Cr(OH) ₂ Cr(phen) ₂] ⁴⁺	2 OH ⁻	phen = 1,10-phenanthroline ¹⁸³⁻¹⁸⁵
[(H ₂ O) ₄ Cr(OH)(SO ₄)Cr(H ₂ O) ₄] ³⁺	1 OH ⁻ , 1 SO ₄ ²⁻	— ¹⁸⁵
[Cr ₂ (φ ₂ PO ₂) ₂ (φ ₂ PO ₂) ₂ (H ₂ O) ₄ (OH) ₂]	2 φ ₂ PO ₂ ⁻	Isomers: 4 meso; 4 inactive (centre of symmetry) 17 <i>d,l</i> pairs ¹⁸⁶ (φ = C ₆ H ₅)
[Cr ₃ (OH) ₂ (HCOO) ₆]HCOO	6 HCOO ⁻	— ^{182b}
[Cr ₃ (CH ₃ COO) ₆ O] ⁺	6 CH ₃ COO ⁻ , 1 O ²⁻	Cr atoms at corners of equilateral triangle, oxygen atom at centre, 2 bridging acetate groups along each side ^{137, 179a}
[Cr ₄ (OH) ₆ en ₆]I ₆ ·4H ₂ O	6 OH ⁻	3 Cr atoms in triangular array with 1 in centre ¹⁸³ or 4 Cr atoms in tetrahedral structure ¹⁸⁷ (en = ethylenediamine)

¹⁷⁵ J. A. Weyh and R. E. Hamm, *Inorg. Chem.* **7** (1968) 2431.

¹⁷⁶ D. A. House and C. S. Garner, *J. Am. Chem. Soc.* **88** (1966) 2156.

¹⁷⁷ D. A. House and C. S. Garner, *Inorg. Chem.* **5** (1966) 2097.

¹⁷⁸ D. A. House and C. S. Garner, *Inorg. Chem.* **6** (1967) 272.

¹⁷⁹ F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience (New York), 2nd edn. (1966): (a) p. 826; (b) p. 161.

¹⁸⁰ D. W. Hoppenjans, J. B. Hunt and L. Penghorn, *Inorg. Chem.* **7** (1968) 1467.

¹⁸¹ P. Pfeiffer, *Z. anorg. Chem.* **58** (1908): with R. Prade and R. Stern, 240; with W. Vorster and R. Storm, 280, 272.

¹⁸² K. H. Gustavson, *The Chemistry of the Tanning Process*, Academic Press, New York (1956); (a) p. 81; (b) p. 10; (c) p. 18; (d) p. 249.

¹⁸³ R. A. D. Wentworth and R. Saillant, *Inorg. Chem.* **6** (1967) 1436.

¹⁸⁴ D. Wolcott and J. B. Hunt, *Inorg. Chem.* **7** (1968) 755.

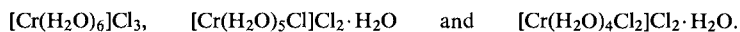
¹⁸⁵ J. E. Finholt, K. Caulton, K. Kimball and E. Uhlenhopp, *Inorg. Chem.* **7** (1968) 610.

¹⁸⁶ B. P. Block and K. D. Maguire, *Inorg. Chem.* **6** (1967) 2107.

¹⁸⁷ C. G. Barraclough, H. B. Gray and L. Dubicki, *Inorg. Chem.* **7** (1968) 844.

(b) *Stereoisomerism*

The number of Cr(III) complexes is large not only because of the great number of ligands but also because of the numerous possibilities for isomerism. Isomeric forms of Cr(III) complexes are illustrated by the three compounds of molecular formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$:



The water of crystallization, 0–2 moles in the three compounds, is readily removed and easily distinguishable from the more strongly bound coordinated water molecules. Isomers of this type were called *hydrate isomers* by Werner, who recognized and described eleven types of isomerism of complex compounds^{151c}.

By far the most important types of isomer are the stereoisomers, i.e. geometrical and optical isomers. Demonstration of the correctness of Werner's views was in large part based on his prediction of stereoisomerism of metal complexes followed by preparation and separation of the numbers and types of isomer predicted. Moreover, study of the mechanisms of reactions of metal complexes often involves consideration of the isomeric relations of reactants, intermediates and products.

The existence of stereoisomers of Cr(III) complexes is possible because of the directed bonds of the Cr(III) structure. With coordination number six, Cr(III) has the octahedral structure (Fig. 3a) with Cr at the centre and the bonds directed toward the six vertices. For convenience, the convention showing only the horizontal plane 2, 3, 4, 5 and the vertical axis 1, 6 of the octahedron is used (Fig. 3b); the six vertices are equivalent even though in the skeleton structure (b) two of them appear to differ from the other four. In counting the number of theoretically possible isomers, it must be remembered that bidentate ligands cannot span *trans* positions.

No stereoisomers are possible for the structures $[\text{CrA}_6]^{3+}$, $[\text{CrX}_6]^{3-}$, $[\text{CrA}_5\text{X}]^{2+}$ and $[\text{CrAX}_5]^{2-}$ since interchanging the positions of the groups leaves the structure unchanged. Geometrical isomerism arises with ions of the types $[\text{CrA}_4\text{X}_2]^+$ and $[\text{CrA}_2\text{X}_4]^-$ illustrated by *cis*-(1,2)- and *trans*-(1,6)- $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ (Fig. 3c, d). The chlorides of the *cis*- and *trans*-isomers are red-violet and green respectively; the analogous Co(III) complexes have the same colors as do the Cr(III) and Co(III) complexes containing two moles of ethylenediamine or propylenediamine in place of the four moles of ammonia. Complexes of the type $[\text{CrA}_3\text{X}_3]$ also have two geometrically isomeric forms, i.e. *cis*-(1,2,3) and *trans*-(1,2,6) (Fig. 3e, f). Examples of such compounds are $[\text{Crpy}_3\text{Cl}_3]$, $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$ and $[\text{Cr}(\text{Nam})_3\text{Cl}_3]$ (py = pyridine; Nam = *N*-substituted amide). In the *cis* form, three like groups are at the corners of a face of the octahedron while in the *trans* form three like groups lie in a plane at right angles to the plane of the other three.

Since even the *cis*-isomers of complexes of the types $[\text{CrA}_4\text{X}_2]^+$ and $[\text{CrA}_2\text{X}_4]^-$ have considerable symmetry, these complexes cannot have optical activity, which does arise, however, in the complexes containing two bidentate chelating ligands in place of the four singly coordinating molecules such as NH_3 . This is illustrated by complexes such as $[\text{Cren}_2\text{Cl}_2]^{3+}$ (Fig. 3g, h); the bracket represents the bidentate ligand. The *trans* form (g) has a high degree of symmetry while the *cis* form (h) has no elements of symmetry. The latter, therefore, has two forms which are related to each other as nonsuperposable mirror images, i.e. these two are optical isomers.

Although no isomers are possible with the types $[\text{CrA}_6]^{3+}$ and $[\text{CrX}_6]^{3-}$, their analogs with chelating ligands, $[\text{Cr}(\widehat{\text{AA}})_3]^{3+}$ and $[\text{Cr}(\widehat{\text{XX}})_3]^{3-}$, exist in *d, l* forms ($\widehat{\text{AA}}$ = bidentate symmetrical neutral chelating ligand such as ethylenediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$; $\widehat{\text{XX}}$ =

bidentate symmetrical negative chelating group such as oxalate, $\text{C}_2\text{O}_4^{2-}$). This is illustrated by the structures (i) of Fig. 3. Chelates of the type $[\text{Cr}(\widehat{\text{AX}})_3]^0$ may also exist in *d, l* pairs ($\widehat{\text{AX}}$ = bidentate ligand such as 1,3-diketonate, or ion of α -amino acid). The enantiomorphous forms are related to each other as three-bladed right- and left-handed propellers.

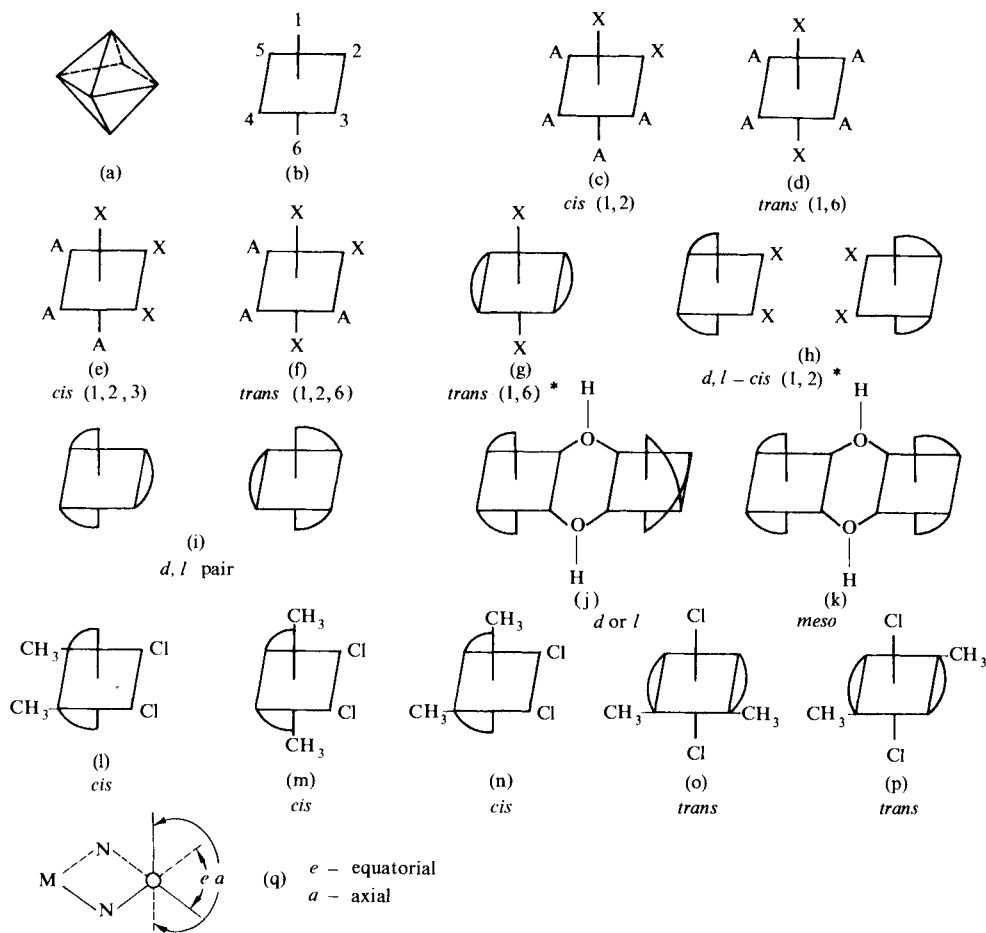


FIG. 3. Stereoisomerism of chromium(III). (a) Octahedral structure, coordination number 6. (b) Formal representation of octahedron; numbering system. (c, d) Geometrical isomers of $[\text{CrA}_4\text{X}_2]^+$ (or $[\text{CrA}_2\text{X}_4]^-$). (e, f) Geometrical isomers of $[\text{CrA}_3\text{X}_3]$. (g, h) Geometrical and optical isomers of $[\text{CrAA}_2\text{X}_2]^+$ (or $[\text{CrA}_2\text{XX}_2]^-$)*. (i) Optical isomers of $[\text{CrAA}_3]^{3+}$ (or $[\text{CrXX}_3]^{3-}$). (j, k) Tartrate-type isomerism possible for $[\text{en}_2\text{M}(\text{OH})_2\text{Men}_2]^{4+}$ or $[(\text{C}_2\text{O}_4)_2\text{M}(\text{OH})_2\text{M}(\text{C}_2\text{O}_4)_2]^{4-}$ (M = Co or Cr; en = ethylenediamine). (l, m, n) Structural isomers of *cis*- $[\text{Crpn}_2\text{Cl}_2]^+$ (pn = propylenediamine). (o, p) Structural isomers of *trans*- $[\text{Crpn}_2\text{Cl}_2]^+$. (q) Conformations of coordinated pn and analogous ligands. * ~ = bidentate ligand.

Tartrate-type isomerism (*d, l* and *meso*) is possible with binuclear complexes (Fig. 3j, k). Chromium complexes of this type are $[\text{en}_2\text{Cr}(\text{OH})_2\text{Cren}_2]^{4+}$ and $[(\text{C}_2\text{O}_4)_2\text{Cr}(\text{OH})_2\text{Cr}(\text{C}_2\text{O}_4)_2]^{4-}$.

The number of possibilities of isomerism increases when the ligand is unsymmetrical.

Complexes of the type $[\text{Cr}(\widehat{\text{AX}})_3]$ have a structure like that of $[\text{CrA}_3\text{X}_3]$ (Fig. 3e, f) except that each A is connected to an X. Thus, if $\widehat{\text{AX}}$ is unsymmetrical, $[\text{Cr}(\widehat{\text{AX}})_3]$ will exist as a pair of geometrical isomers and each of these will be a *d, l* pair, e.g. if $\widehat{\text{AX}}$ is an unsymmetrical 1,3-diketone such as trifluoroacetylacetone. Although acetylacetone (acac) has been classed as a ligand of the $\widehat{\text{AX}}$ type (one neutral and one negative group bonding), no geometrical isomers of $[\text{Cr}(\text{acac})_3]$ exist because resonance in the chelate rings makes it impossible to distinguish between the two oxygen atoms per ligand forming bonds to chromium.

A further increase in possibilities of isomerism arises when a ligand is not only unsymmetrical but also asymmetric as exemplified by propylenediamine, $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$ (pn). The complex $[\text{Crpn}_3]^{3+}$ or $\text{cis-}[\text{Crpn}_2\text{X}_2]^+$ ($\text{X} =$ coordinated ion, such as Cl^-) may contain either the *d* or *l* form of the ligand; the complex ion may have either of the two configurations; and the unsymmetrical structure of the ligand leads to a structural isomerism superimposed on whatever geometrical isomerism is already present in the complex. For example, three structural isomers of the complex $\text{cis-}[\text{Crpn}_2\text{Cl}_2]^+$ are predicted because of the different possible relative positions of the methyl groups (Fig. 3 l, m, n); there would also be two isomers of the *trans* form (Fig. 3 o, p. 48). The amino acids also belong to this class of ligands.

Polydentate ligands may also have different conformations¹⁸⁸. For example, positions on C atoms of ethylenediamine-type ligands could have axial or equatorial orientation as indicated by *a* and *e* respectively of Fig. 3q, e.g. the CH_3 groups of propylenediamine could be either axial or equatorial. In octahedral complexes, the latter is the preferred orientation because of steric interactions that would arise between axial groups and groups in octahedral coordination sites perpendicular to the chelate rings.

In principle, many more isomers of octahedral complexes are possible than have actually been found. For example, the 6-coordinate equivalent of the asymmetric carbon atom Cabcd (representing two isomers, a *d, l* pair) is Mabcdef; for this there are thirty isomers possible (fifteen racemic mixtures). Bailar¹⁸⁹ and Mayper¹⁹⁰ have devised an enumeration scheme for determining the number of isomers possible for any given structure.

(c) Preparation and Separation of Stereoisomers

Geometrical isomers, of course, differ in all their properties, such as color, melting point, solubility, etc.; thus, if both the *cis*- and *trans*-isomers are produced in a synthesis they can be separated by the usual chemical methods. However, since all properties of a pair of optical isomers that are enantiomorphs are identical except optical rotation, separation of the two (or formation of only one) requires introduction of some element of dissymmetry.

Sometimes a reaction produces only one of the possible geometrical isomers which may then be used to prepare others of that particular configuration provided rearrangement does not occur. The NH_4^+ -salt-catalyzed thermal decomposition of $[\text{Cren}_3]\text{X}_3$, for example, produces *cis-}[\text{Cren}_2\text{Cl}_2]\text{Cl} ($\text{X} = \text{Cl}$) and *trans-}[\text{Cren}_2(\text{SCN})_2]\text{SCN} ($\text{X} = \text{SCN}$)^{137, 156b, 163}; chlorination of the latter produces *trans-}[\text{Cren}_2\text{Cl}_2]\text{Cl}¹³⁷.***

Complexes containing two moles of the tridentate ligands iminodiacetate (IDA) and methyliminodiacetate (MIDA) (see Table 17) can have a *cis* and two *trans* forms (with

¹⁸⁸ M. D. Alexander, *Inorg. Chem.* **5** (1966) 2084; E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.* **81** (1959) 2620; F. P. Dwyer, T. E. McDermott and A. M. Sargeson, *J. Am. Chem. Soc.* **85** (1963) 2913.

¹⁸⁹ J. C. Bailar, Jr., *J. Chem. Ed.* **34** (1957) 334, 626.

¹⁹⁰ S. A. Mayper, *J. Chem. Ed.* **34** (1957) 623.

respect to the positions of the N atoms) corresponding to the following relative positions of the bonding atoms of the two molecules¹⁷⁵:

	<i>cis</i>	<i>trans</i> , facial	<i>trans</i> , meridional
(1) N, O, O	1, 2, 3	1, 2, 3	1, 2, 4
(2) N, O, O	4, 5, 6	6, 4, 5	6, 3, 5

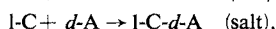
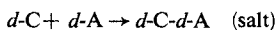
No optical isomers are possible with any of these. By reaction of the sodium salt of the ligand with $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ or adding base to a solution of the ligand acid and $\text{CrCl} \cdot 6\text{H}_2\text{O}$, the following isomers were obtained: *cis*- $\text{Na}[\text{Cr}(\text{IDA})_2] \cdot 2.5\text{H}_2\text{O}$, *cis*- $\text{NH}_4[\text{Cr}(\text{IDA})(\text{MIDA})] \cdot \text{H}_2\text{O}$ and *trans* (facial)- $\text{Na}[\text{Cr}(\text{MIDA})_2]$.

Tetraethylenepentamine is pentadentate and forms complexes of the type $[\text{Cr}(\text{tetren})\text{X}]^{2+}$. There are four possible geometrical isomers¹⁹¹, i.e. with respect to the five N atoms: I—1, 5, 4, 6, 3; II—2, 5, 4, 6, 3; III—1, 5, 4, 3, 6; IV—2, 5, 4, 3, 6. The compounds reported (X = Cl, SCN) are of type I, which has a plane of symmetry. Each of the other three can have *d*, *l* forms.

A fascinating development is the application of chromatographic procedures in stereochemical studies. For example, the geometrical isomers of $[\text{Cr}(\text{tfa})_3]$ (tfa = trifluoroacetylacetone) can be separated by gas chromatography; the peaks appear in the order *trans* (1,2,6)-*cis* (1,2,3). Reaction of Cr(III) with mixtures of trifluoroacetylacetone (tfa) and hexafluoroacetylacetone (hfa) produces seven compounds of the composition $[\text{Cr}(\text{tfa})_x(\text{hfa})_{3-x}]$ all of which can be separated by gas phase chromatography. The order of increasing retention time is: $[\text{Cr}(\text{hfa})_3]$; $[\text{Cr}(\text{hfa})_2\text{tfa}]$; the three geometrical isomers of $[\text{Cr}(\text{hfa})(\text{tfa})_2]$ —*trans-cis*, *cis-cis*, *cis-trans*; *trans*- $[\text{Cr}(\text{tfa})_3]$; *cis*- $[\text{Cr}(\text{tfa})_3]$. This is in accord with what appears to be a general rule, i.e. for complexes of a given metal ion, retention time is reduced by increasing substitution of fluorine for hydrogen¹⁹².

Optically active coordination compounds have been discussed in detail by Kirschner¹⁹³, who has listed many such compounds and described various methods of resolution. In Table 19 are listed some Cr(III) complexes that have been resolved. In the following discussion, *d* and *l* refer to optical rotation.

The most general method of resolving racemic mixtures is separation of diastereoisomers. Resolving agents available are generally the same as those used for resolving racemic mixtures of organic compounds, e.g. for cationic complexes, *d*-tartrate, nitrocamphorsulfonate, bromcamphorsulfonate; for anionic complexes, strychnine, brucine, quinine, *d*-antimonyl tartrate. The principle is illustrated by the following in which C is an optically active cation (racemic) and A is one enantiomorph of an optically active anion such as *d*-tartrate:



The products are optical isomers but not enantiomorphs and therefore can be separated by, for example, difference in solubility.

As Table 19 indicates, sometimes optical isomers of complexes, resolved by use of

¹⁹¹ D. A. House and C. S. Garner, *Inorg. Chem.* **5** (1966) 2097; **6** (1967) 272.

¹⁹² R. Sievers, "Gas Chromatographic and Related Studies of Metal Complexes", in *Coordination Chemistry: Papers Presented in Honor of Professor John C. Bailar, Jr.*, Plenum Press, New York (1969), p. 270.

¹⁹³ S. Kirschner, "Optically Active Coordination Compounds", in *Preparative Inorganic Reactions*, **1**, Interscience, New York (1964).

TABLE 19. SOME OPTICALLY ACTIVE CHROMIUM(III) COMPLEXES

Complex ^a	Resolving agent	Rotation	Refs.
[Cr(phen) ₃] ³⁺	Silver antimonyl <i>d</i> -tartrate	[α] _D = -1320°, +1320°	139
[Cren ₂ C ₂ O ₄] ⁺	K[CoEDTA] ^b	[α] _D = +275°, -305°	194
[Cren ₂ FCI] ⁺	Ammonium α-bromocamphor-π-sulfonate	[α] _D = +191°	195
		[α] ₅₄₆₁ = +625°	
[Cr(dipy) ₂ C ₂ O ₄] ⁺	[Crphen(C ₂ O ₄) ₂] ⁻	[α] _D = -261°, +361°	165
		[α] ₅₄₆₁ = -440°, +611°	
[Cr(phen) ₂ C ₂ O ₄] ⁺	[Crphen(C ₂ O ₄) ₂] ⁻	[α] _D = -562°, +855°	165
		[α] ₅₄₆₁ = -854°, +1290°	
[Cr(dipy)(C ₂ O ₄) ₂] ⁻	[Coen ₂ C ₂ O ₄]Cl	[α] _D = +670°	196
		[α] ₅₄₆₁ = +1200°	
[Crphen(C ₂ O ₄) ₂] ⁻	[Coen ₂ C ₂ O ₄]Cl	[α] _D = +790°	196
		[α] ₅₄₆₁ = +1000°	
<i>cis</i> -[Cr(C ₂ O ₄) ₂ (H ₂ O) ₂] ⁻	Strychnine sulfate	[α] ₅₁₀ = +649°, -619°	170

^a phen = 1,10-phenanthroline; en = ethylenediamine; dipy = 2,2'-dipyridyl.

^b EDTA = ethylenediaminetetraacetate.

natural products, are useful in resolving other complexes. For example, in the following two sequences each substance was resolved by the previous one in the list:

- (1) [Cren₂C₂O₄]⁺ - [Co(EDTA)]⁻ - *cis*-[Coen₂(NO₂)₂]⁺ - potassium antimonyl *d*-tartrate^{194, 197};
- (2) [Cr(dipy)₂C₂O₄]⁺ or [Cr(phen)₂C₂O₄]⁺ - [Crphen(C₂O₄)₂]⁻ - [Coen₂C₂O₄]⁺ - [Co(EDTA)]⁻ - *cis*-[Coen₂(NO₂)₂]⁺ - potassium antimonyl *d*-tartrate^{194, 196, 197}.

One of a pair of enantiomorphs may sometimes be obtained by a partial asymmetric synthesis. For example, *d*-[Cr(phen)₃]³⁺ has been obtained in this way by oxidation (with iodine) of a solution of chromium(II) sulfate, 1,10-phenanthroline and potassium antimonyl *d*-tartrate¹⁵⁹. The diastereoisomer was converted to the perchlorate. The yield was about 80%, i.e. nearly all of the [Cr(phen)₃]³⁺ was obtained in one enantiomorphous form. This product had the same specific rotation ([α]_D = +1320°) as that obtained by resolution (described above).

Such second-order asymmetric processes are also illustrated by the formation of *d*-[Crphen(C₂O₄)₂]⁻ and *d*-[Cr(dipy)(C₂O₄)₂]⁻. These may be obtained in high yield by heating the reaction mixture containing the racemic complexes and the resolving agent (in this case [Coen₂C₂O₄]⁺)¹⁹⁶.

Delepine's "method of active racemates"¹⁹³ is based on the possible formation of three racemic modifications in the solid state that may differ from that of the component enantiomorphs. A *racemic mixture* is composed of equimolar quantities of the two enantiomorphs as crystals with hemihedral facets. A *racemic compound* consists of the two enantiomorphs combined into identical crystals, each containing equal amounts of the two isomers. A *racemic solid solution* sometimes crystallizes, without compound formation, when the two enantiomorphs are isomorphous.

An *active racemate* is defined as an equimolar mixture of one enantiomorph of one complex and the enantiomorph of the opposite configuration of a second isomorphous complex; although physicochemically this is a racemate, it is active because the magnitude of the activity of the two different complexes is not the same. Thus if a mixture of one

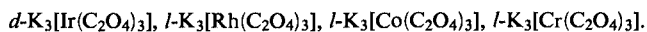
¹⁹⁴ J. W. Vaughn and D. J. Wackwitz, *Inorg. Chem.* **5** (1966) 1082.

¹⁹⁵ J. W. Vaughn, O. J. Stran, Jr., and V. E. Magnuson, *Inorg. Chem.* **7** (1968) 736.

¹⁹⁶ J. A. Broomhead, *Australian J. Chem.* **15** (1962) 228.

¹⁹⁷ F. P. Dwyer and F. L. Garvan, *Inorg. Syn.* **6**, McGraw-Hill, New York (1960), p. 195.

enantiomorph of compound A and one enantiomorph of compound B is a "racemic" mixture in this sense, the two have opposite configurations, but if they form a racemic compound or racemic solid solution they have the same configuration. On this basis, Delepine showed that the following species have the same configuration:



These principles can be used in a resolution procedure which, of course, is limited in application to complexes fulfilling the requirements listed above. If a solution of $d,l\text{-K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ and $d\text{-K}_3[\text{Ir}(\text{C}_2\text{O}_4)_3]$ is evaporated, the racemic compound $d\text{-K}_3[\text{Ir}(\text{C}_2\text{O}_4)_3] \cdot l\text{-K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ crystallizes, leaving $d\text{-K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ in solution. The other isomer could then be obtained by processing the racemic compound.

Adsorption of active solids has been used with somewhat limited success as a method of resolution. A procedure which has just begun to be exploited is gas-phase chromatography. By this technique, Sievers has achieved partial resolution of $d,l\text{-}[\text{Cr}(\text{hfa})_3]$ with a column packed with powdered $d\text{-quartz}$ ¹⁹².

(d) Preparation of Chromium(III) Complexes

The commonly available Cr(III) compounds are salts such as the sulfate and chloride of hexacoordinate Cr(III) ions; almost invariably some of the ligands will be water molecules. The major constituent of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, for example, is $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$. It is frequently difficult or impossible to replace the ligands in these inert complexes directly; when bases that can coordinate (e.g. ethylenediamine) are added to aqueous solutions of salts such as Cr(III) chloride, hydrated chromium oxide precipitates; the diamine complexes generally have to be made by less direct methods. In many other instances, unproductive side reactions such as aquation, hydrolysis, and olation will predominate in aqueous solutions.

There are no really general methods of synthesizing Cr(III) compounds although by some procedures several compounds of a particular type can be prepared. The following exemplify the variety of methods available:

Reactions with Cr(III) in H_2O : $\text{K}_3[\text{Cr}(\text{SCN})_6]$ from chrome alum and KSCN¹³⁷; $[\text{Cr}(\text{acac})_3]$ from $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and acetylacetone (solution neutralized)^{156d}.

Reactions with $\text{Cr}(\text{OH})_3 \cdot \text{XH}_2\text{O}$: with acetylacetone, $[\text{Cr}(\text{acac})_3]$ ^{156b}; with NH_4OH and NH_4NO_3 , $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{NO}_3)_3$ ^{156f}.

Displacement of one ligand by another, dry state reaction: $[\text{Cr}(\text{dbm})_3]$ from $[\text{Cr}(\text{acac})_3]$ and dibenzoylmethane (heated)^{156b}.

Thermal decomposition: $\text{cis-}[\text{Cr}\widehat{\text{AA}}_2\text{Cl}_2]\text{Cl}$ and $\text{trans-}[\text{Cr}\widehat{\text{AA}}_2(\text{SCN})_2]\text{SCN}$ by heating $[\text{Cr}\widehat{\text{AA}}_3]\text{X}$ containing NH_4X as catalyst ($\widehat{\text{AA}}$ =ethylenediamine^{137, 156b, 163, 198}, propylenediamine¹⁹⁹).

Reaction of anhydrous ligand with anhydrous Cr(III) compound: $[\text{Cr}(\text{NH}_3)_6]\text{X}_3$ ^{137, 155, 156a}, $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{X}_2$ ¹³⁷ from CrCl_3 and NH_3 ; $[\text{Cr}\widehat{\text{AA}}_3]_2(\text{SO}_4)_3$ by heating $\text{Cr}_2(\text{SO}_4)_3$ with anhydrous $\widehat{\text{AA}}$ ($\widehat{\text{AA}}$ =ethylenediamine^{137, 155, 156d}, propylenediamine^{155, 156d}); $[\text{Cr}(\text{hfa})_3]$ by heating a suspension of CrCl_3 in a CCl_4 solution of hexafluoroacetylacetone¹⁶⁷.

¹⁹⁸ M. Rock, Ph.D. thesis, University of Maryland (1960).

¹⁹⁹ T. D. O'Brien and J. C. Bailar, Jr., *J. Am. Chem. Soc.* **67** (1945) 1856.

Reactions in nonaqueous solvents: $[\text{CrA}_3\text{Cl}_3]$ by azeotropic dehydration (with benzene) of *N*-substituted amide solution of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (A is, for example *N,N*-dimethylformamide, ϵ -caprolactam)¹⁶⁶.

Reaction of dimeric complexes: $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ by reaction of HCl with erythro compound $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_5\text{Cl}]^{156g}$; *trans*- $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{ClO}_4$ by reaction of acid with chloroerythro chloride¹⁸⁰.

Ligand interchange catalyzed by Cr(II): $[\text{Cr}(\text{THF})_3\text{Cl}_3]^{156i, j}$, $[\text{Cr}(\widehat{\text{AX}})_3]$ ($\widehat{\text{AX}}$ = formylacetone^{156o}, malonaldehyde^{156o}), $[\text{Cr}(\text{C}_2\text{H}_5\text{OH})_3\text{Cl}_3]^{137}$ by reaction of ligand with CrCl_3 in presence of Zn; $[\text{Cr}\widehat{\text{AA}}_3]\text{X}_3$ ($\widehat{\text{AA}}$ = ethylenediamine^{156b, 201}, 1,10-phenanthroline¹⁵⁹, 2,2'-dipyridyl²⁰²), oxidation of Cr(II)-ligand solution.

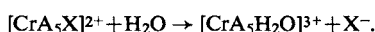
Reduction of Cr(VI): $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]^{137, 156f}$ from $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{H}_2\text{C}_2\text{O}_4$ and $\text{K}_2\text{C}_2\text{O}_4$; Reinecke's salt¹³⁷ $\text{NH}_4[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]$ from $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and NH_4SCN ; $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, reduction of CrO_3 with H_2O_2 ¹⁵⁴ or formic acid²⁰².

Reactions of coordinated ligands^{203, 204}: 3-bromoacetylacetone by bromination of $[\text{Cr}(\text{acac})_3]$; nitration and bromination (on carbon atom 3) of malonaldehyde^{156e} (ma) in $[\text{Cr}(\text{ma})_3]$.

(e) *Hydrolysis of Chromium(III) and Related Processes*²⁰⁵

Chromium(III) is characterized by its marked tendency to form polynuclear complexes. Many compounds of this type have been isolated and characterized (see Table 18). Additionally Cr(III) polymerizes, as a result of hydrolysis and associated reactions, with formation of bridged complexes of less certain composition whose existence is indicated by indirect but substantial evidence. Complexes of this type range from dimers through polymers of colloidal dimensions to precipitated Cr(III) hydroxide. Except under special circumstances to be noted, such reactions are inevitable in neutral and basic solutions and highly probable even in slightly acidic solutions (Fig. 4).

Aquation. Chromium salts (chloride, sulfate, nitrate, etc.) are aquo complexes characterized by ions such as $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$. In aqueous solution, the replacement of coordinated groups by water molecules (aquation) is a common reaction:



The extent of aquation depends on several factors including the relative coordinating tendencies of H_2O and X^- and the concentration of X^- . Thus every aqueous solution of Cr(III) is actually or potentially a solution of aquo complexes. As discussed in Section 2.5.5, Cr(II) (whose complexes are labile) catalyzes such reactions, which are usually quite slow otherwise.

²⁰⁰ D. W. Hoppenjans, J. B. Hunt and C. R. Gregoire, *Inorg. Chem.* **7** (1968) 2506.

²⁰¹ J. H. Balthis and J. C. Bailar, Jr., *J. Am. Chem. Soc.* **58** (1936) 1474.

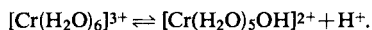
²⁰² E. Deutsch and H. Taube, *Inorg. Chem.* **7** (1968) 1532.

²⁰³ C. L. Rollinson, Ph.D. thesis, University of Illinois (1939).

²⁰⁴ R. F. Gould (ed.), *Reactions of Coordinated Ligands*, American Chemical Society, Washington, D.C. (1963).

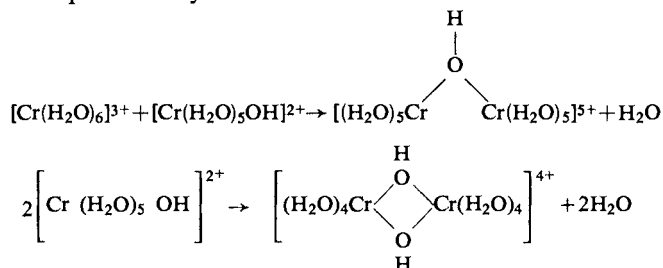
²⁰⁵ C. L. Rollinson, "Olation and Related Processes", in *Chemistry of the Coordination Compounds*, Reinhold, New York (1956); J. C. Bailar, Jr., "Coordination Polymers", in *Preparative Inorganic Reactions*, I, Interscience, New York (1964); F. G. R. Gimblett, "Cationic Aggregation Processes in Solution", in *Inorganic Polymer Chemistry*, Butterworths, London (1963); T. C. Thorstensen, "The Chemistry of the Chromium Salts", in *The Chemistry and Technology of Leather*, **2**, Reinhold, New York (1958).

Hydrolysis. The behavior of aquo complexes as acids leads to far-reaching consequences. The acidity of such solutions is accounted for as follows:



The equilibrium will be displaced to the right by heating and, of course, by addition of base. The order of magnitude of the first hydrolysis constant k is 10^{-4} ; the agreement among numerous reported values is not particularly good as might be expected in view of the side reactions possible and low rate of attainment of equilibrium^{206a}. As the pH of the Cr(III) solution is raised, the equilibrium is shifted and more of the coordinated water molecules may be converted to OH groups.

Olation. A new reaction, *olation*, may now occur, resulting in formation of polynuclear complexes consisting of chains or rings of Cr(III) ions connected by bridging OH groups. The first steps in this process may be as follows:

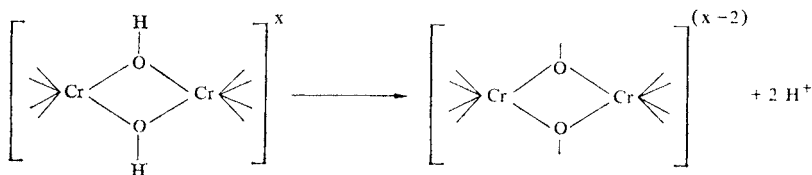


Since the diol produced by the second reaction is stabilized by the 4-membered ring, there is a driving force tending to convert the singly bridged to the doubly bridged complex. This diol is produced by polymerization of $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$, oxidation of Cr(II) by molecular oxygen in dilute acid solution, warming an equimolar mixture of Cr(III) nitrate and NaOH and boiling an aqueous solution of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ^{206b}.

The diol and any other polynuclear products containing water molecules (or groups) that can be displaced by water molecules) can still act as acids, releasing hydrogen ions and leaving coordinated OH groups (Fig. 4). Thus a continued process of olation can occur whose result is formation of larger and larger molecules. Under appropriate conditions, the aggregates may attain colloidal dimensions. The ultimate consequence is precipitation of "chromium hydroxide", the hydrate $\text{Cr}(\text{OH})_3 \cdot \text{XH}_2\text{O}$, a three-dimensional olated complex.

Bridging by groups other than OH^- . Other ligands such as sulfate and acetate (and other carboxylate ions) may also act as bridges. Bifunctional ligands (e.g. ions of dicarboxylic acids) may bridge by coordination of the active groups to different chromium atoms. A maximum of three bridges (alike or different) may be formed between two chromium atoms.

Oxolation. Oxolation may accompany or follow olation, particularly if the reaction mixture is heated. This reaction converts bridging OH^- groups to O^- groups:



²⁰⁶ J. E. Earley and R. D. Cannon, "Aqueous Chemistry of Chromium(III)", in *Transition Metal Chemistry*, 1, Marcel Dekker, New York (1966): (a) p. 69; (b) p. 64; (c) p. 40; (d) p. 34.

Olation and oxolation may account for changes in reactivity of chromium hydroxide as it ages. Freshly precipitated chromium hydroxide usually dissolves quite rapidly in mineral acids, but after standing some hours it becomes difficult to dissolve. Presumably olation continues in the precipitate; since bridged OH^- groups react more slowly with acids than singly coordinated OH^- groups, the reactivity of the precipitated hydroxide progressively diminishes. If the hydrate is heated, there is a drastic decrease in reactivity due to oxolation, a process even more difficult to reverse than olation.

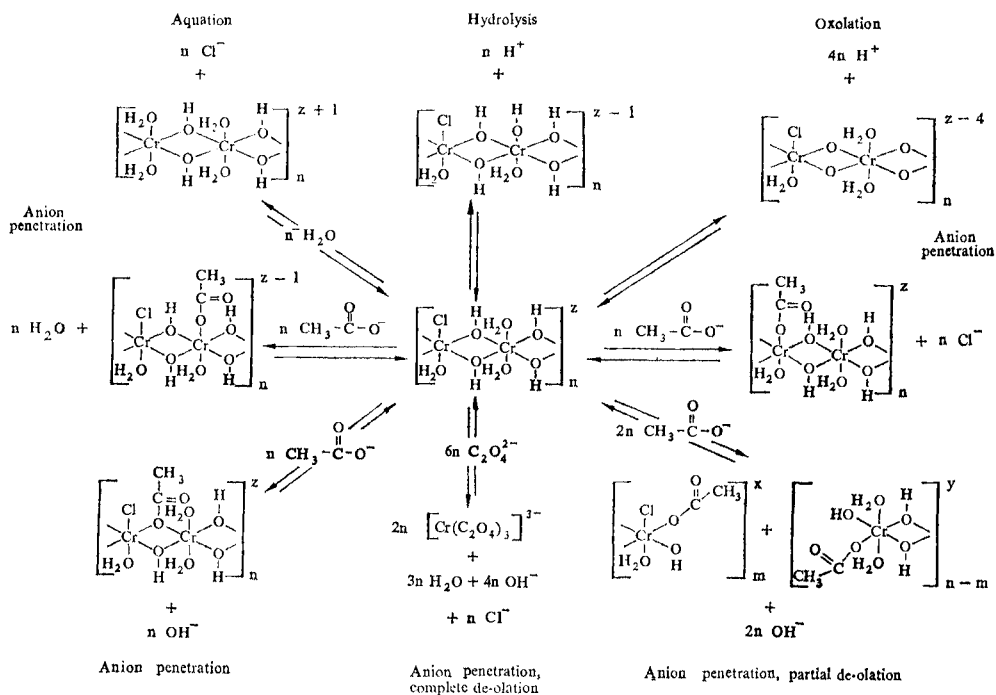


FIG. 4. Reactions of polymeric oxlated Cr(III) complexes.

Anion penetration. Anion penetration comprises displacement by anions in the solution of coordinated water molecules, OH^- groups, OH^- bridges or other ligands (Fig. 4). This reaction can occur with Cr(III) complexes of low ionic weight, with oxlated species in solution, with species of higher molecular weight that may be colloiddally dispersed and even with the precipitated hydrous oxide. Anion penetration accounts for the presence in chromium hydroxide of anionic impurities that cannot be washed out since such anions are integral components of the oxlated complex.

The relative ability of anions to displace coordinated groups in such reactions is a measure of their coordination tendencies. Little or no anion penetration can be expected with weakly coordinating ligands such as Cl^- , ClO_4^- and NO_3^- ; acetate and sulfate have considerably greater coordinating ability. The ligands of greatest coordinating tendency not only displace singly coordinated groups but may even displace bridging OH and other bridging groups, thus causing depolymerization. If the coordinating tendency is great enough, complete depolymerization may occur, with conversion of the

olated complexes (including even the precipitated hydroxide) to mononuclear complexes (Fig. 4). Since chelated structures are generally less reactive than those containing only singly coordinating ligands, ligands such as oxalate and tartrate are particularly effective in preventing olation and causing de-olation. The order of coordinating tendencies of some common ligands is:

oxalate > citrate > tartrate > glycolate > acetate >
formate > sulfate > chloride > nitrate > perchlorate.

Thus if a solution of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, for example, is required, the only anion present should be nitrate or perchlorate since those of greater coordinating tendency may displace one or more of the coordinated water molecules.

Reaction rates. After some parameter of a system containing Cr(III) complexes is changed, the corresponding change in composition of the complexes generally occurs only slowly. Heating a solution (or dispersion) of such complexes promotes olation and oxolation, both of which reverse at a low rate when the system is cooled; reversal of oxolation is much slower than reversal of olation. If the pH of a solution containing olated complexes is reduced to a value at which normally only monomeric Cr(III) complexes would exist, it may take a long time for the state of aggregation corresponding to the new pH to be attained.

Electrodeposition of chromium. The principles outlined have an important application in the production of chromium by electrodeposition from chrome alum solutions²⁰⁷. The chrome alum is crystallized from solutions made by dissolving ferrochrome in a mixture of spent electrolyte, sulfuric acid and filtrates from previous crystallizations.

Iron is removed by crystallization of ferrous ammonium sulfate from the cooled solution. To prevent simultaneous crystallization of chrome alum, Cr(III) must be in some form other than the simple aquo ion required by the chrome alum lattice. By keeping the solution at 50° for some time, the processes of hydrolysis, olation and anion penetration occur with formation of sulfato-, hydroxy- and bridged complexes. When the solution is cooled, the rate of reversal of these processes is so low that the Cr(III) aquo ions required do not have time to form.

After the iron has been removed, the processes described must be reversed to convert Cr(III) into the aquo ions necessary for crystallization of chrome alum. This is accomplished by ageing the solution at 30° for a long time; the solution is then cooled to 0°, the chrome alum crystallizes and the filtrate is returned to the leach circuit.

Chrome tanning. Chrome tanning is another process involving olation, anion penetration and oxolation^{208, 182c}. The hides or skins are made highly acid by pickling in a sulfuric acid-salt solution and then tumbled in a drum in a "basic" chromium sulfate solution, i.e. an acid solution of Cr(III) and SO_4^{2-} in which the $\text{SO}_4^{2-} : \text{Cr}^{3+}$ ratio is less than that corresponding to $\text{Cr}_2(\text{SO}_4)_3$; the composition generally corresponds to CrOHSO_4 . After sufficient agitation to ensure complete penetration of the skins, the pH of the liquor is increased by successive additions of an alkali such as sodium bicarbonate and agitation is continued for several hours.

²⁰⁷ F. E. Bacon, "Chromium and Chromium Alloys", in *Encyclopedia of Chemical Technology*, **5**, Interscience, New York, 2nd edn. (1964), p. 454.

²⁰⁸ E. B. Thorstensen, "Practice of Chrome Tannage", in *The Chemistry and Technology of Leather*, **2**, Reinhold, New York (1958), p. 249.

Prior to the addition of alkali, the state of aggregation of the Cr(III) complexes is low, permitting complete penetration of the skins with essentially no fixation of chromium. As the pH is increased, olation occurs and the olated complexes combine with the hide protein (collagen).

While the mechanism of chrome tanning has not been established unequivocally, the process apparently depends on coordination of chromium in the olated complexes with carboxyl groups of the aspartic and glutamic acid residues of the protein^{182c, 209a}. This is analogous to anion penetration by, for example, acetate ions. The increase in pH not only causes olation of Cr(III) but also promotes coordination of the carboxyl groups as in the synthesis of the Cr(III) complexes of simple ions. Conversion of collagen to leather is a result of bridging of neighboring protein chains by polynuclear Cr(III) complexes. After the leather has been colored (and otherwise processed), it is dried at a relatively high temperature which fixes the tanning complexes essentially irreversibly, presumably that because heating causes oxolation of the complexes. It should be noted, however, powerful enough chelating agents such as oxalate and tartrate can dechrome the leather.

*Competitive reactions*²¹⁰. Whether, and to what extent, olation will occur in an aqueous Cr(III) solution will depend on several factors but in particular on the coordinating tendencies and concentrations of any ligands that may be present, i.e. the state of aggregation and composition of Cr(III) species will be determined by competition of the ligands (including OH⁻) for the coordination positions of Cr(III). If base is added to a solution of CrCl₃·6H₂O, for example, hydrolysis and olation will occur with ultimate precipitation of Cr(OH)₃·XH₂O since no competitive ligand is present; if the solution contained an effective ligand such as acetylacetone^{137, 1561}, olation would be prevented and a complex of the ligand would be formed. Sometimes the chelating agent is not completely effective in competing with OH⁻ ion in syntheses in which the pH of an initially acid Cr(III)-ligand solution is raised. For example, in the preparation of [Cr(AX)₃] (AX = glycinate or alaninate), some of the diol is also produced: [(AX)₂Cr(OH)₂(AX)₂]¹³⁷.

Competition for Cr(III) is also illustrated by the chrome tanning process. Chrome liquors produced by reduction of Na₂Cr₂O₇ by SO₂ are more "astringent" than those obtained by reduction of Na₂Cr₂O₇ by glucose in H₂SO₄ solution. The only species in the former are aquo-, sulfato- and hydroxy-complexes, while the latter also contain complexes of organic ligands (e.g. organic acids) resulting from incomplete oxidation of the glucose. The latter are more highly "masked" than the former and thus do not combine so readily with the skin proteins.

The effect can be reproduced and magnified by adding ligands such as acetate, formate and phthalate to SO₂-reduced liquors^{182d, 209b}. With the unmodified solutions, tanning is usually terminated when the pH of the solution is 3.1–3.3. When the tanning liquor contains a sufficiently high concentration of one of these organic anions the process can be continued to a pH of 5–7 without causing precipitation. To promote the extent of olation required, a higher OH⁻ concentration is necessary in the presence of these competing ions. A sufficient concentration of acetate makes it difficult to exhaust the liquor.

Reactions of chromium(III) with biological ligands. Ingested Cr(III) is presumably converted to its ultimate biologically active chemical form by a sequence of reactions

²⁰⁹ S. G. Shuttleworth, "The Mechanism of Chrome Tannage", in *The Chemistry and Technology of Leather*, 2, Reinhold, New York (1958); (a) p. 293; (b) p. 305.

²¹⁰ C. L. Rollinson, "Problems of Chromium Reactions", in *Radioactive Pharmaceuticals*, CONF-651111, US Atomic Energy Commission, Oak Ridge, Tennessee (1966).

with biological ligands in the mammalian system. The principles outlined above may be applied to this extremely chemical system^{210, 211}. In media of physiological pH, the expected reaction of Cr(III) is ololation except as it may be prevented or minimized by competition of ligands other than OH^- . It may be assumed that extensive ololation would render Cr(III) biologically unavailable since this reaction would presumably be irreversible under the relatively mild conditions of biological systems.

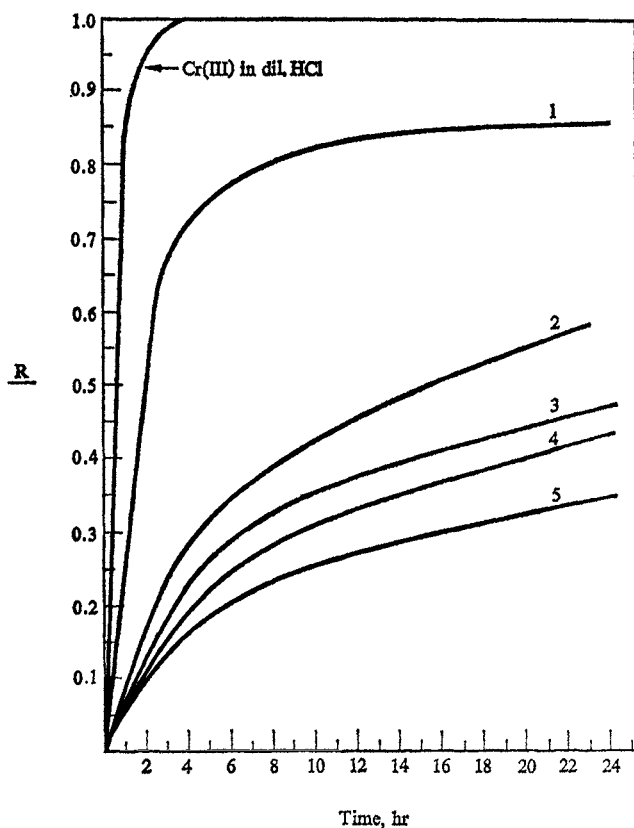


FIG. 5. Sequential dialysis: 10^{-4} M Cr(III), 0.02 M PO_4^{2-} , pH 7.4. Reaction mixture aged: 1, 1 hr; 2, 24 hr; 3, 1 week; 4, 2 weeks; 5, 4 weeks. R , fractional attainment of dialysis equilibrium in closed-system two-compartment dialyzer.

It may therefore be assumed that the chemical form and concentration of biologically active chromium will be determined by competition for Cr(III) by OH^- and other ligands of the biological system. One of the net results of the competition will be the establishing of the average state of aggregation of the Cr(III) product(s) which will be characteristic of a given reaction mixture under a given set of reaction conditions. The rate of transport of the Cr(III) through a membrane will be a function of the state of aggregation.

²¹¹ C. L. Rollinson, E. Rosenbloom and J. Lindsay, "Reactions of Chromium (III) with Biological Substances", in *Proceedings of the VIIth International Congress of Nutrition*, 5, Vieweg, Braunschweig, West Germany (1967).

This has been investigated by the method of *sequential dialysis*²¹². In this procedure successive samples of a Cr(III)-ligand reaction mixture buffered at physiological pH are dialyzed at intervals and curves are plotted showing fractional attainment of dialysis equilibrium vs. time. The area under the dialysis curve is proportional to the rate of diffusion of the Cr(III) and thus inversely proportional to the molecular size of the diffusing species; it is therefore a measure of the effectiveness of the ligand in preventing

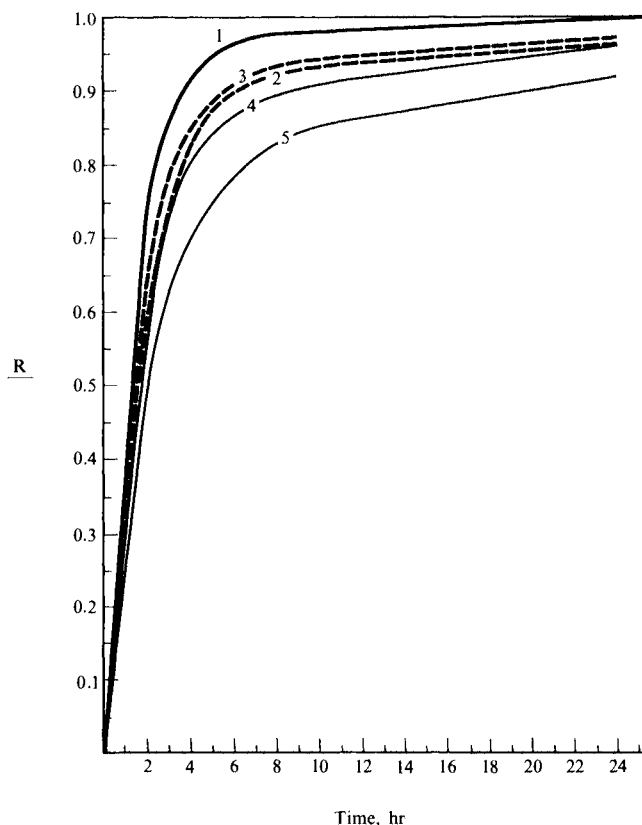


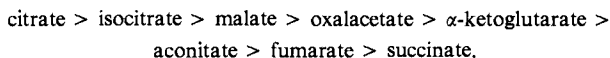
FIG. 6. Sequential dialysis: 10^{-4} M Cr(III), 0.02 M PO_4^{3-} , pH 7.4; ligand-methionine (met). Met concentration, aging of reaction mixture: 0.1 M: 1, 1 hr. 24 hr. 1 week; 0.05 M: 2, 1 hr. 3, 24 hr; 0.01 M: 4, 1 hr. 5, 24 hr. *R*, fractional attainment of dialysis equilibrium in closed-system two-compartment dialyzer.

polymerization (i.e. of the ligand's coordinating tendency). The area progressively decreases when the ligand has relatively low coordinating tendency. With the most effective ligands, the area under the curve is a maximum and remains constant for a long time (e.g. 2–3 weeks). Typical results are shown in Fig. 5 (phosphate buffer only, no effective ligand in reaction mixture) and Fig. 6 (same reaction mixture containing methionine, an effective ligand).

Since the fractional decrease in area under the dialysis curve as the reaction mixture

²¹² C. L. Rollinson and E. W. Rosenbloom, "Coordination in Biochemistry: Reactions of Chromium(III)", in *Coordination Chemistry; Papers Presented in Honor of Professor John C. Bailar, Jr.*, Plenum Press, New York (1969).

ages is inversely proportional to the coordinating ability of the ligand, this procedure makes it possible to establish orders of relative coordinating tendencies. This has been done with many biological ligands, including nearly all the compounds of the Krebs cycle, most of the compounds of the glycolysis chain, numerous amino acids, and various biological phosphates. The order of coordinating tendencies of the Krebs cycle compounds, for example, is:



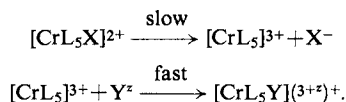
Of the many biological ligands tested, among the most effective (as determined by sequential dialysis) are histidine, ATP, ADP, thiamine pyrophosphate, fructose-1,6-diphosphate, 3-phosphoglycerate, citrate, isocitrate and tartarate^{212, 213}.

(f) *Ligand Substitution Reactions*^{206c, 214-216}

Nearly all of the octahedral complexes of the metals of the first transition series are labile except those of Co(III) and Cr(III). These labile complexes come to equilibrium essentially instantaneously with other ligands, including water. The half-times of uncatalyzed ligand displacement reactions of Cr(III) and Co(III), on the other hand, may range from hours to weeks at ordinary temperatures. Much of the knowledge of ligand replacement reaction mechanisms with octahedral complexes results from investigations of Co(III) complexes. The relative preponderance of information of Co(III) complexes is no doubt in part due to a lower probability of complicating side reactions such as *olation* (see previous section), a reaction often encountered with Cr(III) complexes but of relatively minor importance with Co(III) complexes. In general, however, the principles developed apply to reactions of both Co(III) and Cr(III).

Four important classes of reaction have been studied more or less extensively, i.e. *acid hydrolysis*, *base hydrolysis*, *exchange reactions* and *anation*. Acid hydrolysis (aquation) has been investigated far more extensively than other ligand displacement reactions of Cr(III), probably because of the relative absence of competitive reactions that often accompany the other processes.

Types of reaction^{179b}. Two extreme types of reaction mechanism are recognized: S_N1 (substitution, nucleophilic, unimolecular) and S_N2 (substitution, nucleophilic, bimolecular). In an S_N1 reaction of an octahedral complex, the rate-determining step is dissociation with loss of a ligand to form a pentacoordinate intermediate (square pyramid) which rapidly reacts with the incoming ligand, i.e.:



The rate is evidently dependent only on the concentration of $[\text{CrL}_5\text{X}]^{2+}$ and not on the concentration of the incoming ligand Y^- .

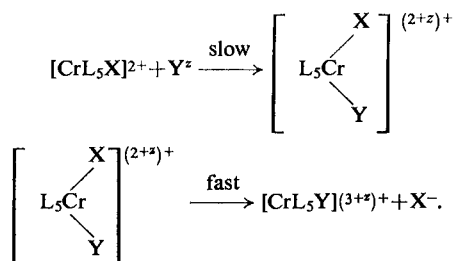
²¹³ C. L. Rollinson and E. W. Rosenbloom, *Chromium Complexes of Insulin and Related Compounds*, Annual Progress Report, Contract No. DA-49-193-MD-2444, US Army Medical Research and Development Command, Washington, DC (1969).

²¹⁴ F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, John Wiley, New York 2nd edn. (1958), chap. 6.

²¹⁵ J. O. Edwards, *Inorganic Reaction Mechanisms*, Benjamin, New York (1964), chap. 6.

²¹⁶ H. B. Gray and C. H. Langford, "Ligand Substitution Dynamics", *Chem. Engng. News* (April 1, 1968), 68.

The active intermediate in an S_N2 reaction is a heptacoordinate complex (pentagonal bipyramid) formed by association of the incoming ligand with the octahedral reactant, followed by ejection of the ligand initially present; the first step is rate controlling:



The rate is thus: $v = k_2[\text{CrL}_5\text{X}^{2+}][\text{Y}^z]$.

Actual reaction mechanisms are almost never as simple as these theoretical extreme types. In a reaction approximating the first of these, some bond formation is likely to occur before bond breaking is complete, i.e. the intermediate is not exactly the ideal square pyramid; and in reactions of the second type, the intermediate may not be actually a complex in which the entering and leaving groups are both strongly bound simultaneously. Nevertheless, these ideal extremes are useful models in considering actual mechanisms.

Acid hydrolysis. Acid hydrolysis consists of displacement of a coordinated ligand by water in acidic solution (aquation). Some acid hydrolysis rate constants for Cr(III) complexes are listed in Table 20 in comparison with the constants for hydrolysis of the analogous Co(III) complexes^{217, 218}.

TABLE 20. ACID HYDROLYSIS RATE CONSTANTS²¹⁷

Complex	Cr(III)		Co(III)	
	k_{acid} (sec ⁻¹)	t (°C)	k_{acid} (sec ⁻¹)	t (°C)
$[\text{M}(\text{NH}_3)_6]^{3+}$	2.5×10^{-5}	25	(very slow)	—
$[\text{M}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	10^{-6}	40	7×10^{-6}	25
$[\text{M}(\text{NH}_3)_5\text{Cl}]^{2+}$	10^{-5}	25	1.7×10^{-6}	25
$[\text{M}(\text{NH}_3)_5\text{Br}]^{2+}$	5×10^{-5}	25	6.3×10^{-6}	25
$[\text{M}(\text{NH}_3)_5\text{I}]^{2+}$	2×10^{-4}	0	10^{-5}	25
$[\text{M}(\text{NH}_3)_5\text{NCS}]^{2+}$	10^{-7}	25	3×10^{-9}	25
<i>cis</i> - $[\text{Men}_2\text{Cl}_2]^+$	3.3×10^{-4}	25	3.5×10^{-4}	25
<i>trans</i> - $[\text{Men}_2\text{Cl}_2]^+$	3.8×10^{-5}	25	3.9×10^{-5}	25
$[\text{Cr}(\text{H}_2\text{O})_5(\text{NCS})]^{2+}$ ^a	9.1×10^{-5}	25	—	—

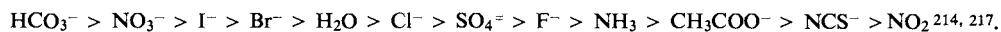
^a Ref. 218.

In acid hydrolysis in aqueous solution, since the entering ligand, H_2O , is present at a concentration of about 55.5 M, and its concentration remains essentially constant, a first-order rate law gives no indication of what the order is with respect to H_2O . Although the question cannot be answered definitely, a predominantly S_N1 mechanism is supported by some of the data. For example, the variation in rate depending on the ligand X follows the

²¹⁷ K. B. Harvey and G. B. Porter, *Introduction to Physical Inorganic Chemistry*, Addison-Wesley, Reading, Massachusetts, (1963), p. 390.

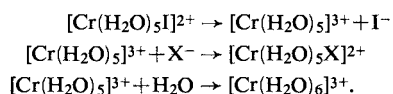
²¹⁸ C. Postmus and E. L. King, *J. Phys. Chem.* **59** (1955) 1208, 1217.

variations of thermodynamic stability of the complex ions, indicating that M–X bond breaking is an important factor in producing the transition state. The order of decreasing lability of the ligand displaced is about the same as the order of the spectrochemical series (increasing ligand field stabilization), i.e.



Numerous investigators have studied the kinetics of aquation of complexes of the type $[\text{Cr}(\text{H}_2\text{O})_5\text{X}]^{2+}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{H}_2\text{PO}_2, \text{N}_3, \text{NCS}$). A recent addition to the list is $[\text{Cr}(\text{H}_2\text{O})_5\text{SO}_4]^+$, which is interesting because the ionic charge is one less than that of the others²¹⁹. Several reaction pathways are available in aquation mechanisms, i.e. depending on $[\text{H}^+]$, $[\text{H}^+]^{-1}$ and $[\text{H}^+]^0$. A trend is discernible in comparing the reaction parameters for the $[\text{H}^+]^{-1}$ pathway with those of the $[\text{H}^+]^0$ and $[\text{H}^+]$ pathways. As the order with respect to $[\text{H}^+]$ becomes more positive, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ become less positive; the only exceptions are the parameters for the sulfato complex. It is concluded that the $[\text{H}^+]$ pathway is important only for complexes containing somewhat basic ligands.

In an acid solution of $[\text{Cr}(\text{H}_2\text{O})_5\text{I}]^{2+}$ containing Cl^- or Br^- , both aquation and anation occur²²⁰. Anation of the product of aquation, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, is excluded since this is known to be slow²²¹. A possible mechanism involves competition by H_2O and X^- for a position on a 5-coordinate intermediate:



Alternatively, the mechanism may involve a *trans* effect²²². In the aquation of $[\text{Cr}(\text{H}_2\text{O})_5\text{I}]^{2+}$ in aqueous HClO_4 containing H_2^{18}O , the product, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, contains two labeled water molecules. One of these is the molecule that displaced the iodide ion; it was concluded that there was exchange of a coordinated water molecule prior to the aquation as a result of a *trans* effect, i.e. labilizing effect by the iodide ion on the *trans* position. Only slow H_2O exchange occurs with $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$.

Replacement of coordinated halide in the following complexes by H_2O occurs with essentially complete retention of configuration²⁰⁰: (1) *cis*- $[\text{Cr}(\text{NH}_3)_4\text{H}_2\text{OCl}]^{2+}$; (2) *trans*- $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$; (3) *trans*- $[\text{Cr}(\text{NH}_3)_4\text{BrCl}]^+$; (4) *trans*- $[\text{Cr}(\text{NH}_3)_4\text{H}_2\text{OCl}]^{2+}$. The first-order rate constants (H^+ , 0.08 to 1.00 M) ranged from 1.13 to $2.90 \times 10^{-4} \text{ sec}^{-1}$. The order of increasing rate was: 4, 1, 2, 3. The trends in reaction rates are the same as those reported for the analogous ethylenediamine complexes^{223–225}.

Effect of CFSE. The rates of aquation of Cr(III) complexes are greater (often by a factor of 10) than the rates with analogous Co(III) complexes. One of the principal reasons for this is the difference in contribution to the activation energy of the change in crystal field stabilization energy (CFSE) resulting from conversion of the octahedral structure of the reactant to the structure of the intermediate activated complex, i.e. to square pyramid (5-coordination), S_N1 mechanism; to pentagonal bipyramid (7-coordination) S_N2

²¹⁹ J. E. Finholt and S. H. Deming, *Inorg. Chem.* **6** (1967) 1533.

²²⁰ M. Ardon, *Inorg. Chem.* **4** (1965) 372.

²²¹ R. J. Baltisberger and E. L. King, *J. Am. Chem. Soc.* **86** (1964) 795.

²²² C. P. Moore, F. Basolo and R. G. Pearson, *Inorg. Chem.* **5** (1966) 223.

²²³ D. J. MacDonald and C. S. Garner, *J. Am. Chem. Soc.* **83** (1961) 4152.

²²⁴ D. J. Macdonald and C. S. Garner, *Inorg. Chem.* **1** (1962) 20.

²²⁵ L. P. Quinn and C. S. Garner, *Inorg. Chem.* **3** (1964) 1348.

mechanism. The difference between the CFSE of the octahedron and the intermediate structure may be considered its contribution, ΔE_a , to the activation energy (Table 21). For ions of the series d^0 to d^{10} , the loss of ligand field energy is a maximum for d^6 (Co^{3+} , strong field) and large for d^3 (Cr^{3+}).

TABLE 21. CRYSTAL FIELD ACTIVATION ENERGIES IN REACTIONS OF CHROMIUM(III) AND COBALT(III) COMPLEXES²¹⁵

	Cr(III) (d^3) (Dq)	Co(III) (d^6)	
		Strong field (Dq)	Weak field (Dq)
Octahedron	12.0	24.0	4.0
S_N1 : octahedron to square pyramid:			
Square pyramid	10.0	20.0	4.57
ΔE_a^a	2.0	4.0	-0.57
S_N2 : octahedron to pentagonal bipyramid:			
Pentagonal bipyramid	7.74	15.48	5.28
ΔE_a^a	4.26	8.52	-1.28

^a CFS contribution to activation energy.

Slow reactions are to be expected when ΔE_a is high and relatively fast reactions when it is zero or negative. The observed relative rates of reaction are in accord with what is predicted from these figures, i.e. Cr(III) and Co(III) (strong field, spin-paired) inert, and Co(III) (weak field, spin-free) labile.

Base hydrolysis. In base hydrolysis, a coordinated ligand is ultimately replaced by OH^- , although the process may not be direct. Some reaction rate constants (k_{OH^-} , $\text{M}^{-1} \text{sec}^{-1}$) are²¹⁴: *cis*- $[\text{Men}_2\text{Cl}_2]^+$: Cr(III), 2.7×10^{-2} (25°); Co(III), 10^3 (25°); *trans*- $[\text{Men}_2\text{Cl}_2]^+$: 3.7×10^{-2} (25°); 3×10^3 (25°). The rates for the Co(III) complexes are about 10^5 times those for the Cr(III) complexes.

It is apparent that the mechanisms cannot be the same. It has been suggested that some Co(III) complexes of NH_3 and amines can react by the $S_N1\text{CB}$ mechanism²¹⁷ (substitution, nucleophilic, unimolecular, conjugate base) in which the fast reaction is a combination of OH^- with a proton from, for example, NH_3 , leaving a coordinated NH_2^- , followed by a slow (rate-controlling) reaction with water converting the NH_2^- back to NH_3 and coordinating the resulting OH^- .

Exchange reactions^{206c, 216}. Exchange of a ligand with the coordinated ligand can be followed by use of isotopic tracers. The inert character of Cr(III) complexes is demonstrated by the low rate of exchange of H_2^{18}O with coordinated water of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$; the rate constant (at 27°) is 2 to $5 \times 10^{-6} \text{min}^{-1}$, depending on the salt concentration, and is constant over the range of $[\text{H}^+]$ 10^{-2} to 1.5 M. The activation energy is about 24 kcal/mole. The question whether this reaction is S_N1 or S_N2 has not been answered; either type fits the rate law

$$v = k[\text{Cr}(\text{H}_2\text{O})_6^{3+}].$$

In the study of exchange reactions with ligands other than water, aquation may cause complications. For example, the exchange of urea with $[\text{Cr}(\text{NH}_2\text{CONH}_2)_6]^{3+}$ is slow in

water and cannot be followed readily because of rapid aquation although the exchange has been measured in methanol.

Anation^{206c}. In general, the rate of reaction of an aquo ion with a ligand is not strongly affected by the nature of the ligand and the rates for a given ion are about the same as the

TABLE 22. STABILITY OF SOME CHROMIUM(III) COMPLEXES AT 25° 206^d

X ⁻	[Cr(H ₂ O) ₅ X] ²⁻			X ⁻ S ^{a, c}
	log <i>k</i>	<i>H</i> ^b	Δ <i>S</i> ^c	
OH ⁻	10.2	-4.0	33	-2.5
F ⁻	4.4	2.6	30	-2.3
NCS ⁻	3.1	-2.1	6.9	—
Cl ⁻	0.7	6.1	17.2	13.2
Br ⁻	-2.6	5.1	4.9	19.3
SO ₄ ²⁻	1.3	7.2	29.3	4.2

^a For reaction [Cr(H₂O)₆]³⁺ + X⁻ ⇌ [Cr(H₂O)₅X]²⁺ + H₂O.

^b kcal/mole.

^c e.u.

rate of exchange of water for that ion. Presumably these facts are accounted for by a reaction mechanism comprising two steps: (1) formation of outer-sphere complex of the aquo ion and the ligand; (2) elimination of water from the aquo ion^{179b}. The following are

TABLE 23. STABILITIES OF CHROMIUM(III) AND COBALT(III) COMPLEXES^{206^d}

System	log <i>k</i>	
	Cr	Co
[M(H ₂ O) ₆] ³⁺ -SO ₄ ²⁻	1.0	1.3
-OH ⁻	9.7	12.3
-EDTA	23.4	36
-biguanide	21.9	42.7
[M(NH ₃) ₅ H ₂ O] ³⁺ -Cl ⁻	1.6	0.6
-OH ⁻	8.8	7.6
[Men ₂ (H ₂ O) ₂] ³⁺ -en	< 10.2	14.0

examples of anations whose mechanisms have been studied: reaction of C₂O₄²⁻ or HC₂O₄⁻ with *cis*-[Cr(C₂O₄)₂(H₂O)₂]⁻ ^{226, 227}; C₂O₄²⁻ with [Cr(C₂O₄)_{*n*}(H₂O)_{6-2*n*}]^{3-2*n*} ²²⁸; acetate and citrate with [Cr(H₂O)₆]³⁺ ²²⁹; NCS⁻ with [Cr(H₂O)₆]³⁺ ²¹⁸. The last is first order with respect to NCS⁻ up to 0.1 M. There is also a pH dependence indicating reaction of NCS⁻ with [Cr(H₂O)₅OH]²⁺ and [Cr(H₂O)₄(OH)₂]⁺ as well as with [Cr(H₂O)₃]³⁺; the rate of reaction increased with decreasing positive charge of the reacting species, i.e. the OH⁻ ion exerts a labilizing effect for replacement of water.

²²⁶ H. Kelm and G. M. Harris, *Inorg. Chem.* **6** (1967) 706.

²²⁷ K. V. Krishnamurty and G. M. Harris, *J. Phys. Chem.* **64** (1960) 346.

²²⁸ R. E. Hamm and R. E. Davis, *J. Am. Chem. Soc.* **75** (1953) 3085.

²²⁹ R. E. Davis, *J. Am. Chem. Soc.* **80** (1958) 4469.

Stability of chromium(III) complexes. Generally, Co(III) complexes are more stable than analogous Cr(III) complexes. Earley and Cannon^{206d}, summarizing considerable thermodynamic data, conclude that the difference in stability of Co(III) and Cr(III) complexes increases in the order: I^- , $Br^- < Cl^-$, $S^{2-} < N_3^-$, NCS^- , $F^- < H_2O$, OH^- , $C_2O_4^{2-} < en < NO_2^- < biguanide$ (en = ethylenediamine). Some data for complexes of the type $[Cr(H_2O)_6X]^{2+}$ are summarized in Table 22; data for some analogous Co(III) and Cr(III) complexes are listed in Table 23.

2.7. OXIDATION STATE IV

2.7.1. Anhydrous Chromium(IV) Halides and Halide Complexes²³⁰⁻²³²

Chromium(IV) fluoride may be obtained by fluorinating Cr, CrF_3 , or $CrCl_3$, a process which also produces some CrF_5 . The tetrachloride is produced by reaction of Cl_2 with $CrCl_3$ at 600° , and it may also be formed in the $NaCl$ - $CrCl_3$ system at 900° . The fluoride can be heated without decomposition to a temperature above its melting point (estimated²³² at 277°). The chloride, however, decomposes into Cl_2 and $CrCl_3$ at relatively low temperatures. The fluoride is quite stable toward chemical reagents. The halides $CrBr_4$ and CrI_4 may exist in the vapor phase at high temperatures in the presence of a high vapor pressure of free halogen.

The complexes $M_2[CrF_6]$ ($M = K, Rb, Cs$) are prepared by fluorinating a mixture of MCl and $CrCl_3$. The potassium salt is isomorphous with $K_2[MnF_6]$. It decomposes to $K_3[CrF_6]$ and CrF_5 at 300° . Complexes of the type $M[CrF_5]$ ($M = K, Rb$) are also known. The complex fluorides hydrolyze readily.

2.7.2. Chromates(IV)

Chromium(IV) forms several mixed oxides, or chromates(IV), formulated as $MCrO_3$, $M_2^{II}CrO_4$, $M_3^{II}CrO_5$ and $M_4^{II}CrO_6$ (M = alkaline earth ion)²³³. These are not too well characterized except for Ba_2CrO_4 and Sr_2CrO_4 . These compounds are stable in air and contain discrete CrO_4^{4-} ions.

Ba_2CrO_4 is prepared from Cr_2O_3 and $BaCrO_4$ by heating a mixture of stoichiometric quantities of the pure dry reactants, containing a little $Ba(OH)_2$, in nitrogen²³⁴. The product is a microcrystalline emerald green powder soluble in dilute acids and hydrolyzed by water. If too much $Ba(OH)_2$ is used in the reaction mixture, blackish-green $Ba_3Cr^{IV}O_5$ is formed.

Several $BaCrO_3$ polytypes have been prepared in a tetrahedral anvil apparatus at high temperature and high pressure by reaction of CrO_2 with BaO or Ba_2CrO_4 ; $BaCrO_3$ was not formed at pressures less than 3000 atm²³⁵. The $BaCrO_3$ variants may be described on the basis of stacking sequences of close-packed BaO_3 layers. The unit cell of the layered

²³⁰ R. D. Peacock, "Some Fluorine Compounds of the Transition Metals", in *Progress in Inorganic Chemistry*, **2**, Interscience, New York (1960), pp. 207, 209, 213.

²³¹ G. W. A. Fowles, "Halide and Oxyhalide Complexes of Elements of the Titanium, Vanadium and Chromium Subgroups", in *Preparative Inorganic Reactions*, **1**, Interscience, New York (1964), pp. 128, 132.

²³² J. E. Fergusson, "Halide Chemistry of Chromium, Molybdenum and Tungsten", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 242.

²³³ F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 2nd edn. (1966), p. 830.

²³⁴ F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965), p. 1393.

²³⁵ B. L. Chamberland, *Inorg. Chem.* **8** (1969) 286.

structures is determined by the number of BaO_3 layers per cell. For layer types $4H$, $6H$, $9R$, $12R$, $14H$ and $27R$, the value of a varied from 5.62 to 5.662 Å; c ranged from 9.359 Å ($4H$) to 62.705 Å ($27R$) (numeral designates number of layers; H , R , hexagonal and rhombohedral symmetries respectively).

2.7.3. Chromium(IV) Oxide

While information about Cr(IV) is generally scanty, considerable information about CrO_2 is available, much of it recent. One of the reasons for the great interest in this compound is its magnetic properties, which make it particularly suitable for recording tapes.

When CrO_3 is heated in a bomb it decomposes to lower oxides and oxygen; the final product is Cr_2O_3 ²³⁶. One of the intermediate oxides is CrO_2 which can also be produced by heating chromyl chloride and by thermal decomposition of CrO_3 in the presence of water vapor at high pressure^{237, 238}. The other oxides decompose and pure CrO_2 is obtained; the oxygen required to stabilize CrO_2 is furnished by the decomposition of CrO_3 .

Chromium(IV) oxide suitable for magnetic recording tapes is made by hydrothermal heating of a chromium oxide Cr_xO_y at 250–500° and in the pressure range 50–3000 atm²³⁸. The thermal decomposition is carried out with water or aqueous acid as the reaction medium.

Oxides Cr_xO_y suitable as starting materials may be prepared, for example, by heating CrO_3 in oxygen at atmospheric pressure for several days at 250° or by heating $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at atmospheric pressure at 250–400°. The ratio $2y/x$ is greater than 4 and less than 6; this range includes Cr_3O_8 and Cr_2O_5 in which the average oxidation states are respectively 5.33 and 5.00. The advantage of such oxides is their smaller solubility in water than that of CrO_3 . Various modifying agents (e.g. Sb_2O_3 , RuO_2 , iron oxide) may be used to extend the range over which the magnetic properties of the product (e.g. coercive force, remanence ratio, Curie temperature) can be varied.

Various temperatures from 250° to 500° have been reported for the decomposition of CrO_2 (which is metastable in air) to Cr_2O_3 . Some experimental evidence²³⁹ indicates that it can be heated for at least 48 hr at 400° unless it has first been nucleated with Cr_2O_3 by rapid heating to about 475°. Thus previously reported decomposition temperatures may be significant only for each particular set of experimental conditions since the transformation of CrO_2 to Cr_2O_3 is dependent on the history and composition of the CrO_2 sample used. It can be kept without decomposition for short times (at least 2 min) up to 2000° and for longer times (at least 60 min) up to 1200°, at 60–65 kb pressure²⁴⁰.

Chromium(IV) oxide has been grown epitaxially in oriented layers on {100}, {110}, {210} and {001} surfaces of rutile (TiO_2) single crystals and on the {0001} planes of Al_2O_3 (sapphire) and Fe_2O_3 (hematite) single crystals²⁴¹. Such layers are obtained by decomposition of CrO_3 on the substrate in a pressure vessel at 4000 psi and 425°. The area of the oriented layers is limited by the size of the single crystal substrates. The epitaxial CrO_2 is identical with the bulk material.

²³⁶ B. Kubota, *J. Am. Ceramic Soc.* **44** (5) (1961) 239.

²³⁷ T. J. Swoboda, P. Arthur, Jr., N. L. Cox, J. N. Ingraham, A. L. Oppegard and M. S. Sadler, *J. App. Phys.*, Supplement, **32** (1961) 374S.

²³⁸ P. Arthur, Jr. and J. N. Ingraham, "Process for the Preparation of Ferromagnetic Chromium Dioxide", US Patent 3,117,093 (to du Pont), January 7, 1964.

²³⁹ D. S. Rodbell and R. C. DeVries, General Electric Report No. 67-C-007, January, 1967.

²⁴⁰ R. C. DeVries, *Mat. Res. Bull.* **2** (1967) 999.

²⁴¹ R. C. DeVries, *Mat. Res. Bull.* **1** (1966) 83.

Chromium(IV) oxide has a tetragonal rutile-type crystal structure^{237, 242}, space group $P4/nmn$, $a = 4.421 \text{ \AA}$, $c = 2.917 \text{ \AA}$. The chromium ions are at the corners and body-centre of the unit cell. The density of CrO_2 is 4.9 g/cm^3 .

Chromium(IV) oxide is ferromagnetic and its magnetic properties have been investigated in considerable detail^{243, 244}. The coercivity can be varied from 25 to over 700 oersteds. The saturation flux density is 6100 gauss. At room temperature, the saturation specific magnetization varies from 89 to 92 e.m.u./g (powdered samples, 4000 oe); extrapolation of experimental magnetic data to infinite field results in limiting values of 98–100 e.m.u./g²³⁷. The Curie temperature is about 126° ²³⁷.

Chromium(IV) oxide is characterized by metallic conductance. Resistivities of particle compactions are in the range 4×10^{-2} to $2 \times 10^{-3} \text{ ohm cm}^{243}$. The resistivity of the $\{100\}$ plane of a single crystal is $2.5 \pm 0.5 \times 10^{-4} \text{ ohm cm}^{245}$.

2.7.4. Chromium(IV) Alkoxides

By reaction of $\text{Cr}(\text{Net}_2)_4$ with alcohols, blue monomeric alkoxides, $\text{Cr}(\text{OR})_4$, are obtained²³³. The *tert*-butoxide has been prepared in 80% yield by heating $\text{Cr}(\text{C}_6\text{H}_5)_2$, di-*tert*-butyl peroxide in benzene or petroleum ether at 90° in a sealed tube²⁴⁶. At 300°K , μ_{eff} for these compounds is about 2.8 B.

2.7.5. Chromium(IV) Reaction Intermediates

Chromium(IV) apparently has no solution chemistry except for the formation of Cr(IV) intermediates in redox reactions, discussed in Section 2.9.3.

2.8. OXIDATION STATE V

2.8.1. Anhydrous Chromium(V) Halogen Compounds^{247–250}

The only chromium pentahalide known is CrF_5 . Pyrolysis of $\text{K}_2[\text{CrF}_6]$ produces CrF_5 and $\text{K}_3[\text{CrF}_6]$. Chromium(V) fluoride has been prepared by fluorination of Cr, CrCl_3 , or CrF_3 at 300° . It is a fiery red solid (m.p. 30° , b.p. 117° , with decomposition). It is hard to prepare in pure form because it is easily hydrolyzed. The reactivity of the Group VIB pentafluorides increases in the order $\text{W} < \text{Mo} < \text{Cr}$. Of the highest fluorides of Cr, Mo and W (CrF_5 , MoF_6 and WF_6), CrF_5 is the most reactive²⁵¹; CrF_6 is unstable above -100° ²⁵².

²⁴² W. H. Cloud, D. S. Schreiber and K. R. Babcock, *J. Appl. Phys.*, Supplement, **33** (1962) 1193.

²⁴³ F. J. Darnell and W. H. Cloud, *Bull. Soc. Chim. France* (1965) 1164.

²⁴⁴ J. S. Kouvel and D. S. Rodbell, *Magnetic Critical-point Behavior of CrO_2* , General Electric Report No. 66-C-423, November, 1966; *The Magnetic Equation of State for CrO_2 and Nickel Near their Curie Points*, General Electric Report No. 66-C-499, December, 1966; D. S. Rodbell, *J. Phys. Soc. Japan*, **21** (1966) 1224.

²⁴⁵ D. S. Rodbell, J. M. Lommel and R. C. DeVries, *J. Phys. Soc. Japan*, **21** (1966) 2430.

²⁴⁶ N. Hagihara and H. Yamazaki, *J. Am. Chem. Soc.* **81** (1959) 3160.

²⁴⁷ R. D. Peacock, "Some Fluorine Compounds of the Transition Metals", in *Progress in Inorganic Chemistry*, **2**, Interscience, New York (1960), pp. 215, 217.

²⁴⁸ G. W. A. Fowles, "Halide and Oxyhalide Complexes of Elements of the Titanium, Vanadium and Chromium Subgroups", in *Preparative Inorganic Reactions*, **1**, Interscience, New York (1964), pp. 126, 132, 134, 137.

²⁴⁹ J. E. Fergusson, "Halide Chemistry of Chromium, Molybdenum and Tungsten", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 243.

²⁵⁰ A. D. Beveridge and H. C. Clark, "Pentahalides of the Transition Metals", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), pp. 186, 192, 199, 217.

²⁵¹ T. A. O'Donnell and D. F. Stewart, *Inorg. Chem.* **5** (1966) 1434.

²⁵² O. Glemser, H. Roesky and K. H. Hellberg, *Angew. Chem.* **75** (1963) 346.

Two oxyhalides are known, CrOF_3 and CrOCl_3 . They are easily hydrolyzed. The chloro compound is stable only at low temperature in the dark; above 0° , disproportionation occurs (to Cr(VI) and Cr(III)). The fluoro compound is prepared by reaction of CrO_3 with BF_3 or ClF_3 at room temperature; the product always contains some BrF_3 or ClF_3 , probably as solvate molecules. The chloro compound, CrOCl_3 , can be made by reaction of thionyl chloride, sulfuryl chloride or boron(III) chloride with chromyl chloride or CrO_3 at low temperature.

Two types of oxyhalide complex are known, $[\text{CrOX}_4]^-$ ($X = \text{F}, \text{Cl}$) and $[\text{CrOCl}_5]^{2-}$. Salts of $[\text{CrOF}_4]^-$ are obtained by reducing the dichromate with BrF_3 or ClF_3 at low temperature. Reduction of Cr(IV) with HCl in acetic acid is a route to the compounds $\text{M}_2[\text{CrOCl}_5]$ ($M = \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$, organic bases) and $\text{M}[\text{CrOCl}_4]$ ($M = \text{pyridine}, \text{quinoline}, \text{etc.}$). These complexes are easily hydrolyzed.

2.8.2. Chromium(V) Oxygen Compounds

A few alkali and alkaline earth chromates(V) have been described²⁵³. They are hygroscopic black or blue-black solids. They hydrolyze with disproportionation to Cr(III) and Cr(VI) . The magnetic susceptibility of Na_3CrO_4 corresponds to one unpaired electron. The CrO_4^{3-} ions of M_3CrO_4 ($M = \text{Li}, \text{Na}$) and $\text{M}_3^{II}(\text{CrO}_4)_2$ are apparently discrete and tetrahedral.

Chromium(V) oxide is apparently formed in the thermal decomposition of CrO_3 , the final product of which is Cr_2O_3 ²⁵⁴. The Cr_2O_5 phase formed always has a ratio O:Cr smaller than the theoretical value, 2.5; it ranges from 2.385 to 2.430. This oxide starts to decompose in air at about 380° ; the activation energy of decomposition is 61.7 kcal/mole.

2.8.3. Chromium(V) Reaction Intermediates

There appears to be no solution chemistry of chromium(V) other than the occurrence of Cr(V) intermediates in redox reactions, dealt with in Section 2.9.3.

2.9. OXIDATION STATE VI

2.9.1. Chromium(VI) Fluoride^{255, 256}

The only hexahalide of Cr(VI) reported is CrF_6 , a yellow compound that is thermally unstable, decomposing to CrF_5 and F_2 even at -100° . It has been prepared by reaction of Cr and F_2 in an autoclave (400° , 200 atm).

2.9.2. Chromium(VI) Oxy Compounds

Chromium(VI) forms a large number and a considerable variety of oxygen compounds most of which may be regarded as derived from Cr(VI) oxide. These include the oxy-halogen complexes and chromyl compounds, chromates, dichromates, trichromates, tetrachromates and basic chromates. All of these Cr(VI) compounds are, of course, quite potent oxidizing agents, although kinetically they cover a wide range. Chromium(VI) does not appear to

²⁵³ F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 2nd edn. (1966), p. 830.

²⁵⁴ B. Kubota, *J. Am. Ceramic Soc.* **44** (1961) 239.

²⁵⁵ J. E. Fergusson, "Halide Chemistry of Chromium Molybdenum and Tungsten", in *Halogen Chemistry*, 3, Academic Press, New York (1967), p. 245.

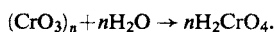
²⁵⁶ O. Glemser, J. Roesky and K. H. Hellberg, *Angew. Chem.* **75** (1963) 346.

have anywhere near the capability of forming isopoly anions so characteristic of molybdenum and tungsten.

(a) *Chromium(VI) Oxide ("Chromic Acid")*^{257, 258a}

Although it is the anhydride of chromic acid, CrO_3 has for a long time been designated *chromic acid* in industry. It is an orange-red compound that can be precipitated from aqueous solutions of chromates and dichromates by addition of H_2SO_4 . It is produced^{259a} by evaporating the water from a reaction mixture of $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ and concentrated H_2SO_4 or by precipitation from a slurry of sodium dichromate and excess concentrated H_2SO_4 . When CrO_3 is heated above its melting point, it loses oxygen by stages with ultimate formation of the stable product Cr_2O_3 . By means of X-ray analysis, Cr_3O_8 , Cr_2O_5 , CrO_2 and Cr_2O_3 were identified as the products of decomposition of CrO_3 under high oxygen pressures²⁶⁰.

Chromium trioxide is a linear polymer of chromium and oxygen atoms with two additional oxygen atoms attached to each Cr atom^{261a}. The structure consists of distorted CrO_4 octahedra with a Cr-O bond distance of about 1.8 Å. Chromium trioxide is not very soluble in acetic acid or most of the common nonhydroxylic solvents, but dissolves in water, acetic anhydride, *t*-butyl alcohol, pyridine, etc., with accompanying depolymerization, e.g.



When CrO_3 is dissolved in *t*-butyl alcohol, chromate esters may be formed.

Chromium trioxide forms many adducts, with organic compounds, of the general formula $\text{CrO}_3 \cdot 2\text{L}$, in which L may be, for example, pyridine, picolines, lutidines and quino-line. A few adducts contain more than two moles of base per mole of CrO_3 ^{258a, 262a, b}.

(b) *Chromates and Dichromates*^{258b, 259a, 265}

Dozens of chromates and dichromates are known, including those of the ammonium ion and all the common metallic ions²⁶⁶. The chromates of colorless cations are yellow. They contain the CrO_4^{2-} ion which is tetrahedral in solution and in the crystal lattice. The alkali metal chromates and magnesium chromate are soluble in water.

Among the slightly soluble chromates are those of silver, lead and the alkaline earth metals; the solubilities of the last decrease in the order $\text{Ca} > \text{Ba} > \text{Sr} > \text{Ra}$. The

²⁵⁷ F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 2nd edn. (1966), p. 828.

²⁵⁸ J. Amiel, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959); (a) p. 208; (b) p. 218; (c) p. 150.

²⁵⁹ W. H. Hartford and R. L. Copson, "Chromium Compounds", in *Encyclopedia of Chemical Technology*, **5**, Interscience, New York, 2nd edn. (1964); (a) p. 484; (b) p. 497.

²⁶⁰ B. Kubota, *J. Am. Ceramic Soc.* **44** (5) (1961) 239.

²⁶¹ K. B. Wiberg, "Oxidation by Chromic Acid and Chromyl Compounds", in *Oxidation in Organic Chemistry*, Part 4, Academic Press, New York (1965); (a) p. 69; (b) p. 161; (c) p. 94.

²⁶² (a) O. E. Accountius, J. Bush and H. H. Sisler, *Inorg. Syn.* **4**, McGraw-Hill, New York (1953), p. 94; (b) S. Hein and F. Herzog, in *Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965), p. 1385.

²⁶³ R. Keller, *Basic Tables in Chemistry*, McGraw-Hill, New York (1967), p. 228.

²⁶⁴ P. Moore, S. P. Kettle and R. G. Wilkins, *Inorg. Chem.* **5** (1966) 220.

²⁶⁵ M. C. Udy, "The Physical and Chemical Properties of Compounds of Chromium", in *Chromium*, **2**, Reinhold, New York (1956), p. 137.

²⁶⁶ F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965), p. 1384.

solubility product²⁶³ (at 25°) of some slightly soluble chromates are: PbCrO_4 , 1.8×10^{-14} ; Ag_2CrO_4 , 9.0×10^{-12} ; BaCrO_4 , 3.0×10^{-10} ; SrCrO_4 , 3.0×10^{-5} ; CaCrO_4 , 2.3×10^{-2} .

The chromates are converted to dichromates by acids. The latter are usually hydrated. If the cation is colorless, the dichromate is orange; in aqueous solutions of these compounds, the color change is easily visible as the solution is made basic or acid. Some of the pH-dependent equilibria of Cr(VI) solutions are shown in Table 24. Only CrO_4^{2-} ions exist

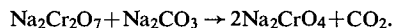
TABLE 24. SOME EQUILIBRIA IN CHROMIUM(VI) SOLUTIONS

Equilibria	$k(25^\circ)$ ^a	Reference
$\text{H}_2\text{CrO}_4 \rightleftharpoons \text{HCrO}_4^{2-} + \text{H}^+$	4.2, 5	264
$\text{HCrO}_4 \rightleftharpoons \text{CrO}_4^{2-} + \text{H}^+$	$10^{-5.9}$ (3); $10^{-6.5}$ (0)	264
$\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCrO}_4$	$10^{-2.2}$ (3); $10^{-1.6}$ (0)	264
$\text{HCr}_2\text{O}_7 \rightleftharpoons \text{H}^+ + \text{Cr}_2\text{O}_7^{2-}$	0.85	261(a)
$\text{H}_2\text{CrO}_4 \rightleftharpoons \text{H}^+ + \text{HCr}_2\text{O}_7^-$	large	261(a)
$\text{Cr}_2\text{O}_7^{2-} + \text{OH}^- \rightleftharpoons \text{HCrO}_4^- + \text{CrO}_4^{2-}$	—	264
$\text{HCrO}_4^- + \text{HO}^- \rightleftharpoons \text{CrO}_4^{2-} + \text{H}_2\text{O}$	—	264

^a Numbers in parentheses indicate ionic strengths.

above pH 8. As the pH is lowered the equilibria shift; in the pH range 2–6, HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions are in equilibrium. These equilibria are modified if ions such as chloride are present that react to form substituted chromates. At high Cr(VI) concentrations, polychromates may form.

The most important of these compounds industrially are sodium chromate and dichromate from which most other chromium compounds are produced^{259a}. Sodium chromate is made by roasting chromite with soda ash or a mixture of soda ash and lime followed by extraction with water; presence of lime prevents leaching of aluminate along with Na_2CrO_4 . Sodium chromate is crystallized from a solution prepared by adding Na_2CO_3 to a solution of $\text{Na}_2\text{Cr}_2\text{O}_7$:



Most industrial Cr(III) compounds, such as chrome alum, $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, are made from Cr(III) solutions obtained by reducing acidic dichromate solutions, usually with SO_2 ^{259a}. Various reducing agents, including SO_2 and glucose, have been used in reducing dichromates to produce the basic chromium sulfates used in chrome tanning.

Other chromates may be produced by, for example, reaction of CrO_3 with bases and carbonates; chromates or bichromates with salts of cations whose chromates are insoluble^{262b, 265}. Double decomposition reactions of bichromates with salts are used to produce other bichromates which can also be obtained by reaction of CrO_3 with metal oxides and carbonates^{262b, 265}.

Many double chromates have been reported; of these, the double potassium chromates appear to be the most numerous. They can be produced by: reaction of bases with bichromates; reaction of bichromates with chromates; reaction of one chromate with another²⁶⁵.

Numerous basic chromates are also known²⁶⁵. Among these are many groups of compounds of the type $a\text{M}_x\text{O}_y \cdot b\text{CrO}_3$ in which M_xO_y is a metal oxide, and a/b has several values, e.g. $a\text{CaO} \cdot b\text{CrO}_3$, $a/b = 2/1, 2/3$; $a\text{PbO} \cdot b\text{CrO}_3$, $a/b = 2/1, 3/1, 4/1, 5/1, 3/2, 7/2$; $a\text{NiO} \cdot b\text{CrO}_3 \cdot n\text{H}_2\text{O}$, $a/b = 2/1, 4/1$ ($n = 6$), $3/1$ ($n = 3$); $a\text{TiO}_2 \cdot b\text{CrO}_3 \cdot n\text{H}_2\text{O}$, $a/b = 3/2$ ($n = 1$), $2/1$ ($n = 2$), $3/1$ ($n = 3$).

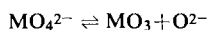
(c) *Polychromates*^{258b, 265}

While many chromates and dichromates have been described, polychromates are far less numerous and appear to be limited to trichromates and tetrachromates. Although several such compounds have been isolated as solids, there is little evidence for the complex equilibria in aqueous solution of the type characteristic of molybdenum and tungsten, leading to formation of polymeric "isopoly" anions containing up to eight Mo atoms and twelve W atoms. Typical trichromates and tetrachromates are: $M_2Cr_3O_{10}$, $M = Na, K, Rb, Cs, NH_4$; $M_2Cr_3O_{10}$, $M = Ba, Sr, Cd, Cu, Ni, Zn$; $M_2Cr_4O_{13}$, $M = NH_4, Na, K, Rb, Cs$; $M_2Cr_4O_{13}$, $M = Ca, Mg, Cu$.

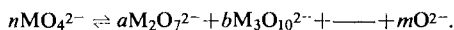
(d) *Condensation of Cr(VI) in Anhydrous Melts*

In terms of the Lux-Flood concept, in which an acid is defined as an oxide ion acceptor, the polymeric oxides CrO_3 , MoO_3 and WO_3 are acids since they react with basic solvents, depolymerizing to smaller units, ultimately to the ortho anion, MO_4^{2-} . Thus these oxides act as acids in fused salts such as KNO_3 ²⁶⁷; furthermore, it has been shown that $Cr_2O_7^{2-}$ has acidic properties in fused alkali nitrates²⁶⁸.

It is therefore to be expected that the reverse reaction can occur, i.e. condensation of the ortho anions MO_4^{2-} , with increasing acidity of the melt²⁶⁹. Formation of an oxide ion from MO_4^{2-} could presumably result from dissociation



or from a process of condensation with formation of higher polymers,



It was found that $[O^{2-}]$ varies with the square of the MO_4^{2-} concentration, which corresponds to the first step in the condensation process, i.e. formation of $M_2O_7^{2-}$. The order of decreasing basicity of MO_4^{2-} is $W > Mo > Cr$ in the equimolar $NaNO_3$ - KNO_3 melt, in agreement with conclusions reached by other investigators²⁶⁷.

(e) *Chromyl Halides*^{255, 258c, 272} and *Halochromates*^{255, 271, 273}

Four chromyl halides are known. The methods of preparation are:

CrO_2F_2 : fluorination of CrO_3 with SeF_4 , SF_4 , HF , IF_5 , or CoF_3 ; fluorination of $K_2Cr_2O_7$ with HF or SeF_4 .

CrO_2FCl : reaction of CrO_2F_2 with CrO_2Cl_2 *in vacuo*.

CrO_2Cl_2 : distilling a mixture of $NaCl$, H_2SO_4 and an alkali metal chromate or bichromate²⁶⁶ or a mixture of $Na_2Cr_2O_7$ and HCl ^{274a}; chlorinating CrO_3 with HCl ²⁷³, PCl_5 , $ClSO_3H$, $SOCl_2$, SO_2Cl_2 , or $AlCl_3$.

²⁶⁷ A. M. Shams El Din and A. A. El Hosary, *J. Electroanal. Chem.* **9** (1965) 349.

²⁶⁸ A. Bystrom and K. A. Wilhelmi, *Acta Chem. Scand.* **4** (1950) 1131.

²⁶⁹ R. N. Kust, *Inorg. Chem.* **6** (1967) 157.

²⁷⁰ R. N. Kust, *Inorg. Chem.* **6** (1967) 2239.

²⁷¹ R. D. Peacock, "Some Fluorine Compounds of the Transition Metals", in *Progress in Inorganic Chemistry*, **2**, Interscience, New York (1960), p. 241.

²⁷² E. L. Muetterties and C. W. Tullock, "Binary Fluorides", in *Preparative Inorganic Reactions*, **2**, Interscience, New York (1965), pp. 281, 285.

²⁷³ G. W. A. Fowles, "Halide and Oxyhalide Complexes of Elements of the Titanium, Vanadium and Chromium Subgroups", in *Preparative Inorganic Reactions*, **1**, Interscience, New York (1965), p. 126.

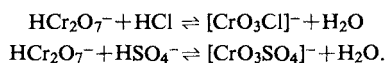
²⁷⁴ H. H. Sisler, *Inorg. Syn.* **2**, McGraw-Hill, New York (1946): (a) p. 205; (b) p. 208.

CrO_2Br_2 : reaction of CrO_3 with CF_3COBr and HBr in presence of P_2O_5 ; reaction of CrO_2Cl_2 with excess HBr .

It has also been reported that fluorination of Cr produces CrOF_4 ²⁷⁵.

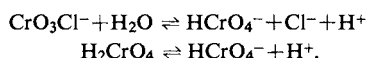
Pure chromyl fluoride consists of violet-red crystals, m.p. 31.6° (885 mm)²⁷⁶; older reports describing it as a liquid are based on work with impure samples. However, under the influence of light, the red vapor polymerizes to a poorly defined white solid (m.p. about 200°). Chromyl chloride is a dark red liquid (density, 1.92 g/cm^3 ; m.p., -96.5° ; b.p. 117°), soluble in inorganic acid halides and organic liquids (e.g. POCl_3 , CCl_4 , CHCl_3 , C_6H_6). The oxyfluoride and oxychloride are quite stable when kept dry in the dark; decomposition is promoted by light and impurities. The bromide decomposes above -70° . The chromyl halides are easily hydrolyzed.

In the equilibria listed in Table 24, the only chromium species involved are chromate, acid chromate, dichromate and acid dichromate. These equilibria exist only in HNO_3 and HClO_4 solutions; when other acid anions are present, the equilibria are modified because of the formation of substituted chromates, e.g. chlorochromate and sulfatochromate:



When a hot solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in HCl is cooled, potassium chlorochromate crystallizes; the analogous fluoro-, bromo- and iodochromates can be prepared in a similar way. The expected oxidation of Cl^- , Br^- and I^- does not occur because $\text{Cr}_2\text{O}_7^{2-}$ is a kinetically slow oxidizer of these ions²⁵⁷.

In acid solutions of CrO_3Cl^- , the predominant equilibria are²⁷⁷



The equilibrium constant for the first of these decreases with increasing $[\text{H}^+]$, presumably because of the changing relative importance of the second. ΔH and ΔS for the dissociation of CrO_3Cl^- were found to be -1.13 kcal and -8.6 e.u. respectively.

Several salts $\text{M}[\text{CrO}_3\text{X}]$ have been described ($\text{X} = \text{F}$, $\text{M} = \text{K}$, NH_4 , Rb , Cs ; $\text{X} = \text{Cl}$, $\text{M} = \text{Na}$, K , NH_4 , and possibly Li and Cs). Salts of $[\text{CrO}_3\text{Br}]^-$ and $[\text{CrO}_3\text{I}]^-$ have been reported but their existence is doubtful. Salts of the anions $[\text{CrO}_4\text{F}]^{3-}$ and $[\text{CrO}_2\text{F}_4]^{2-}$ have also been described. Salts of the type $\text{M}[\text{CrOX}_3]$ are prepared by reaction of CrO_3 with MX or of the bichromate with HX . The salt $\text{K}[\text{CrO}_3\text{Cl}]$ (monoclinic) is readily prepared by reaction of K_2CrO_4 with chromyl chloride^{274b}.

The oxyhalide complexes are orange-brown. The anions $[\text{CrO}_3\text{X}]^-$ ($\text{X} = \text{Cl}$, F) have distorted octahedral symmetry C_{3v}^{10} . They are easily hydrolyzed and decompose when heated. The chlorochromate ion is a relatively poor oxidizing agent compared to CrO_4^{2-} ; however, it reacts vigorously with ammonia by which it is reduced to Cr(III) .

(f) Other Chromyl Compounds and Substituted Chromates

In addition to chromyl chloride and fluoride, numerous other chromyl compounds CrO_2Y_2 have been described ($\text{Y} = \text{nitrate}$, perchlorate, fluorosulfonate, sulfate, borate, acetate, trichloroacetate, azide and benzoate)²⁶¹.

²⁷⁵ A. J. Edwards, *Proc. Chem. Soc.* **1963**, 205.

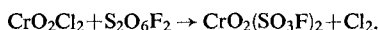
²⁷⁶ A. Engelbrecht and A. V. Grosse, *J. Am. Chem. Soc.* **74** (1952) 5262.

²⁷⁷ J. Y. Tong and R. L. Johnson, *Inorg. Chem.* **5** (1966) 1902.

Chromyl nitrate, $\text{CrO}_2(\text{NO}_3)_2$, is prepared by reaction of N_2O_5 with CrO_3 ²⁶⁶. It is a red liquid (m.p. -27°) that is easily hydrolyzed. It decomposes at about 120° .

By reaction of CrO_3 with Cl_2O_3 , chromyl perchlorate, $\text{CrO}_2(\text{ClO}_4)_2$ is produced²⁶⁶. It is a red liquid (b.p. 175°), soluble in CCl_4 . It is a powerful oxidizing agent and often explodes at 80° , although it is stable for a long time in the dark at low temperature.

Chromyl fluorosulfate²⁷⁸ is obtained by the reaction:



The product is a green solid which is quite stable if kept dry. It reacts violently with water and finally dissolves; the products of hydrolysis are presumably H_2CrO_4 , H_2SO_4 and HF . By heating the green compound *in vacuo* at 75° , brown crystals are obtained which, on the basis of chemical, infrared and X-ray data, have the same composition as the green compound. It may be that the green and brown compounds are respectively an amorphous and a crystalline form of chromyl fluorosulfate or perhaps the green form is slightly polymerized.

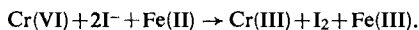
Many salts of the type $\text{M}[\text{CrO}_3\text{Y}]$ have been described in the older literature²⁷⁹, e.g. $\text{Y} =$ iodate, sulfate, selenate, acetate, NH_2 and NH .

2.9.3. Chromium(VI) in Redox Reactions

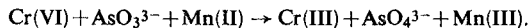
The conversion of Cr(VI) to Cr(III) (and the reverse) involves a 3-electron change which has only a low probability of occurring in a single step. This implies the formation of chromium in intermediate oxidation states in such reactions. Kinetics and mechanism studies have provided considerable evidence for formation of transient intermediates containing Cr(IV) and Cr(V) in redox reactions; furthermore, some Cr(IV) and Cr(V) compounds, which are unstable in water, have been isolated (see Sections 2.7 and 2.8).

(a) Induced Oxidation

Studies of induced oxidation^{261a, 280a} have produced some of the most compelling evidence for formation of chromium in oxidation states IV and V in redox reactions. In the reduction of chromic acid by iodide, for example, the rate of reaction is very low in dilute acid and low concentrations of reactants. If Fe(II) is added, the rate is greatly increased; the rate of reduction of Fe(III) by I^- is low under the reaction conditions. These results indicate that iodide is oxidized by some species other than Cr(VI) or Fe(III) . When $[\text{I}^-]$ is large compared with Fe(II) , the stoichiometry is:



Another example of induced oxidation^{261a, 280a} is the reduction of chromic acid by arsenious acid. This reaction induces the oxidation of bromide, iodide and Mn^{2+} . When Mn^{2+} is present in excess, the stoichiometry is



Several other induced oxidations by Cr(VI) have been investigated^{261a}. For example,

²⁷⁸ W. V. Rochat and G. L. Gard, *Inorg. Chem.* **8** (1969) 158.

²⁷⁹ R. Duval and C. Duval, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959), p. 537.

²⁸⁰ J. O. Edwards, *Inorganic Reaction Mechanisms*, Benjamin, New York (1964): (a) p. 149; (b) p. 130.

iodide is oxidized when the inductor is VOSO_4 , $(\text{VO})_2\text{SO}_4$, VSO_4 , Ti(III) and UOSO_4 ; bromide is oxidized when the inductor is Fe(II) , VOSO_4 and Ti(III) .

(b) *Chromium(VI) in Redox Reactions with Inorganic Substances*^{261a, 280a, 281}

In Table 25 are listed proposed mechanisms for several redox reactions involving the transformation $\text{Cr(III)} \rightarrow \text{Cr(VI)}$ or the reverse. A coordination number change must occur in some step since the coordination numbers of Cr(III) and Cr(VI) are six and four respectively. Thus quite drastic molecular rearrangement is necessary as well as high energy

TABLE 25. MECHANISMS OF REDOX REACTIONS INVOLVING CHROMIUM(VI)^a

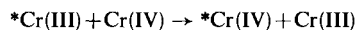
Oxidant	Reductant		Reference
Cr(VI)	Fe(II)	$\text{Fe(II)} + \text{Cr(VI)} \rightleftharpoons \text{Fe(III)} + \text{Cr(V)}$ (fast)	261(a), 280(b), 281
		$\text{Fe(II)} + \text{Cr(V)} \rightarrow \text{Fe(III)} + \text{Cr(IV)}$ (rate-determining)	
		$\text{Fe(II)} + \text{Cr(IV)} \rightarrow \text{Ce(III)} + \text{Cr(III)}$ (fast)	
Cr(VI)	V(IV)	$\text{V(IV)} + \text{Cr(VI)} \rightleftharpoons \text{V(V)} + \text{Cr(V)}$ (fast)	261(a), 281
		$\text{V(IV)} + \text{Cr(V)} \rightarrow \text{V(V)} + \text{Cr(IV)}$ (rate-determining)	
		$\text{V(IV)} + \text{Cr(IV)} \rightarrow \text{V(V)} + \text{Cr(III)}$ (fast)	
Cr(VI)	Np(V)	$\text{Np(V)} + \text{Cr(VI)} \rightleftharpoons \text{Np(VI)} + \text{Cr(V)}$ (rate-determining)	281
		$\text{Np(V)} + \text{Cr(V)} \rightarrow \text{Np(VI)} + \text{Cr(IV)}$ (fast)	
		$\text{Np(V)} + \text{Cr(IV)} \rightarrow \text{Np(VI)} + \text{Cr(III)}$ (fast)	
Ce(IV)	Cr(III)	$\text{Cr(III)} + \text{Ce(IV)} \rightleftharpoons \text{Cr(IV)} + \text{Ce(III)}$ (fast)	280(a), 281
		$\text{Cr(IV)} + \text{Ce(IV)} \rightarrow \text{Cr(V)} + \text{Ce(III)}$ (rate-determining)	
		$\text{Cr(V)} + \text{Ce(IV)} \rightarrow \text{Cr(VI)} + \text{Ce(III)}$ (fast)	
Cr(VI)	*Cr(III) ^b	$\text{Cr(III)} + 2\text{Cr(VI)} \rightleftharpoons 3\text{Cr(V)}$ (fast)	261(a), 280(a)
		$*\text{Cr(III)} + \text{Cr(V)} \rightarrow \text{Cr(III)} + *\text{Cr(V)}$ (rate-determining)	
		$*\text{Cr(V)} + \text{Cr(VI)} \rightarrow *\text{Cr(VI)} + \text{Cr(V)}$ (fast)	
Cr(VI) ^b	Cr(II)	$\text{Cr(VI)} + \text{Cr(II)} \rightarrow *\text{Cr(V)} + \text{Cr}^{3+}$ (fast)	282
		$\sim 80\% \rightarrow *\text{Cr(IV)} + \text{Cr}^{3+}$	
		$*\text{Cr(V)} + \text{Cr(III)} \xrightarrow{\sim 20\%} *\text{Cr}^{3+} + \text{Cr(IV)}$ (rate-determining)	
		$*\text{Cr(IV)} + \text{Cr(II)} \rightarrow [* \text{Cr(OH)}_2\text{Cr}]^{4+}$ (fast)	
		$\text{Cr(IV)} + \text{Cr(II)} \rightarrow [\text{Cr(OH)}_2\text{Cr}]^{4+}$ (fast)	

^a In acid solutions.

^b * indicates radioactively tagged atom.

of activation for the particular electron transfer involved. This appears to be the $\text{Cr(IV)}-\text{Cr(V)}$ step since this is rate-determining in the $\text{Cr(VI)}-\text{Fe(II)}$, $\text{Cr(VI)}-\text{V(IV)}$ and $\text{Cr(III)}-\text{Ce(IV)}$ reactions. Presumably Cr(V) is present in the form of an oxyacid, e.g. H_3CrO_4 .

This difference in coordination numbers is also involved in the exchange-reactions^{261a, 280a, 282}:



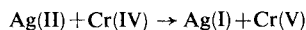
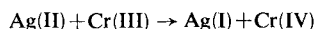
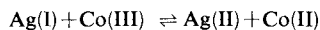
The first of these is very slow; in the last step (Table 25) rapid electron exchange occurs between Cr(VI) which is tetrahedral and Cr(V) which is also presumed to be tetrahedral.

²⁸¹ A. G. Sykes, "Further Advances in the Study of Mechanisms of Redox Reactions", in *Advances in Inorganic Chemistry and Radiochemistry*, **10**, Academic Press, New York (1967), p. 219.

²⁸² L. S. Hegeudus and A. Haim, *Inorg. Chem.* **6** (1967) 664.

The last step of the Cr(II)–Cr(VI) exchange involves electron exchange between six-coordinate Cr species.

Although Co(III) does not oxidize Cr(III) rapidly, the reaction is catalyzed by Ag(I); an equilibrium concentration of Ag(II) is attained in the first step²⁸¹:



(c) *Oxidation of Organic Substances by Chromium(VI)*²⁶¹

Chromium(VI) compounds are vigorous oxidizing agents and are extremely useful as oxidants in organic syntheses. Compounds often used are chromic acid, dichromates, chromyl chloride, chromyl acetate, chromium trioxide–pyridine complex and *t*-butyl chromate. A wide range of oxidations can be accomplished with these reagents including the following: aryl alkanes and polycyclic aromatic hydrocarbons to aromatic acids with chromic acid and aqueous dichromate; oxidation of aryl alkanes to aldehydes and ketones by chromyl chloride and to acetates with chromyl acetate. One of the major uses of Cr(VI) in synthetic chemistry is oxidation of primary alcohols to aldehydes and secondary alcohols to ketones. The mechanisms of many systems have been investigated; as with oxidation of

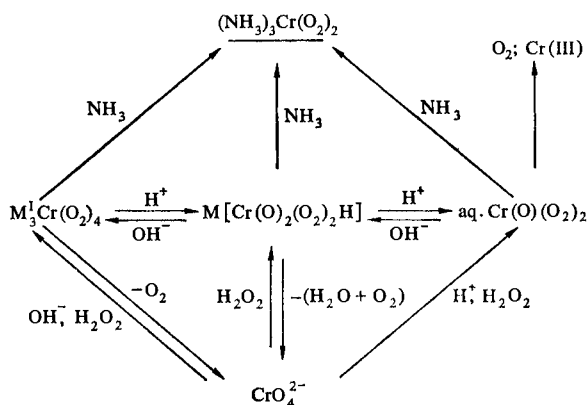


FIG. 7. Relationships among peroxychromium species.

(Reprinted from ref. 284, p. 313, © 1965, by permission of Academic Press, Inc.)

inorganic substances with Cr(VI), the mechanisms of these organic oxidations involve Cr(IV) and Cr(V) intermediates. Sometimes chromate esters and other organic compounds of chromium are postulated as intermediates^{261b}.

Probably the best known of these oxidations is Étard's reaction^{261c}, the oxidation of an aryl alkane to an aldehyde, e.g. toluene to benzaldehyde. In this reaction, carried out in, for example, CS₂ or CCl₄, an addition compound precipitates, usually of the composition 1 hydrocarbon : 2 CrO₂Cl₂; this is added to water or sodium bisulfite solution to obtain the final products. Some mechanisms proposed for these reactions involve intermediate Cr(IV) esters.

2.10. PEROXYCHROMIUM COMPOUNDS²⁸³⁻²⁸⁵

Peroxy compounds are formed by chromium in oxidation states IV, V and VI. These include adducts of $\text{CrO}(\text{O}_2)_2$ (deep blue), the violet peroxychromates, the red peroxychromates and addition compounds of $[\text{Cr}(\text{O}_2)_2]$. They are all quite unstable in solution and more or less unstable in the solid state, although some can be kept in the dry state for a long

TABLE 26. SOME PEROXYCHROMIUM COMPOUNDS²⁸³⁻²⁸⁵

Compounds ^a	Properties ^b	Structure	Preparative method
$\text{Cr}^{\text{VI}}\text{O}(\text{O}_2)_2 \cdot \text{A}$ (A = H_2O , ether, py, qu, phen)	Blue; py adduct monomeric in benzene, diamagnetic; <i>S</i>	py adduct—pentagonal pyramid with oxide oxygen at apex	Extraction of H_2O_2 — $\text{Cr}_2\text{O}_7^{2-}$ — H^+ solution with ether, addition of base ²⁸⁶
$(\text{NH}_4)_2[\text{Cr}_2\text{O}_2(\text{O}_2)_5] \cdot 2\text{H}_2\text{O}$	Violet-black crystalline powder, converted to $(\text{NH}_4)_2\text{CrO}_4$ after 24 hr; exposed to air, decomposes violently to Cr_2O_3 at 50°	—	Reaction of H_2O_2 with CrO_3 in presence of NH_4Cl and HCl ²⁸⁷
$\text{M}[\text{Cr}^{\text{VI}}\text{O}(\text{O}_2)_2\text{OH}]$; M = K, NH_4 , Tl	Blue-violet salts, violently explosive, diamagnetic; <i>S</i>	—	Reaction of H_2O_2 with neutral or slightly acidic solution of $\text{M}_2[\text{Cr}_2\text{O}_7]$
$\text{M}_3[\text{Cr}^{\text{V}}(\text{O}_2)_4]$	Red-brown; paramagnetic with one unpaired electron per formula unit; solid salts stable for several months at room temperature	CrO_8^{3-} —quasi dodecahedral (D_{2d}); Cr to O_2 bond lengths 1.89 and 1.94 Å; K_3CrO_8 forms mixed crystals with K_3MVO_8 (M = Nb, Ta)	Reaction of 30% H_2O_2 with alkaline chromate solution ²⁸⁷
$(\text{NH}_3)_3[\text{Cr}^{\text{IV}}(\text{O}_2)_2]^c$	Brown crystals; two unpaired electrons per formula unit; stable for months at room temperature	Deformed pentagonal bipyramid; bonds to 2NH_3 groups at 90° to plane containing the third NH_3 , 4 oxygen atoms and Cr atom	Reaction mixture for $(\text{NH}_4)_3[\text{Cr}_4(\text{O}_2)_4]$ heated to 50° and cooled to 0° ^{287, 288}
$\text{K}_3[\text{Cr}^{\text{IV}}(\text{O}_2)_2(\text{CN})_3]$	—	—	Reaction of $(\text{NH}_3)_3[\text{Cr}(\text{O}_2)_2]$ with KCN in aqueous solution

^a py = pyridine, qu = quinoline, phen = 1,10-phenanthroline.

^b *S*, solid compounds have been isolated.

^c Analogous ethylenediamine and hexamethylenediamine derivatives have been obtained²⁸³.

²⁸³ P. Pascal, p. 19; J. Amiel, p. 302; in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959).

²⁸⁴ J. A. Connor and E. A. V. Ebsworth, "Peroxy Compounds of Transition Metals", in *Advances in Inorganic Chemistry and Radiochemistry*, **6**, Academic Press, New York (1965), p. 300.

²⁸⁵ F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 2nd edn. (1966), p. 831.

²⁸⁶ P. Moore, S. F. A. Kettle and R. G. Wilkins, *Inorg. Chem.* **5** (1966) 466.

²⁸⁷ F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965), p. 1391.

²⁸⁸ G. B. Kauffman and G. Acero, *Inorg. Syn.* **8**, McGraw-Hill, New York (1966), p. 132.

time at room temperature. Some properties of the most important peroxychromium compounds are listed in Table 26. The relationships among these species are shown in Fig. 7.

Recently several new diperoxy compounds of Cr(IV) have been described, i.e. $[\text{CrenH}_2\text{O}(\text{O}_2)_2] \cdot \text{H}_2\text{O}^{289}$, $[\text{Crdien}(\text{O}_2)] \cdot \text{H}_2\text{O}^{289}$, $[\text{Cren}(\text{NH}_3)(\text{O}_2)_2] \cdot \text{H}_2\text{O}^{290}$, $[\text{CrpnH}_2\text{O}(\text{O}_2)_2] \cdot 2\text{H}_2\text{O}^{290}$ and $[\text{CribnH}_2\text{O}(\text{O}_2)_2] \cdot \text{H}_2\text{O}^{290}$ (en = ethylenediamine, dien = diethylenetriamine, pn = propylenediamine, ibn = isobutylenediamine). The diperoxychromium(IV) compounds (in particular $(\text{NH}_3)_3\text{Cr}(\text{O}_2)_2$) are useful starting materials for making Cr(III) complexes²⁹¹.

II. Molybdenum

1. THE ELEMENT

1.1. DISCOVERY AND HISTORY²⁹²⁻²⁹⁴

Until the latter part of the nineteenth century, molybdenum disulfide (molybdenite), a soft black mineral, was confused with graphite, which it resembles, and both were called *molybdän* or *molybdenum*; it was sometimes considered a lead mineral. Bengt Qvist investigated this mineral (1745) and found it to contain iron and copper (and tin, in some specimens); he concluded, however, that it contained some metal other than these. He also showed that it contained sulfur.

In 1778 Carl Wilhelm Scheele analyzed molybdenite; by repeated evaporation of the ore with nitric acid, he obtained an acidic oxide which Torbern Bergman suggested might be the oxide of a new metal. Peter Jacob Hjelm obtained the metal by reducing the oxide with carbon formed by pyrolysis of linseed oil used to make a paste with the oxide. From correspondence of Scheele and Bergman, it appears that Hjelm's work was accomplished in 1781, although his first paper was published much later. Justus C. H. Heyer also obtained molybdenum by reducing the oxide (1787) and synthesized molybdenite, as Scheele had done, by heating a mixture of molybdic acid and sulfur. In 1785 B. Pelletier showed that the ore that had been called "molybdenum" is a sulfide of the metal.

Metallic molybdenum started to become commercially important about 1910 when Coolidge and Fink (General Electric Company) first prepared the metal in ductile form. Molybdenum became available in quantities with the opening of an enormous deposit of molybdenum ore at Climax, Colorado, in 1917. Slow development of large-scale uses occurred from about 1920. Production of byproduct molybdenum from copper sulfide ores was started in 1939. A resurgence of interest in molybdenum as an engineering material started after World War II.

A tremendous amount of work on molybdenum compounds was accomplished in the nineteenth century, from about 1817, and the early part of the twentieth; much of this has not been repeated and confirmed by modern methods. Recently, interest in molybdenum compounds has been increasing, with the result that many papers have been appearing reporting synthesis, spectra, structure and biological activity of molybdenum compounds.

²⁸⁹ D. A. House and C. S. Garner, *Inorg. Chem.* **5** (1966) 840.

²⁹⁰ D. A. House, R. G. Hughes and C. S. Garner, *Inorg. Chem.* **6** (1967) 1077.

²⁹¹ R. G. Hughes, E. A. V. Ebsworth and C. S. Garner, *Inorg. Chem.* **7** (1968) 882.

²⁹² M. E. Weeks and H. M. Leicester, *Discovery of the Elements*, Journal of Chemical Education, Easton, Penna., 7th edn. (1968), p. 261.

²⁹³ L. Northcott, *Molybdenum*, Academic Press, New York (1956) p. 1.

²⁹⁴ J. Z. Briggs, "Molybdenum and Molybdenum Alloys", in *Encyclopedia of Chemical Technology*, **13**, Interscience, New York, 2nd edn. (1967), p. 635.

time at room temperature. Some properties of the most important peroxychromium compounds are listed in Table 26. The relationships among these species are shown in Fig. 7.

Recently several new diperoxy compounds of Cr(IV) have been described, i.e. $[\text{CrenH}_2\text{O}(\text{O}_2)_2] \cdot \text{H}_2\text{O}^{289}$, $[\text{Crdien}(\text{O}_2)] \cdot \text{H}_2\text{O}^{289}$, $[\text{Cren}(\text{NH}_3)(\text{O}_2)_2] \cdot \text{H}_2\text{O}^{290}$, $[\text{CrpnH}_2\text{O}(\text{O}_2)_2] \cdot 2\text{H}_2\text{O}^{290}$ and $[\text{CribnH}_2\text{O}(\text{O}_2)_2] \cdot \text{H}_2\text{O}^{290}$ (en = ethylenediamine, dien = diethylenetriamine, pn = propylenediamine, ibn = isobutylenediamine). The diperoxychromium(IV) compounds (in particular $(\text{NH}_3)_3\text{Cr}(\text{O}_2)_2$) are useful starting materials for making Cr(III) complexes²⁹¹.

II. Molybdenum

1. THE ELEMENT

1.1. DISCOVERY AND HISTORY²⁹²⁻²⁹⁴

Until the latter part of the nineteenth century, molybdenum disulfide (molybdenite), a soft black mineral, was confused with graphite, which it resembles, and both were called *molybdän* or *molybdenum*; it was sometimes considered a lead mineral. Bengt Qvist investigated this mineral (1745) and found it to contain iron and copper (and tin, in some specimens); he concluded, however, that it contained some metal other than these. He also showed that it contained sulfur.

In 1778 Carl Wilhelm Scheele analyzed molybdenite; by repeated evaporation of the ore with nitric acid, he obtained an acidic oxide which Torbern Bergman suggested might be the oxide of a new metal. Peter Jacob Hjelm obtained the metal by reducing the oxide with carbon formed by pyrolysis of linseed oil used to make a paste with the oxide. From correspondence of Scheele and Bergman, it appears that Hjelm's work was accomplished in 1781, although his first paper was published much later. Justus C. H. Heyer also obtained molybdenum by reducing the oxide (1787) and synthesized molybdenite, as Scheele had done, by heating a mixture of molybdic acid and sulfur. In 1785 B. Pelletier showed that the ore that had been called "molybdenum" is a sulfide of the metal.

Metallic molybdenum started to become commercially important about 1910 when Coolidge and Fink (General Electric Company) first prepared the metal in ductile form. Molybdenum became available in quantities with the opening of an enormous deposit of molybdenum ore at Climax, Colorado, in 1917. Slow development of large-scale uses occurred from about 1920. Production of byproduct molybdenum from copper sulfide ores was started in 1939. A resurgence of interest in molybdenum as an engineering material started after World War II.

A tremendous amount of work on molybdenum compounds was accomplished in the nineteenth century, from about 1817, and the early part of the twentieth; much of this has not been repeated and confirmed by modern methods. Recently, interest in molybdenum compounds has been increasing, with the result that many papers have been appearing reporting synthesis, spectra, structure and biological activity of molybdenum compounds.

²⁸⁹ D. A. House and C. S. Garner, *Inorg. Chem.* **5** (1966) 840.

²⁹⁰ D. A. House, R. G. Hughes and C. S. Garner, *Inorg. Chem.* **6** (1967) 1077.

²⁹¹ R. G. Hughes, E. A. V. Ebsworth and C. S. Garner, *Inorg. Chem.* **7** (1968) 882.

²⁹² M. E. Weeks and H. M. Leicester, *Discovery of the Elements*, Journal of Chemical Education, Easton, Penna., 7th edn. (1968), p. 261.

²⁹³ L. Northcott, *Molybdenum*, Academic Press, New York (1956) p. 1.

²⁹⁴ J. Z. Briggs, "Molybdenum and Molybdenum Alloys", in *Encyclopedia of Chemical Technology*, **13**, Interscience, New York, 2nd edn. (1967), p. 635.

One of the most active areas is the chemistry of molybdenum carbonyl (synthesized for the first time in 1910) and the molybdenum organometallic compounds.

1.2. OCCURRENCE AND DISTRIBUTION

Molybdenum ranks fifty-third in order of abundance of the elements in the earth's crust²⁹⁵ (1.5 ppm). Its distribution²⁹⁶ in various materials is shown in Table 27. In

TABLE 27. DISTRIBUTION OF MOLYBDENUM

Material	Mo (ppm) ^a	Ref. 296 (page)
Soils	0.2–5 (median, 2)	39, 192
Igneous rocks	1.5	16, 192
Shales	2.6	16, 192
Sandstones	0.2	16, 192
Limestones	0.4	16, 192
Coal	10	16
Fresh water	0.00035	192
Sea water	0.01	20, 192
Land plants	0.9	192
Marine plants	0.45	192
Land animals	< 0.2 ^b	192
Marine animals	0.6–2.5	192
Plant tissues	0.13–1.5	68
Mammalian tissues	0.07–2.8	76
Hard tissues (marine organisms)	0.1–0.7	72
Mammalian blood	0.0041	81
Red cells	< 0.008	81

^a Results for soils and biological materials reported on oven-dried basis.

^b Highest in mammalian liver and kidney.

biogeochemical prospecting, indicators of excess molybdenum in soils are yellow–orange coloration and stunted growth of plants²⁹⁷.

Molybdenite, (MoS₂), is the only molybdenum mineral of great commercial importance²⁹⁸. The most important deposit is at Climax, Colorado. The ore is an altered granite containing several other minerals such as molybdenite and wolframite. Some other molybdenum minerals are: wulfenite, PbMoO₄; molybdenite or molybdenum ochre, Fe₂O₃·3MoO₆·7.5H₂O (composition varies); powellite, PbMoO₄.

1.3. PRODUCTION AND INDUSTRIAL USE^{299, 300}

The free world consumption of molybdenum in 1968 approached 60,000 tons^{301a}. Molybdenite (MoS₂) is the principal source of molybdenum. Its concentration in ores is low;

²⁹⁵ K. B. Krauskopf, *Introduction to Geochemistry*, McGraw-Hill, New York (1967), p. 639.

²⁹⁶ H. J. M. Bowen, *Trace Elements in Biochemistry*, Academic Press, London (1966).

²⁹⁷ H. L. Cannon, *Science*, **132** (1960) 591.

²⁹⁸ D. H. Killeffer and A. Linz, *Molybdenum Compounds*, Interscience, New York (1952), p. 5.

²⁹⁹ J. Z. Briggs, "Molybdenum and Molybdenum Alloys"; J. C. Bacon, "Molybdenum Compounds", in *Encyclopedia of Chemical Technology*, **13**, Interscience, New York, 2nd edn. (1967).

³⁰⁰ B. H. Danziger and C. H. Kline, *Chem. Engng. News*, January 25, 1925, 268.

³⁰¹ (a) *Chem. Engng. News*, April 14, 1969, 15; (b) *Chem. Engng. News*, March 2, 1964, 55; December 5, 1966, 31; April 21, 1969, 21.

about 7 lb of molybdenite (4 lb of Mo) is obtained from a ton of ore. From the crushed ore the molybdenite is recovered by flotation.

The concentrate (about 90–95% MoS_2) is roasted to MoO_3 . This may be purified by sublimation or converted to ammonium molybdate by NH_4OH . Recently a process has been put into operation to recover molybdic oxide from the ferric molybdate that is found associated with the molybdenite from which it was produced by oxidation^{301b}. The molybdate is reduced to molybdenum blue which is adsorbed on activated charcoal from which it is recovered by extraction and oxidation as ammonium paramolybdate; this is calcined to MoO_3 . Molybdenum powder is obtained by reducing molybdenum trioxide or ammonium molybdate with hydrogen at 500–1150°.

Molybdenum in massive form is produced by powder metallurgy^{302a}. Molybdenum powder is compressed hydraulically in dies at 15–20 tons/in²; the bars ($1.5 \times 1.5 \times 24$ to 30 in) are sintered electrically in hydrogen at 2200–2300°. Larger bars are produced by longer sintering in hydrogen at lower temperatures (16 hr at 1600–1700°). In the first process, ingots weighing up to 30 lb are obtained; in the second, they may weigh over 500 lb. Even larger ingots (up to 1800 lb) may be produced by arc-casting in which a continuously formed compacted Mo bar serves as a consumable electrode^{302b}.

Processes used to convert the ingots to rods, bars, and sheets include rolling, forging and swaging at 1200–1400°. Wire is produced by drawing Mo rods through tungsten carbide dies. As these operations proceed, the temperature is lowered.

Molybdenum metal is used to make many electric and electronic parts such as heaters of vacuum tubes and supports and hooks for filaments in lamps. Molybdenum is deposited (by an oxy-acetylene process) in thin layers on other metals such as aluminum and steel. The surface thus formed has outstanding resistance to friction and wear, as required by the bearing surfaces of machine tools such as lathe beds.

Molybdenum finds one of its most important applications as an alloying element in steels. It imparts to such steels strength, toughness and wear resistance. Some molybdenum steels are characterized by high strength and good corrosion resistance at high temperatures and are thus particularly useful for fabricating steam and gas turbine parts. Molybdenum imparts additional corrosion resistance to stainless steels.

Molybdenum sulfide has excellent lubricating properties resulting from its laminar structure, each lamina comprising two layers of sulfur atoms separated by a layer of molybdenum atoms^{303a}. It is a particularly valuable lubricant for high pressure–high temperature conditions under which other lubricants would be squeezed out; even under these conditions, MoS_2 adheres to metals and prevents galling of the contacting surfaces.

Molybdenum sulfide is also useful as a catalyst in hydrogenations and dehydrogenations of complex hydrocarbon mixtures^{303a}. The disulfide is formed by reaction of H_2S with ammonium molybdate or by decomposition of ammonium thiomolybdate; usually it is deposited on a carrier.

³⁰² (a) D. J. Jones, "Practical Aspects of Sintering Tungsten and Molybdenum"; (b) A. R. Ross and D. T. Richards, "The Arc-Melting of Niobium, Tantalum and Tungsten", in *Niobium, Tantalum, Molybdenum and Tungsten*, Elsevier, Amsterdam (1966).

³⁰³ (a) *Properties of Molybdenum Disulfide*, Cdb-5a (February, 1962); (b) *Properties of Molybdic Oxide*, Cdb-1 (August, 1954); (c) *Properties of the Simple Molybdates*, Cdb-4 (October, 1962); (d) *Refractory Metal Borides*, Cdb-8 (March, 1956); bulletins, Climax Molybdenum Company, New York.

Uses of some other molybdenum compounds are as follows^{303b-d, 304}:

MoO_3 : hydrogenation and cracking catalyst (deposited on carriers such as Al_2O_3 and SiO_2); with CaO , added to molten steel to provide Mo.

$(\text{NH}_4)_2\text{MoO}_4$, Na_2MoO_4 : electrolysis for deposition of black coatings on metal surfaces.

PbMoO_4 : constituent of *molybdate orange* pigment (PbMoO_4 , PbCrO_4 , PbSO_4).

CaMoO_4 , SrMoO_4 : corrosion-resistant pigments.

CaMoO_4 : additive to steel for providing Mo.

12-heteropolymolybdates: precipitants for basic dyes to form color lakes.

Refractory borides: corrosion and abrasion resistant materials for dies, plungers of automatic presses, cutting tools, etc.

1.4. PREPARATION OF PURE MOLYBDENUM^{305, 306}

Pure molybdenum can be obtained by reduction of pure MoO_3 . Technical MoO_3 is dissolved in excess NH_4OH ; silica and iron oxides are precipitated. As the filtrate evaporates ammonium paramolybdate crystallizes. When this is ignited in an oxidizing atmosphere at 500° , pure MoO_3 is produced. Pure MoO_3 can also be obtained by subliming the technical oxide. The fumes, carried out of the furnace by a stream of air, are passed through a filter; the purity of the MoO_3 so obtained is 99.98–100%. The oxide is reduced with hydrogen.

1.5. ALLOTROPES

Molybdenum (body-centred cubic, type *A2*, $a = 3.140 \text{ \AA}$)³⁰⁷ apparently has no allotropes³⁰⁸, at least up to 2125° .

1.6. NUCLEAR PROPERTIES³⁰⁹

Naturally occurring molybdenum is a mixture of seven isotopes of mass numbers (*A*) 92–100. Their abundances and some of their properties are listed in Table 28.

Thirteen radioactive species of molybdenum are known, including two pairs of nuclear isomers ($A = 91, 93$). The nuclide $A = 99$ (66–67.0 hr half-life) is commonly used in tracer

³⁰⁴ G. A. Tsigdinos, *Heteropoly Compounds of Molybdenum and Tungsten*, Bulletin Cdb-12a, Climax Molybdenum Company, New York (September, 1966).

³⁰⁵ J. Aubry, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959), p. 559.

³⁰⁶ F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965), p. 1401.

³⁰⁷ C. J. Smithells, *Metals Reference Book*, **1**, Plenum Press, New York (1967), p. 157.

³⁰⁸ L. Northcott, *Molybdenum*, Academic Press, New York (1956), p. 30.

³⁰⁹ C. M. Lederer, J. M. Hollander and I. Perlman, *Table of Isotopes*, John Wiley, New York, 6th edn. (1967), p. 44.

TABLE 28. STABLE MOLYBDENUM ISOTOPES

A^a	%	Δ (meV) ^b	σ_c^c
92	15.86	-86.804	< 0.3 (to ⁹³ Mo) < 0.006 (to ^{93m} Mo)
94	9.12	-88.407	—
95	15.70	-87.709	14
96	16.50	-88.794	1
97	9.45	-87.539	2
98	23.75	-88.110	0.51
100	9.62	-86.185	0.2

^a Mass number.

^b Mass excess = $M - A$ (M = isotopic weight),
¹²C = 0.

^c Thermal neutron capture cross-section (barns).

investigations; it is usually supplied as MoO₃ or a molybdate solution. The properties of the molybdenum radio-isotopes are listed in Table 29.

TABLE 29. RADIOISOTOPES OF MOLYBDENUM

A^a	Half-life ^b	Δ (meV) ^c	Mode of decay, radiations, energies (meV) ^d	Mode of formation ^e
88	27 m	—	β^+ , 2.5; [EC]; γ , 2.69; $\gamma^\pm$	Nb (p); Mo (p)
89	7 m	—	β^+ , 4.9; [EC]; $\gamma^\pm$	Mo (p)
90	5.67–6.3 h	-80.17	β^+ , 1.2 (25%); EC (75%); e^- , 0.104–0.255 (4); γ , 0.445–1.46 (5); $\gamma^\pm$	⁹³ Nb (p, 4n); ⁹⁰ Zr (α , 4n)
91	15.5 m	-82.3	β^+ , 3.44; $\gamma^\pm$	⁹² Mo (n, 2n)
91m	64–75 s	-81.6	(a) IT, β^+ , 3.99, EC; (b) IT, β^+ , 2.78; EC; e^- , 0.638; γ , 0.658, 1.21, 1.53; $\gamma^\pm$	⁹² Mo (γ , n)
93	> 100 y	-86.79	EC; Nb and Mo X-rays	⁹² Mo (n, γ); ⁹³ Nb (p, n)
93m	6.75–6.95 h	-84.36	IT; e^- , 0.244, 0.261; γ , 0.264, 0.685, 1.479, Mo X-rays	⁹³ Nb (d, 2n); ⁹⁰ Zr (α , n); ⁹³ Nb (p, n)
99	66.0–67.0 h	-85.96	B^- , 1.23; γ , 0.041–0.780 (5); Tc X-rays	⁹⁸ Mo (n, γ); nf
101	14.6 m	-83.50	β^- , 2.23; e^- , 0.170; γ , 0.191–2.08 (8)	¹⁰⁰ Mo (n, γ)
102	11–12 m	-84	β^- , 1.2	nf (parent ^{99m} Tc)
103	62–70 s	—	[β^-]	nf (parent ¹⁰³ Tc)
104	1.1–1.6 m	—	β^- , 4.8; γ , 0.070	nf (parent ¹⁰⁴ Tc)
105	40–42 s	—	β^-	nf (parent ¹⁰⁵ Tc)

^a Mass number; m , nuclear isomer.

^b s, seconds; m, minutes; h, hours; y, years.

^c $\Delta = M - A$ (M = isotopic weight), ¹²C = 0.

^d EC, electron capture; β^- , beta decay; β^+ , positron decay; IT, internal transition; e^- , conversion electron; $\gamma^\pm$, $e^- + e^+$, annihilation radiation; maximum energy given for β^- and β^+ ; [], inferred; number in (), number of different energies.

^e n, neutron; p, proton; γ , gamma; α , ⁴He; nf, nuclear fission.

1.7. PHYSICAL PROPERTIES

Some of the physical properties of molybdenum are listed in Table 30. The references cited list many others. Ranges of values of several properties are presented in graphical form in the compilation of Goldsmith *et al.*³¹⁵.

TABLE 30. SOME PHYSICAL PROPERTIES OF MOLYBDENUM

Property	Value			Reference
Color	Metallic silver			310
Atomic number, (<i>Z</i>)	42			310
Atomic weight	95.94			310
Density	10.28 g/cm ³ (20°C)			311
Atomic volume	9.32 cm ³ /mole			
Crystal structure	Body-centred cubic, type <i>A2</i> , space group O_h^9 ; $a = 3.140 \text{ \AA}$; closest approach of atoms, 2.725 $\text{\AA}$; lattice energy, 165.7 kcal/mole			312
Melting point (m.p.)	$2620 \pm 10^\circ\text{C}$			310
Heat of fusion (ΔH_f)	6.66 kcal/mole			310
Boiling point (b.p.)	4825°C			310
Heat of vaporization (ΔH_v)	128.42 kcal/mole (at b.p.)			310
Heat of sublimation (ΔH_s)	158.7 kcal/mole (25°)			312
Heat capacity (C_p ; cal/mole/°C)	Mo(s), 5.61 (25°C)			310
	$C_p = 5.77 + 0.28 \times 10^{-3}T + 0.54 \times 10^{-6}T^2$ ($T = ^\circ\text{K}$)			312
	Mo(g), 4.968 (25°C)			310
	25°C	2227°C		314
Entropy (cal/mole/°C)	Mo(s)	6.83	21.52	
	Mo(g)	43.46	54.11	
Vapor pressure (mm Hg)		1378°C	3.36×10^{-6}	314
		2189	2.21×10^{-4}	
		m.p.	3.36×10^{-2}	
Configuration and ground state: un-ionized atom	$4d^5 5s$ (7S_3)			314
Atomic radius	1.40 $\text{\AA}$			314
Ionization potentials (eV)	1st:	7.131	4th: 46.4	314
	2nd:	15.72	5th: 61.2	
	3rd:	29.6	6th: 67	
Bond energies of inner electrons (keV)	<i>K</i>	<i>L_I</i>	<i>L_{II}</i>	314
	20.039	2.873	2.633	
<i>K</i> X-ray emission spectra ($\text{\AA}$)	α'	α	β	314
	0.71354	0.70894	0.63225	
Electron affinity	1.8 eV			314
Reflectivity	46% (5000 $\text{\AA}$); 93% (10 ⁵ $\text{\AA}$)			313
Magnetic susceptibility	0.93×10^{-6} e.m.u./g at 25°			313
Resistivity (ρ , microhm cm)	5 (20°C) to 60 (2000°C)			314

³¹⁰ R. Keller, *Basic Tables in Chemistry*, McGraw-Hill, New York (1967).

³¹¹ J. Aubry, in *Nouveau Traité de Chimie Minérale*, 14, Masson et Cie, Paris (1959).

³¹² C. J. Smithells, *Metals Reference Book*, 1, Plenum Press, New York, 4th edn. (1967).

³¹³ E. N. Simons, "Molybdenum", in *Guide to Uncommon Metals*, Hart, New York (1967).

³¹⁴ G. V. Samsonov (ed.), *Handbook of the Physicochemical Properties of the Elements*, Plenum Press, New York (1968).

³¹⁵ A. Goldsmith, T. E. Waterman and H. J. Hirschhorn, *Handbook of Thermophysical Properties*, 1, Macmillan, New York, revised edn. (1961), pp. 413-427.

1.8. CHEMISTRY AND CHEMICAL PROPERTIES³¹⁶⁻³¹⁸

Molybdenum is inert to oxygen and air at room temperature but at red heat burns to the trioxide. It reacts with F_2 at room temperature; with Cl_2 and Br_2 above about $325^\circ C$; it is not attacked by I_2 . It reacts with carbon, phosphorus, sulfur, selenium, tellurium and silicon at high temperature to form the respective binary compounds.

It does not react with water but at red heat is converted to MoO_3 by water vapor. It is oxidized to MoO_3 by NO , NO_2 or N_2O at red heat. Molybdenum reacts with CO_2 above 1000° .

Molybdenum does not react significantly with solutions of bases unless they contain oxidizing agents such as $KClO_3$. It is not attacked by HCl , HF , or H_2SO_4 ; it reacts initially with HNO_3 but soon becomes passive. It dissolves slowly in aqua regia or a mixture of HF and HNO_3 . It is rapidly attacked by fused oxidizing agents such as Na_2O_2 , $KClO_3$ and KNO_3 .

Molybdenum is a typical transition element with outermost electron structure $4d^5 5s^1$. It has oxidation states from $2-$ to $6+$; the lowest oxidation states ($2-$, $1-$, 0 , $1+$) are exemplified only by organometallic compounds and compounds of π -acceptor ligands. Except in the formation of such compounds, neither molybdenum nor tungsten resembles chromium closely. In particular, the extensive coordination chemistry of oxidation state III is almost entirely lacking in the chemistry of molybdenum and tungsten. These resemble each other in many respects, e.g. in the relative stabilities of the different oxidation states and in forming many analogous compounds such as iso- and heteropoly acids. With both elements, the higher oxidation states ($4+$, $5+$, $6+$) are the more stable.

1.9. BIOLOGICAL ACTIVITY^{319, 320a}

Molybdenum is an essential element in plant and animal metabolism. It is a constituent of several flavoprotein enzymes such as xanthine oxidases from milk and animal tissues (which also contain iron) and aldehyde oxidases. As a constituent of the nitrate reductase of plants and microorganisms, it is essential in plant growth. It is also involved in the function of the nitrogen-fixing enzyme nitrogenase³²¹ and in a hydrogenase of bacterial origin (see Section 2.8.5).

Molybdenum is poisonous under certain circumstances. Cattle ingesting excessive amounts of molybdenum become ill with a disease ("teart") characterized by severe diarrhea. The illness is treated successfully by use of copper sulfate in the diet. Molybdenum in the diet of ruminants affects copper metabolism. Sheep ingesting abnormally low amounts of molybdenum accumulate toxic concentrations of copper in their livers. On the other hand, an excess of molybdenum causes a depletion of copper stores and results in

³¹⁶ G. V. Samsonov (ed.), *Handbook of the Physicochemical Properties of the Elements*, Plenum Press, New York (1968), pp. 580, 707, 737, 746, 754, 778, 788, 810, 827.

³¹⁷ F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 2nd edn. (1966), p. 930.

³¹⁸ J. Aubry, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959), p. 581.

³¹⁹ E. S. West and W. R. Todd, *Textbook of Biochemistry*, Macmillan, New York, 3rd edn. (1961): pp. 1252, 1257.

³²⁰ (a) E. C. de Renzo, "Molybdenum", p. 483; (b) S. J. Adelstein and B. L. Vallee, "Copper", p. 382, in *Mineral Metabolism*, **2B**, Academic Press, New York (1962).

³²¹ L. R. Melby, *Inorg. Chem.* **8** (1969) 349.

copper deficiency. Sulfate is also involved in the Mo–Cu antagonism; the toxicity of molybdenum is enhanced by increased ingestion of inorganic sulfate.

In view of the reciprocal effects of Mo and Cu, there is a question whether a similar antagonism exists in man, and specifically whether Mo may be involved in Wilson's disease³²². This is a hereditary disease characterized by pathologic changes of the liver, kidneys and central nervous system, reflecting excessive absorption of copper from the intestine, increased excretion of copper in the urine and low levels of plasma copper combined with the protein ceruloplasmin³²⁰. It has been shown that urinary excretion of molybdenum is diminished in patients having Wilson's disease³²². Elimination of molybdenum is roughly proportional to that of copper in these and normal individuals, but the rates are entirely different; it is far greater with the Wilson's disease patients.

Biogeochemical prospecting has been investigated as a means of locating molybdenum, ores^{323a}. As in animals, there appears to be an inverse relation between copper and molybdenum uptake by plants^{323b}, i.e. the higher the copper content the lower the molybdenum content, and vice versa.

1.10. ANALYTICAL CHEMISTRY³²⁴

Molybdenum has been determined gravimetrically by precipitation of CaMoO_4 , BaMoO_4 , PbMoO_4 , Ag_2MoO_4 and Hg_2MoO_4 . The first three are ignited to constant weight; Ag_2MoO_4 is dried (110–250°), and Hg_2MoO_4 is ignited to MoO_3 . Molybdenum trisulfide has also been used; this can be weighed as MoS_3 after drying in a CO_2 atmosphere, ignited to MoO_3 , or converted to PbMoO_4 . The composition of MoS_3 is not always stoichiometric. Compact precipitates that are easy to filter are formed if sulfide ion is produced by decomposition of thiocarbonic acid, thioacetic acid or thioacetamide. In any procedure that includes igniting MoO_3 , errors may be introduced by volatilization, which becomes noticeable at 500–600°.

Of these methods, the PbMoO_4 procedure has been quite widely used. The lead molybdate is precipitated by $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, washed with $\text{NH}_4\text{C}_2\text{H}_3\text{O}$ solution and ignited to constant weight. Chromate, vanadate and tungstate must be absent as well as cations other than Pb^{2+} such as Ag^+ and Hg^+ that form insoluble molybdates in acetic acid solution.

Numerous organic precipitants have been used, including α -benzoinoxime, *o,o'*-dianisidine, quinine, codeine, strychnine and brucine. The precipitates are oxidized to MoO_3 or converted to PbMoO_4 . These methods, as well as those utilizing inorganic precipitates, are limited by numerous interferences including ions of fifth and sixth subgroup elements.

Of the organic precipitants, α -benzoinoxime has been applied and studied the most. Interferences include W, V, Cr, Pd, Nb, Ta and Au. Tungsten must be removed or determined and corrected for. Interference of chromate and vanadate is eliminated by reduction of these ions, to Cr^{3+} and V^{4+} respectively, with SO_2 . Molybdate is precipitated from the cooled solution by addition of 2% ethanol solution of α -benzoinoxime and a little Br_2 is added to ensure that all the molybdenum is Mo(VI). The precipitate is filtered, washed and ignited to MoO_3 (500–525°).

Oxine is also a useful reagent, particularly when used with EDTA for masking and

³²² A. Galli, *Ann. Biol. Clin.* **26** (1968) 976.

³²³ D. P. Malyuga, *Biogeochemical Methods of Prospecting*, Consultants Bureau, New York (1964): (a) p. 135; (b) p. 73.

³²⁴ R. A. Chalmers, "Molybdenum", in *Comprehensive Analytical Chemistry*, **1C**, Elsevier, Amsterdam (1962); J. J. Lingane, "Chromium", in *Analytical Chemistry of Selected Metallic Elements*, Reinhold, New York (1966).

preventing the precipitation of Fe(III), Be(II), Zn(II), Ni(II), Co(II), Mn(II), Pt(II), Cd(II), Bi(III), Cu(II) and Hg(II); Ti, W, V and U, however, are interferences in this procedure. The oxine precipitate, $\text{MoO}_2(\text{C}_9\text{H}_6\text{ON})_2$ (23.07% Mo), is dried to constant weight at 130–140°.

In titrimetric precipitation methods, the precipitate is generally PbMoO_4 , although Ag^+ , Ba^{2+} and Hg^+ have also been investigated as precipitants of MoO_4^{2-} . In direct titrations with Pb^{2+} , indicators studied include alizarin red, cochineal test paper, and carminic acid test paper; an excess of precipitant may be added and back-titrated with ferrocyanide. End-points may also be determined potentiometrically and conductimetrically.

Redox titrimetric procedures include: titration of Mo(VI) with $\text{M}^{\text{II}}\text{Cl}_2$ ($\text{M}^{\text{II}} = \text{Sn}^{2+}$, Cr^{2+} , Ti^{3+}); reduction to Mo(V) with SnCl_2 , Bi, Bi amalgam, Cu, Ag, TiCl_3 and titration with permanganate, vanadate, dichromate or ceric sulfate; reduction to Mo(III) with Zn, Cd, Al, Mg, Rose's metal and Wood's metal and amalgams of Zn, Cd, Pb, Sn and Bi.

Methods utilizing the Jones reductor (Zn) and Walden reductor (Ag) are quite satisfactory. The tip of the Jones reductor is immersed in ferric sulfate solution and the Fe^{2+} formed is titrated with permanganate. The Ag-reduced solution may be titrated with ceric sulfate (ferroin indicator). Of course, substances other than Mo that form soluble reduction products must be absent. Several colorimetric methods are available of which one of the best depends on the orange-red complex of Mo^{5+} with CNS^- in acid solution.

Numerous chelating agents have been evaluated as reagents for molybdenum. Donor atoms in such agents are oxygen, sulfur, nitrogen and selenium. The following systems have been encountered: $-\text{O}-\text{Mo}-\text{O}-$; $-\text{O}-\text{Mo}-\text{S}-$; $-\text{S}-\text{Mo}-\text{S}-$; $-\text{O}-\text{Mo}-\text{N}-$; $-\text{S}-\text{Mo}-\text{N}-$; $-\text{Se}-\text{Mo}-\text{N}-$; $-\text{N}-\text{Mo}-\text{N}-$. This field is the subject of a recent comprehensive review^{325a}. Another recent review includes numerous examples of use of chelating agents as precipitants for molybdenum^{325b}.

With a neutron flux of 10^{13} n/cm²/sec, the estimated sensitivity of activation analysis for Mo is 1.5×10^{-9} g and 1.1×10^{-7} g with 150 hr and 1 hr irradiation respectively (product species 67-hr ⁹⁹Mo)³²⁶. The analytical sensitivity of activation analysis has been compared with the sensitivities of other methods useful in geochemical analysis (emission spectroscopy, X-ray fluorescence and colorimetric analysis of solutions)³²⁶.

2. MOLYBDENUM COMPOUNDS

2.1. INTERMETALLIC PHASES IN BINARY MOLYBDENUM ALLOYS^{327–330}

The chemistry of alloys is extensive, complex and specialized. It involves principles which are generally not encountered in other areas of chemistry, e.g. those which are used

³²⁵ (a) R. Püschel and E. Lassner, "Chelates and Chelating Agents in the Analytical Chemistry of Molybdenum and Tungsten", in *Chelates in Analytical Chemistry*, 1, Marcel Dekker, New York (1967); (b) F. H. Firsching, "Chelating Agents as Metal Precipitants: Advances, 1960–1965", *ibid.* 2 (1969).

³²⁶ J. H. Winchester, "Radioactivation Analysis in Inorganic Geochemistry", in *Progress in Inorganic Chemistry*, 2, Interscience, New York (1960).

³²⁷ M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York (1958), index to all systems, pp. ix–xvi.

³²⁸ R. P. Elliott, *Constitution of Binary Alloys, First Supplement*, McGraw-Hill, New York (1965), cumulative index to all systems, pp. ix–xxx.

³²⁹ J. H. Westbrook (ed.), *Intermetallic Compounds*, John Wiley, New York (1967), compound index, pp. 639–663.

³³⁰ I. I. Kornilov, *The Chemistry of the Metallides*, Consultants Bureau, New York (1966).

preventing the precipitation of Fe(III), Be(II), Zn(II), Ni(II), Co(II), Mn(II), Pt(II), Cd(II), Bi(III), Cu(II) and Hg(II); Ti, W, V and U, however, are interferences in this procedure. The oxine precipitate, $\text{MoO}_2(\text{C}_9\text{H}_6\text{ON})_2$ (23.07% Mo), is dried to constant weight at 130–140°.

In titrimetric precipitation methods, the precipitate is generally PbMoO_4 , although Ag^+ , Ba^{2+} and Hg^+ have also been investigated as precipitants of MoO_4^{2-} . In direct titrations with Pb^{2+} , indicators studied include alizarin red, cochineal test paper, and carminic acid test paper; an excess of precipitant may be added and back-titrated with ferrocyanide. End-points may also be determined potentiometrically and conductimetrically.

Redox titrimetric procedures include: titration of Mo(VI) with $\text{M}^{\text{II}}\text{Cl}_2$ ($\text{M}^{\text{II}} = \text{Sn}^{2+}$, Cr^{2+} , Ti^{3+}); reduction to Mo(V) with SnCl_2 , Bi, Bi amalgam, Cu, Ag, TiCl_3 and titration with permanganate, vanadate, dichromate or ceric sulfate; reduction to Mo(III) with Zn, Cd, Al, Mg, Rose's metal and Wood's metal and amalgams of Zn, Cd, Pb, Sn and Bi.

Methods utilizing the Jones reductor (Zn) and Walden reductor (Ag) are quite satisfactory. The tip of the Jones reductor is immersed in ferric sulfate solution and the Fe^{2+} formed is titrated with permanganate. The Ag-reduced solution may be titrated with ceric sulfate (ferroin indicator). Of course, substances other than Mo that form soluble reduction products must be absent. Several colorimetric methods are available of which one of the best depends on the orange-red complex of Mo^{5+} with CNS^- in acid solution.

Numerous chelating agents have been evaluated as reagents for molybdenum. Donor atoms in such agents are oxygen, sulfur, nitrogen and selenium. The following systems have been encountered: $-\text{O}-\text{Mo}-\text{O}-$; $-\text{O}-\text{Mo}-\text{S}-$; $-\text{S}-\text{Mo}-\text{S}-$; $-\text{O}-\text{Mo}-\text{N}-$; $-\text{S}-\text{Mo}-\text{N}-$; $-\text{Se}-\text{Mo}-\text{N}-$; $-\text{N}-\text{Mo}-\text{N}-$. This field is the subject of a recent comprehensive review^{325a}. Another recent review includes numerous examples of use of chelating agents as precipitants for molybdenum^{325b}.

With a neutron flux of 10^{13} n/cm²/sec, the estimated sensitivity of activation analysis for Mo is 1.5×10^{-9} g and 1.1×10^{-7} g with 150 hr and 1 hr irradiation respectively (product species 67-hr ⁹⁹Mo)³²⁶. The analytical sensitivity of activation analysis has been compared with the sensitivities of other methods useful in geochemical analysis (emission spectroscopy, X-ray fluorescence and colorimetric analysis of solutions)³²⁶.

2. MOLYBDENUM COMPOUNDS

2.1. INTERMETALLIC PHASES IN BINARY MOLYBDENUM ALLOYS^{327–330}

The chemistry of alloys is extensive, complex and specialized. It involves principles which are generally not encountered in other areas of chemistry, e.g. those which are used

³²⁵ (a) R. Püschel and E. Lassner, "Chelates and Chelating Agents in the Analytical Chemistry of Molybdenum and Tungsten", in *Chelates in Analytical Chemistry*, 1, Marcel Dekker, New York (1967); (b) F. H. Firsching, "Chelating Agents as Metal Precipitants: Advances, 1960–1965", *ibid.* 2 (1969).

³²⁶ J. H. Winchester, "Radioactivation Analysis in Inorganic Geochemistry", in *Progress in Inorganic Chemistry*, 2, Interscience, New York (1960).

³²⁷ M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York (1958), index to all systems, pp. ix–xvi.

³²⁸ R. P. Elliott, *Constitution of Binary Alloys, First Supplement*, McGraw-Hill, New York (1965), cumulative index to all systems, pp. ix–xxx.

³²⁹ J. H. Westbrook (ed.), *Intermetallic Compounds*, John Wiley, New York (1967), compound index, pp. 639–663.

³³⁰ I. I. Kornilov, *The Chemistry of the Metallides*, Consultants Bureau, New York (1966).

to account for the composition of compounds in which the elements appear to have anomalous oxidation states. Some of these principles have been stated in Part I, Section 2.1, in which three important types of phases were discussed, i.e. σ phases (berthollides), Laves phases (daltonides) and compounds of the Cr_3Si type (daltonides).

TABLE 31. SIGMA^{331a, 332}, LAVES^{331b, 332} AND Cr_3Si -TYPE^{331c, 333} PHASES^a IN BINARY MOLYBDENUM ALLOYS, Mo_xX_y

Compound	X (atom %)	<i>T</i> (°C)	<i>a</i> (Å)	<i>r</i> _A / <i>r</i> _B	<i>e</i> / <i>A</i> ^b	Type
—	Mn, 62–73	1175	—	1.07	6.62–6.73	<i>S</i>
—	Fe, 50–65	1180–1540	—	1.10	7.00–7.12	<i>S</i>
—	Co, 40	1340–1550	—	1.12	7.20	<i>S</i>
—	Tc, ~ 75	700	—	1.03	6.75	<i>S</i>
—	Ru, 40	1200	—	1.04	6.75	<i>S</i>
—	Re, 48–67	1200	—	1.02	6.48–6.67	<i>S</i>
—	Os, 37.5	1200	—	1.03	6.75	<i>S</i>
—	Ir, ~ 30	near m.p.	—	1.03	6.90	<i>S</i>
MoBe_2^c , ^d	—	—	4.442	1.241	3.33	<i>L</i>
MoFe_2^c	—	—	—	—	—	<i>L</i>
ZrMo_2^e	—	—	7.560	1.129	5.33	<i>L</i>
HfMo_2^e	—	—	7.590	1.144	5.33	<i>L</i>
Mo_3Al	—	—	4.950	0.978	—	<i>C</i>
Mo_3Si	—	—	4.888	1.061	—	<i>C</i>
Mo_3Ga	—	—	4.940	0.992	—	<i>C</i>
Mo_3Ge	—	—	4.933	1.023	—	<i>C</i>
MoTc^f	—	—	4.934	1.029	—	<i>C</i>
Mo_3Os	—	—	4.973	1.035	—	<i>C</i>
Mo_3Ir	—	—	4.973	1.032	—	<i>C</i>

^a Strukturbericht types: σ (*S*), $D8_8$ (tetragonal); Laves (*L*), $C15$ (cubic), $C14$, $C36$, hexagonal; Cr_3Si (*C*), $A15$ (cubic).

^b Electron: atom ratio.

^c $C14$.

^d MoBe_2 : $c = 7.356$ Å, $c/a = 1.656$.

^e $C15$.

^f Note abnormal composition.

In Table 31 are listed molybdenum intermetallic phases of these types. Molybdenum forms many intermetallic phases other than those listed in the tables but forms none with numerous metals (e.g. alkali, alkaline earth and rare earth metals, coinage metals, etc.).

2.2. BINARY COMPOUNDS OF MOLYBDENUM WITH NONMETALS^{334–335}

The chemistry of compounds of molybdenum with nonmetallic elements is an extensive and somewhat specialized field that includes a wide range of compounds from berthollides to daltonides. Some of the principles involved have been discussed in Part I, Section 2.2. (Halides and oxides are dealt with elsewhere.) References 334 and 335 contain phase diagrams for several of the binary systems mentioned below.

³³¹ M. V. Nevitt, "Alloy Chemistry of Transition Elements", in *Electronic Structure and Alloy Chemistry of the Transition Elements*, Interscience, New York (1963): (a) p. 105; (b) p. 146; (c) p. 123.

³³² J. H. Wernick, "Topologically Close-packed Structures", in ref. 329, p. 197.

³³³ M. V. Nevitt, "Miscellaneous Structures of Fixed Stoichiometry", in ref. 329, p. 217.

³³⁴ M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York (1958), index to all systems, pp. ix–xvi.

³³⁵ R. P. Elliott, *Constitution of Binary Alloys, First Supplement*, McGraw-Hill, New York (1965), cumulative index to all systems, pp. ix–xxx.

Molybdenum borides (Mo_xB_y) are prepared by reduction of molybdenum oxides with boron carbide *in vacuo* ($x:y = 2:1; 3:2; 1:1; 1:2; 2:5$). They are solid refractory compounds that have metallic electrical conductivity^{336a, 337a, 338a, 339, 340}.

The carbides of molybdenum (Mo_2C , MoC) may be synthesized from the elements in a reducing atmosphere at high temperature. They have melting points above 2700° ^{336b, 337b, 338b, 339-341}.

Molybdenum silicides (Mo_xSi_y) have metallic bonds between molybdenum and silicon atoms and covalent bonds between silicon atoms ($x:y = 3:1; 5:3; 1:2$). They have high melting points and can be made by synthesis from the elements^{336c, 337c, 338c, 339, 340}.

Nitrides of the transition metals are "interstitial phases" (products of insertion of nitrogen atoms into the crystal lattices of the metals). Most such nitrides satisfy Hagg's rule (radius of nonmetallic atom/radius of metal atom ≤ 0.59). Molybdenum nitrides Mo_xN_y ($x:y = 3:1; 2:1; 1:1$) are prepared by reaction of a mixture of N_2 and H_2 with MoO_3 at high temperature or by heating MoCl_5 in dry NH_3 ^{336d, 337d, 338c, 339, 340}.

Molybdenum phosphides Mo_xP_y are refractory and corrosion resistant ($x:y = 3:1; 1:1; 1:2$)^{336e, 337e}.

Molybdenite (MoS_2) is the principal ore of molybdenum. Molybdenum disulfide is an excellent lubricant particularly under severe service conditions. The crystal is hexagonal ($C7$, $a = 3.15 \text{ \AA}$, $C = 12.30 \text{ \AA}$); the Mo-S distance is $2.41 \text{ \AA}$; the Mo-Mo distance within a layer is $3.15 \text{ \AA}$ and between layers $6.26 \text{ \AA}$. MoS_3 precipitates from an acidified solution of K_2MoS_3 . Two other sulfides are known, Mo_2S_3 and Mo_2S_5 . A hydrated sulfide precipitates when H_2S is passed into an acid solution of Mo(III) ^{336f, 337f, 338d, 340, 342}.

Selenides and tellurides of the transition elements are isomorphous with the corresponding sulfides (Mo_xSe_y : $x:y = 1:1; 2:3; 1:2; 2:5; 1:3$; Mo_xTe_y : $x:y = 2:3, 1:2$)^{336g, 337f, 340}. At high temperatures and pressures, rhombohedral MoSe_2 (and MoS_2) can be synthesized from the elements; the usual form is hexagonal³⁴³.

2.3. MOLYBDENUM COMPOUNDS OF π -ACCEPTOR LIGANDS

Innumerable compounds of transition metals with π -acceptor ligands have been isolated and characterized. Some of the principles of this field of chemistry have been stated in Part I, Section 2.3.

Molybdenum forms many compounds analogous to those of chromium including a

³³⁶ G. V. Samsonov (ed.), *Handbook of the Physicochemical Properties of the Elements*, Plenum Press, New York (1968): (a) pp. 737, 743; (b) pp. 746, 752; (c) pp. 754, 760; (d) pp. 762, 776; (e) pp. 778, 786; (f) pp. 810, 823; (g) pp. 827, 834.

³³⁷ J. Aubry, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959): (a) p. 742; (b) p. 728; (c) p. 739; (d) p. 724; (e) p. 726; (f) p. 649.

³³⁸ (a) *Refractory Molybdenum Borides*, Cdb-8 (March, 1956); (b) *Refractory Molybdenum Carbides and Nitrides*, Cdb-7 (February, 1956); (c) *Refractory Metal Silicides*, Cdb-6A (May, 1963); (d) *Properties of Molybdenum Disulfide*, Cdb-5a (February, 1962); bulletins, Climax Molybdenum Company, New York.

³³⁹ I. I. Kornilov, *The Chemistry of the Metallides*, Consultants Bureau, New York (1966), pp. 23-27.

³⁴⁰ C. J. Smithells, "Crystal Chemistry", in *Metals Reference Book*, **1**, Plenum Press, New York, 4th edn. (1967), pp. 167-178.

³⁴¹ E. K. Storms, "The Molybdenum-Molybdenum Carbide System", in *The Refractory Carbides*, Academic Press, New York (1967).

³⁴² F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965), p. 1415.

³⁴³ M. S. Silverman, *Inorg. Chem.* **6** (1967) 1063.

stable hexacarbonyl³⁴⁴, $\text{Mo}(\text{CO})_6$, and a great number of related compounds³⁴⁵⁻³⁴⁸. One or more of the CO groups can be displaced by any of a large number of ligands such as NO³⁴⁹, CN, NH_3 , halides, amines, nitriles, phosphines, arsines, etc. Among these compounds are anionic and substituted anionic carbonyls such as $[\text{Mo}(\text{CO})_5]^{2-}$, $[\text{Mo}(\text{CO})_5\text{X}]^-$ and $[\text{Mo}(\text{CO})_4\text{X}_2]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). Bridged dinuclear anions^{350a} are also known, e.g. $[\text{M}_2(\text{CO})_{10}]^{2-}$, $[\text{M}_2(\text{CO})_{10}\text{I}]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). Recently halogen-bridged mixed dinuclear anions such as $[\text{MoCr}(\text{CO})_{10}\text{I}]^-$ have been prepared^{350a}.

Another quite recent development is the synthesis of compounds having metal-metal bonds between two different metals, e.g. $[\text{MnMo}(\text{CO})_{10}]^-$ ^{350b}; $\phi_4\text{AsM}(\text{CO})_5\text{M}'\text{Cl}_3$ ($\phi = \text{C}_6\text{H}_5$; $\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{M}' = \text{Sn}, \text{Ge}$)³⁵¹; $\text{dipy}(\text{CO})_3\text{XMM}'\text{X}_3$ ($\text{M} = \text{Mo}, \text{W}$; $\text{M}' = \text{Sn}, \text{Ge}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{dipy} = 2,2'$ -dipyridyl)³⁵²; $\text{dipy}(\text{CO})_3\text{ClMSnRCl}_2$ ($\text{M} = \text{Mo}, \text{W}$; $\text{R} = \phi, \text{C}_2\text{H}_5, \text{CH}_3, \text{C}_4\text{H}_9$)³⁵²; $\text{phen}(\text{CO})_3\text{ClMSnCH}_3\text{Cl}_2$ ($\text{M} = \text{Mo}, \text{W}$; $\text{phen} = 1,10$ -phenanthroline)³⁵².

The compound $\text{dipy}(\text{CO})_3\text{ClMoSnCH}_3\text{Cl}_2$ is monoclinic ($a = 6.73 \text{ \AA}$, $b = 11.14 \text{ \AA}$, $c = 24.46 \text{ \AA}$, $\beta = 90.5^\circ$). The Mo-Sn bond length is $2.753 \text{ \AA}$; there is a Cl bridging group; Mo and Sn are 7-coordinate and 5-coordinate respectively³⁵³.

On the basis of studies of the rate of displacement of CO from $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) by phosphine and phosphite, it has been established that the enthalpies of activation decrease in the order $\text{Cr}(\text{CO})_6 \sim \text{W}(\text{CO})_6 > \text{Mo}(\text{CO})_6$ ³⁵⁴. The order of lability of numerous ligands (L) in *cis*- $\text{M}(\text{CO})_4\text{L}_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) has been determined. For a given leaving group, the order of reactivity is $\text{Mo} > \text{Cr} > \text{W}$ ³⁵⁵.

For further information about this rapidly expanding field of chemistry, the reader is referred to the chapters on carbonyl, nitrosyl and cyanide complexes and compounds involving metal-metal bonds.

2.4. ORGANOMETALLIC COMPLEXES OF MOLYBDENUM^{346, 356-359}

Molybdenum and tungsten form many organometallic complexes closely resembling those of chromium. What distinguishes these compounds from those of π -acceptor ligands

³⁴⁴ F. Calderazzo, R. Ercoli and G. Natta, "Metal Carbonyls: Preparation, Structure and Properties", in *Organic Syntheses via Metal Carbonyls*, 1, Interscience, New York (1968).

³⁴⁵ F. Calderazzo, "Halogeno Metal Carbonyls and Related Compounds", in *Halogen Chemistry*, 3, Academic Press, New York (1967), p. 401.

³⁴⁶ G. R. Dobson, I. W. Stolz and R. K. Sheline, "Substitution Products of the Group VIB Metal Carbonyls", in *Advances in Inorganic Chemistry and Radiochemistry*, 8, Academic Press, New York (1965).

³⁴⁷ T. A. Manuel, "Lewis Base-Metal Carbonyl Complexes", in *Advances in Organometallic Chemistry*, 3, Academic Press, New York (1965), p. 196.

³⁴⁸ R. B. King, "Reactions of Alkali Metal Derivatives of Metal Carbonyls and Related Compounds", in *Advances in Organometallic Chemistry*, 2, Academic Press, New York (1964), p. 182.

³⁴⁹ F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.* 3 (1964) 1609.

³⁵⁰ J. K. Ruff, *Inorg. Chem.* 7 (1968): (a) 1821; (b) 1818.

³⁵¹ J. K. Ruff, *Inorg. Chem.* 6 (1967) 1502.

³⁵² R. Kummer and W. A. G. Graham, *Inorg. Chem.* 7 (1968) 310.

³⁵³ M. Elder and D. Hall, *Inorg. Chem.* 8 (1969) 1268.

³⁵⁴ J. R. Graham and R. J. Angelici, *Inorg. Chem.* 6 (1967) 7082.

³⁵⁵ M. Graziani, F. Zingales and U. Belluco, *Inorg. Chem.* 6 (1967) 1582.

³⁵⁶ G. E. Coates, M. L. H. Green, P. Powell and K. Wade, *Principles of Organometallic Chemistry*, Methuen, London (1968).

³⁵⁷ E. O. Fischer and H. Werner, *Metal π -Complexes*, 1, Elsevier, Amsterdam (1966).

³⁵⁸ M. L. H. Green and P. L. Nagy, "Allyl Metal Complexes"; J. Birmingham, "Synthesis of Cyclopentadienyl Metal Compounds", in *Advances in Organometallic Chemistry*, 2, Academic Press, New York (1964).

³⁵⁹ J. J. Eisch, *The Chemistry of Organometallic Compounds*, Macmillan, New York (1967); *Transition Metal Organometallic Chemistry*, Academic Press, New York (1969).

is that the bond between the metal and the π -acceptor ligand lies in the plane of the ligand while in the organometallic compounds the plane of the ligand (e.g. benzene) is at right

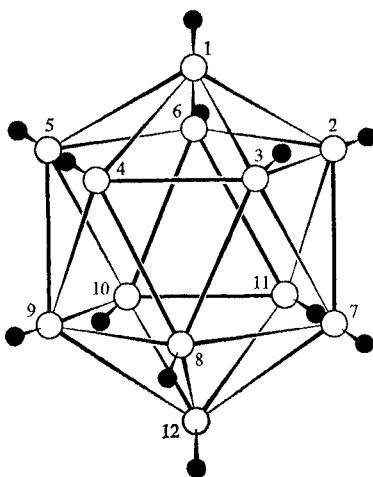


FIG. 8. Icosahedral structure and numbering system of $B_{10}C_2H_{12}$ carboranes and derivatives. (Reprinted from ref. 367, © 1968, by permission of the American Chemical Society.)

angles to the bond. The effective atomic number rule (rare gas rule) has been very useful in this field of chemistry. For further discussion of the principles involved the reader is referred to Part I, Section 2.4.

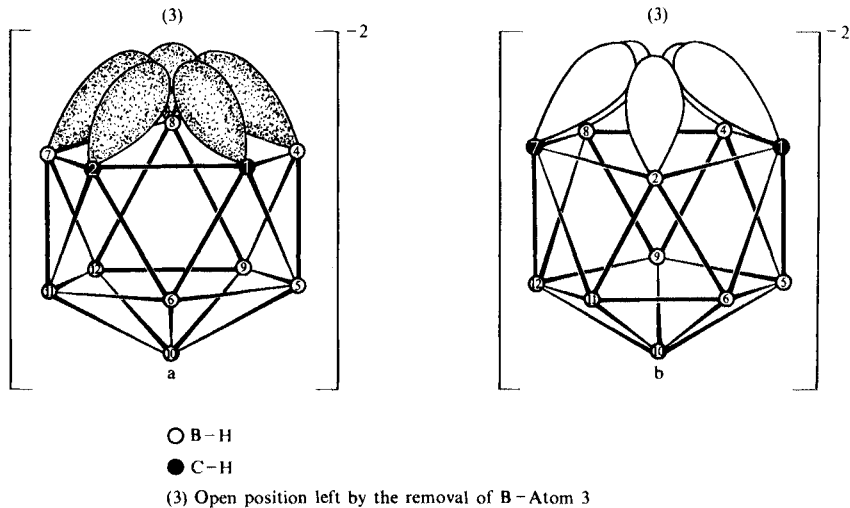


FIG. 9. Proposed structures of the two isomeric $B_9C_2H_{11}^{2-}$ (dicarbollide) ions; (a) 1,2; (b) 1,7. (Reprinted from ref. 367, © 1968, by permission of the American Chemical Society.)

The ligands in these compounds may be, for example, benzene and other aromatic molecules, unsaturated molecules such as butadiene, cyclobutadiene, cycloheptatriene and unsaturated radicals, e.g. π -allyl, π -cyclopentadienyl, etc. Typical compounds are:

$(C_6H_6)_2Mo^{360}$; $\sigma\text{-}CH_3Mo(CO)_3(\pi\text{-}C_5H_5)^{361}$; $\pi\text{-}C_5H_5Mo(CO)_3H^{362}$; $C_7H_8Mo(CO)_3^{363}$; $\pi\text{-}C_5H_5Mo(CO)_3X$ ($X = Cl, Br, I$).

Ligands of these types stabilize low oxidation states of the metal and make possible formation of types of compounds that otherwise do not exist. For example, there are no simple hydrides of Mo and W but complex hydrides $\pi\text{-}C_5H_5M(CO)_3H$ ($M = Cr, Mo, W$) are well known^{362, 364}. The hydrogens are acidic and the complex hydrides dissolve in alkali

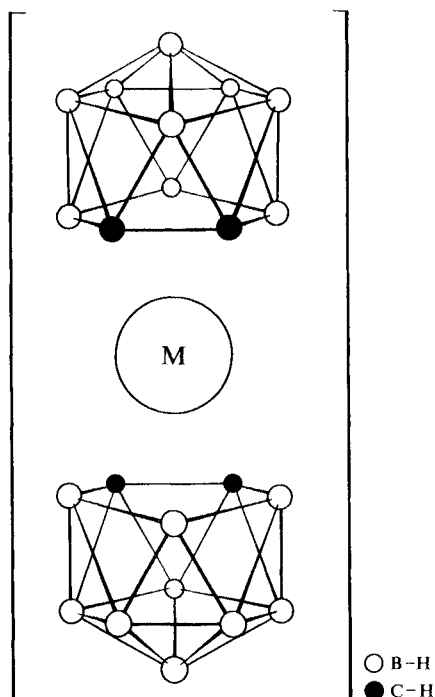


FIG. 10. Structure of dicarbollide-metal sandwich compounds ($M = Cr, Mo, W$). (Reprinted from ref. 367, © 1968, by permission of the American Chemical Society.)

metal hydroxide solutions to form the anions $[M(CO)_3(C_5H_5)]^-$. The thermal stability and resistance to oxidation in air of the three carbonyl hydrides increases in the order $Cr > Mo < W$.

Currently a very active area of organometallic chemistry is the syntheses and characterization of compounds having metal-metal bonds, and in particular bonds between two different metals, e.g.: $(CH_3)_{3-n}Cl_nSnMo(CO)_3(\pi\text{-}C_5H_5)$ ($n = 0, 1, 2, 3$)³⁶⁵; $R_3MM'(CO)_3(\pi\text{-}C_5H_5)$ ($R = CH_3, C_6H_5$; $M = Cr, Mo, W$; $M' = Ge, Sn, Pb$)³⁶⁶.

A recent and most fascinating development is the synthesis of transition metal complexes

³⁶⁰ F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965), p. 1402.

³⁶¹ W. L. Jolly, *Inorg. Syn.* **11**, McGraw-Hill, New York (1968), p. 116.

³⁶² E. O. Fischer, *Inorg. Syn.* **7**, McGraw-Hill, New York (1963), p. 136.

³⁶³ F. A. Cotton, J. A. McCleverty and J. E. White, *Inorg. Syn.* **9**, McGraw-Hill, New York (1967), p. 121.

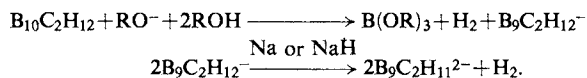
³⁶⁴ B. L. Shaw, *Inorganic Hydrides*, Pergamon Press, Oxford (1967), p. 86.

³⁶⁵ N. A. D. Carey and H. C. Clark, *Inorg. Chem.* **7** (1968) 94.

³⁶⁶ H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.* **5** (1966) 1401.

of carborane radicals^{367, 368}. The best known of these radicals are the icosahedral dicarbollide ions 1,2- and 1,7-B₉C₂H₁₁²⁻ derived from the carboranes 1,2- and 1,7-B₁₀C₂H₁₂ (Fig. 8). Other icosahedral ligands are B₁₀CH₁₁³⁻ and B₁₀H₁₀S²⁻.

The isomeric icosahedral carboranes, 1,2-, 1,7- and 1,12-B₁₀C₂H₁₂ are converted to the 11-particle ions B₉C₂H₁₂⁻ by reaction with strong bases; these can be reduced to the dicarbollide ions:



The dicarbollide ion closely resembles the cyclopentadienide ion with five molecular orbitals (Fig. 9) and thus can form "sandwich" compounds, e.g. Cr(π -(3)-1,2-B₉C₂L₁₁)₂³⁶⁹ (Fig. 10).

By photochemical reaction of M(CO)₆ (M = Cr, Mo, W), the ions [π -(3)-1,2-B₉C₂H₁₁M(CO)₃]²⁻ are formed, analogs of the cyclopentadienyl complexes,

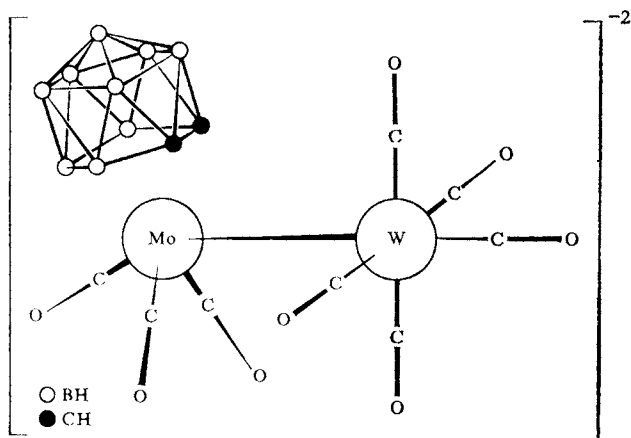
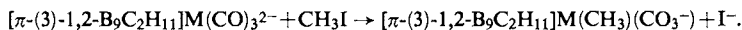


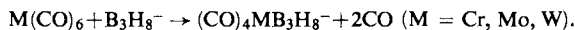
FIG. 11. Probable structure of the dinuclear metal carbonyl, [π -(3)-1,2-B₉C₂H₁₁]Mo(CO)₃W(CO)₅]²⁻. (Reprinted from ref. 367 by permission of the American Chemical Society.)

[π -C₅H₅M(CO)₃]⁻. The carbollide complexes resemble the cyclopentadienyl complexes in nucleophilic character:



The dianions are also reversibly protonated to acidic metal hydride derivatives. What is of even greater significance is the formation of a new series of dinuclear metal carbonyl derivatives by nucleophilic displacement of one CO from M(CO)₆ (M = M, W) by these dianions (Fig. 11).

Less complex borane fragments also form complexes with transition metals³⁶⁸, e.g. triborohydride ion:



For further information about the extensive and expanding area of organometallic chemistry the reader is referred to the chapters on metal carbonyls, organometallic compounds and metal-metal bonds.

³⁶⁷ M. F. Hawthorne, *Accounts of Chemical Research*, **1** (1968) 281.

³⁶⁸ F. Klanberg, E. L. Muetterties and L. J. Guggenberger, *Inorg. Chem.* **7** (1968) 2272.

³⁶⁹ H. W. Ruhle and M. F. Hawthorne, *Inorg. Chem.* **7** (1968) 2279.

2.5. OXIDATION STATE II

2.5.1. Molybdenum(II) Halogen Compounds and Their Derivatives^{370, 371}

To a large extent the chemistry of Mo(II) is the chemistry of the halides and compounds derived from them. The chemistry of Mo(II) (and of W(II)) is quite unusual because in this oxidation state there is often strong metal-metal bonding and formation of metallic clusters^{372, 373}. These clusters remain intact in chemical reactions except under quite drastic conditions.

Molybdenum(II) chloride is prepared by disproportionation of MoCl₃, oxidation of Mo with COCl₂³⁷⁴, or fusion of the pentachloride, trichloride or tetrachloride with Mo. The crude product is purified by dissolving it in HCl and isolating the chloro-acid, which is converted to the chloride by heating to 200° *in vacuo*. The bromide is obtained by dissociation of MoBr₃, bromination of Mo at 600–650°, or melting a mixture of MoCl₂ and LiBr followed by extraction (with water) of the LiCl formed; the iodide can be made similarly by reaction of MoCl₂ with LiI. The iodide can also be prepared by reaction of Mo(IV) or Mo(VI) oxide with AlI₃, or reaction of Mo and I₂ above the temperature of decomposition of MoI₃. Some of the properties of the Mo(II) halides have been summarized by Fergusson³⁷¹.

The dihalides MX₂ (M = Mo, W; X = Cl, Br) are isomorphous. The structural unit of the Mo(II) halides is [Mo₆X₈]⁴⁺. The six Mo atoms are at the corners of an octahedron with direct metal-metal bonds. This octahedron is inside a cube with each vertex (i.e. Mo atom) in the centre of a cube face; the corners of the cube are occupied by the halogen atoms (Fig. 12). The metal-metal distance in the [Mo₆Cl₈]⁴⁺ cluster is 2.63 Å as compared to 2.73 Å in Mo metal.

Each of the metal atoms can bond one more group. In the halides, these will be six halogen atoms, four of which bridge between adjacent clusters to form a two-dimensional structure. Thus any one cluster [Mo₆X₈]⁴⁺ acquires its electrical neutrality from two halogen atoms associated only with it and from $\frac{1}{2} \times 4$, or 2 more, from the four it shares equally with adjacent clusters. A general formulation for these halides is thus [Mo₆X₈]Y₄; X and Y may be the same but the mixed halides for all the X, Y combinations (X = Cl, Br, I) can also be prepared.

The [Mo₆X₈]⁴⁺ cluster persists as a chemical entity, acting as a hexacoordinate center. The eight X's are inert in aqueous solution but many ligands can occupy the six available positions on the cluster and these can be replaced by others without disturbing the cluster. Thus MoBr₂ and MoI₂ dissolve in acids HX to form H₂[(Mo₆Br₈)X₆] and H₂[(Mo₆I₈)X₆] which decompose on heating to [Mo₆Br₈]X₄ and [Mo₆I₈]X₄ (X = Cl, Br, I). Stable salts of these acids are formed with pyridinium and tetraethylammonium cations.

Cotton and Curtis³⁷⁵ prepared compounds of the types [Mo₆Cl₈L₆](ClO₄)₄,

³⁷⁰ J. D. Corbett, "Metal Halides in Low Oxidation States", in *Preparative Inorganic Reactions*, **3**, Interscience, New York (1966), p. 7.

³⁷¹ J. E. Fergusson, "Halide Chemistry of Chromium, Molybdenum and Tungsten", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 249.

³⁷² M. C. Baird, "Metal-Metal Bonds in Transition Metal Compounds", in *Progress in Inorganic Chemistry*, **9**, Interscience, New York (1968), pp. 3, 24–26.

³⁷³ D. L. Kepert and K. Vrieze, "Halides Containing Multi-centred Metal-Metal Bonds", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 26.

³⁷⁴ F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965), p. 1403.

³⁷⁵ F. A. Cotton and N. F. Curtis, *Inorg. Chem.* **4** (1965) 241.

$[\text{Mo}_6\text{Cl}_8\text{L}_2(\text{CH}_3\text{SO}_3)_4]$ and $[\text{Mo}_6\text{Cl}_{12}\text{L}_2]$ ($\text{L} = N,N$ -dimethylformamide, dimethylsulfoxide). The perchlorate ions do not coordinate while all L molecules and CH_3SO_3^- ions are coordinated to the Mo atoms via oxygen atoms. The Mo_6Cl_8 cluster always binds six

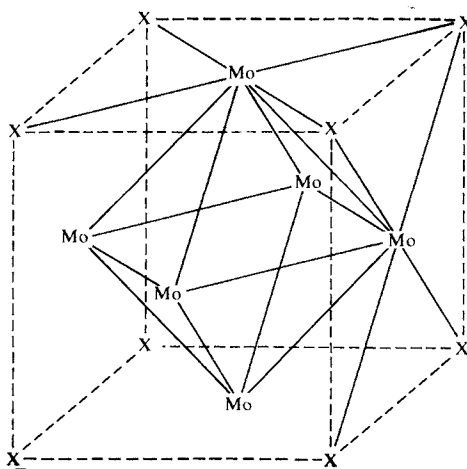


FIG. 12. Structure of the Mo_6X_8 cluster.

(Adapted from ref. 371, p. 250, © 1967, by permission of Academic Press.)

additional singly coordinating ligands. With polydentate ligands, compounds of the following type are formed: $[(\text{Mo}_6\text{Cl}_8)\text{X}_2\text{B}_2]\text{X}_2$ and $[(\text{Mo}_6\text{Cl}_8)\text{X}_3\text{T}]\text{X}$ (B = bidentate ligand such as dipyridyl, *o*-phenanthroline; T = tridentate ligand such as terpyridyl)³⁷¹.

All of these results indicate the persistence of the $[\text{Mo}_6\text{Cl}_8]^{4+}$ cluster. Somewhat drastic treatment is required to disrupt this structure. It remains intact on reaction of Mo(II) halides with sodium methoxide and sodium ethoxide at room temperature in an inert atmosphere³⁷⁶; the products are crystalline coordination compounds, $\text{Na}_2[(\text{Mo}_6\text{X}_8)(\text{OR})_6]$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$). However, if the solvent is distilled away, and the temperature of the reaction mixture is increased to 150° , it appears that the chlorides of the cluster are replaced, and the product is $\text{Na}_2\{[\text{Mo}_6(\text{OCH}_3)_8](\text{OCH}_3)_6\}$. Cotton, Wing and Zimmerman³⁷⁷ studied the far infrared spectra of a series of compounds $\text{M}_2[\text{Mo}_6\text{X}_8\text{Y}_6]$ in which $\text{X} = \text{Cl}$ or Br and $\text{Y} = \text{Cl}, \text{Br}, \text{I}$ (or other related species) and $\text{M} = (\text{n-C}_4\text{H}_9)_4\text{N}, (\text{C}_6\text{H}_5)_4\text{N}, (\text{C}_6\text{H}_5)_4\text{As},$ or Cs . The effect of changing the cation is negligible. The Mo-Mo stretching frequency is about 230 cm^{-1} .

In metal atom cluster compounds, for bonds of various orders between a given pair of atoms, a plot of bond order vs. bond length is a smooth curve concave upward³⁷⁸. Thus it appears possible to estimate bond orders from bond length and *vice versa*, as illustrated by data in Table 32.

Multiple metal-metal bonds were first encountered in the $[\text{Re}_2\text{Cl}_8]^{2-}$ ion and are supposed to exist in $[\text{Mo}_2(\text{CH}_3\text{COO})_4]$ ³⁷⁹ (see below). By reaction of this Mo(II) compound with aqueous HCl , compounds of the type $\text{M}_x^+[\text{Mo}_y\text{Cl}_z] \cdot w\text{H}_2\text{O}$ have been prepared³⁸⁰. Red crystals of $\text{K}_4[\text{Mo}_2\text{Cl}_8]$ can be obtained from the cold HCl solution.

³⁷⁶ P. Nannelli and B. P. Block, *Inorg. Chem.* **7** (1968) 2423.

³⁷⁷ F. A. Cotton, R. M. Wing and R. A. Zimmerman, *Inorg. Chem.* **6** (1967) 11.

³⁷⁸ F. A. Cotton, *Inorg. Chem.* **4** (1965) 335.

³⁷⁹ D. Lawton and R. Mason, *J. Am. Chem. Soc.* **87** (1965) 921.

³⁸⁰ J. V. Brencic and F. A. Cotton, *Inorg. Chem.* **8** (1969) 7.

TABLE 32. RELATION OF BOND ORDER AND METAL-METAL DISTANCE³⁷⁸

Cluster	Bond order	Metal-metal distance (Å)
[Nb ₆ X ₁₂] ²⁺	~ $\frac{2}{3}$	~ 2.9
[Ta ₆ Cl ₁₂] ²⁺	~ $\frac{2}{3}$	~ 2.9
[Mo ₆ Cl ₈] ⁴⁺	~ 1	~ 2.65
[Re ₃ Cl ₉]	~ 2	~ 2.48
[Re ₂ Cl ₈] ²⁻	~ 4	~ 2.24

The [Mo₂Cl₈]⁴⁻ ion has an approximately cubical structure, the eight Cl's occupying the corners; within the cube a pair of Mo atoms is centred along a fourfold axis; or it can be described as two MoCl₄ groups bound via a very short Mo-Mo bond (2.14 Å). The [Mo₂Cl₈]⁴⁻ ion is isostructural with [Re₂Cl₈]³⁻ and [Tc₂Cl₈]³⁻. It is concluded that the ion has the type of quadruple bond (σ , 2π , δ) previously attributed to the [Re₂X₈]²⁻ compounds and their derivatives.

2.5.2. Molybdenum(II) Acetate

The structure of the acetates of Mo(II)³⁷⁹, Cr(II), Cu(II) and Rh(II), established by X-ray crystallography³⁸², is shown in Fig. 2 (p. 659). In all of these except the Mo(II) compound, neutral ligands L are present. Molybdenum(II) acetate, [Mo₂(CH₃COO)₄], is triclinic, space group *P*1, with the following parameters: *a*, *b*, *c*, respectively 8.35, 5.46, and 7.50 Å; α , β , γ , respectively 82.9°, 105.1° and 105.1°. It is centrosymmetric with an Mo-Mo distance of 2.1 Å, which is short enough to indicate metal-metal bonding (Mo-Mo distance in the metal, 2.725 Å).

2.5.3. Potassium Cyanomolybdate(II)³⁸¹

By reduction of K₄[Mo(CN)₈] with H₂ (330–390°), HCN is evolved and the Mo(II) complex K₄[Mo(CN)₆] is obtained. Aqueous solutions of this compound reduce hydrogen peroxide, iodine and Ag⁺. When the green K₄[Mo(CN)₆] is extracted (under anhydrous conditions) with methanol, the complex is oxidized to K₃[Mo(CN)₆].

2.5.4. Molybdenum(II) Oxide

By reduction of oxygen-containing Mo compounds with potassium, K_{0.66}MoO₂ and K_{1.5}MoO₃ are obtained. When these react with alcohol or water, the products are K₂MoO₄, hydrogen and a black insoluble residue whose composition approaches MoO. This oxide is cubic (*a* = 5.019 Å)³⁸³. Some of the thermodynamic properties of MoO as an ideal gas are³⁸⁴:

ΔH°_{f298}	92.5 ± 15 kcal/mole
ΔG°_{f298}	84.887 kcal/mole
S°_{298}	56.9 ± 2 gibbs/mole.

³⁸¹ J. S. Yoo, E. Griswold and J. Kleinberg, *Inorg. Chem.* **4** (1965) 365.

³⁸² M. J. Bennett, K. G. Caulton and F. A. Cotton, *Inorg. Chem.* **8** (1969) 1.

³⁸³ J. Aubry, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959), p. 635.

³⁸⁴ JANAF Thermochemical Tables, Third Addendum, PB-168-370-3, National Bureau of Standards, Washington, DC (1968).

2.6. OXIDATION STATE III

2.6.1. Molybdenum(III) Halides and Complex Halides^{385, 386}

Some preparative methods for MoX_3 ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) are as follows:

MoF_3 : reduction of MoF_5 with Mo (sealed tube at 400° ; reduction of MoF_5 with H_2 or SbF_3 .

MoCl_3 : reduction of MoCl_5 with Mo, H_2 ³⁸⁷ or a hydrocarbon; oxidation of Mo with Hg_2Cl_2 .

MoBr_3 : reduction of MoBr_4 ; oxidation of Mo with Br_2 ^{387, 388} or Hg_2Br_2 .

MoI_3 : reaction of Mo and I_2 in a sealed tube at 300° (if the temperature is too high, MoI_2 is formed).

Aqueous solutions of MoCl_3 may be obtained by electrolytic reduction of a concentrated HCl solution of MoO_3 ^{387, 389}.

The Mo(III) halides are quite inert and insoluble in water. Their colors and estimated melting points are: chloride, brown-red, 1027° ; bromide, green, 977° ; iodide, black, 927° . The fluoride is stable up to about 600° *in vacuo*. The chloride decomposes before melting to a mixture of products, including Mo, MoCl_5 , MoCl_4 and MoCl_3 .

Halide complexes of the following types are known: $\text{M}_3[\text{MoF}_6]$ ($\text{M} = \text{NH}_4, \text{K}$); $\text{M}_2[\text{MoX}_5\text{H}_2\text{O}]$ and $\text{M}_3[\text{MoX}_6]$ ($X = \text{Cl}, \text{Br}$; $\text{M} = \text{alkali metal or NH}_4$); $(\text{NH}_4)[\text{MoCl}_6] \cdot \text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$; $\text{K}_3[\text{MoCl}_6] \cdot 4\text{KCl} \cdot 6\text{H}_2\text{O}$; $\text{M}_3[\text{Mo}_2\text{X}_9]$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{amines}$; $X = \text{Cl}, \text{Br}$). There are reports in the older literature of oxyhalides such as $\text{MoOCl} \cdot 4\text{H}_2\text{O}$, $\text{MoOBr} \cdot 4\text{H}_2\text{O}$ and $\text{MoOF} \cdot 3.5\text{H}_2\text{O}$; and oxyhalide complexes, e.g. $[\text{MoOCl}_3 \cdot 3\text{H}_2\text{O}]^-$, $[\text{MoOHCl}_3 \cdot 3\text{H}_2\text{O}]^-$, $[\text{MoF}_4]^-$ and $[\text{Mo}_2\text{F}_9]^-$.

The brown complex $\text{K}_3[\text{MoF}_6]$ (cubic) is prepared by fusing a mixture of $\text{K}_3[\text{MoCl}_6]$ and KHF_2 . It has six M-F bonds at $1.95 \text{ \AA}$ and a magnetic moment of 3.2 B (25°). The red complex mono-Mo chlorides are obtained by reducing HCl solutions of MoO_3 electrolytically^{387, 389} or with potassium amalgam. They are stable in dry air and in HCl solution and are strong reducing agents. Disproportionation of $[\text{MoX}_6]^{2-}$ in liquid NH_3 produces the binuclear complexes (insoluble in the reaction mixture) and soluble ammonobasic Mo(V) complexes.

Metal-metal bonding^{390a} may exist in the Mo(III) halides, as indicated by magnetic properties and Mo-Mo distances. Molybdenum(III) chloride exists in two forms. One has a structure similar to that of $\gamma\text{-TiCl}_3$ with alternating Mo-Mo distances of 2.77 and $3.70 \text{ \AA}$; the Mo-Mo distance in the metal is $2.725 \text{ \AA}$. The other apparently has a cluster-type structure Mo_3Cl_9 . The tribromide and triiodide resemble $\beta\text{-TiCl}_3$ and have MoX_6 octahedra joined through opposite faces in infinite chains. The Mo-Mo distance in MoBr_3 is $3.07 \text{ \AA}$. The dimeric ion $[\text{Mo}_2\text{Cl}_9]^{3-}$ is diamagnetic and may have a structure like that of $[\text{W}_2\text{Cl}_9]^{3-}$,

³⁸⁵ J. D. Corbett, "Metal Halides in Low Oxidation States", in *Preparative Inorganic Reactions*, **3**, Interscience, New York (1966), p. 7.

³⁸⁶ J. E. Fergusson, "Halide Chemistry of Chromium, Molybdenum and Tungsten", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 254.

³⁸⁷ F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965), p. 1404.

³⁸⁸ P. J. H. Carnell, R. E. McCarley and R. D. Hogue, *Inorg. Syn.* **10**, McGraw-Hill, New York (1967), p. 49.

³⁸⁹ K. H. Lohman and R. C. Young, *Inorg. Syn.* **4**, McGraw-Hill, New York (1953), p. 97.

³⁹⁰ M. C. Baird, "Metal-Metal Bonds in Transition Metal Compounds", in *Progress in Inorganic Chemistry*, Interscience, New York (1968): (a) pp. 2, 24, 26; (b) p. 28.

i.e. two distorted MoCl_6 octahedra with a common face with a short metal-metal distance indicating metal-metal bonding.

2.6.2. Molybdenum(III) Coordination and Chelate Compounds

Molybdenum(III) apparently does not form many coordination compounds like the thousands so characteristic of the chemistry of Cr(III). However, a few are known such as the analogs of $[\text{Crpy}_3\text{Cl}_3]$ (py = pyridine), $[\text{Mopy}_3\text{X}_3]$ (X = Cl, Br) which are formed by the reaction of the Mo(III) halide with anhydrous pyridine. The chloride is prepared by heating the reactants at 270° in a sealed tube; the bromide is formed by refluxing the reaction mixture of MoBr_3 and pyridine³⁸⁷. The chloride can also be prepared by reaction of pyridine with $\text{K}_3[\text{MoCl}_6]$ ³⁹¹.

In contrast to the action of pyridine, monoethyl amine and dimethylamine cause solvolysis³⁹² of MoBr_3 , producing $\text{MoBr}(\text{NHCH}_3)_2 \cdot \text{NH}_2\text{CH}_3$ (brown) and $\text{MoBr}_2 \cdot \text{N}(\text{CH}_3)_2 \cdot \text{NH}(\text{CH}_3)_2$ (violet); these compounds are insoluble in the amine and in benzene. On the other hand, alkyl cyanides form adducts, $\text{MoBr}_3 \cdot 3\text{RCN}$ ³⁹³; these are useful in the preparation of other compounds.

Molybdenum(III) forms an isothiocyanato ion $[\text{Mo}(\text{NCS})_6]^{3-}$. The compound $\text{K}_3[\text{Mo}(\text{CNS})_6] \cdot 4\text{H}_2\text{O}$ (isomorphous with $\text{K}_3[\text{Cr}(\text{NCS})_6] \cdot 4\text{H}_2\text{O}$) is somewhat unstable in air but the adducts $\text{M}[\text{Mo}(\text{CNS})_6] \cdot \text{H}_2\text{O} \cdot \text{L}$ (M = K, NH_4 ; L = HCl, KHC_2O_4 , $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_3\text{H}_7\text{OH}$, CH_3COOH) are quite stable³⁹⁴. The structure of the complex ion was determined by single crystal X-ray diffraction study of the acetic acid adduct. The compound is orthorhombic (space group $\text{Pm}2_1n$); a , b , c are respectively 13.547, 8.568 and 9.660 Å. The structure of the complex ion is octahedral with six SCN groups bonded to Mo via the N atoms; thus the Mo is 6-coordinate; the H_2O molecule is not coordinated to the metal.

Black crystals of a complex Mo(III) cyanide can be precipitated by ethanol from a reaction mixture of KCN and $\text{K}_3[\text{MoCl}_6]$ (or $\text{K}_2[\text{MoCl}_5 \cdot \text{H}_2\text{O}]$ in air-free water³⁹⁵). The magnetic moment³⁹⁶ (1.75 B) is not compatible with an octahedral ion $[\text{Mo}(\text{CN})_6]^{3-}$; the anion may be $[\text{Mo}(\text{CN})_7]^{4-}$ or $[\text{Mo}(\text{CN})_7\text{H}_2\text{O}]^{4-}$; whether it is 8-coordinate is questionable. The compound is oxidized in air to $\text{K}_4[\text{Mo}(\text{CN})_8]$.

Fusion of $\text{K}_4[\text{Mo}(\text{CN})_8]$ with KCN at 550° produces the dark red $\text{K}_2[\text{Mo}(\text{CN})_5]$, which has a magnetic moment of 0.6 B in the solid state and 0.9 B in solution³⁹⁷. Since these values are much lower than the values for $\text{K}_4[\text{Mo}(\text{CN})_7\text{H}_2\text{O}]$ (1.75) and Mo(III)-6-coordinate complexes (3.70–3.80)³⁹⁸, there is a possibility of metal-metal bonding in $[\text{Mo}(\text{CN})_5]^{2-}$.

Reduction of $\text{K}_4[\text{Mo}(\text{CN})_8]$ with H_2 produces the Mo(II) complex $\text{K}_4[\text{Mo}(\text{CN})_6]$. When this is extracted with methanol in dry air, oxidation occurs and the Mo(III) complex, $\text{K}_3[\text{Mo}(\text{CN})_6]$, is formed³⁹⁹.

The acetylacetone (acac) complex $[\text{Mo}(\text{acac})_3]^{400}$ may be prepared by neutralizing a

³⁹¹ H. B. Jonassen and L. J. Bailin, *Inorg. Syn.* **7**, McGraw-Hill, New York (1963), p. 140.

³⁹² D. A. Edwards and G. W. A. Fowles, *J. Less-Common Metals*, **4** (1962) 512.

³⁹³ E. A. Allen, K. Feenan and G. W. A. Fowles, *J. Chem. Soc.* (1965) 1636.

³⁹⁴ J. R. Knox and K. Eriks, *Inorg. Chem.* **7** (1968) 84.

³⁹⁵ R. C. Young, *J. Am. Chem. Soc.*, **54** (1932) 1402.

³⁹⁶ W. P. Griffith, *Quart. Rev. (London)* **16** (1962) 188.

³⁹⁷ W. L. Magnuson, E. Griswold and J. Kleinberg, *Inorg. Chem.*, **3** (1964) 88.

³⁹⁸ J. Lewis, R. S. Nyholm and P. W. Smith, *J. Chem. Soc.* (1961) 4590.

³⁹⁹ J. S. Yoo, E. Griswold and J. Kleinberg, *Inorg. Chem.* **4** (1965) 365.

⁴⁰⁰ M. L. Larson and F. W. Moore, *Inorg. Syn.* **8**, McGraw-Hill, New York (1966), p. 153.

solution of $(\text{NH}_4)_2[\text{MoCl}_5 \cdot \text{H}_2\text{O}]$ and acetylacetone, or a solution of acetylacetone and Mo(III) ion produced by electrolytic reduction of a molybdate solution, or by refluxing a mixture of Mo(CO)_6 and acetylacetone. This chelate is a purple crystalline solid (m.p. 228–230°). It oxidizes in air to form products containing Mo(V) . It can be sublimed *in vacuo*. It is soluble in benzene, benzophenone, pyridine and CCl_4 without decomposition. It is not decomposed by boiling water. Although its properties generally resemble those of the analogous chromium chelate, there is a marked contrast between the inertness of the chromium compound and the ease of oxidation of the molybdenum compound. Oxalato complexes such as $[\text{Mo}_2\text{O}(\text{C}_2\text{O}_4)_2] \cdot 6\text{H}_2\text{O}$ and $[\text{Mo}_4\text{O}_3(\text{C}_2\text{O}_4)_3] \cdot 12\text{H}_2\text{O}$ have been described^{401a}.

2.6.3. Molybdenum(III) Oxide and Hydroxide^{401b}

Watt and Davies prepared Mo_2O_3 by dehydrating Mo(OH)_3 or by action of potassium on a liquid ammonia solution of MoO_3 . This amorphous oxide is converted to the hydrate by action of water and dissolves in HCl to give a red solution of Mo(III) .

The hydroxide, Mo(OH)_3 , has been prepared by catalytic hydrogenation of an ammonium molybdate solution or by action of bases on Mo^{3+} solutions; the latter can be obtained by reduction of molybdate solutions by metals such as Zn , Cd , Pb , or their amalgams (in the absence of air), or electrolytic reduction of molybdate solutions.

2.7. OXIDATION STATE IV

2.7.1. Molybdenum(IV) Halogen Compounds^{402–404}

Preparative methods for the Mo(IV) halides include the following:

MoF_4 : pyrolysis of Mo_2F_9 from reaction of Mo(CO)_6 and F_2 at -75° ; the non-volatile green solid is MoF_4 (Mo_2F_9 may be a mixed valence compound, perhaps $[\text{MoF}_3]^+[\text{MoF}_6]^-$); reaction of MoS_2 and SF_4 at 350° .

MoCl_4 : reduction of MoCl_5 with C_6H_6 ; reaction of Mo with CCl_4 and O_2 ; disproportionation of MoCl_3 (500°) or MoCl_2 (700°); reaction of MoCl_3 with MoCl_5 at 250° .

MoBr_4 : bromination of MoBr_3 ⁴⁰⁵ (60°) or Mo(CO)_6 .

The existence of MoI_4 is uncertain.

The Mo(IV) halides are easily oxidized and hydrolyzed and disproportionate when heated, e.g. the chloride to MoCl_5 and MoCl_3 (above 170°), or to MoCl_3 and Cl_2 (*in vacuo* at 150°); the bromide to MoBr_3 and Br_2 ; MoI_4 (if it exists) to MoI_3 and I_2 ; the tungsten compounds are more stable in this respect. The estimated melting points are⁴⁰⁴: chloride, 317° ; bromide, 337° ; iodide, 417° . Thermodynamic properties of these compounds have been summarized by Fergusson⁴⁰⁴; a considerable part of the data is based on estimates.

⁴⁰¹ J. Aubrey, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959): (a) p. 737; (b) pp. 634, 637.

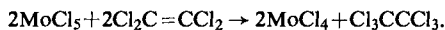
⁴⁰² G. W. A. Fowles, "Halide and Oxyhalide Complexes of Elements of the Titanium, Vanadium and Chromium Subgroups", in *Preparative Inorganic Reactions*, **1**, Interscience, New York (1964), pp. 128, 132, 134.

⁴⁰³ J. D. Corbett, "Metal Halides in Low Oxidation States", in *Preparative Inorganic Reactions*, **3**, Interscience, New York (1966), p. 7.

⁴⁰⁴ J. E. Fergusson, "Halide Chemistry of Chromium, Molybdenum and Tungsten", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 259.

⁴⁰⁵ P. J. H. Carnell, R. E. McCarley and R. D. Hogue, *Inorg. Syn.* **10**, McGraw-Hill, New York (1967), p. 49.

Preparation of MoCl_4 is conveniently accomplished by refluxing (2.5–4 days, under dry oxygen-free conditions) a reaction mixture of MoCl_5 and tetrachloroethylene in CCl_4 ^{406, 407}:



The yield of the black MoCl_4 may be as high as 85–95%. Not only is this an elegant method but also the product (α - MoCl_2) is different from that obtained with high temperature methods (β - MoCl_4). X-ray powder patterns show that α - MoCl_4 is similar to MoCl_4 obtained by reduction of MoCl_5 by benzene and is isomorphous with NbCl_4 and WCl_4 (monoclinic), both of which are characterized by direct metal–metal bonding. Heating α - MoCl_4 (250°) converts it to β - MoCl_4 .

Beta- MoCl_4 has a structure consisting of MoCl_6 octahedra sharing edges. The magnitudes of the magnetic moment (2.42 B) and shortest Mo–Mo distance (3.50 Å) show that there is no Mo–Mo bonding in β - MoCl_4 . The effective magnetic moment of α - MoCl_4 (room temperature) is low (0.85 B); there may be marginal Mo–Mo bonding in this compound.

Complex fluoro anions of Mo(IV) are difficult to obtain because of their sensitivity to hydrolysis; $\text{Na}_2[\text{MoF}_6]$ has been prepared by reduction of MoF_6 with NaI in liquid SO_2 ; it slowly decomposes in air. The chloro complexes $\text{M}[\text{MoCl}_6]$ (M = alkali metal such as Cs or Rb, or an amine) are obtained by melting a mixture of MCl and MoCl_5 , or by reaction of MCl and MoCl_5 in ICl or liquid SO_2 ; the bromo complexes can be obtained by similar methods. The amine salts are readily prepared by reaction of the amine hydrochloride with $\text{MoCl}_4 \cdot 2\text{RCN}$ (R = methyl or *n*-propyl)⁴⁰⁸. The salts of $[\text{MoCl}_6]^{2-}$ and $[\text{MoBr}_6]^{2-}$ have magnetic moments in the range 2.08–2.44 B at room temperature. The salt $\text{K}_2[\text{MoCl}_6]$ has a cubic structure with Mo–Cl distance of 2.31 Å. These compounds hydrolyze in moist air.

There appears to be only one oxyhalide of Mo(IV), the bronze MoOCl_3 , which can be made by reaction of MoCl_3 with MoO_3 or by the reaction of Cl_2 with MoS_2 . This compound may have a polymeric structure like that of the analogous Nb and Ta compounds.

2.7.2. Molybdenum(IV) Coordination and Chelate Compounds

Molybdenum(IV) chloride forms adducts, with organic molecules, that may be regarded as hexacoordinate Mo(IV) complexes^{409, 410}. Molybdenum(V) chloride is usually reduced by nitrogen-containing ligands⁴¹¹ (e.g. pyridine; 2,2'-dipyridyl; RCN, R = methyl, ethyl, *n*-propyl, phenyl) with formation of Mo(IV) complexes of the types MoX_4L_2 and MoX_4B (L = singly-coordinating ligand; B = bidentate ligand). Other complexes, $\text{MoCl}_4 \cdot 2\text{L}$, can be made by replacement of the cyanide in $\text{MoCl}_4 \cdot 2\text{RCN}$ (R = *n*-propyl) by, for example, tetrahydrofuran, pentamethylene oxide, α -picoline, pyridine triphenylphosphine oxide; and complexes of the type $\text{MoCl}_4 \cdot \text{B}$ (B = bidentate ligand) by replacement of the cyanide with 2,2'-dipyridyl or 1,10-phenanthroline.

The Mo(IV) halides are sufficiently unstable to make the direct preparation of such

⁴⁰⁶ T. M. Brown and E. L. McCann III, *Inorg. Chem.* **7** (1968) 1227.

⁴⁰⁷ D. L. Kepert and R. Mandyczewsky, *Inorg. Chem.* **7** (1968) 2091.

⁴⁰⁸ E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J. Chem. Soc.* (1963) 4649.

⁴⁰⁹ E. Allen, B. J. Brisdon and G. W. A. Fowles, *J. Chem. Soc.* (1964) 4531.

⁴¹⁰ E. Allen, K. Feenan and G. W. A. Fowles, *J. Chem. Soc.* (1965) 1936.

⁴¹¹ T. M. Brown and B. Ruble, *Inorg. Chem.* **6** (1967) 1335.

complexes difficult, and furthermore, they are often oxidized by oxygen-containing ligands. By excluding air and moisture, Brown and associates⁴¹² were able to prepare adducts of MoX_4 by direct reaction of MoX_4 with various N-containing ligands, i.e. $\text{MoCl}_4 \cdot 2\text{RCN}$ ($\text{R} = \text{CH}_3, \text{C}_3\text{H}_7, \text{C}_6\text{H}_5$); $\text{MoCl}_4 \cdot 2\text{py}$ ($\text{py} = \text{pyridine}$); $\text{MoCl}_4 \cdot \text{B}$ ($\text{B} = 2,2'$ -dipyridyl or N,N,N',N' -tetramethylethylenediamine). The bromide, however, formed complexes only with $2,2'$ -dipyridyl, acetonitrile and benzonitrile. With long reaction times, pyridine reduces MoCl_4 and MoBr_4 , producing the complexes $[\text{Mopy}_3\text{Cl}_3]$ and $[\text{Mopy}_3\text{Br}_3]$, which are also obtained by reaction of pyridine with the trihalide (see Section 2.6.2).

Several cyano complexes of Mo(IV) are known^{413, 414}. The octacyanomolybdate, $\text{K}_4[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$, is prepared by reduction of Mo(IV) in the presence of KCN ⁴¹⁵. In the crystal, $[\text{Mo}(\text{CN})_8]^{6-}$ is dodecahedral, as indicated by X-ray diffraction studies. On the basis of Raman and infrared data, it has been concluded that the ion in solution has an Archimedean antiprism structure^{414a}. At pH 10, exchange of labeled CN^- with $[\text{Mo}(\text{CN})_8]^{4-}$ occurs slowly in the light but is negligible in the dark (pH 4–12). Exchange of ^{99}Mo between $[\text{Mo}(\text{CN})_8]^{4-}$ and $[\text{Mo}(\text{CN})_8]^{3-}$ is rapid since this is an electron-transfer between two very similar ions and thus the activation energy is negligible⁴¹³.

The red-violet *trans*-dioxo complex, $\text{K}_4[\text{MoO}_2(\text{CN})_4] \cdot 6\text{H}_2\text{O}$, is obtained by reaction of KCN and KOH with $\text{MoO}(\text{OH})_3$; this hydroxide is precipitated by NH_4OH from a solution of ammonium paramolybdate reduced with hydrazine. The anhydrous salt is tan but dissolves in water to give a blue solution, as does the hydrate. By adjusting the pH of the solution to 11, the blue $\text{K}_3[\text{MoO}(\text{OH})(\text{CN})_4]$ is obtained; at pH 7.0, $\text{K}_2[\text{Mo}(\text{OH})_2(\text{CN})_4]$ (green) is formed⁴¹⁶. The aqueous solutions are somewhat sensitive to air oxidation, but this is not rapid if the pH is 8 or more⁴¹⁶. After a considerable time, aqueous solutions of $\text{K}_2[\text{Mo}(\text{OH})_2(\text{CN})_4]$ are oxidized with precipitation of $\text{MoO}(\text{OH})_3$ (brown); in alcohol solutions, the hydroxy complex is oxidized to a blue compound, $\text{K}_6[\text{Mo}_2^{\text{IV}}\text{Mo}^{\text{VI}}(\text{CN})_8\text{O}_6] \cdot 2\text{H}_2\text{O}$.

The photochemical decomposition of $[\text{Mo}(\text{CN})_8]^{4-}$ has been studied by many investigators⁴¹². According to Balzani and co-workers⁴¹⁷, the primary process (caused by radiation in the $d-d$ bands, 365 $m\mu$) is a photoaquation:



These investigators reject the alternative hypothesis of the formation of "supercomplexes" such as $[\text{Mo}(\text{CN})_4(\text{H}_2\text{O})_2]^{4-}$ (10-coordinate) as intermediates. This primary process is followed by thermal reactions that are very rapid in alkaline solution and release up to four CN^- ions. The specific anion or anions present will depend on the pH if this is 8 or above and the solid product recovered will depend on the procedure used⁴¹⁵.

Only a few octacoordinate Mo(IV) complexes are known^{414b}; one of these is the octacyanide ion, $[\text{Mo}(\text{CN})_8]^{4-}$. Previous reports of the supposedly 8-coordinate complex

⁴¹² T. T. Brown, D. K. Pings, L. R. Lieto and S. J. DeLong, *Inorg. Chem.* **5** (1966) 1695.

⁴¹³ B. M. Chadwick and A. G. Sharpe, "Transition Metal Cyanides and Their Complexes", in *Advances in Inorganic Chemistry and Radiochemistry*, **8**, Academic Press, New York (1965), p. 99.

⁴¹⁴ S. J. Lippard, "Eight-Coordination Chemistry", in *Progress in Inorganic Chemistry*, **8**, Interscience. New York (1967): (a) p. 158; (b) p. 165.

⁴¹⁵ J. van de Poel and H. M. Neumann, *Inorg. Syn.* **11**, McGraw-Hill, New York (1968), p. 53; N. H. Furmen and C. O. Miller, *ibid.* **3** (1950), p. 160.

⁴¹⁶ J. van de Poel and H. M. Neumann, *Inorg. Chem.* **7** (1968) 2086.

⁴¹⁷ V. Balzani, M. F. Manfrin and L. Moggi, *Inorg. Chem.* **8** (1969) 47.

$K_4[Mo(CN)_4(OH)_4] \cdot 2H_2O$ are incorrect. It has been shown by X-ray structural investigation that this is the red-violet trans-dioxo complex, $K_4[MoO_2(CN)_4] \cdot 6H_2O$ ⁴¹⁸. Other octa-coordinate anions⁴¹⁹ are the oxalato and carbonato complexes, $[Mo(C_2O_4)_4]^{4-}$ and $[Mo(CO_3)_4]^{4-}$.

2.7.3. Molybdenum(IV) Oxide

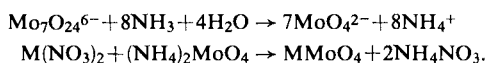
Molybdenum(IV) oxide⁴²⁰ can be prepared by several methods including controlled oxidation of Mo and controlled reduction of MoO_3 with hydrogen. The pure oxide suitable for structure determination has been prepared by electrolysis of a polymolybdate ($K_2O \cdot 5MoO_3$) solution. Molybdenum(IV) oxide is insoluble in water: it is inert in solutions of nonoxidizing acids or bases, but is dissolved by oxidizing solutions. It dissociates to Mo and MoO_3 at high temperatures ($\sim 1100^\circ$).

Crystalline MoO_2 is violet or brown. Its deformed rutile structure consists of infinite chains of MoO_6 octahedra sharing opposite edges along the chain direction with Mo-Mo distances alternately long (3.10 Å) and short (2.50 Å)⁴²¹. It is diamagnetic and semi-conducting; metal-metal bonds are present⁴²². Some of its thermodynamic properties are as follows⁴²³:

$$\begin{array}{ll} \Delta G_f^\circ_{298} & -172.415 \text{ kcal/mole} \\ \Delta H_f^\circ_{298} & -140.5 \text{ kcal/mole} \\ S^\circ_{298} & 11.954 \text{ gibbs/mole.} \end{array}$$

2.7.4. Molybdates(IV)

Barium and strontium molybdates(IV) are prepared by reducing $BaMoO_4$ and $SrMoO_4$ with hydrogen^{424, 425}. The starting materials are obtained from ammonium paramolybdate as follows ($M = Ba, Sr$):



Barium molybdate(IV) is purple-red and $SrMoO_3$ is brick-red. They have the cubic perovskite structure with cell constants 4.0400 Å ($BaMoO_3$) and 3.9751 Å ($SrMoO_3$). This structure is appropriate for studying cation-anion-cation or superexchange interactions. These compounds show metallic behavior; for example, their resistivity increases with increasing temperature (-190 to 180°). Bouchard and Sienko⁴²⁵ have suggested the same structure for these compounds as that which successfully accounts for the properties of the tungsten bronzes, i.e. a host structure of MoO_3 with Ba or Sr acting as an interstitial donor contributing two valence electrons to the collective electron assembly.

⁴¹⁸ S. J. Lippard and B. J. Russ, *Inorg. Chem.* **6** (1967) 1943; V. W. Day and J. L. Hoard, *J. Am. Chem. Soc.* **90** (1968) 3374.

⁴¹⁹ M. C. Steele, *Australian J. Chem.* **10** (1957) 367.

⁴²⁰ J. Aubry, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959), p. 632; F. Hein and S. Herzog, in *Handbook of Preparative Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965), p. 1409.

⁴²¹ F. A. Cotton and S. M. Morehouse, *Inorg. Chem.* **4** (1965) 1377; D. B. Rogers, R. D. Shannon, A. W. Sleight and J. L. Gillson, *Inorg. Chem.* **8** (1969) 841.

⁴²² M. C. Baird, "Metal-Metal Bonds in Transition Metal Compounds", in *Progress in Inorganic Chemistry*, **9**, Interscience, New York (1968), p. 28.

⁴²³ *JANAF Thermochemical Tables, Third Addendum*, PB-168-370-3, National Bureau of Standards, Washington, DC (1968).

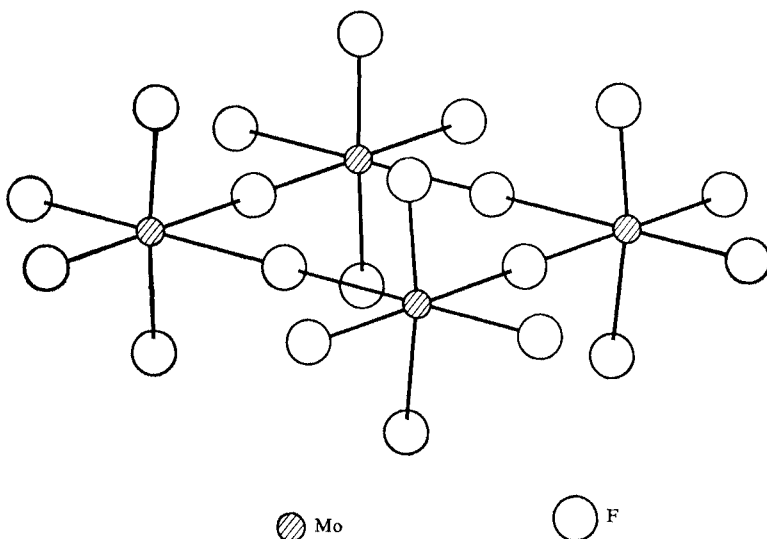
⁴²⁴ J. DeLuca, A. Wold and L. H. Brixner, *Inorg. Syn.* **11**, McGraw-Hill, New York (1968), p. 1.

⁴²⁵ G. H. Bouchard, Jr. and M. J. Sienko, *Inorg. Chem.* **7** (1968) 441.

2.8. OXIDATION STATE V

2.8.1. Molybdenum(V) Halides⁴²⁶⁻⁴²⁹

Molybdenum(V) fluoride can be prepared by reduction of MoF_6 with Mo (300–400°), PF_3 or $\text{Mo}(\text{CO})_6$ (or $\text{W}(\text{CO})_6$) (25°). Some tetrafluoride is usually formed but the pentafluoride is easily separated because of its much greater volatility. Generally F_2 and BF_3 cannot be used because these reagents oxidize Mo and Mo compounds to Mo(VI). However, reaction of F_2 with $\text{Mo}(\text{CO})_6$ at -75° produces Mo_2F_9 (which may be $[\text{MoF}_3]^+[\text{MoF}_6]^-$

FIG. 13. Structure of MoF_5 ^{428, 429}.

(Reprinted from ref. 428, p. 182, © 1967, by permission of Academic Press.)

or a mixture of MoF_4 and MoF_5) from which, at 170° , MoF_5 distills, leaving MoF_4 as a nonvolatile residue.

An excellent method for preparing MoCl_5 involves reaction of boiling hexachloropropene with MoO_3 , resulting in about 90% yield in 15 min (WCl_6 can also be prepared by this method)⁴³⁰. Several other methods have been described, e.g. chlorination of Mo^{431a} , or of MoS_2 at 400–500°; reaction of MoO_3 with CCl_4 ⁴³², Cl_2 , COCl_2 or SO_2Cl_2 , or reaction of MoS_2 with CCl_4 .

⁴²⁶ R. D. Peacock, "Some Fluorine Compounds of the Transition Metals", in *Progress in Inorganic Chemistry*, **2**, Interscience, New York (1960), pp. 215, 217.

⁴²⁷ E. L. Muetterties and C. W. Tullock, "Binary Fluorides", in *Preparative Inorganic Reactions*, **2**, Interscience, New York (1965), pp. 257, 268.

⁴²⁸ A. D. Beveridge and H. C. Clark, "Pentahalides of the Transition Metals", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 185.

⁴²⁹ J. E. Fergusson, "Halide Chemistry of Chromium, Molybdenum and Tungsten", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 265.

⁴³⁰ W. W. Porterfield and S. Y. Tyree, Jr., *Inorg. Syn.* **9**, McGraw-Hill, New York (1967), p. 133.

⁴³¹ F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965): (a) p. 1405; (b) p. 1413.

⁴³² E. R. Epperson, S. M. Horner, K. Knox and S. Y. Tyree, Jr., *Inorg. Syn.* **7**, McGraw-Hill, New York (1963), p. 163.

Molybdenum(V) fluoride is a yellow solid (m.p. 70° , b.p. 209.9°). At 165° , it disproportionates to MoF_4 and MoF_6 . The chloride (black, m.p. $190\text{--}194^\circ$, b.p. 268°) dissociates at high temperatures to MoCl_4 and Cl_2 . These compounds hydrolyze readily. They are less stable than the tungsten analogs. Thermodynamic and other properties of MoF_5 and MoCl_5 have been summarized by Beveridge and Clark⁴²⁸ and by Fergusson⁴²⁹. The pentabromide and -iodide apparently have not been prepared.

Molybdenum(V) fluoride, like NbF_5 , has a tetrameric structure^{428, 429}. The four Mo atoms are in a plane, each pair joined by a bridging fluorine atom (Fig. 13). The bond lengths are: Mo-terminal F, 1.85 and 1.70 Å; Mo-bridging F, 2.06 Å. The short Mo-terminal F distances may imply some back-bonding.

The chloride in the solid state has a dimeric octahedral structure with the following bond distances in Å: Mo-terminal Cl, 2.24; Mo-Cl bridge, 2.53; Mo-Mo, 3.83. In the gas phase it is monomeric with a trigonal bipyramidal structure.

2.8.2. Molybdenum(V) Halide and Oxyhalide Complexes^{426, 428, 429, 433}.

The complex fluorides $\text{M}[\text{MoF}_6]$ can be made by reaction of MI with MoF_6 in IF_5 or liquid SO_2 ; or by heating a mixture of MF, $\text{Mo}(\text{CO})_6$ and SF_4 in a sealed tube at 165° ($\text{M} = \text{Li, Na, K, Rb, Cs, Tl}$). The nitrosyl salt is obtained by reaction of Mo with $\text{NO}(\text{HF})_3$ or MoF_6 with NO. The octafluoride $\text{K}_3[\text{MoF}_8]$ is prepared by reaction of $\text{Mo}(\text{CO})_6$ with KI in IF_5 . The hexachloro salt $(\text{C}_2\text{H}_5)_4\text{N}[\text{MoCl}_6]$ has been prepared by reaction of $(\text{C}_2\text{H}_5)_4\text{I}$ and MoCl_5 in chloroform; the potassium salt may exist in fused $\text{MoCl}_5\text{--KCl}$, which has the spectrum predicted for $[\text{MoCl}_6]^-$.

Since these compounds are easily hydrolyzed, they cannot be isolated from aqueous solutions. They are sensitive to traces of moisture, undergoing irreversible changes accompanied by a color change from white to deep blue. They are quite stable, even when heated, if kept dry.

The $[\text{MoF}_6]^-$ ion has a distorted tetragonal structure with four long and two short M-F bonds. The potassium and sodium salts have, respectively, the $\text{K}[\text{NbF}_6]$ structure (tetragonal) and the NaCl structure (cubic). The octafluoro complex $\text{K}_3[\text{MoF}_8]$ has a cubic structure and a magnetic moment of 1.23 B at room temperature.

Two complex oxyfluoro Mo(V) salts have been described, i.e. $\text{K}_2[\text{MoOF}_5]$ and $(\text{NH}_4)_2[\text{MoOF}_5]$. Two series of oxychloro and oxybromo complexes have been reported. Salts of the type $\text{M}_2[\text{MoOX}_5]$ are prepared by reaction of MX with MoX_5 in aqueous HX solution; electrolytic reduction of an acid solution of MoO_3 is a convenient way of obtaining Mo(V)^{431b}. Salts of the type $\text{M}[\text{MoOX}_4]$ may be obtained by reaction of MX with MoX_5 in liquid SO_2 ; with RbCl and CsCl, the products of the reaction are mixtures of $\text{M}[\text{Mo}^\text{v}\text{OCl}_4]$ and $\text{M}_2[\text{Mo}^\text{v}\text{Cl}_6]$.

Many salts of these types have been reported, including the following:

$\text{M}_2[\text{MoOCl}_5]$: $\text{M} = \text{NH}_4, \text{K, Rb, Cs, pyH, quH, CH}_2\text{NH}_3, (\text{CH}_3)_2\text{NH}_2, (\text{CH}_3)_3\text{NH}$
(py = pyridine; qu = quinoline).

$\text{M}[\text{MoOCl}_4]$: $\text{M} = \text{Rb, Cs, NH}_4, \text{pyH, quH, C}_2\text{H}_5\text{NH}_2; (\text{CH}_3)_3\text{NH}$.

$\text{M}_2[\text{MoOBr}_5]$: $\text{M} = \text{NH}_4, \text{K, Rb, Cs, pyH, quH}$.

$\text{M}[\text{MoOBr}_4]$: $\text{M} = \text{Li, pyH, quH}$.

⁴³³ G. W. A. Fowles, "Halide and Oxyhalide Complexes of Elements of the Titanium, Vanadium and Chromium Subgroups", in *Preparative Inorganic Reactions*, 1, Interscience, New York (1964), pp. 126, 132, 134.

The color of these salts is green–yellow to brown. They are stable if kept dry; hydrolysis causes color changes to red and then blue. The far infrared spectra of $M_2[MoOX_5]$ and $M_2[WOX_5]$ ($M = Rb, Cs$; $X = Cl, Br$) have been reported⁴³⁴; the structure of the complex ions $[MoOX_5]^{2-}$ and $[WOX_5]^{2-}$ belongs to the point group C_{4v} ⁴³⁴. The $[MoOX_5]^{2-}$ ion is essentially octahedral but considerable tetragonal distortion is imposed on the structure by the $Mo=O$ bond, and this tends to destroy the spin-orbit coupling; the magnetic moments (~ 1.7 B) of the $[MoOX_5]^{2-}$ salts approach the spin-only values⁴²⁹. There will also be some distortion of the $[MoOX_4]^-$ structure; the magnetic moments of salts of this ion are also about 1.7 B.

Ultraviolet spectroscopy has been used to study the equilibria existing in HBr solutions of Mo(V) and Mo(VI), which are shown to be dimeric⁴³⁵. The spectra of Mo(V) in HBr solutions (1.0–8.6 M) may be interpreted in terms of four different dimeric species. At the highest HBr concentration the predominant species is $[MoOBr_4]_2^{2-}$. If Mo is 6-coordinate, the compounds $pyH[MoOBr_4]$, $quH[MoOBr_4]$, $pyH[MoO_2Cl_2] \cdot H_2O$ and $Mo_2O_4(OH)Cl \cdot H_2O$ are to be formulated as doubly bridged dimers. This is consistent with the structure of $MoCl_5$ in the solid state; the same basic structure has been proposed for the $[Mo_2O_4(NCS)_6]^{4-}$ ion.

2.8.3. Molybdenum Oxyhalides; Adducts of $MoOCl_3$ with Organic Ligands^{428, 429}

Two Mo(V) oxyhalides are quite well characterized, i.e. $MoOCl_3$ (brown–black, m.p. 295°) and $MoOBr_2$. The oxychloride can be obtained in over 90% yield by reduction of $MoOCl_4$ with chlorobenzene⁴³⁶:



The oxychloride has also been prepared by: chlorination of Mo(IV) compounds in air; reaction (in molten state) of $MoCl_5$ and MoO_2Cl_2 (or MoO_3) (which also produces $MoCl_4$); reaction of $MoCl_5$ with SO_2 or SO_2Cl_2 ; heating $MoOCl_4$ in an inert atmosphere at 120° . The chloride is one of several products formed by electrolytic reduction of Mo(VI)^{431b} compounds in HCl. The bromide can be made by reaction of MoO_2Br_2 and PBr_5 in boiling CCl_4 . When heated, the oxyhalides sublime and dissociate to Mo(VI) and Mo(III) compounds.

Many organic molecules form complexes with $MoOCl_3$. Several procedures have been described for preparing them from $MoOCl_4$, $MoCl_5$ and $MoOCl_3$, e.g. reduction of $MoOCl_4$ by ligand in CCl_4 ⁴³⁶; reaction of ligands with $MoCl_5$ in solution in wet ether⁴³⁷, ethanol^{437–439} or moist CCl_4 ⁴⁴⁰; reaction of $MoCl_5$ with oxygen-containing ligands without a solvent⁴⁴¹; reaction of ligands with solid $MoOCl_3$ ^{436, 441, 442}; reaction of ligands with $MoOCl_3$ in benzene⁴⁴¹; displacement of one ligand by another^{436, 442}. In Table 33 are listed examples of these compounds, which are of two types, $MoOCl_3 \cdot L$ and $MoOCl_3 \cdot 2L'$.

⁴³⁴ A. Sabatini and I. Bertini, *Inorg. Chem.* **5** (1966) 204.

⁴³⁵ J. F. Allen and H. M. Neumann, *Inorg. Chem.* **3** (1964) 1612.

⁴³⁶ M. L. Larson and F. W. Moore, *Inorg. Chem.* **5** (1966) 801.

⁴³⁷ W. Wardlaw and H. Webb, *J. Chem. Soc.* (1930) 2100.

⁴³⁸ S. M. Horner and S. Y. Tyree, Jr., *Inorg. Chem.* **1** (1962) 122.

⁴³⁹ M. D. Joesten, *Inorg. Chem.* **6** (1967) 1598.

⁴⁴⁰ P. C. H. Mitchell, *J. Inorg. Nucl. Chem.* **25** (1963) 963.

⁴⁴¹ K. Feenan and G. W. A. Fowles, *Inorg. Chem.* **4** (1965) 310.

⁴⁴² D. A. Edwards, *J. Inorg. Nucl. Chem.* **27** (1965) 303.

TABLE 33. COMPLEXES OF MoOCl_3 , $\text{MoOCl}_3 \cdot \text{L}$ AND $\text{MoOCl}_3 \cdot 2\text{L}'$

L	L'
Acetylacetone ⁴³⁶	Ethyl ether ⁴³⁷
Benzophenone ⁴³⁶	Tetrahydrofuran ⁴⁴¹
Ethyl ether ⁴³⁷	Pentamethylene oxide ⁴⁴¹
Dioxane ⁴⁴¹	Tetrahydrothiophene ⁴⁴¹
Ethylene glycol dimethyl ether ⁴⁴¹	Dimethyl sulfoxide ⁴⁴¹
Thioxane ⁴⁴¹	Pentamethylene sulfide ⁴⁴¹
R_2S ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7$) ⁴⁴¹	Triphenyl phosphine ⁴⁴²
2,2'-dipyridyl ^{440, 442}	Triphenyl phosphine oxide ⁴³⁸
1,10-phenanthroline ^{440, 442}	Triphenyl arsine oxide ⁴³⁸
	Pyridine ⁴³⁶
	RCN ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7$) ⁴⁴²
	Octamethylpyrophosphoramide ⁴³⁹

The complexes of MoOCl_3 generally have magnetic moments close to the spin-only value; the spin-orbit coupling constant is reduced by the strong $\pi\text{-Mo-O}$ bonding. Most of these complexes are octahedral with considerable tetragonal distortion due to the Mo-O bond⁴⁴¹. Ultraviolet and visible absorption spectra indicate that octamethylpyrophosphoramide bonds to Mo(V) via the oxygen atoms; the complex, in which the Mo(V) is 6-coordinate, is soluble in acetonitrile in which it is a nonelectrolyte⁴³⁹.

2.8.4. Molybdenum(V) Complex and Chelate Compounds

The coordination chemistry of molybdenum is nowhere near as extensive as that of chromium and a large fraction of the molybdenum complexes are compounds in which the metal has the oxidation state 5+ rather than 2+ and 3+ as is the case with chromium. Molybdenum(V) has a marked tendency to form dimeric complexes⁴⁴³. The structural feature of particular interest is the pairing of spins of two Mo(V) atoms to form diamagnetic compounds.

(a) 2,4,6-Trimethylpyridine Complex

Although MoCl_5 is reduced by ligands such as pyridine, acetonitrile and benzonitrile (see Section 2.7) a stable Mo(V) complex is obtained by reaction of MoCl_5 with 2,4,6-trimethylpyridine (L)⁴⁴⁴. It has a conductivity characteristic of a 1:1 electrolyte in nitromethane and is therefore formulated $[\text{MoCl}_4\text{L}_2]\text{Cl}$. Comparison of solution and reflectance spectra indicates that it exists in this form also in the solid state. The magnetic moment (1.4 B) is somewhat lower than the spin-only value but in the range reported for other Mo(V) complexes. Similar W(V) complexes have been prepared. Molybdenum(V) chloride also reacts (without reduction) with tertiary alkyl amines to form complexes of the type $\text{MoCl}_5 \cdot \text{NR}_3$ ⁴⁴⁵.

(b) Acetylacetone Complexes

Under mild conditions, MoOCl_3 forms an adduct with neutral acetylacetone⁴³⁶ (see preceding section), but when it reacts with acetylacetone in refluxing benzene, H^+ of the

⁴⁴³ L. V. Haynes and D. T. Sawyer, *Inorg. Chem.* **6** (1967) 2146.

⁴⁴⁴ T. M. Brown and B. Ruble, *Inorg. Chem.* **6** (1967) 1335.

⁴⁴⁵ D. A. Edwards and G. W. A. Fowles, *J. Chem. Soc.* (1961) 24.

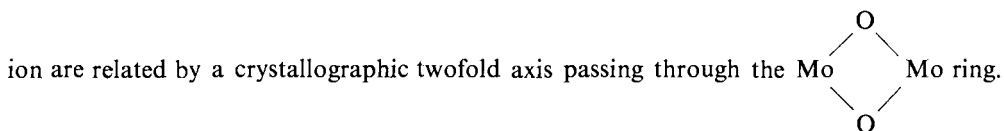
ketone is displaced, HCl is evolved, and the monomeric chelate compound $[\text{MoOCl}(\text{C}_5\text{H}_7\text{O}_2)_2]$ is formed⁴³⁶. This dark red solid is soluble in chloroform. Exposed to the atmosphere, it undergoes slow decomposition by hydrolysis, oxidation or both.

Beta-diketone chelates of the type $(\text{C}_2\text{H}_5)_4\text{N}[\text{MoOX}_3\text{B}]$ have been characterized by conductance, magnetic susceptibility, infrared, visible and ultraviolet spectroscopy and electron paramagnetic resonance ($\text{X} = \text{Cl}, \text{Br}$; $\text{B} = \text{benzoyltrifluoroacetone, dibenzoylmethane, hexafluoroacetylacetone, thenoyltrifluoroacetone}$)⁴⁴⁶. These compounds are monomeric in solution and the solid state as indicated by their magnetic susceptibilities (μ_{eff} , 1.63–1.87) and e.p.r. spectra (g values, 1.947–1.982). The magnetic moments approach the spin-only values because of reduction of the spin-orbit coupling, reflecting a high degree of covalency of the oxo group–Mo bond. Presumably the diketone group lies in the plane perpendicular to this bond. With this structure, the ions belong to point group C_3 if the β -diketone is symmetrical and C_1 otherwise.

The binuclear molybdenyl(V) acetylacetonate⁴⁴⁷ is prepared by reaction of $(\text{NH}_4)_2[\text{MoOCl}_5]$ with acetylacetone in aqueous solution; Mo(V) for this synthesis may also be prepared by reducing (with Mo) a solution of MoO_3 in HCl and neutralizing the reduced solution. The composition of the complex is considered to be $[(\text{C}_5\text{H}_7\text{O}_2)_2\text{Mo}=\text{O}]_2\text{O}$ containing a nonlinear $\text{O}=\text{Mo}-\text{O}$ group. The compound is diamagnetic, presumably because of $d\pi-\pi\pi$ interaction along the $\text{Mo}-\text{O}-\text{Mo}$ bridge.

(c) Oxalato Complex^{390b}

The oxalato complex, $\text{Ba}[\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2]\cdot 5\text{H}_2\text{O}$ (dark red crystals) may be prepared by reaction of $\text{H}_2\text{C}_2\text{O}_4$ with $(\text{NH}_4)_2[\text{MoOCl}_5]$ ⁴⁴⁸. The anion is shown by X-ray diffraction⁴⁴⁹ to be binuclear with the composition $[\text{MoO}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]_2\text{O}_2^{2-}$. The structure consists of two hexacoordinated Mo atoms in distorted octahedra sharing an edge; the two halves of the



The Mo–Mo distance is 2.541 Å; it is thus possible that the diamagnetism of the ion is due to a metal–metal bond (Mo–Mo distance in the metal, 2.725 Å). The Mo–O bond lengths (Å) are: Mo–O₁ (oxalate), 2.11; Mo–O₅ (oxalate), 2.14; Mo–O₃ (H_2O), 2.22; Mo–O₄ (bridge), 1.93; Mo–O₄ (bridge), 1.88; Mo–O₂ (terminal), 1.70.

(d) Dialkyldithiocarbamate and Xanthate Complexes

The complexes $[(\text{R}_2\text{NCS})_2\text{Mo}=\text{O}]_2\text{O}$ have been prepared by reaction of the dialkyldithiocarbamate with $(\text{NH}_4)_2[\text{MoOCl}_5]$ ⁴⁵⁰ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$). The xanthate complexes, $[(\text{ROCS}_2)_2\text{Mo}=\text{O}]_2\text{O}$ (green, $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$), are obtained by reducing a molybdate–xanthate solution with SO_2 ⁴⁴⁹. The diethyl xanthate complex has a linear Mo–O–Mo bridge; its diamagnetism is due to pairing of electrons via the bridge⁴⁵¹.

⁴⁴⁶ H. E. Pence and J. Selbin, *Inorg. Chem.* **8** (1969) 353.

⁴⁴⁷ M. L. Larson and F. W. Moore, *Inorg. Chem.* **2** (1963) 881.

⁴⁴⁸ R. G. James and W. Wardlaw, *J. Chem. Soc.* (1927) 2152.

⁴⁴⁹ F. A. Cotton and S. M. Morehouse, *Inorg. Chem.* **4** (1965) 1377.

⁴⁵⁰ F. W. Moore and M. L. Larson, *Inorg. Chem.* **6** (1967) 998.

⁴⁵¹ A. B. Blake, F. A. Cotton and J. S. Wood, *J. Am. Chem. Soc.* **86** (1964) 3024.

(e) *Cysteine and Cysteine Ester Complexes*⁴⁵²

By reaction of sodium cysteinate with Mo(V) in aqueous solution, crystalline doubly bridged binuclear complexes are obtained that contain one mole of ligand per Mo. Cysteine ester hydrochlorides ($R = CH_3, C_2H_5$) react with Mo(V) to form singly bridged species; when these purple microcrystalline solids are dissolved in organic solvents (e.g. acetone, acetonitrile), ligand expulsion occurs with formation of yellow crystalline double-bridged cysteine ester complexes analogous to the cysteine complexes.

(f) *Histidine Complex*⁴⁵³

The rate of oxidation of Mo(V) in slightly acidic solutions (pH 4.6) is greatly decreased by the presence of histidine, apparently because of formation of a histidine–Mo(V) complex (1:1); this is much less stable than the Mo(VI)–histidine complex (see Section 2.9). Since no e.p.r. signal was obtained with solutions of Mo(V) and histidine over a wide range of field strengths, the solutions contain no paramagnetic species, i.e. the complex is dimeric.

(g) *Some Aminoacetate Complexes*⁴⁴³

In addition to the dimeric complexes discussed above, Mo(V) forms dimeric complexes with some aminoacetates (as determined by protein n.m.r. measurements), e.g. ethylenediaminetetraacetate (EDTA), *dl*-1,2-propylenediaminetetraacetate (PDTA), *N*-methyliminodiacetate (MIDA) and nitrilotriacetate (NTA). The EDTA, PDTA and NTA complexes were isolated; the first two contain dioxo-bridged binuclear molybdenum units while the nature of the bridging in the NTA complex was not determined. The dimeric nature of the MIDA complex was established by n.m.r. measurements of MIDA–Mo(V) solutions.

(h) *Cyanomolybdates(V)*^{454–456}

In aqueous solution, $[Mo(CN)_8]^{4-}$ can be oxidized, by MnO_4^- , Ce^{4+} , etc., to $[Mo(CN)_8]^{3-}$ which can be separated as the slightly soluble Ag^+ salt. This can be converted to the potassium salt by action of KCl. Salts of $[Mo(CN)_8]^{3-}$ are yellow, photosensitive and easily reduced.

The Mo(IV) and Mo(V) cyanide complexes and their derivatives are of great interest as examples of coordination number eight. For eight equivalent ligands, the following five structures, with their symmetries, are possible: cube, O_h ; Archimedean antiprism, D_{4d} ; dodecahedron, D_{2d} ; trigonal prism with ligands centred on two end faces, D_{3h} ; and trigonal prism with ligands centred on two side faces, C_{2v} .

The $[Mo^V(CN)_8]^{3-}$ ion has the Archimedean antiprism configuration in solution, as indicated by electron spin resonance (e.s.r.) investigation of frozen glycerine solutions of $K_3[Mo(CN)_8]$. The g values for $[Mo^V(CN)_8]^{3-}$ were obtained from e.s.r. spectra of this ion trapped in the crystal lattice of $K_4[Mo^IV(CN)_8]$. The results were consistent with a dodecahedral structure for the ion in the solid state.

⁴⁵² L. R. Melby, *Inorg. Chem.* **8** (1969) 349.

⁴⁵³ J. T. Spence and J. Y. Lee, *Inorg. Chem.* **4** (1965) 385.

⁴⁵⁴ B. M. Chadwick and A. G. Sharpe, "Transition Metal Cyanides and Their Complexes", in *Advances in Inorganic Chemistry and Radiochemistry*, **8**, Academic Press, New York (1965), p. 101.

⁴⁵⁵ B. R. McGarvey, *Inorg. Chem.* **5** (1966) 476.

⁴⁵⁶ S. J. Lippard, "Eight-Coordination Chemistry", in *Progress in Inorganic Chemistry*, **8**, Interscience, New York (1967), p. 165.

The $[\text{Mo}^{\text{IV}}(\text{CN})_8]^{4-}$ ion is dodecahedral in the solid state; there is some question whether it has a dodecahedral or Archimedean antiprism structure in solution (see Section 2.7.2.).

2.8.5. Bioinorganic Chemistry of Molybdenum(V)

As a result of increasing interest in the inorganic constituents of living organisms, a definable field of chemistry encompassing all the inorganic chemistry of biological systems is developing. Since most of the essential metal ions are those of transition metals and many biological substances can act as ligands, a most important aspect of "bioinorganic chemistry" is coordination chemistry, which is particularly important in connection with metallo-enzymes and other enzymes whose action depends on metal ions^{457, 458}.

Molybdenum is an essential cofactor for several enzymes including xanthine oxidase, aldehyde reductase and nitrate reductase. Xanthine oxidase contains eight Fe atoms, two Mo atoms and two flavin adenine nucleotide molecules bound to the protein molecule. It is believed to be a thiol enzyme with Mo-S bonds and there is some reason to believe that Mo is similarly bound in nitrate reductase.

Important recent investigations related to the bioinorganic chemistry of molybdenum have involved synthesis of Mo(V) complexes of ligands of biological interest (see preceding section). These include the S-containing ligands dialkylthiocarbamates⁴⁵¹, alkyl xanthates⁴⁵¹, cysteine⁴⁵² and cysteine esters⁴⁵²; in complexes of these substances there are apparently Mo-S bonds as is supposedly the case in the molybdo-enzymes. In several enzymes, histidine residues are involved in binding metals and it is thus of particular interest that histidine forms complexes with Mo(V) and Mo(VI)⁴⁵³.

Another most interesting development is the application of e.s.r. measurements in the study of formation and reactions of molybdenum enzymes and other complexes⁴⁵⁹. Results of such studies indicate that in reactions of these enzymes an electron is transferred by the metal ion to or from the flavin coenzyme. Flavin free radicals (semiquinones) are apparently formed in the reactions of flavoenzymes; semiquinone-Mo(V) interactions are probable in Mo-flavoproteins such as xanthine oxidase.

Evidently Mo(V) in molybdo-enzymes is monomeric; an e.s.r. signal for Mo(V) (a $1d$ ion) is observed in xanthine oxidase in presence of substrate (and also in nearly neutral solutions of Mo(V) and thiols). On the other hand, in aqueous solutions in the absence of ligands, Mo(V) dimerizes to diamagnetic species ($< 2 \text{ M HCl}$); only the monomer exists in solutions more than 10 M in HCl while a monomer and a paramagnetic dimer exist in the range $4\text{--}10 \text{ M}$ ⁴⁶⁰.

Molybdenum(V) monomer is formed in the reduction of Mo(VI) by reduced flavins at pH 6-7 and by several other reducing agents over a range of acidity up to pH 6 in presence of tartrate⁴⁶⁰. The rate of disappearance of the monomer is a function of pH and tartrate buffer concentration, as determined by e.s.r. studies. It was concluded that a high concen-

⁴⁵⁷ C. L. Rollinson and E. W. Rosenbloom, "Coordination in Biochemistry: Reactions of Chromium-(III)", in *Coordination Chemistry; Papers Presented in Honor of Professor John C. Bailar, Jr.*, Plenum Press, New York (1969).

⁴⁵⁸ U. Weser, *Naturwissenschaften*, **56** (1969) 506.

⁴⁵⁹ H. Beinert and W. H. Orme-Johnson, "Electron Spin Relaxation as a Probe for Active Centers of Paramagnetic Enzyme Species"; R. C. Brey, P. F. Knowles and L. S. Meriwether, "ESR and the Role of Molybdenum in Enzymic Catalysis by Milk Xanthine Oxidase"; J. T. Spence, M. Heydanek and P. Hemmerich, "An ESR Study of Molybdenum-Flavin Model Reactions"; F. Müller, A. Ehrenberg and L. E. G. Eriksson, "Flavin-Radical Metal Complexes", in *Magnetic Resonance in Biological Systems*, Pergamon Press, Oxford (1967).

⁴⁶⁰ J. T. Spence and M. Heydanek, *Inorg. Chem.* **6** (1967) 1489.

tration of Mo(V) monomer could exist even at biological pH in the presence of an appropriate ligand. Since molybdenum enzymes apparently contain monomeric Mo(V), these results are of considerable significance; see p. 680 for a discussion of the aggregation of Cr(III) in media of physiological pH.

2.8.6. Molybdenum(V) Oxide and Hydroxide

Molybdenum(V) oxide (Mo_2O_5) is a violet compound obtained by heating a mixture of Mo and MoO_3 , in stoichiometric quantities, at 750° . It is soluble in warm acids. When solutions of Mo_2O_5 are made ammoniacal, $\text{MoO}(\text{OH})_3$ precipitates; and this is converted to Mo_2O_5 by heating⁴⁶¹.

Solutions containing Mo(V) can readily be prepared by controlled electrochemical reduction of Mo(VI) solutions; reduction can also be accomplished by HI, Ag or Hg under controlled conditions of acidity⁴⁶². When a hydroxide or sodium acetate is added to such a solution, a brown precipitate forms, which may be $\text{Mo}(\text{OH})_5$, that dehydrates to a brown-red product, $\text{MoO}(\text{OH})_3$. The same product, together with Mo(VI), is formed by disproportion of "molybdenum blue" (p. 737) suspended in base solutions and by air oxidation of solutions of $\text{K}_2[\text{Mo}(\text{OH})_2(\text{CN})_4]$ ⁴⁶³.

2.9. OXIDATION STATE VI

2.9.1. Molybdenum(VI) Halides⁴⁶⁴⁻⁴⁶⁶

The only Mo(VI) halide reported is the fluoride. This can be obtained in excellent yield by fluorination of MoO_3 with SF_4 in a sealed reactor at 350° ⁴⁶⁷. It has also been prepared by fluorination of MoO_3 with BrF_3 and reaction of Mo with F_2 , BrF_3 , or ClF_3 . It has been reported that ClF reacts at room temperature with Mo and MoS_2 to produce MoF_6 but whether these are useful preparative reactions is not stated⁴⁶⁸.

Molybdenum(VI) fluoride is a white solid (m.p. 17.4° , b.p. $34-35^\circ$) that reacts vigorously with organic matter and is easily reduced and hydrolyzed. The average Mo-F bond energy is 105 kcal/mole⁴⁶⁹. Formation data are as follows⁴⁶⁶: ΔH° , kcal/mole: 388.6 (l), 372.4 (g); $-\Delta G^\circ$, kcal/mole: 361.2 (l), 350.8 (g); $-\Delta S^\circ$, e.u. 72.1 (g); ΔS_{vap} , e.u. 22.5, 20.6. The relative reactivities of the highest fluorides of Cr, Mo and W are in the order $\text{CrF}_5 > \text{MoF}_6 > \text{WF}_6$. Metal-F bonding is stronger in WF_6 than in MoF_6 ; the bond-stretching force constants are respectively 5.13 and 4.73⁴⁶⁹. The solubility of MoF_6 in anhydrous HF (room temperature) is 1.50 moles per 1000 g HF ⁴⁷⁰; the conductivity of the solution (0°) is 0.1 $\text{ohm}^{-1} \text{cm}^{-1} \text{mole}^{-1}$.

⁴⁶¹ F. A. Cotton and G. A. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 2nd edn. (1966), p. 934.

⁴⁶² J. Aubry, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959), p. 636.

⁴⁶³ J. van de Poel and H. M. Neumann, *Inorg. Chem.* **7** (1968) 2086.

⁴⁶⁴ R. D. Peacock, "Some Fluorine Compounds of the Transition Metals", in *Progress in Inorganic Chemistry*, **2**, Interscience, New York (1960), p. 223.

⁴⁶⁵ E. L. Muetterties and C. W. Tullock, "Binary Fluorides", in *Preparative Inorganic Reactions*, **2**, Interscience, New York (1965), pp. 241, 249, 257, 281.

⁴⁶⁶ J. E. Fergusson, "Halide Chemistry of Chromium, Molybdenum and Tungsten", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 276.

⁴⁶⁷ A. L. Oppegard, W. C. Smith, E. L. Muetterties and V. A. Engelhardt, *J. Am. Chem. Soc.* **82** (1960) 3835.

⁴⁶⁸ J. J. Pitts and A. W. Jache, *Inorg. Chem.* **7** (1968) 1661.

⁴⁶⁹ T. A. O'Donnell and D. F. Stewart, *Inorg. Chem.* **5** (1966) 1434.

⁴⁷⁰ B. Frlc and H. H. Hyman, *Inorg. Chem.* **6** (1967) 1596.

Molybdenum(VI) fluoride is octahedral (space group O_h). The vapor is monomeric. Like other transition metal hexafluorides (e.g. WF_6 , ReF_6 , etc.), it exists in a cubic modification near room temperature and in a lower symmetry phase at lower temperatures⁴⁷¹. The transition temperature is -9.6° . The dimensions ($\text{\AA}$) of the unit cells are: a , 6.23 (5°); a , b , c , 9.61, 8.75, 5.07 respectively (-36°).

2.9.2. Molybdenum(VI) Oxyhalides^{464, 466}

The molybdenum oxyhalides that are well established are MoO_2X_2 ($X = F, Cl, Br$) and $MoOX_4$ ($X = F, Cl$). The preparative methods are as follows:

MoO_2F_2 : reaction of MoO_2Cl_2 with HF; fluorination of MoO_3 with SeF_4 or IF_5 .

$MoOF_4$: reaction of $MoOCl_4$ with HF; reaction of Mo with F_2 and HNO_3 (or O_2); reaction of MoO_3 with F_2 , SeF_4 or IF_5 .

MoO_2Cl_2 : reaction of MoO_3 , MoS_3 or MoO_4^{2-} with: HCl ; $NaCl$; Cl_2 - O_2 mixture; CCl_4 ; S_2Cl_2 - Cl_2 mixture; CCl_4 - O_2 mixture; $TiCl_4$; $MoCl_5$; reaction of Mo with Cl_2 .

$MoOCl_4$: reaction of MoO_2Cl_2 or MoO_3 with: S_2Cl_2 - Cl_2 mixture; $MoCl_5$; $SOCl_2$; reaction of $MoCl_5$ with dry O_2 ⁴⁷² or with CCl_4 in air.

MoO_2Br_2 : reaction of Mo with Br_2 - O_2 mixture or of MoO_3 with Br_2 .

Ward and Stafford have described a method for generating Mo(VI) and W(VI) oxyhalides in the gas phase for infrared studies⁴⁷³. The compounds are made from a fused mixture of a lithium halide and the metal trioxide. A boat containing the mixture is heated inside a tube (stainless steel for the fluorides and mullite for the other halides) fitted with end windows. The authors recommend this as an easily controllable method for producing the oxyhalides in either the gas or condensed phase.

The Mo(VI) compounds thus prepared were MoO_2X_2 ($X = F, Cl, Br$) and $MoOX_4$ ($X = F, Br$). Some spectral evidence was obtained indicating formation of a molybdenum oxydide from a reaction mixture MoO_3 -LiI. While the spectra of the oxyhalides in the solid state, in solution or in the vapor state, are quite different, the metal-oxygen stretching frequencies are all in the range 900 – 1100 cm^{-1} , considered to be indicative of a terminal metal-oxygen double bond. The solid and liquid phases contain polymeric species, while the vapor phases are predominantly monomeric.

Molybdenum(VI) dioxodichloride (MoO_2Cl_2) is an orange-white solid, m.p. 175° . The oxytetrachloride⁴⁷⁴ (dark green crystals, m.p. 100 – 103°) can be purified by sublimation *in vacuo* at 70 – 80° . It has a magnetic moment of 0.34 B . It is hydrolyzed by atmospheric moisture and reacts with water to form soluble "molybdenum blue" (oxide hydrate of indefinite composition with average oxidation state of Mo between $5+$ and $6+$). It is easily reduced to $MoOCl_3$ (see Section 2.8.3) and is decomposed by ultraviolet radiation to $MoCl_3$ and Cl_2 . It dissolves in CCl_4 or $CHCl_3$ (red-brown solution) in which it is monomeric and undissociated.

2.9.3. MoO_2Cl_2 Adducts with Organic Molecules

The dioxodichloride forms adducts $MoO_2Cl_2 \cdot 2L$ with many organic molecules. For example, L may be: (1) acid anhydrides, esters, ethers, ketones, aldehydes, nitriles^{474, 475};

⁴⁷¹ S. Siegel and D. A. Northrop, *Inorg. Chem.* **5** (1966) 2187.

⁴⁷² A. K. Mallock, *Inorg. Syn.* **10**, McGraw-Hill, New York (1967), p. 54.

⁴⁷³ B. G. Ward and F. E. Stafford, *Inorg. Chem.* **7** (1968) 2569.

⁴⁷⁴ M. L. Larson and F. W. Moore, *Inorg. Chem.* **5** (1966) 801.

⁴⁷⁵ H. L. Krauss and W. Huber, *Chem. Ber.* **94** (1961) 2864.

(2) $(\text{C}_6\text{H}_5)_3\text{PO}$, $(\text{CH}_3)_2\text{SO}$, $(\text{C}_6\text{H}_5)_3\text{AsO}$, $\text{C}_5\text{H}_5\text{NO}$ ^{474, 476}; (3) *N,N*-dimethylformamide, *N,N*-dimethylacetamide, *N,N*-dibutylacetamide⁴⁷⁴; (4) tetrahydrofuran⁴⁷⁷; (5) alkyl cyanides (which under different reaction conditions give complexes $\text{MoO}_2\text{Cl}_2\text{L}$)⁴⁷⁸. Methods of preparation⁴⁷⁸ include reaction of MoO_2Cl_2 with ligands with or without a solvent⁴⁷⁴⁻⁴⁷⁶, oxidation of substituted molybdenum carbonyls and reaction of MoCl_5 with oxygen-containing ligands.

The hexacoordinated complexes (1) are colorless crystals, sensitive to hydrolysis, and soluble in benzene in which they are monomeric. The compounds (2) have some solubility in organic solvents and are less sensitive to moisture. The amide complexes (3) are thermally stable and are not hydrolyzed by atmospheric moisture. The amide molecules are bonded to Mo via the oxygen atom, as shown by the infrared spectra. A neutral acetylacetonate adduct, $\text{MoO}_2\text{Cl}_2 \cdot \text{C}_5\text{H}_8\text{O}_2$, is formed by reaction of acetylacetonate with MoO_2Cl_2 suspended in benzene^{474, 475}.

The structure of $\text{MoO}_2\text{Cl}_2 \cdot 2\text{dmf}$ ($\text{dmf} = N,N$ -dimethylformamide) has been determined by single-crystal X-ray diffraction⁴⁷⁹. The structure is that of discrete monomers with the dmf molecules *cis* to each other, the oxogroups *cis* to each other and the chlorine atoms *trans* to each other. The compound is monoclinic (space group $C2/c$); *a*, *b* and *c* are respectively 20.90, 7.717 and 11.99 Å; β is $139^\circ 52'$ (four molecules per unit cell). The Mo—O distance of 1.68 Å is close to that in the complex oxalato salts (discussed below), i.e. 1.69 Å (K salt) and 1.70 Å (Ba salt). This is consistent with the expected bond order of 2.5.

2.9.4. Complex Molybdenum(VI) Halides and Oxyhalides^{466, 469}

Two types of complex halogen salts are known, $[\text{MoF}_7]^-$ and $[\text{MoF}_8]^{2-}$. For the first, the cations are NO, NO₂, Rb, Cs and NH₄; for the second, Na, K, Rb and Cs. These may be prepared by reaction of MoF_6 with MI in IF₅ or ClF₃; reaction of MoF_6 with MF has also been reported as a preparative method, but there is some question whether reaction occurs if the reactants are pure and dry. The complexes $\text{Na}[\text{MoF}_7]$ and $\text{Na}_2[\text{MoF}_8]$ are formed rapidly by reaction of $\text{MoF}_6(\text{g})$ with NaF when the latter is formed by decomposition of $\text{UF}_6 \cdot 2\text{NaF}$ ⁴⁸⁰. Chlorine monoxide reacts with $\text{M}_2[\text{MoO}_4]$ at 300° to produce $\text{M}_2[\text{MoF}_8]$ ($\text{M} = \text{Na}, \text{K}$), but it is not stated whether this is a satisfactory preparative method⁴⁶⁸. These white compounds are stable in dry air but are easily hydrolyzed. Infrared studies indicate that the structure of the $[\text{MoF}_7]^-$ ion is a distorted octahedron.

The oxyfluoro complexes and methods of preparing them are:

$\text{M}_3[\text{MoO}_4\text{F}]$: reaction of MF and M_2MoO_4 in molten state; hydrolysis of $[\text{MoO}_3\text{F}_3]^{2-}$.

$\text{M}_3[\text{MoO}_3\text{F}_3]$: reaction of MF and MoO_3 in molten state; reaction of MoO_3 and MF in aqueous HF.

$\text{M}_2[\text{MoO}_3\text{F}_2]$, $\text{M}_2[\text{MoO}_2\text{F}_4]$: reaction of MoO_3 and MF in aqueous HF, generally with $\text{MF}/\text{MoO}_3 > 6/1$.

$\text{M}[\text{MoOF}_5]$: $\text{MF}_6 + \text{moist MF}$ in I₂, SO₂ or N₂O₄.

M is generally an alkali metal or NH₄ (and NO or NO₂ with $[\text{MoOF}_5]^-$). In the old literature there are also reports of $(\text{NH}_4)_3[\text{MoO}_2\text{F}_5]$.

⁴⁷⁶ S. M. Horner and S. Y. Tyree, Jr., *Inorg. Chem.* **1** (1962) 122.

⁴⁷⁷ K. Feenan and G. W. A. Fowles, *Inorg. Chem.* **4** (1965) 310.

⁴⁷⁸ B. J. Brisdon, *Inorg. Chem.* **6** (1967) 1791.

⁴⁷⁹ L. R. Florian and E. R. Corey, *Inorg. Chem.* **7** (1968) 722.

⁴⁸⁰ S. Katz, *Inorg. Chem.* **5** (1966) 666.

These complexes are generally stable in a dry inert atmosphere but readily undergo hydrolysis. The oxychloride complexes $\text{K}[\text{MoO}_2\text{Cl}_3] \cdot 7\text{H}_2\text{O}$ and $\text{M}_2[\text{MoO}_2\text{Cl}_4] \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{K}, \text{NH}_4$) have been reported.

By means of ultraviolet spectrophotometry, the species present in HBr solutions of Mo(V) and Mo(VI) were determined⁴⁸¹. In 8.6 M HBr, Mo(VI) (from paramolybdate) reacts to form an equilibrium mixture of Mo(VI), Mo(V) and Br_3^- ; presumably both Mo(V) and Mo(VI) are dimeric in this solution (in the form of oxybromide anions).

2.9.5. Molybdenum(VI) Complex and Chelate Compounds

The oxychloride $\text{Mo}_2\text{O}_2\text{Cl}_2$ is a source of molybdenyl ion and thus reacts to form molybdenyl chelates, e.g. with acetylacetone to form the orange-red $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$ ⁴⁷⁴; this compound (m.p., with decomposition, 184–185°) can also be prepared by reaction of MoO_3 with refluxing acetylacetone⁴⁸². It dissolves in acetone with decomposition. It has limited solubility in methylene chloride and chloroform in which it decomposes with liberation of acetylacetone. It is slowly hydrolyzed by atmospheric moisture.

By single-crystal X-ray diffraction⁴⁸³, it has been shown that the structure of the bi-nuclear complex ion in $\text{K}_2[\text{MoO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]_2\text{O}$ belongs to space group $P2_1/c$ with unit cell⁴⁸⁴ dimensions a , b and c respectively 7.508, 14.235 and 6.602 Å; $\beta = 94^\circ 33'$. The bridging oxygen atom is at the crystallographic center of symmetry, and thus the Mo–O–Mo bridge is linear and symmetrical. The set of six oxygens (Mo–O bond lengths, 1.680–2.330 Å) forms a distorted octahedron; the Mo to terminal O and the Mo to bridging O distances are respectively 1.680 and 1.876 Å. The O–Mo–O bond angles range from 73.77° to 106.51°. It is observed that there is a tendency of ligands coordinated *trans* to multiple M–O bonds to have abnormally long bonds to the metal.

In marked contrast, the complex Mo-oxalato ion in $\text{NaNH}_4[\text{MoO}_3(\text{C}_2\text{O}_4)] \cdot 2\text{H}_2\text{O}$ has a structure of infinite Mo–O–Mo–O chains; the structure of each Mo unit is a distorted octahedron. The Mo–O–Mo bridges are bent and unsymmetrical with Mo–O distances of 2.33 and 1.87 Å. The two terminal Mo–O bond lengths are 1.815 and 1.850 Å⁴⁸⁵.

Molybdenum(VI) oxide reacts with diethylenetriamine (dien) to form the monomeric crystalline complex $\text{MoO}_3 \cdot \text{dien}$ ⁴⁸⁶. The molybdenum in the molecules is coordinated in a distorted octahedron⁴⁸⁷ by three mutually *cis*-oxygen atoms and three nitrogen atoms; the average Mo–O and Mo–N distances are respectively 1.736 and 2.324 Å. There is extensive intermolecular hydrogen bonding.

As indicated by polarography, coulometry and polarimetry, Mo(VI) forms complexes with gluconate (pH 2–10)⁴⁸⁸. At lower pH values, the ratio of gluconate to Mo(VI) is 2:1; at higher pH values, apparently there is a mixture of complexes perhaps because of change of state of polymerization of Mo(VI).

Results of n.m.r. and polarimetric studies show that histidine forms a 1:1 complex with

⁴⁸¹ J. F. Allen and H. M. Neumann, *Inorg. Chem.* **3** (1964) 1612.

⁴⁸² W. C. Fernelius, K. Terada and B. E. Bryant, *Inorg. Syn.* **6**, McGraw-Hill, New York (1960) p. 147.

⁴⁸³ F. A. Cotton, S. M. Morehouse and J. S. Wood, *Inorg. Chem.* **3** (1964) 1603; **4** (1965) 922; J. Donohue, **4** (1965) 921.

⁴⁸⁴ B. Lucas and E. Sandor, *Acta Cryst.* **16** (1963) 854.

⁴⁸⁵ L. O. Atomovniyan and G. B. Bokii, *Zh. Strukt. Khim.* **4** (1963) 576 (quoted by Cotton, Morehouse and Wood, ref. 483, 1964).

⁴⁸⁶ W. F. Marzluff, *Inorg. Chem.* **3** (1964) 395.

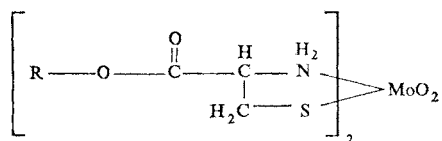
⁴⁸⁷ F. A. Cotton and R. C. Elder, *Inorg. Chem.* **3** (1964) 397.

⁴⁸⁸ J. T. Spence and G. Kallos, *Inorg. Chem.* **2** (1963) 710.

Mo(VI) in the pH range 5–7; the ratio of histidine to Mo(VI) is higher at lower pH values⁴⁸⁹. Similar results were obtained with L-histidine methyl ether, but there is no evidence of complex formation with L-alanine or N-acetyl-L-histidine. Histidine apparently bonds to Mo(VI) via the α -amino group and the l-nitrogen of the imidazole ring.

Molybdenum(VI) dithiocarbamate complexes, $\text{MoO}_2(\text{R}_2\text{NCS})_2$ (R = methyl, ethyl n-butyl) are obtained by acidifying solutions of molybdate ions and the sodium dialkyl-dithiocarbamate⁴⁹⁰. These compounds, as well as others of the same formulation, MoO_2L_2 , contain *cis* (bent) MoO_2 groups as indicated by the two strong $\text{Mo}=\text{O}$ stretching modes in the 900 cm^{-1} region (L = R_2NCS_2^- , acetylacetonate, benzoylacetonate, oxinate)⁴⁹¹. This is confirmed for the dithiocarbamates by their large dipole moments and for the diketone complexes by their n.m.r. spectra. The complexes MoO_2L_2 are undissociated in CH_3NO_2 and $\text{HCON}(\text{CH}_3)_2$ as shown by conductivity measurements.

On the basis of spectroscopic studies, it has been reported that cystine (L) and Mo(VI) form several complexes having L:Mo(VI) ratios from 3:1 to 1:1 in the pH range 3–6⁴⁹². By reaction of MoO_2Cl_2 with the sodium salt of methyl or ethyl cysteinate in aqueous solution, yellow crystalline chelates of the composition



can be prepared in good yield. Alternatively the starting materials may be sodium molybdate and the cysteine ester hydrochlorides.

Simple relationships exist among Mo–O stretching force contents *a*, Mo–O bond lengths *b*, and bond orders *c*, i.e. plots of *a* vs. *b*, *b* vs. *c* and *a* vs. *c* are smooth curves. These conclusions are based on structural and infrared data⁴⁹³.

2.9.6. Molybdenum(VI) Oxides

(a) MoO_3

When molybdenum and molybdenum compounds such as MoS_2 , MoS_3 and lower oxides are heated in oxygen, the final product is MoO_3 , which may also be produced by calcination of ammonium paramolybdate, $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ ^{494a} ^{495a} and by dehydrating a hydrate such as H_2MoO_4 ($\text{MoO}_3 \cdot \text{H}_2\text{O}$)^{496a}. Molybdenum oxide for production of Mo is produced by roasting MoS_2 in air and may be purified by dissolution in NH_4OH from which the paramolybdate is crystallized and ignited to MoO_3 ^{494b}.

Although MoO_3 is the anhydride of molybdic acid, it does not form hydrates readily. Two hydrates^{494c}, $\text{MoO}_3 \cdot \text{H}_2\text{O}$ ^{496a} and $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$, can be obtained by acidifying molybdate

⁴⁸⁹ J. T. Spence and J. Y. Lee, *Inorg. Chem.* **4** (1965) 385.

⁴⁹⁰ F. W. Moore and M. L. Larson, *Inorg. Chem.* **6** (1967) 998.

⁴⁹¹ F. W. Moore and R. E. Rice, *Inorg. Chem.* **7** (1968) 2510.

⁴⁹² L. R. Melby, *Inorg. Chem.* **8** (1969) 349.

⁴⁹³ F. A. Cotton and R. M. Wing, *Inorg. Chem.* **4** (1965) 867.

⁴⁹⁴ (a) L. Malaprade, p. 656; (b) J. Aubry, p. 560; (c) L. Malaprade, p. 664; (d) J. Aubry, p. 638, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959).

⁴⁹⁵ F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 2nd edn. (1966): (a) p. 933; (b) p. 938.

⁴⁹⁶ F. Hein and S. Herzog, *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965): (a) p. 1411; (b) p. 1416.

solutions^{494b, 495a}. Molybdic oxide and its hydrates readily dissolve in solutions of excess bases to form molybdates.

Molybdenum(VI) is orthorhombic with crystal dimensions as follows (Å): *a*, 3.966; *b*, 13.88; *c*, 3.703^{494a}. The Mo–Mo and Mo–O distances are, respectively, 3.43 Å and 1.8–2.35 Å. The solid has a layer structure consisting of parallel rows of distorted MoO₆ octahedra; the octahedra within one layer are connected by shared edges in one direction and by shared corners in the other⁴⁹⁷; the layers are infinite in two dimensions.

(b) MoO_x ($2 < x < 3$)^{497, 498}

Several molybdenum oxides with composition between MoO₃ and MoO₂ have been prepared, for example, by heating MoO₃ *in vacuo*⁴⁹⁷ or reducing MoO₃ with Mo^{496a}. These oxides have the following formulas (*x* in parentheses): Mo₉O₂₆, monoclinic (2.889); Mo₁₈O₅₂, triclinic (2.889); Mo₈O₂₃ (2.875); Mo₅O₁₄ (2.80); Mo₁₇O₄₇ (2.765); Mo₄O₁₁, monoclinic and triclinic (2.75). Although these oxides are nonstoichiometric in the sense that the Mo:O ratios are “abnormal”, they are “daltonides”, not “berthollides”, since they are stable phases without extended homogeneity ranges. Since the formal oxidation state of Mo in these oxides is between 4+ and 6+, they may be regarded as mixed valence compounds⁴⁹⁸ containing Mo⁶⁺ and Mo⁵⁺ or Mo⁶⁺ and Mo⁴⁺.

On the basis of results of differential thermal analysis and X-ray diffraction studies (primarily the work of G. Hägg, A. Magneli, L. Kihlberg and their collaborators), the structural principles involved have been established. All of the structures are built up of MoO₆ octahedra, MoO₄ tetrahedra, and MoO₇ pentagonal bipyramids. The seven mixed valence oxides belong to three structural classes, i.e. ReO₃, MoO₃ and what has been called the “mixed-polygonal” type.

The ReO₃ structure consists of Mo₆ octahedra connected only at the corners. In one of its configurations, the chains of octahedra extend infinitely in three dimensions (e.g. WO₃). The basic structure may extend infinitely in only two dimensions; in this case slabs of finite width are present which may be connected in two different ways.

One way is by the sharing of edges of the octahedra of adjacent slabs. This structure is exemplified by Mo₈O₂₃ and monoclinic Mo₉O₂₆. These oxides are members of a “homologous” series Mo_{*n*}O_{3*n*-1} in which the widths are determined by the value of *n*. Molybdenum oxides in which *n* = 9 and 10 are known and mixed Mo–W oxides have been obtained in which *n* = 10, 11, 12 and 14⁴⁹⁸.

In the second way, slabs of octahedra are connected by tetrahedra sharing corners with the octahedra of the two adjacent slabs; there is no sharing of edges in this structure. Examples are the two forms of Mo₄O₁₁; in these the slabs have the same thickness in both, but the rows of octahedra are parallel and reversed respectively in the monoclinic and orthorhombic structures. Homologous series of oxides of this type are possible.

In the oxygen-deficient oxides such as Mo₁₈O₅₂, the structure within a layer is the same as in MoO₃, i.e. zigzag rows of octahedra sharing edges, the rows connected by shared corners. In MoO₃, the layers are stacked so that the lowest octahedral corner of one layer is situated above the hole formed between four octahedra in the layer below. In Mo₁₈O₅₂

⁴⁹⁷ L. Kihlberg, “The Crystal Chemistry of Molybdenum Oxides”, in *Advances in Chemistry Series*, **39**, American Chemical Society, Washington, DC (1963).

⁴⁹⁸ M. B. Robin and P. Day, “Mixed Valence Chemistry—a Survey and Classification”, in *Advances in Inorganic Chemistry and Radiochemistry*, **10**, Academic Press, New York (1967), p. 335.

there is increased edge-sharing, i.e. six octahedra at each end of every zigzag row share edges with six octahedra of a row in the adjacent strip in a structure known as a "step lattice"⁴⁹⁷.

In the "mixed polygonal" type ($\text{Mo}_{17}\text{O}_{47}$, Mo_5O_{14} , $\text{MoW}_{11}\text{O}_{36}$, $\text{MoW}_{14}\text{O}_{45}$, $\text{W}_{18}\text{O}_{49}$), there is a complex linking pattern in two dimensions involving three-, four- and five-membered rings. In the third dimension perpendicular to the rings, the connection is through shared corners⁴⁹⁷.

All of the compounds of this type except $\text{Mo}_{17}\text{O}_{47}$ have been described as "tunnel compounds" because they contain wide empty tunnels that pass straight through the structures (Fig. 14A)⁴⁹⁷. The tunnels are linked by rings of five or six octahedra. In $\text{Mo}_{17}\text{O}_{47}$, the

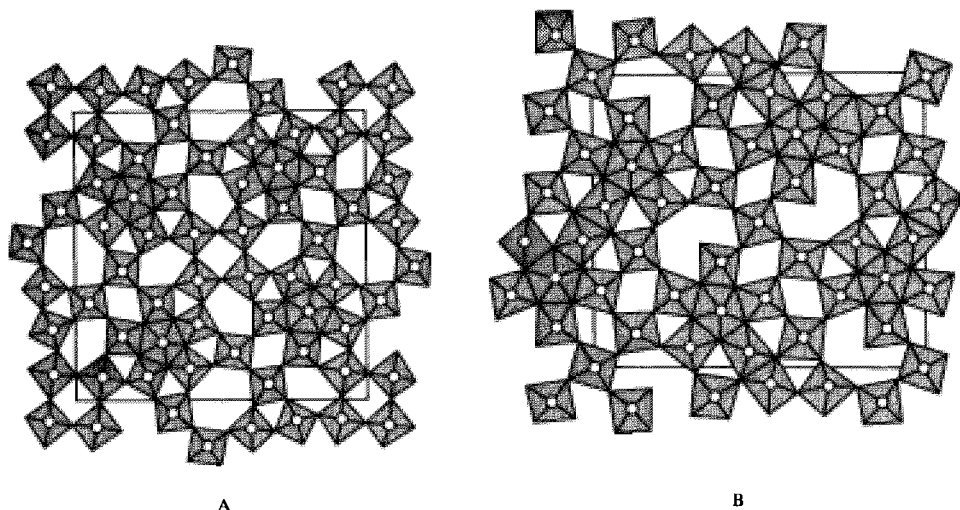


FIG. 14. Crystal structures of Mo_5O_{14} (A) and $\text{Mo}_{17}\text{O}_{47}$ (B) in line of sight identical networks joined by common apices. (Reprinted from ref. 497, © 1963, by permission of the American Chemical Society.)

tunnels are blocked by oxygen atoms in the middle of the six-membered rings (Fig. 14B). In the molybdenum and tungsten bronzes (*q.v.*), the alkali (or other metal) atoms are situated in the tunnels of the host oxide.

2.9.7. Molybdenum Blues^{494d, 495a, 498}

The molybdenum blues are mixed valence oxide-hydroxides containing Mo(V) and Mo(VI). They are formed by partial reduction of acidified molybdate solutions by, for example, Sn(II) , SO_2 , N_2H_4 and H_2S and by partial oxidation of Mo in oxidation state V or lower. Since some of the products are transient, some are colloidal and they may contain different ratios $\text{Mo(VI)}:\text{Mo(V)}$, it has been difficult to isolate solid products of reproducible composition, particularly with respect to degree of hydration. Apparently a series of compounds exists with MoO(OH)_3 and MoO_3 as the limits; the blue compounds have compositions intermediate between these limits (i.e. with mean oxidation states between 5+ and 6+).

Blue anhydrous oxides and crystalline hydrates have been prepared. The compounds $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ ^{496a} and $\text{Mo}_8\text{O}_{15}(\text{OH})_{16}$, which have been characterized by X-ray diffraction, are insoluble in water and stable toward alkali. Water-soluble amorphous blues have also

been obtained. When MoO_3 in concentrated HCl is reduced with Zn , the final product is a crystalline green Mo(IV) compound, $\text{Mo}_5\text{O}_5(\text{OH})_{10}$, which loses hydrogen *in vacuo* with formation of the mixed valence red compound $\text{Mo}_5\text{O}_7(\text{OH})_8$.

2.9.8. Molybdenum Bronzes⁴⁹⁹

The tungsten bronzes were first prepared by Wöhler in 1823, while bronzes of other metals, including molybdenum, were not obtained until quite recently. In view of this fact and the close similarity of the molybdenum and tungsten bronzes, they are discussed together in Part III, Section 2.9.6 (see also the chapter on tungsten bronzes).

2.9.9. Molybdates^{494a, 495a, 500}

Preparative methods for molybdates (M_2MoO_4 or $\text{M}_2\text{MoO}_4 \cdot \text{XH}_2\text{O}$) include the following⁵⁰⁰: fusion of M_2O or M_2CO_3 with MoO_3 (M = alkali metal); fusion of M_2O with MoO_3 (M = $\frac{1}{2}\text{Mg}$, $\frac{1}{2}\text{Be}$, $\frac{1}{2}\text{Zn}$); neutralization of MoO_3 slurry with MOH or M_2CO_3 (M = alkali metal, $\frac{1}{2}\text{Fe}$, $\frac{1}{2}\text{Ni}$, $\frac{1}{2}\text{Co}$, $\frac{1}{2}\text{Cu}$); crystallization from solution of M^+ and MoO_4^{2-} (M = alkali metal, $\frac{1}{2}\text{Fe}$, $\frac{1}{2}\text{Co}$, $\frac{1}{2}\text{Ni}$, $\frac{1}{2}\text{Mn}$); precipitation of insoluble molybdate from molybdate solution by metal ion (M = $\frac{1}{2}\text{Ca}$, $\frac{1}{2}\text{Sr}$, $\frac{1}{2}\text{Ba}$, $\frac{1}{2}\text{Pb}$, $\frac{1}{2}\text{Zn}$, $\frac{1}{2}\text{Cd}$, $\frac{1}{2}\text{Hg}$, Ag , Hg , Tl); fusion of Na_2MoO_4 with MCl_2 (M = $\frac{1}{2}\text{Zn}$, $\frac{1}{2}\text{Cd}$, $\frac{1}{2}\text{Mn}$, $\frac{1}{2}\text{Fe}$, $\frac{1}{2}\text{Co}$, $\frac{1}{2}\text{Ni}$, $\frac{1}{2}\text{Cu}$).

The three ammonium molybdates are made as follows:

$(\text{NH}_4)_2\text{MoO}_4$: crystallization from aqueous solutions (made by dissolving MoO_3 or $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ in NH_3 solution containing excess NH_3).

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 24\text{H}_2\text{O}$: made in the same way except the solution is kept at the boiling point for an hour.

$(\text{NH}_4)_2\text{Mo}_8\text{O}_{26} \cdot 5\text{H}_2\text{O}$: acidification of heptamolybdate solutions⁵⁰⁰.

Many molybdate crystals contain discrete tetrahedral MoO_4^{2-} ions, e.g. those of the alkaline earths, lead, sodium, lithium and silver⁵⁰¹. It is probable that MoO_4^{2-} is also tetrahedral in solution^{495a}. Nearly all the molybdates are insoluble in water except those of ammonium, alkali metal, magnesium, and thallous ions^{495a}. The molybdates are quite easily reduced but they are not powerful oxidizing agents like CrO_4^{2-} . On acidification of molybdate solutions, polymerization occurs with formation of isopolymolybdates (*q.v.*).

Single crystals of scheelite-type molybdates of the following compositions have been obtained by slow crystallization from melts: $\text{Sr}_{0.9}\text{M}_{0.1}\text{MoO}_4$ (M = Gd , Eu); $\text{Na}_{0.5}\text{M}_{0.5}\text{MoO}_4$ (M = Pr , Tm , Dy); $\text{Li}_{0.5}\text{Dy}_{0.5}\text{MoO}_4$. In these tetragonal crystals, a and c range from 5.179 to 5.315 Å and 11.168 to 11.791 Å respectively; a and c for the isomorphous SrMoO_4 are 5.36 and 11.94 Å⁵⁰².

Polymorphs of AMoO_4 (A = Mg , Mn , Fe , Co , Ni , Zn) have been prepared by reaction of: MoO_3 with an oxide of A at 1000° at normal pressure; MoO_3 with an oxide of A in presence of H_2O at 700° and 3000 atm; divalent metal chloride with Na_2MoO_4 in aqueous solution followed by drying the precipitated molybdate at 400° *in vacuo*⁵⁰³. Ferrous molybdates were also prepared from mixtures of Fe_2O_3 , MoO_3 and Mo or Fe_2O_3 , MoO_3

⁴⁹⁹ E. Banks and A. Wold, "Oxide Bronzes", in *Preparative Inorganic Reactions*, **4**, Interscience, New York (1968).

⁵⁰⁰ *Properties of the Simple Molybdates*, bulletin Cdb-4, Climax Molybdenum Company, New York (October, 1962).

⁵⁰¹ G. M. Clark and W. P. Doyle, *Spectrochim. Acta* **22** (1966) 1441.

⁵⁰² M. M. Schieber, *Inorg. Chem.* **4** (1965) 762.

⁵⁰³ A. W. Sleight and B. L. Chamberland, *Inorg. Chem.* **7** (1968) 1672.

and Fe^{504} . All the high-pressure modifications have a structure related to that of NiWO_4^{503} .

Rhombohedral crystals $3\text{R}_2\text{O}_3 \cdot \text{MoO}_3$ ($\text{R} = \text{Tm}, \text{Yb}, \text{Lu}$) are obtained by high-temperature reaction of R_2O_3 and MoO_3^{505} .

The equilibrium



has been shown to exist in solutions of Na_2MoO_4 in equimolar NaNO_3 – KNO_3 melt (see Part I, Section 2.9.2(d))^{506, 507}.

Ammonium tetrathiomolybdate $(\text{NH}_4)_2\text{MoS}_4^{496b, 508}$ is obtained by reaction of H_2S with ammonium paramolybdate in concentrated NH_4OH solution. In more dilute NH_4OH , the dithiomolybdate $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$ is obtained.

2.9.10. Iso- and Heteropoly Anions of Molybdenum(VI)

When solutions of molybdates, tungstates and similar ions are acidified, polymerization occurs with formation of isopolyanions. In attempts to establish the species formed, numerous methods⁵⁰⁹ have been used including dialysis, diffusion, pH titrations, conductometric titrations, cryoscopy, light scattering, ion exchange, ultracentrifugation, ultraviolet spectroscopy and Raman spectroscopy. One of the difficulties encountered in investigations of isopolyanions is the low rate at which equilibria are established.

Although some uncertainty still exists with respect to the reactions occurring in acidified molybdate solutions, the following conclusions appear to be valid^{495b, 500, 509}. Down to pH 4–5 and with molybdenum concentrations up to 0.25 M, the system appears to be represented best by an equilibrium between molybdate, MoO_4^{2-} , and the heptamolybdate, $\text{Mo}_7\text{O}_{24}^{6-}$. When acidification is carried past the heptamer stage, the predominant species is the octamolybdate $\text{Mo}_8\text{O}_{26}^{4-}$. With more than 1.5 protons bound per molybdenum atom, species of higher degree of aggregation are formed and the rates of the reactions become very low.

The heteropoly complexes are prepared by heating and acidifying solutions of a molybdate (or a tungstate, vanadate or niobate) with a salt of the central atom in the appropriate oxidation state⁵¹⁰. The number of ions that can function as heteroatoms is close to 40; some examples are Be^{2+} , B^{3+} , Si^{4+} , P^{3+} , P^{5+} , V^{5+} , Te^{6+} , I^{7+} .

The following are examples of the principal types of heteropolymolybdates:

1:6 series: $[\text{Te}^{\text{VI}}\text{Mo}_6\text{O}_{24}]^{6-}$, $[\text{I}^{\text{VII}}\text{Mo}_6\text{O}_{24}]^{5-}$, $[\text{Cr}^{\text{III}}\text{Mo}_6\text{O}_{24}\text{H}_6]^{3-}$.

1:9 series: $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$.

1:12 A series: $[\text{P}^{\text{V}}\text{Mo}_{12}\text{O}_{40}]^{3-}$; $[\text{S}^{\text{IV}}\text{Mo}_{12}\text{O}_{40}]^{4-}$ ⁵¹¹.

1:12 B series: $[\text{Ce}^{\text{IV}}\text{Mo}_{18}\text{O}_{62}]^{6-}$.

1:10, 1:11 and 2:17 series are also known.

Isopolymolybdates such as



⁵⁰⁴ A. W. Sleight, B. L. Chamberland and J. F. Weiher, *Inorg. Chem.* **7** (1968) 1093.

⁵⁰⁵ E. A. Aitken, S. F. Bartram and E. F. Juenke, *Inorg. Chem.* **3** (1964) 949.

⁵⁰⁶ R. N. Kust, *Inorg. Chem.* **6** (1967) 2239.

⁵⁰⁷ A. Navrotsky and O. J. Kleppa, *Inorg. Chem.* **6** (1967) 2119.

⁵⁰⁸ F. W. Moore and M. L. Larson, *Inorg. Chem.* **6** (1967) 998.

⁵⁰⁹ J. Aveston, E. W. Anacker and J. S. Johnson, *Inorg. Chem.* **3** (1964) 735.

⁵¹⁰ G. A. Tsigdinos, *Heteropoly Compounds of Molybdenum and Tungsten*, bulletin Cdb-12a, Climax Molybdenum Company, New York (September, 1966).

⁵¹¹ E. O. North and W. Haney, *Inorg. Syn.* **1**, McGraw-Hill, New York (1939), p. 127.

can be crystallized from isopolymolybdate solutions. X-ray investigation of the last two shows that the Mo atoms are arranged in heptameric and octameric units, respectively, in the crystals (Figs. 15 and 16)⁵¹². The structures of some heteropolymolybdates and

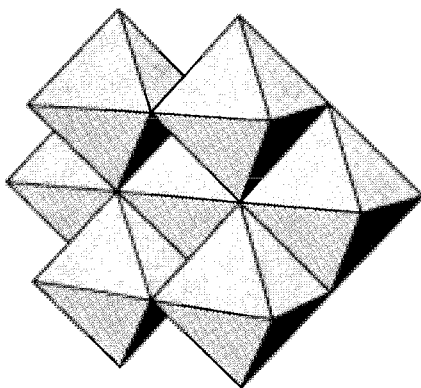


FIG. 15. Structure of the paramolybdate ion $[\text{Mo}_7\text{O}_{24}]^{6-}$.

heteropolytungstates of the 1:6, 1:9, 2:18 and 1:12 series have also been determined by X-ray diffraction.

In the iso- and heteropoly anions of molybdenum and tungsten, the molybdenum and tungsten atoms are in the centres of octahedra of oxygen atoms which share corners and

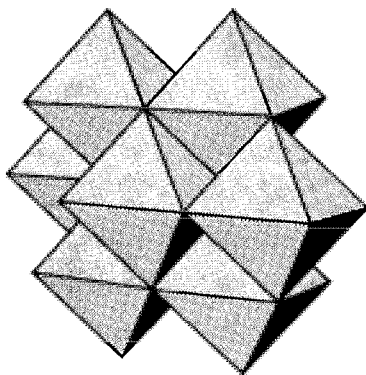


FIG. 16. Structure of the octamolybdate ion, $[\text{Mo}_8\text{O}_{26}]^{4-}$; one MoO_6 octahedron is hidden by the seven that show.

edges but not faces. In the heteropoly anions, the coordination of the central (hetero) atom may be^{495b, 513}: (1) tetrahedral, as in many 1:12 and 2:18 heteropolymolybdates and heteropolytungstates (Fig. 17); (2) octahedral, as in $[\text{Te}^{\text{VI}}\text{Mo}_6\text{O}_{24}]^{6-}$ and $[\text{M}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{9-}$ ($\text{M}(\text{III})$ = trivalent metal ion such as Cr^{3+} or Fe^{3+}); (3) icosahedral as in $[\text{Ce}^{\text{IV}}\text{Mo}_{12}\text{O}_{42}]^{8-}$.

In the crystal there are large interstices between the large heteropolyanions which apparently are linked by hydrogen bonding via molecules of water of hydration. Other

⁵¹² I. Lindqvist, *Arkiv. Kemi* **2** (1951) 325, 349.

⁵¹³ D. L. Kepert, *Inorg. Chem.* **8** (1969) 1556.

water molecules appear to be zeolitic, i.e. they are lost continuously when the crystal is heated instead of stepwise at specific temperatures⁵¹⁰.

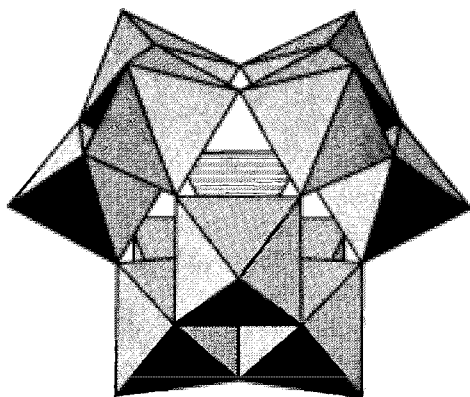


FIG. 17. Structure of the 1:12 series heteropolyanions $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ ($M = Mo$; $X^{n+} = P^V$, As^V , Ti^{IV} , Zr^{IV} ; $M = W$; $X^{n+} = B^{III}$, Ge^{IV} , Si^{IV} , As^V).

For further details, see the chapter on polyacids.

2.10. PEROXYMOLYBDENUM COMPOUNDS^{514, 515}

Molybdenum(VI) forms several series of peroxy compounds. These include salts in which the $(O_2):Mo$ ratio is 4:1, 3:1, 2:1 and 1:1 as well as compounds of less well-defined ratios.

By the action of excess H_2O_2 on neutral or slightly alkaline solutions of MoO_4^{2-} , red salts of the type $M[Mo(O_2)_4]$ are obtained ($M = 2Na, 2K, Ca, Sr, Ba, Co, Zn(NH_3)_4$ ⁵¹⁶); some of these can be obtained by double decomposition reactions. It appears that the ion $[Mo(O_2)_4]^{2-}$ is present in the solid state, although it may hydrolyze readily in solution.

There is some question, however, about the composition of these salts. The sodium salt $Na_2MoO_8 \cdot 2H_2O$ cannot be dehydrated without loss of peroxide oxygen, which has been interpreted as indicating presence of H_2O_2 of crystallization. However, the anhydrous potassium salt, K_2MoO_8 , can be obtained.

These compounds are quite unstable. They explode when struck or heated. The final product of their decomposition is molybdate, MoO_4^{2-} . Intermediate decomposition products have been reported that contain 3, 2 or 1 atom of peroxy oxygen, per Mo atom.

By thermal decomposition of the tetraperoxy molybdates described, the triperoxy compounds $M[MoO(O_2)_3]$ are obtained ($M = Ca, Sr$). The Sr compound is brick-red. These peroxides may not be true chemical species; what is formulated as $[MoO(O_2)_3]^{2-}$ may be a mixture of $[Mo(O_2)_4]^{2-}$ and the dimeric ion $[(O_2)_2OMoOMoO(O_2)_2]^{2-}$ which is thought to be in equilibrium with $[Mo(O_2)_4]^{2-}$ in aqueous solution.

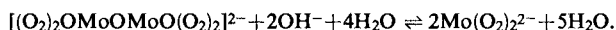
The 2:1 species $[MoO_2(O_2)_2]^{2-}$ are apparently dimers, $[(O_2)_2OMoOMoO(O_2)_2]^{2-}$. The

⁵¹⁴ L. Malaprade, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959), p. 711.

⁵¹⁵ J. A. Connor and E. A. V. Ebsworth, "Peroxy Compounds of Transition Metals", in *Advances in Inorganic Chemistry and Radiochemistry*, **6**, Academic Press, New York (1964), p. 313.

alkali metal salts are obtained from acid solutions of alkali metal molybdates containing a high concentration of H_2O_2 ⁵¹⁶.

The 2:1 peroxymolybdates are thermally more stable than the tetraperoxy compounds. The product of thermal decomposition is molybdate; monoperoxy compounds may be formed as intermediates. In solutions containing a high concentration of H_2O_2 , the following equilibrium exists:



Salts of the 1:1 peroxy anion $[\text{MO}_3(\text{O}_2)]^-$ have been prepared by neutralizing solutions of H_2O_2 and molybdic acid, by action of H_2O_2 on molybdates and as products of decomposition of peroxymolybdates of higher ratio.

Many peroxy compounds of $(\text{O}_2):\text{Mo}$ ratio between 0 and 1 have been described in the older literature. Such products have been obtained from molybdate and polymolybdate solutions containing low concentrations of H_2O_2 . They have sometimes been formulated as peroxypolymolybdates, e.g. $\text{Ba}_5\text{Mo}_{12}\text{O}_{38} \cdot (\text{O}_2)_3 \cdot 18\text{H}_2\text{O}$.

Other peroxy-Mo compounds that have been reported include peroxyfluoromolybdates, peroxyoxalates, sulfatoperoxy complexes and compounds resulting from reactions of organic phosphates with molybdic acid and H_2O_2 .

III. Tungsten

1. THE ELEMENT

1.1. DISCOVERY AND HISTORY^{517, 518}

Tungsten was discovered by the Swedish chemist Carl Wilhelm Scheele in 1781. Scheele isolated a new oxide (tungstic acid) from the white mineral then called tungsten ("heavy stone") and now known as scheelite, whose principal constituent is calcium tungstate, CaWO_4 . This oxide, obtained by reaction of nitric acid with the mineral, was found to be quite similar to molybdic oxide but to differ from it in important details, e.g. in being less volatile and more acidic.

In 1783 two Spanish chemists, the d'Elhuyar brothers (there are several variants of the spelling of their name), obtained this oxide not only from tungsten but also from wolfram or wolframite (an iron-manganese tungstate). Scheele and Bergman had suggested that a new metal might be obtained by reducing tungstic acid, which was accomplished by the d'Elhuyar brothers by heating a mixture of the oxide with charcoal in a luted crucible. The product was a brown metallic button which crumbled to microscopic globules of the metal.

Tungsten steel was invented in 1855 by the Austrian chemist Franz Koller^{519a}. Mushet started to manufacture high-carbon-vanadium-manganese-tungsten steels in England in 1868. These steels had the advantage of hardening on cooling without requiring quenching,

⁵¹⁶ F. Hein and S. Herzog, in *Handbook of Preparative Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965), p. 1414.

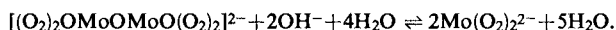
⁵¹⁷ M. E. Weeks and H. M. Leicester, *Discovery of the Elements*, Journal of Chemical Education, Easton, Penna., 7th edn. (1968), p. 241.

⁵¹⁸ B. Kopelman, "Tungsten and Tungsten Alloys", in *Encyclopedia of Chemical Technology*, **14**, Interscience, New York, 1st edn. (1955), p. 353.

⁵¹⁹ (a) H. R. Schubert, "The Steel Industry", p. 64; (b) D. F. Galloway, "Machine Tools", p. 640; (c) R. Chadwick, "New Extraction Processes for Metals", p. 98, in *A History of Technology*, **5**, Oxford University Press, London (1958).

alkali metal salts are obtained from acid solutions of alkali metal molybdates containing a high concentration of H_2O_2 ⁵¹⁶.

The 2:1 peroxymolybdates are thermally more stable than the tetraperoxy compounds. The product of thermal decomposition is molybdate; monoperoxy compounds may be formed as intermediates. In solutions containing a high concentration of H_2O_2 , the following equilibrium exists:



Salts of the 1:1 peroxy anion $[\text{MO}_3(\text{O}_2)]^-$ have been prepared by neutralizing solutions of H_2O_2 and molybdic acid, by action of H_2O_2 on molybdates and as products of decomposition of peroxymolybdates of higher ratio.

Many peroxy compounds of $(\text{O}_2):\text{Mo}$ ratio between 0 and 1 have been described in the older literature. Such products have been obtained from molybdate and polymolybdate solutions containing low concentrations of H_2O_2 . They have sometimes been formulated as peroxypolymolybdates, e.g. $\text{Ba}_5\text{Mo}_{12}\text{O}_{38} \cdot (\text{O}_2)_3 \cdot 18\text{H}_2\text{O}$.

Other peroxy-Mo compounds that have been reported include peroxyfluoromolybdates, peroxyoxalates, sulfatoperoxy complexes and compounds resulting from reactions of organic phosphates with molybdic acid and H_2O_2 .

III. Tungsten

1. THE ELEMENT

1.1. DISCOVERY AND HISTORY^{517, 518}

Tungsten was discovered by the Swedish chemist Carl Wilhelm Scheele in 1781. Scheele isolated a new oxide (tungstic acid) from the white mineral then called tungsten ("heavy stone") and now known as scheelite, whose principal constituent is calcium tungstate, CaWO_4 . This oxide, obtained by reaction of nitric acid with the mineral, was found to be quite similar to molybdic oxide but to differ from it in important details, e.g. in being less volatile and more acidic.

In 1783 two Spanish chemists, the d'Elhuyar brothers (there are several variants of the spelling of their name), obtained this oxide not only from tungsten but also from wolfram or wolframite (an iron-manganese tungstate). Scheele and Bergman had suggested that a new metal might be obtained by reducing tungstic acid, which was accomplished by the d'Elhuyar brothers by heating a mixture of the oxide with charcoal in a luted crucible. The product was a brown metallic button which crumbled to microscopic globules of the metal.

Tungsten steel was invented in 1855 by the Austrian chemist Franz Koller^{519a}. Mushet started to manufacture high-carbon-vanadium-manganese-tungsten steels in England in 1868. These steels had the advantage of hardening on cooling without requiring quenching,

⁵¹⁶ F. Hein and S. Herzog, in *Handbook of Preparative Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965), p. 1414.

⁵¹⁷ M. E. Weeks and H. M. Leicester, *Discovery of the Elements*, Journal of Chemical Education, Easton, Penna., 7th edn. (1968), p. 241.

⁵¹⁸ B. Kopelman, "Tungsten and Tungsten Alloys", in *Encyclopedia of Chemical Technology*, **14**, Interscience, New York, 1st edn. (1955), p. 353.

⁵¹⁹ (a) H. R. Schubert, "The Steel Industry", p. 64; (b) D. F. Galloway, "Machine Tools", p. 640; (c) R. Chadwick, "New Extraction Processes for Metals", p. 98, in *A History of Technology*, **5**, Oxford University Press, London (1958).

and were especially valuable as materials for metal cutting tools. The "high speed steels" were developed by Taylor and White at the end of the nineteenth century^{519b}. Cutting tools made of these steels (containing tungsten, chromium and vanadium) retain their hardness at high metal cutting speeds even when they become red hot.

Perhaps because of its high melting point and consequent experimental difficulties, metallic tungsten was to a considerable extent neglected until 1909, when W. D. Coolidge succeeded in making ductile tungsten from the metal powder by a combination of heat treatment and mechanical working; tungsten was the first metal to be produced by the methods of "powder metallurgy". Use of tungsten as a lamp filament had started about 1904^{519c}, and for a long time this was its principal application. Recently there has been increasing interest in tungsten and its alloys as materials for high temperature applications, as in nozzles of rocket motors.

The history of tungsten parallels that of molybdenum in that, following its discovery, the literature of tungsten compounds grew very rapidly as shown by the hundreds of references cited in such encyclopedias as those of Gmelin and Pascal, with subsequent relative neglect of these compounds, and currently a resurgence of interest. As is the case with chromium and molybdenum, one of the most active areas of research in tungsten chemistry is the chemistry of the carbonyls and organometallic compounds.

Since the metal was first produced from tungstic acid obtained from wolframite, some authorities have contended that the appropriate name for the element is *wolfram*. At one time, the International Union of Pure and Applied Chemistry recommended replacing the name tungsten by wolfram, but since the name tungsten had become too well established to be abolished, they later approved the use of both names. Still later, their Commission on Atomic Weights recommended dropping the name wolfram, which, however, is widely used in the German literature.

1.2. OCCURRENCE AND DISTRIBUTION

Tungsten is fifty-fourth in order of abundance of the elements in the earth's crust (1.55 ppm)⁵²⁰. Tungsten deposits have been discovered by geobotanical prospecting; the indicator is anomalous W content of plants⁵²¹. Table 34 shows the distribution of W in various materials⁵²².

TABLE 34. DISTRIBUTION OF TUNGSTEN

Material	W (ppm)*	Material	W (ppm)*
Soils	1 ^{522a}	Marine plants	0.035 ^{522a}
Igneous rocks	1.5 ^{522a, b}	Land plants	0.07 ^{522a, c}
Shales	1.8 ^{522a, b}	Marine animals	0.0005–0.05 ^{522a}
Sandstones	1.6 ^{522a, b}	Land animals	0.00025–0.005 ^{522b, d, c}
Limestones	0.6 ^{522a, b}	Mammalian blood	0.001 ^{522f}
Sea water	0.0001 ^{522a}	Red cells	0.002 ^{522f}

* Results for soils and biological materials reported on oven-dried basis.

⁵²⁰ K. B. Krauskopf, *Introduction to Geochemistry*, McGraw-Hill, New York (1967), p. 639.

⁵²¹ H. L. Cannon, *Science*, **132** (1960) 591.

⁵²² J. H. M. Bowen, *Trace Elements in Biochemistry*, Academic Press, London (1966): (a) p. 208; (b) p. 17; (c) p. 68; (d) p. 71; (e) p. 78; (f) p. 82.

Tungsten ores are widely distributed. The principal minerals are scheelite (CaWO_4) and wolframite ($(\text{Fe}, \text{Mn})\text{WO}_4$) (a mixed crystal of hubnerite, MnWO_4 , and ferberite, FeWO_4). The ores usually contain other minerals, particularly those of tin. The major deposits are in China, and much smaller deposits are located in the United States, South America and Korea. The most important European deposits are in Portugal⁵²³.

1.3. PRODUCTION AND INDUSTRIAL USE⁵²³⁻⁵²⁵

The estimated 1970 US consumption of tungsten is about 7000 tons⁵²⁶. The commercially important ores are scheelite (CaWO_4) and wolframite ($(\text{Fe}, \text{Mn})\text{WO}_4$). Since the ores contain only 2–3% W, they are ground and processed by gravity separations and/or flotation to produce concentrates of at least 60% WO_3 .

Scheelite (or CaWO_4 produced from wolframite) is decomposed to tungstic acid by hydrochloric acid. Calcium tungstate is obtained from wolframite by roasting with sodium carbonate and sodium nitrate, leaching, filtering to remove Fe_2O_3 and Mn_3O_4 ; or digestion with MOH solution ($\text{M} = \text{Na}$ or K); precipitation of CaWO_4 from the tungstate solutions by CaCl_2 . The tungstic acid may be purified by dissolution in sodium hydroxide solution and re-precipitation, or by extraction with ammonium hydroxide solution from which ammonium paramolybdate crystallizes.

The tungstic oxide (or ammonium paramolybdate) is calcined to WO_3 which is reduced to metal with hydrogen. The powdered tungsten is pressed into bars which are sintered (in hydrogen) to produce massive tungsten^{527a}. Bars so produced are mechanically processed further by hot swaging and hot drawing. Arc-melting may be used for producing larger ingots^{527b}.

Pure tungsten is used for filaments for incandescent lamps and in the manufacture of elements for vacuum tubes, rods, contacts and other parts of electrical equipment.

The chief use of tungsten is as an alloying element in various steels; the tungsten is usually added to the steel as ferrotungsten, produced by reduction of wolframite by coke in an electric furnace. Tungsten is used in a wide variety of steels including tungsten stainless steels, heat-resistant steels and high-speed tool steels (18–20% W). The tungsten forms wear-resistant carbides in the steel; tools made of high-speed steels retain hardness and sharp cutting edges at high cutting speeds (i.e. high temperatures).

Of the numerous nonferrous alloys, copper–tungsten and silver–tungsten alloys are used to make switches and circuit breakers. The Stellites have compositions as follows: 12–16% W, 2.5% C, 48–53% Co, 28–32% Cr; some fraction of each of these may be replaced by other elements. Since these precipitation-hardenable alloys have high resistance to corrosion and wear even at high-temperatures, they are useful for equipment for handling corrosive chemicals, dies and punches, and shears for hot metals.

⁵²³ G. D. Rieck, *Tungsten and Its Compounds*, Pergamon Press, Oxford (1967), p. 4.

⁵²⁴ B. Kopelman, "Tungsten and Tungsten Alloys", "Tungsten Compounds", in *Encyclopedia of Chemical Technology*, 14, Interscience, New York, 1st edn. (1955).

⁵²⁵ A. Chretien and W. Freundlich, in *Nouveau Traité de Chimie Minérale*, 14, Masson et Cie, Paris (1959), p. 747.

⁵²⁶ *Chem. Engng. News*, September 1, 1969, 49a.

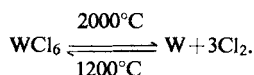
⁵²⁷ (a) D. J. Jones, "Practical Aspects of Sintering Tungsten and Molybdenum"; (b) A. R. Moss and D. T. Richards, "The Arc-Melting of Niobium, Tantalum, Molybdenum and Tungsten", in *Niobium, Tantalum, Molybdenum and Tungsten*, Elsevier, Amsterdam (1961).

Except for tungsten carbide, there are no very important uses of tungsten compounds. Tungsten carbide is produced by reaction of tungsten or tungstic oxide at high temperature in an inert atmosphere. The product is crushed to powder and sintered with cobalt powder. The cemented tungsten carbide is almost as hard as diamond and is thus useful for dies, tools, bits for rock drilling and other applications requiring extreme hardness and wear-resistance. Steels can be hard-faced with tungsten carbide.

1.4. PREPARATION OF PURE TUNGSTEN

The purity of tungsten metal obtained by reduction of WO_3 is dependent on the purity of the oxide. It may be purified by repeated dissolution in alkali and re-precipitation by acid or by solution in ammonium hydroxide and crystallization as ammonium paramolybdate^{528, 529a} (which is calcined to WO_3).

Pure tungsten may also be made from volatile tungsten compounds (e.g. halides, carbonyl) which can be purified by distillation^{529b}. The van Arkel process^{529b} depends on the reactions



A wire at 1200° is attacked by Cl_2 and the WCl_6 formed is decomposed on another wire at the higher temperature. Other procedures include thermal decomposition of WBr_5 and reduction of WCl_6 (or a tungsten oxychloride) with H_2 ^{529b}.

1.5. ALLOTROPES

The ordinary stable form of tungsten is α -W, type A2 (cubic, O_h^9 , $a = 3.16 \text{ \AA}$)⁵³⁰.

An allotrope, β -W (A15, cubic O_h^3 , $a = 5.04 \text{ \AA}$), has also been described, either metastable or stable only below 630°C ⁵³⁰. However, there is a question whether it exists since some investigators have been unable to prepare it by reported methods⁵³¹. Moreover, if it does exist a further question arises whether it is really an allotrope or an oxide W_3O ; at any rate, exclusion of oxygen is reported to prevent its formation⁵³⁰.

1.6. NUCLEAR PROPERTIES⁵³²

Naturally occurring tungsten is a mixture of five stable isotopes, whose characteristics are listed in Table 35.

Fifteen radioactive species of tungsten have been described; there are three pairs of nuclear isomers ($A = 179, 183, 185$). The nuclides $A = 185$ (beta, 75 days) and 187 (beta, 23.7–24.0 hr) are generally used for tracer work and are usually obtained as the metal or a solution of tungstate. The properties of the tungsten isotopes are summarized in Table 36.

⁵²⁸ F. Hein and S. Herzog, in *Handbook of Preparative Chemistry*, 2, Academic Press, New York, 2nd edn. (1965), p. 1417.

⁵²⁹ G. D. Rieck, *Tungsten and Its Compounds*, Pergamon Press, Oxford (1967): (a) p. 38; (b) pp. 40, 58.

⁵³⁰ Ref. 529, p. 11; Ref. 525, p. 771.

⁵³¹ M. V. Nevitt, "Miscellaneous Structures of Fixed Stoichiometry", in *Intermetallic Compounds*, John Wiley, New York (1967), p. 217.

⁵³² C. M. Lederer, J. M. Hollander and I. Perlman, *Table of Isotopes*, John Wiley, New York, 6th edn. (1967), p. 107.

TABLE 35. STABLE TUNGSTEN ISOTOPES⁵³²

A^a	%	Δ (meV) ^b	σ_c^c
180	0.135	-49.37	< 20
182	26.4	-48.16	20 (to ¹⁸³ W) 0.5 (to ^{183m} W)
183	14.4	-46.27	11
184	30.6	-45.62	2.1 (to ¹⁸⁵ W) 0.001 (to ^{185m} W)
186	28.4	-42.44	40

^a Mass number.^b Mass excess = $M - A$ (M = isotopic weight), ¹²C = 0.^c Slow neutron capture cross-section (barns).TABLE 36. RADIOISOTOPES OF TUNGSTEN⁵³²

A^a	Half-life ^b	Δ (meV) ^c	Mode of decay radiations, energies (meV) ^d	Mode of formation ^e
173	16.5 m		EC	¹⁸¹ Ta (p, 9n)
174	31 m		[EC]	Er(¹² C)
175	34 m		EC; γ , 0.26-1.6 (4)	¹⁸¹ Ta (p, 7n)
176	2.3 h, 2.7 h	-50	EC; e^- , 0.017-0.083 (6); γ , 0.034, 0.100	¹⁸¹ Ta (p, 6n)
177	130 m, 132 m, 135 m	-50	EC; e^- , 0.020-0.360 (9); γ , 0.0-1.00 (5)	¹⁸¹ Ta (p, 5n)
178	21.5 d, 22.0 d	-50	EC	¹⁸¹ Ta (p, 4n)
179	37.5 m, 38 m	-49	EC; e^- , 0.020, 0.029; γ , 0.031	¹⁸¹ Ta (p, 3n); ¹⁸⁰ W (p, 2n): ¹⁷⁹ Re (EC)
179m	5.2 m, 7.0 m	-49	IT; e^- , 0.152, 0.211; W X-rays	daughter ¹⁷⁹ Re; ¹⁸¹ Ta (p, 3n)
181	120 d, 126 d, 140 d, 145 d	-48.24	EC; e^- , 0.004, 0.006; γ , 0.006, 0.136, 0.152	¹⁸¹ Ta (d, 2n); ¹⁸¹ Ta (p, n); ¹⁸⁰ W (n, γ)
183m	5.1 s, 5.3 s, 5.5 s	-45.96	IT; e^- 0.034, 0.040; 0.046-0.160 (6), W X-rays	daughter ¹⁸³ Ta; ¹⁸² W (n, γ)
185	75 d	-43.30	β^- , 0.429	¹⁸⁴ W (n, γ); ¹⁸⁷ Re (d, α)
185m	1.55 m, 1.62 m, 1.85 m	-42.93	IT, 0.075-0.17 (4); W X-rays	¹⁸⁴ W (n, γ); ¹⁸⁶ W (γ , n)
187	23.7 h, 23.9 h, 24.0 h	-39.83	β^- , 1.31, 0.63; e^- , 0.063-0.8; γ , 0.072-0.773 (7)	¹⁸⁶ W (n, γ)
188	69.4 d	-38.44	β^- , 0.349; γ , 0.227, 0.290	¹⁸⁷ W (n, γ)
189	11 m, 11.5 m	-35.3	β^- , 2.5, 2.0; γ , 0.032-0.96 (8)	¹⁹² Os (n, α)

^a Mass number; m , nuclear isomer.^b s, seconds; m, minutes; h, hours; d, days.^c $\Delta = M - A$ (M = isotopic weight), ¹²C = 0.^d EC, electron capture; β^- , beta decay; IT, internal transition; e^- , conversion electrons; maximum energy given for β decays; [], inferred.^e n, neutron; p, proton; d, deuteron; γ , gamma; α , $\frac{4}{2}\text{He}$.

1.7. PHYSICAL PROPERTIES

Some of the physical properties of tungsten are listed in Table 37. Discrepancies in values of some properties reported by different authorities may be accounted for by

TABLE 37. SOME PHYSICAL PROPERTIES OF TUNGSTEN

Property	Value		Reference
Color	Steel gray		533
Atomic number (<i>Z</i>)	74		533
Atomic weight	183.85		534
Density	18.7–19.3 g/cm ³ (20°C) ^a		533
Atomic volume	10.46 cm ³ /mole		
Crystal structure	α (stable): body-centred cubic, type <i>A2</i> , space group <i>O</i> _h ⁹ , <i>a</i> = 3.165 Å; closest approach of atoms, 2.741 Å; lattice energy, 216.1 kcal/mole		533
	β (low temperature) ^b : cubic type, <i>A15</i> , space group <i>O</i> _h ³ , <i>a</i> = 5.04 Å		535
Melting point (m.p.)	3410 ± 20°C		533
Heat of fusion (ΔH_f)	8.42 kcal/mole		534
Boiling point (b.p.)	5500–5900°C		533
Heat of vaporization (ΔH_v)	184.58 kcal/mole (at b.p.)		534
Heat of sublimation (ΔH_s)	202.5 kcal/mole (25°)		536
Heat capacity (<i>C_p</i> , cal/mole/°C)	W(s) 5.97 (25°)		534
	<i>C_p</i> = 5.74 + 0.76 × 10 ⁻³ <i>T</i> ² (<i>T</i> = °K)		536
	W(g) 5.0903		534
Entropy (cal/mole/°C)	25°C	2227°C	535
	W(s)	8.04	
	W(g)	41.54	
Vapor pressure	°C	mm Hg	535
	2016	6.8 × 10 ⁻⁹	
	2384	6.4 × 10 ⁻⁷	
	2744	8.7 × 10 ⁻⁵	
	m.p.	3.3 × 10 ⁻²	
Configuration and ground state: un-ionized atom	5 <i>d</i> ⁴ 6 <i>s</i> ² ; ⁵ <i>D</i> ₀		535
Atomic radius	W ¹⁺ 5 <i>d</i> ⁴ 6 <i>s</i> ; ⁶ <i>D</i> _{3/2}		535
Ionization potentials (eV)	1.46 Å		535
	1st: 7.98		535
	2nd: 17.7		535
Bond energies of inner electrons (keV)	<i>K</i>	<i>L_I</i>	535
	69.645	12.116	
	<i>L_{II}</i>	<i>L_{III}</i>	535
	11.560	10.219	
	<i>M_I</i>	<i>M_{II}</i>	535
	2.820	2.575	
<i>K</i> X-ray emission spectra (Å)	α'	α	535
	0.21395	0.20927	
	β	γ	535
	0.18473	0.17976	
Electron affinity	1.7 eV		535
Work function	4.56 eV		537
Magnetic susceptibility	0.29 × 10 ⁻⁶ e.m.u./g		533
Resistivity (microhm cm)	5 (20°C)–60 (2000°C)		535

^a Density of sintered metal depends on extent of working; theoretical maximum, 19.254 g/cm³ 533.^b May be W₃O (see Section 1.5).533 G. D. Rieck, *Tungsten and Its Compounds*, Pergamon Press, Oxford (1967).534 R. Keller, *Basic Tables in Chemistry*, McGraw-Hill, New York (1967).535 G. V. Samsonov (ed.), *Handbook of the Physicochemical Properties of the Elements*, Plenum Press, New York (1968).536 C. J. Smithells, *Metals Reference Book*, 1, Plenum Press, New York, 4th edn. (1967).537 E. N. Simons, "Tungsten", in *Guide to Uncommon Metals*, Hart, New York (1967).

differences in specimens due to the manner and extent of mechanical processing, since tungsten, like molybdenum, is fabricated by powder-metallurgical processes.

In addition to the compilation to which specific reference has been made, the compendium⁵³⁸ of Goldsmith *et al.* is also very useful.

1.8. CHEMISTRY AND CHEMICAL PROPERTIES⁵³⁹⁻⁵⁴¹

At room temperature, tungsten is inert in air and oxygen; it burns to the trioxide at red heat. It reacts with fluorine at room temperature, with chlorine at about 300°C and with iodine at about 800°C. At high temperatures it combines with B, C, Si, N₂, S, Se and Te to form the binary compounds of these elements; tungsten also reacts with CO to form carbides and with NH₃ to form nitrides at a lower temperature than with N₂.

Tungsten does not react with water except at high temperatures at which it is oxidized to WO₃. It is also oxidized to WO₃ by N₂O, NO and NO₂ at elevated temperatures. It reacts with CO₂ above 1200°C.

Tungsten is not attacked by solutions of KOH in the absence of oxygen unless they contain oxidizing agents such as KNO₂, KNO₃, KClO₃ or PbO₂. It reacts slowly with fused NaOH in the presence of oxygen and rapidly with mixtures of NaOH and the oxidizing agents listed. It is not attacked by H₂SO₄, HCl, HNO₃ or HF at ordinary temperature and only insignificantly on heating. Tungsten dissolves rapidly in a mixture of HF and HNO₃; it is not attacked by aqua regia at room temperature but is dissolved rapidly on heating.

Tungsten is a transition element whose outermost electron structure is 5d⁴ 6s². Its oxidation states are the same as those of molybdenum, i.e. 2- to 6+. The lowest oxidation states (2- to 1+) occur only in organometallic compounds and compounds of π -acceptor ligands. Tungsten resembles molybdenum closely in many ways, e.g. in formation of the compounds mentioned, in formation of iso- and heteropoly acids, in the greater stability of the higher oxidation states and in the absence of extensive coordination chemistry of oxidation state III, which is a characteristic aspect of chromium chemistry.

1.9. BIOLOGICAL ACTIVITY

There is no evidence that tungsten has a biological role, nor that tungsten compounds (except possibly in massive amounts) are poisonous. A molybdenum-tungsten antagonism, however, has been demonstrated⁵⁴². Tungstate in considerable quantities inhibits utilization of molybdenum in formation of xanthine oxidase in rats. Although molybdenum deficiency was not induced in chickens fed a molybdenum-deficient (but otherwise adequate) diet, molybdenum deficiency was induced by adding tungstate to the diet.

⁵³⁸ A. Goldsmith, T. E. Waterman and H. J. Hirschhorn, *Handbook of Thermophysical Properties*, 1, Macmillan, New York, revised edn. (1961), pp. 675-689.

⁵³⁹ G. V. Samsonov (ed.), *Handbook of the Physicochemical Properties of the Elements*, Plenum Press, New York (1968), pp. 582, 708, 737, 746, 754, 762, 778, 788, 810.

⁵⁴⁰ F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 2nd edn. (1966), p. 930.

⁵⁴¹ A. Chretien and W. Freundlich, in *Nouveau Traité de Chimie Minérale*, 14, Masson et Cie, Paris (1959), p. 787.

⁵⁴² E. C. De Renzo, "Molybdenum", in *Mineral Metabolism*, 2B, Academic Press, New York (1962), p. 492.

1.10. ANALYTICAL CHEMISTRY^{543, 544}

Tungsten is usually determined as WO_3 , particularly in steel analysis, in which the sample is dissolved in acid which leaves silica and tungstic acid as insoluble residues. The silica can be removed by digestion of the precipitate with HF . The tungstic acid is ignited to WO_3 ; the temperature must be kept below 900° to avoid volatilization.

Since several other elements may be precipitated under the conditions of formation of tungstic acid, prior separation of the tungsten is often required. The same difficulty arises with gravimetric methods based on precipitation of insoluble tungstates MWO_4 ($\text{M} = \text{Pb}, \text{Ba}, \text{Ca}, \text{Cd}$).

Tungstate can be precipitated by many organic compounds but since the precipitates do not have well-defined compositions, they are ignited to WO_3 . Most of the organic precipitants are amines, e.g. benzidine, α -naphthylamine, o -anisidine; the alkaloids quinine, strychnine, brucine, totaquine and cinchonine have also been used.

Cinchonine and oxine seem to be the best of the organic reagents. When tungstic acid is precipitated, some tungsten is left in solution which can be recovered by precipitation with cinchonine. In contrast to many other organic reagents, oxine forms a stoichiometric compound $\text{WO}_2(\text{C}_9\text{H}_6\text{ON})_2$, which can be dried at 120 – 180° or ignited to WO_3 .

The use of chelating agents in analysis of tungsten has been reviewed recently^{545a} and another review contains several examples of chelating agents as precipitants for tungsten^{545b}.

Titrimetric procedures are not very useful because of numerous interferences. Among those reported are: precipitation methods with Pb^{2+} and Ba^{2+} ; redox methods involving reduction of W(VI) to W(V) by Cr(II) or by Ag or Zn in reductors; reduction of W(VI) to W(IV) by Wood's and Rose's alloys and various amalgams. Generally the reduced solution is collected in excess ferric solution and the Fe^{2+} produced is titrated.

With a flux of 10^{13} n/cm²/sec, the estimated sensitivity of neutron activation analysis for W is 0.021×10^{-9} g and 0.73×10^{-9} g (150 hr and 1 hr radiation respectively; product species 24 hr ^{187}W)⁵⁴⁶. The analytical sensitivity of this method has been compared with those of other methods useful in geochemical analysis.

2. TUNGSTEN COMPOUNDS

2.1. INTERMETALLIC PHASES IN BINARY TUNGSTEN ALLOYS^{547–554}

In the corresponding sections dealing with chromium and molybdenum, examples of three important classes of intermetallic phases were listed, i.e. σ , Laves and Cr_3Si -type

⁵⁴³ J. J. Lingane, "Tungsten", in *Analytical Chemistry of Selected Metallic Elements*, Reinhold, New York (1966).

⁵⁴⁴ R. A. Chalmers, "Tungsten", in *Comprehensive Analytical Chemistry*, IC, Elsevier, Amsterdam (1962).

⁵⁴⁵ (a) R. Püschel and E. Lassner, "Chelates and Chelating Agents in the Analytical Chemistry of Molybdenum and Tungsten", in *Chelates in Analytical Chemistry*, 1, Marcel Dekker, New York (1967); (b) F. H. Firsching, "Chelating Agents as Metal Precipitants: Advances, 1960–1965", *ibid.* 2 (1969).

⁵⁴⁶ J. H. Winchester, "Radioactivation Analysis in Inorganic Geochemistry", in *Progress in Inorganic Chemistry*, 2, Interscience, New York (1960).

⁵⁴⁷ M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York (1958), index to all systems, pp. ix–xvi.

⁵⁴⁸ R. P. Elliott, *Constitution of Binary Alloys, First Supplement*, McGraw-Hill, New York (1965), cumulative index to all systems, pp. ix–xxx.

⁵⁴⁹ J. H. Westbrook (ed.), *Intermetallic Compounds*, John Wiley, New York (1967), compound index, pp. 639–663.

⁵⁵⁰ I. I. Kornilov, *The Chemistry of the Metallides*, Consultants Bureau, New York (1966).

1.10. ANALYTICAL CHEMISTRY^{543, 544}

Tungsten is usually determined as WO_3 , particularly in steel analysis, in which the sample is dissolved in acid which leaves silica and tungstic acid as insoluble residues. The silica can be removed by digestion of the precipitate with HF. The tungstic acid is ignited to WO_3 ; the temperature must be kept below 900° to avoid volatilization.

Since several other elements may be precipitated under the conditions of formation of tungstic acid, prior separation of the tungsten is often required. The same difficulty arises with gravimetric methods based on precipitation of insoluble tungstates MWO_4 ($\text{M} = \text{Pb}, \text{Ba}, \text{Ca}, \text{Cd}$).

Tungstate can be precipitated by many organic compounds but since the precipitates do not have well-defined compositions, they are ignited to WO_3 . Most of the organic precipitants are amines, e.g. benzidine, α -naphthylamine, o -anisidine; the alkaloids quinine, strychnine, brucine, totaquine and cinchonine have also been used.

Cinchonine and oxine seem to be the best of the organic reagents. When tungstic acid is precipitated, some tungsten is left in solution which can be recovered by precipitation with cinchonine. In contrast to many other organic reagents, oxine forms a stoichiometric compound $\text{WO}_2(\text{C}_9\text{H}_6\text{ON})_2$, which can be dried at 120 – 180° or ignited to WO_3 .

The use of chelating agents in analysis of tungsten has been reviewed recently^{545a} and another review contains several examples of chelating agents as precipitants for tungsten^{545b}.

Titrimetric procedures are not very useful because of numerous interferences. Among those reported are: precipitation methods with Pb^{2+} and Ba^{2+} ; redox methods involving reduction of W(VI) to W(V) by Cr(II) or by Ag or Zn in reductors; reduction of W(VI) to W(IV) by Wood's and Rose's alloys and various amalgams. Generally the reduced solution is collected in excess ferric solution and the Fe^{2+} produced is titrated.

With a flux of 10^{13} n/cm²/sec, the estimated sensitivity of neutron activation analysis for W is 0.021×10^{-9} g and 0.73×10^{-9} g (150 hr and 1 hr radiation respectively; product species 24 hr ^{187}W)⁵⁴⁶. The analytical sensitivity of this method has been compared with those of other methods useful in geochemical analysis.

2. TUNGSTEN COMPOUNDS

2.1. INTERMETALLIC PHASES IN BINARY TUNGSTEN ALLOYS^{547–554}

In the corresponding sections dealing with chromium and molybdenum, examples of three important classes of intermetallic phases were listed, i.e. σ , Laves and Cr_3Si -type

⁵⁴³ J. J. Lingane, "Tungsten", in *Analytical Chemistry of Selected Metallic Elements*, Reinhold, New York (1966).

⁵⁴⁴ R. A. Chalmers, "Tungsten", in *Comprehensive Analytical Chemistry*, IC, Elsevier, Amsterdam (1962).

⁵⁴⁵ (a) R. Püschel and E. Lassner, "Chelates and Chelating Agents in the Analytical Chemistry of Molybdenum and Tungsten", in *Chelates in Analytical Chemistry*, 1, Marcel Dekker, New York (1967); (b) F. H. Firsching, "Chelating Agents as Metal Precipitants: Advances, 1960–1965", *ibid.* 2 (1969).

⁵⁴⁶ J. H. Winchester, "Radioactivation Analysis in Inorganic Geochemistry", in *Progress in Inorganic Chemistry*, 2, Interscience, New York (1960).

⁵⁴⁷ M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York (1958), index to all systems, pp. ix–xvi.

⁵⁴⁸ R. P. Elliott, *Constitution of Binary Alloys, First Supplement*, McGraw-Hill, New York (1965), cumulative index to all systems, pp. ix–xxx.

⁵⁴⁹ J. H. Westbrook (ed.), *Intermetallic Compounds*, John Wiley, New York (1967), compound index, pp. 639–663.

⁵⁵⁰ I. I. Kornilov, *The Chemistry of the Metallides*, Consultants Bureau, New York (1966).

phases. In this section examples of only the first two are given (Table 38). There is a decreasing tendency of elements in a group to form Cr_3Si -type phases with increasing period number; thus Hf and W (third period) do not form this phase. Although this trend has not been explained, it may be of electronic origin^{551a}.

TABLE 38. SIGMA^{551b} AND LAVES^{551c} PHASES^a IN BINARY TUNGSTEN ALLOYS, W_xX_y

Compound	X (atom %)	T (°C)	c (Å)	a (Å)	c/a	r_A/r_B	e/A^b	Type
—	Tc, 75	700	—	—	—	1.04	6.75	S
—	Ru, 40	1650	—	—	—	1.05	6.80	S
—	Re, 42–63	1200	—	—	—	1.02	6.42–6.63	S
—	Os, 21–32	2200	—	—	—	1.04	6.42–6.70	S
—	Ir, 30	near m.p.	—	—	—	1.04	6.90	S
WBe ₂ ^c	—	—	7.289	4.446	1.639	1.248	3.33	L
WFe ₂ ^c	—	—	7.719	4.736	1.627	1.105	7.33	L
WOs ₂ ^d	—	—	—	—	—	—	—	L
ZrW ₂ ^d	—	—	—	7.615	—	1.138	5.33	L
HfW ₂ ^d	—	—	—	7.571	—	1.122	5.33	L

^a Strukturbericht types: δ (S), $D8_b$ (tetragonal); Laves (L), C15 (cubic), C14, C36, hexagonal.

^b Electron: atom ratio.

^c C14.

^d C15.

2.2. BINARY COMPOUNDS OF TUNGSTEN WITH NONMETALS^{547, 548, 553, 554}

The binary compounds of tungsten with nonmetallic elements resemble closely those of molybdenum and corresponding compounds are often isomorphous. Some of the principles of this area of chemistry have been stated in Part I, Section 2.2; see also Part II) Section 2.2. References 553 and 554 contain phase diagrams of some of the W-nonmetal systems.

Tungsten borides (W_xB_y) are prepared by reaction of the elements ($x:y = 2:1; 1:1; 2:5; 1:4$). They are refractory solids with metallic electrical conductivity^{555a, 556a, 557, 558}.

Tungsten carbides (W_2C , WC) can be made by reaction of the elements in a reducing atmosphere at high temperature. They have melting points $>1600^\circ\text{C}$. They are of great

⁵⁵¹ M. V. Nevitt, "Alloy Chemistry of Transition Elements", in *Electronic Structure and Alloy Chemistry of the Transition Elements*, Interscience, New York (1963): (a) p. 127; (b) p. 105; (c) p. 146.

⁵⁵² J. H. Wernick, "Topologically Close-Packed Structures", in *Intermetallic Compounds*, John Wiley, New York (1967).

⁵⁵³ W. E. Pearson, *Handbook of Lattice Spacings and Structures of Metals, I*, Pergamon Press, Oxford (1958).

⁵⁵⁴ W. E. Pearson, *Handbook of Lattice Spacings and Structures of Metals, II*, Pergamon Press, Oxford (1967).

⁵⁵⁵ C. V. Samsonov (ed.), *Handbook of the Physicochemical Properties of the Elements*, Plenum Press, New York (1968): (a) pp. 737, 743; (b) pp. 746, 752; (c) pp. 754, 760; (d) pp. 762, 776; (e) pp. 778, 786; (f) pp. 810, 823; (g) pp. 827, 834.

⁵⁵⁶ A. Chretien and W. Freundlich, in *Nouveau Traité de Chimie Minérale, 14*, Masson et Cie, Paris (1959): (a) p. 900; (b) p. 877; (c) p. 896; (d) p. 873; (e) p. 874; (f) p. 868.

⁵⁵⁷ E. K. Storms, "The Tungsten-Tungsten Carbide System", in *The Refractory Carbides*, Academic Press, New York (1967).

⁵⁵⁸ Ref. 550, pp. 23–27.

utility because of their extreme hardness, which makes them suitable materials for rock drills, metal-cutting tools and wire-drawing dies^{555b, 556b, 557}.

The tungsten silicides (W_xSi_y) ($x:y = 3:1; 5:3; 1:2$) are prepared by synthesis from the elements. They have high melting points and high resistance to oxidation and action of chemicals^{555c, 556c, 558, 559}.

Tungsten nitrides (W_xN_y) are typical berthollides, having high hardness and wear resistance but low strength ($x:y = 2:1; 1:1; 1:2$). They are interstitial compounds^{555d, 556d, 558, 559}.

Tungsten phosphides (WP, WP_2) resemble the molybdenum phosphides; they are refractory and corrosion resistant^{555e, 556e, 559}.

Tungsten disulfide, like MoS_2 , is a naturally occurring compound. It can be synthesized by reaction of the elements, reaction of H_2S and the oxide, and by fusion of WO_3 with S^{560} ; it has the same structure as MoS_2 . WS_3 is obtained by acidification of potassium thiotungstate^{555f, 556f, 559, 560}.

Selenides and tellurides of W (WSe_2 , WSe_3 , WTe_2), like those of Mo, are isomorphous with the corresponding sulfides. These compounds are stable in dilute nonoxidizing acids at room temperature but dissolve on heating^{555g, 556f, 559}. WSe_2 is a semiconductor⁵⁶¹. The usual form of WSe_2 (and of WS_2) is hexagonal; rhombohedral WSe_2 and WS_2 can be synthesized at high temperature and pressure⁵⁶².

2.3. TUNGSTEN COMPOUNDS OF π -ACCEPTOR LIGANDS

Tungsten, like molybdenum and chromium, forms many compounds of π -acceptor ligands, such as the hexacarbonyl⁵⁶³, carbonyl halides^{563, 564}, and many other compounds derived from the carbonyl by substitution of one or more CO molecules by other ligands such as NO^{565} , CN, halides, NH_3 , amines, nitriles, phosphines, arsines, etc.^{566, 567}. These include anionic carbonyls and substituted anionic carbonyls⁵⁶⁸, such as $[W(CO)_5]^{2-}$, $[W(CO)_5X]^-$, $[W(CO)_4X_2]^{2-}$ ($X = \text{halide}$); CO-bridged dinuclear anions, e.g. $[W_2(CO)_{10}]^{2-}$; halogen-bridged dinuclear anions, e.g. $[W_2(CO)_{10}I]^-$; halogen-bridged anions containing two different metals such as $[CrW(CO)_{10}X]^-$ ($X = I, Br$)^{569a}. By insertion reactions between $[W_2(CO)_{10}]^{2-}$ and metal halides, mixed metal complexes $[W_2(CO)_{10}MI_2]^{2-}$ ($M = Sn, Ge$) are formed⁵⁷⁰.

⁵⁵⁹ C. J. Smithells, "Crystal Structure", in *Metals Reference Book*, **1**, Plenum Press, New York, 4th edn. (1967), pp. 167–178.

⁵⁶⁰ F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965), p. 1425.

⁵⁶¹ R. Kershaw, M. Vlasse and A. Wold, *Inorg. Chem.* **6** (1967) 1599.

⁵⁶² M. S. Silverman, *Inorg. Chem.* **6** (1967) 1063.

⁵⁶³ F. Calderazzo, R. Ercoli and G. Natta, "Metal Carbonyls: Preparation, Structure and Properties", in *Organic Synthesis via Metal Carbonyls*, **1**, Interscience, New York (1968).

⁵⁶⁴ F. Calderazzo, "Halogeno Metal Carbonyls and Related Compounds", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 401.

⁵⁶⁵ F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.* **3** (1964) 1609.

⁵⁶⁶ G. R. Dobson, I. W. Stolz and R. K. Sheline, "Substitution Products of the Group VIB Metal Carbonyls", in *Advances in Inorganic Chemistry and Radiochemistry*, **8**, Academic Press, New York (1965).

⁵⁶⁷ T. A. Manuel, "Lewis Base-Metal Carbonyl Complexes", in *Advances in Organometallic Chemistry*, **3**, Academic Press, New York (1965), p. 196.

⁵⁶⁸ R. B. King, "Reactions of Alkali Metal Derivatives of Metal Carbonyls and Related Compounds", in *Advances in Organometallic Chemistry*, **2**, Academic Press, New York (1964), p. 182.

⁵⁶⁹ J. K. Ruff, *Inorg. Chem.* **7** (1968): (a) 1821; (b) 1818.

⁵⁷⁰ J. K. Ruff, *Inorg. Chem.* **6** (1967) 2080.

Compounds containing two different metals with metal-metal bonds have recently been prepared. The following are examples of such compounds: $[\text{WCo}(\text{CO})_9]^-$, $[\text{WMn}(\text{CO})_{10}]^-$ ^{569b}; $[\text{W}(\text{CO})_5\text{M}'\text{Cl}_3]^-$ ($\text{M}' = \text{Sn}, \text{Ge}$)⁵⁷¹; $\text{dipy}(\text{CO})_3\text{XWM}'\text{X}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}; \text{M}' = \text{Sn}, \text{Ge}$)⁵⁷²; $\text{dipy}(\text{CO})_3\text{ClW}\text{SnRCl}_2$ ($\text{R} = \text{C}_6\text{H}_5, \text{C}_2\text{H}_5, \text{CH}_3, \text{C}_4\text{H}_9$)⁵⁷²; $\text{dipy}(\text{CO})_3\text{ClWGeC}_6\text{H}_5\text{Cl}_2$ ⁵⁷²; $\text{phen}(\text{CO})_3\text{ClW}\text{SnRCl}_2$ ($\text{R} = \text{C}_2\text{H}_5, \text{CH}_3\text{O}$; $\text{dipy} = 2,2'$ -dipyridyl; $\text{phen} = 1,10$ -phenanthroline)⁵⁷².

In the mixed metal complex $[\text{DTH}(\text{CO})_3\text{WSnCH}_3\text{Cl}_2]$ ($\text{DTH} = \text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_2$, 2,5-dithiahexane), tungsten is 7-coordinate and tin is 5-coordinate^{573a}. There are four molecules per unit cell with the following parameters: a , 7.458 Å; b , 15.044 Å; c , 16.228 Å; β , 110.75°. The W-Sn bond length is 2.759 Å. In a similar Mo complex^{573b}, the Mo-Sn bond length is 2.753 Å; the near-equality of these lengths indicates that the covalent radii of W and Mo are very close (see Part II, Section 2.3).

Rates of displacement of CO from $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) by phosphite and phosphine indicate that the enthalpies of activation decrease in the order $\text{Cr}(\text{CO})_6 \sim \text{W}(\text{CO})_6 > \text{Mo}(\text{CO})_6$ ⁵⁷⁴. An order of lability of numerous ligands L has been established for *cis*- $[\text{M}(\text{CO})_4\text{L}_2]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$)⁵⁷⁵. For a given leaving group, the order of reactivity is $\text{Mo} > \text{Cr} > \text{W}$.

More detailed and extensive information about this very active field of chemistry will be found, for example, in the chapters on carbonyl, nitrosyl and cyanide complexes and compounds involving metal-metal bonds. Some of the applicable principles have been discussed in Part I, Section 2.3; see also Part II, Section 2.3.

2.4. ORGANOMETALLIC COMPLEXES OF TUNGSTEN⁵⁷⁶⁻⁵⁸¹

The organometallic complexes of tungsten closely resemble those of chromium and molybdenum (see Part I, Section 2.4, and Part II, Section 2.4). Currently there is great interest in organometallic complexes containing metal-metal bonds between two different metals, e.g. $(\text{CH}_3)_3\text{SnW}(\text{CO})_3(\pi\text{-C}_5\text{H}_5)$, $(\text{CH}_3)_2\text{ClSnW}(\text{CO})_3(\pi\text{-C}_5\text{H}_5)$ ⁵⁸²; $\text{R}_3\text{MM}'(\text{CO})_3(\pi\text{-C}_5\text{H}_5)$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$; $\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{M}' = \text{Ge}, \text{Sn}, \text{Pb}$)⁵⁸³. Another important recent development is the synthesis of and characterization of metal complexes of carborane ions^{584, 585} such as the dicarbollide ion $\text{B}_9\text{C}_2\text{H}_{11}^{2-}$ and of borohydride ions (e.g. B_3H_8^-)⁵⁸⁵.

⁵⁷¹ J. K. Ruff, *Inorg. Chem.* **6** (1967) 1502.

⁵⁷² K. Kummer and W. A. G. Graham, *Inorg. Chem.* **7** (1968) 310.

⁵⁷³ M. Elder and D. Hall, *Inorg. Chem.* **8** (1969): (a) 273; (b) 1268.

⁵⁷⁴ J. R. Graham and R. J. Angelici, *Inorg. Chem.* **6** (1967) 2082.

⁵⁷⁵ M. Graziani, F. Zingales and U. Belluco, *Inorg. Chem.* **6** (1967) 1582.

⁵⁷⁶ G. E. Coates, M. L. H. Green, P. Powell and K. Wade, *Principles of Organometallic Chemistry*, Methuen, London (1968).

⁵⁷⁷ E. O. Fischer and H. Werner, *Metal π -Complexes*, **1**, Elsevier, Amsterdam (1966).

⁵⁷⁸ M. L. H. Green and P. L. Nagy, "Allyl Metal Complexes"; J. Birmingham, "Synthesis of Cyclopentadienyl Metal Compounds", in *Advances in Organometallic Chemistry*, **2**, Academic Press, New York (1964).

⁵⁷⁹ G. R. Dobson, I. W. Stolz and R. K. Sheline, "Substitution Products of Group VIB Metal Carbonyls", in *Advances in Inorganic Chemistry and Radiochemistry*, **8**, Academic Press, New York (1965).

⁵⁸⁰ E. O. Fischer, *Inorg. Syn.* **7**, McGraw-Hill, New York (1963), p. 136.

⁵⁸¹ B. L. Shaw, *Inorganic Hydrides*, Pergamon Press, Oxford (1967), p. 86.

⁵⁸² N. A. D. Carey and H. C. Clark, *Inorg. Chem.* **7** (1968) 94.

⁵⁸³ H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.* **5** (1966) 1401.

⁵⁸⁴ M. F. Hawthorne, *Accounts of Chemical Research* **1** (1968) 281.

⁵⁸⁵ F. Klanberg, E. L. Muetterties and L. J. Guggenberger, *Inorg. Chem.* **7** (1968) 2272.

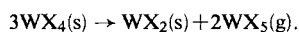
More detailed discussion of organometallic chemistry will be found in the chapters on organometallic compounds, metal carbonyls and metal-metal bonds.

2.5. OXIDATION STATE II

2.5.1. Tungsten(II) Halogen Compounds and Their Derivatives⁵⁸⁶⁻⁵⁸⁹

The chemistry of tungsten in the +2 oxidation state is essentially the chemistry of the halides and their derivatives. The isostructural halides MoCl_2 , MoBr_2 , WCl_2 and WBr_2 are characterized by the $[\text{M}_6\text{X}_8]^{4+}$ cluster (see Part II, Section 2.5.1).

Tungsten and molybdenum apparently do not form difluorides; reaction of the bromides with HF produces the hexafluorides. It is more difficult to obtain the other W(II) halides in the pure state than the Mo(II) halides. Production of WCl_2 by reduction of WCl_6 with Al, H_2 or P appears to be unsatisfactory. Tungsten(II) chloride and bromide can be prepared in good yield by disproportionation of the tetrahalides at 450–500°⁵⁹⁰:



The dibromide can also be prepared by reduction of the pentabromide—for example, by H_2 at 400–450°. It has been reported that the iodide can be prepared by reducing WCl_6 with HI vapor, or reaction of I_2 with W at red heat. Estimated thermodynamic data for these halides have been summarized by Fergusson⁵⁸⁷.

In the $[\text{W}_6\text{X}_8]^{4+}$ cluster the metal atoms are bonded to each other in an octahedron; each W atom (at a vertex of the octahedron) is at the center of a face of a surrounding cube at each corner of which is a halogen atom (see Fig. 12). Each W atom can bind one more group; and thus whenever complexes are formed with these halides, the $[\text{W}_6\text{X}_8]^{4+}$ cluster acts as hexacoordinate center, i.e. the number of donor atoms bound external to the cage is six as in $[\text{W}_6\text{Cl}_8]\text{B}_2\text{Cl}_2$ in which B is a bidentate ligand such as *o*-phenanthroline.

In the halides themselves, these atoms are, of course, halogen atoms, four of which (in a plane) bridge to adjacent clusters to form a two-dimensional structure; the other two are above and below the cube. Thus, of the four halogens required for electrical neutrality, any $[\text{W}_6\text{X}_8]^{4+}$ unit has two associated only with itself and four shared equally with adjacent units; this composition may be formulated $[\text{W}_6\text{X}_8]\text{X}_2\text{X}_{4/2}$. The W(II) halides are diamagnetic, as expected.

Although the $[\text{W}_6\text{X}_8]^{6+}$ cluster remains intact in some chemical reactions, the W(II) halides are less stable than the Mo(II) halides; for example, they are oxidized even by water and it is easier to substitute the halogen atoms by other halogens. The bromide W_6Br_{12} can be oxidized to bromides in which W has a higher oxidation state and any of these are converted back to W_6Br_{12} by strong heating; it appears that the W_6 cluster persists in these reactions and the various compounds may therefore be formulated WB_6F_{12} , W_6Br_{16} and W_6Br_{18} . The average W–W distance in the W_6 cluster is 2.64 Å as compared with 2.741 Å in the metal.

⁵⁸⁶ J. D. Corbett, "Metal Halides in Low Oxidation States", in *Preparative Inorganic Reactions*, **3**, Interscience, New York (1966), p. 8.

⁵⁸⁷ J. E. Fergusson, "Halide Chemistry of Chromium, Molybdenum and Tungsten", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 249.

⁵⁸⁸ R. V. Parish, "The Inorganic Chemistry of Tungsten", in *Advances in Inorganic Chemistry and Radiochemistry*, **9**, Academic Press, New York (1966), pp. 320, 324, 331, 345.

⁵⁸⁹ M. C. Baird, "Metal-Metal Bonds in Transition Metal Compounds", in *Progress in Inorganic Chemistry*, **9**, Interscience, New York (1968), p. 23.

⁵⁹⁰ R. E. McCarley and T. M. Brown, *Inorg. Chem.* **3** (1964) 1232.

Tungsten(II) chloride dissolves in HCl. From the solution, the yellow crystalline compound $\text{H}_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]\cdot 8\text{H}_2\text{O}$, can be precipitated; it decomposes in air but can be kept over HCl. The complexes $\text{H}_2[(\text{M}_6\text{Cl}_8)\text{X}_2]\cdot 8\text{H}_2\text{O}$ ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{Cl}, \text{Br}$) are isomorphous.

2.5.2. Potassium Cyanotungstate(II)⁵⁹¹

By reduction of $\text{K}_4[\text{W}(\text{CN})_8]$ with H_2 ($330\text{--}390^\circ$), HCN is evolved and the W(II) complex, $\text{K}_4[\text{W}(\text{CN})_6]$, is produced. When this is extracted with methanol in dry air, it is oxidized to the W(III) complex, $\text{K}_3[\text{W}(\text{CN})_6]$. The analogous Mo compounds are formed by similar reactions.

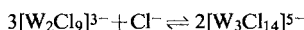
2.6. OXIDATION STATE III

2.6.1. Tungsten(III) Halogen Compounds^{592, 593}

Apparently the only W(III) halide known is the bromide. If W(II) bromide is left in contact with liquid bromine at 50° for a long time, a black compound, WBr_3 , is formed which decomposes to WBr_2 above 80° ⁵⁹⁴.

The W(III) complex $\text{K}_3[\text{W}_2\text{Cl}_9]$ may be crystallized from a W(III) solution obtained by electrolytic reduction of an acid K_2WO_4 solution^{595, 596}. This salt (yellowish-green hexagonal crystals) decomposes slowly in air. It is soluble in water but only slightly soluble in concentrated HCl or ethanol. A solution of W(III) can also be obtained by reducing K_2WO_4 (in concentrated HCl) with Sn and from this solution $\text{K}_3[\text{W}_2\text{Cl}_9]$ can be crystallized⁵⁹⁷.

From the latter solution, another product was obtained, supposed to be $\text{K}_5[\text{W}_3\text{Cl}_{14}]$. Presumably there was an equilibrium⁵⁹⁷:



and it was reported that either $\text{K}_2[\text{W}_2\text{Cl}_9]$ or $\text{K}_5[\text{W}_3\text{Cl}_{14}]$ could be obtained by adjusting the KCl concentration during the reduction. The second product is more soluble; its aqueous solutions are deep red and it is more easily oxidized than $\text{K}_5[\text{W}_2\text{Cl}_9]$. It has since been shown (by, among other methods, X-ray diffraction) that the product thought to be $\text{K}_5[\text{W}_3\text{Cl}_{14}]$ is a mixture of $\text{K}_3[\text{W}_2\text{Cl}_9]$ and $\text{K}_2[\text{W}(\text{OH})\text{Cl}_5]$ ⁵⁹⁸; reports of the ions $[\text{W}_3\text{Cl}_{17}]^{8-}$ and $[\text{Mo}_3\text{F}_{14}]^{5-}$ may also be erroneous for similar reasons.

Several salts of the $[\text{W}_2\text{Cl}_9]^{3-}$ ion have been prepared. The cations are: NH_4^+ , K^+ , Rb^+ , Cs^+ , Tl^+ , $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$, $[\text{Ag}(\text{NH}_3)_2]^+$, $\text{C}_6\text{H}_5\text{NH}_3^+$, pyH^+ ($\text{py} = \text{pyridine}$); the salts of the first four are isomorphous. They are all either diamagnetic or only weakly paramagnetic. In the $[\text{W}_2\text{Cl}_9]^{3-}$ ion, each W is octahedrally surrounded by six chloride ions,

⁵⁹¹ J. S. Yoo, E. Griswold and J. Kleinberg, *Inorg. Chem.* **6** (1965) 365.

⁵⁹² J. E. Fergusson, "Halide Chemistry of Chromium, Molybdenum and Tungsten", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 254.

⁵⁹³ R. V. Parish, "The Inorganic Chemistry of Tungsten", in *Advances in Inorganic Chemistry and Radiochemistry*, **9**, Academic Press, New York (1966), pp. 321, 324, 331.

⁵⁹⁴ R. E. McCarley and T. M. Brown, *J. Am. Chem. Soc.* **84** (1962) 3216; R. Siepmann and H. Schaffer, *Naturwissenschaften*, **52** (1965) 344.

⁵⁹⁵ H. B. Jonassen, A. R. Tarsey, S. Cantor and G. F. Helferich, *Inorg. Syn.* **5**, McGraw-Hill, New York (1957), p. 139.

⁵⁹⁶ F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965), p. 1427.

⁵⁹⁷ R. A. Laudise and R. C. Loring, *Inorg. Syn.* **6**, McGraw-Hill, New York (1960), p. 149.

⁵⁹⁸ E. König, *Inorg. Chem.* **2** (1963) 1238.

the two octahedra sharing a trigonal face; the structure is distorted because the W-W distance is very short (2.41 Å), indicating W-W bonding.

Although the W-Cl bond lengths are not all the same, all the chloride ions appear to be equally labile. Investigation with radioactive chloride indicates that complete exchange of all the nine chloride ions occurs. Attempts to replace the chloride with iodide or bromide cause decomposition with oxidation and formation of hydrated WO₂; the complex also oxidizes in aqueous solution.

Reaction of hot pyridine with K₃[W₂Cl₉] has been reported to produce [W₂Cl₆py₃]⁵⁹⁶, but more recent investigations show that the product is [W₂Cl₆py₄] (diamagnetic)^{599, 600}; K₃[CrCl₉], however, reacts with pyridine to form monomeric [CrCl₃py₃]. In the conversion of K₃[W₂Cl₉] to [W₂Cl₉py₄], the W-W distance increases to only 2.6 Å, indicating considerable interaction remaining between the two W atoms. Other compounds of this type, [W₂Cl₆L₄], were also obtained with 4-picoline and 4-isopropylpyridine⁵⁹⁹. The structure of these compounds is presumably two octahedra sharing an edge, resulting from the breaking of one bridging bond in [W₃Cl₉]³⁻.

The stability of the [W₂Cl₉]³⁻ ion is such that oxidation (or loss of electrons involved in the metal-metal bonding) is necessary to produce mononuclear compounds. For example, reaction of this ion with CN⁻ produces [W(CN)₈]⁴⁻ and heating of a mixture of (NH₃)₃[W₂Cl₉] and 8-hydroxyquinoline forms the 8-coordinate W(IV) chelate.

There are no W(III) halogen complexes analogous to the Mo(III) complexes [MoX₆]³⁻ (X = Cl, Br, I). In the older literature there are reports of compounds such as KWF₄·9H₂O.

2.6.2. Potassium Cyanotungstate(III)

When K₄[W(CN)₈] is heated in H₂ (330–390°), reduction occurs with production of HCN and K₄[W(CN)₆]. When this is extracted (in air) with methanol, it is oxidized to K₃[W(CN)₆]⁶⁰¹.

2.7. OXIDATION STATE IV

2.7.1. Tungsten(IV) Halogen Compounds^{602–605}

The W(IV) halides may be prepared as follows: *fluoride*: reaction of WF₆ with benzene in a bomb at 110°; *chloride*: reduction of WCl₆ with Al⁶⁰⁶ or white P; *bromide*: reduction of WBr₅ with Al or W or disproportionation of WBr₅ at 180° *in vacuo*; *iodide*: reduction of WCl₆ with HI or reaction of WO₂ with AlI₃. The mixed halide WBrCl₃ is obtained by oxidations of [W₂Cl₉]³⁻ with Br₂.

These tetrahalides are easily hydrolyzed and oxidized. When heated, they react as follows: WF₄ decomposes at 800° *in vacuo*; WX₄ (X = Cl, Br) decomposes to WX₅ and

⁵⁹⁹ R. Saillant, J. L. Hayden and R. A. D. Wentworth, *Inorg. Chem.* **6** (1967) 1497.

⁶⁰⁰ R. Saillant and R. A. D. Wentworth, *Inorg. Chem.* **7** (1968) 1606.

⁶⁰¹ J. S. Yoo, E. Griswold and J. Kleinberg, *Inorg. Chem.* **4** (1965) 365.

⁶⁰² J. E. Fergusson, "Halide Chemistry of Chromium, Molybdenum and Tungsten", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 259.

⁶⁰³ J. D. Corbett, "Metal Halides in Low Oxidation States", in *Preparative Inorganic Reactions*, **3**, Interscience, New York (1966), pp. 7, 8.

⁶⁰⁴ G. W. A. Fowles, "Halide and Oxyhalide Complexes", in *Preparative Inorganic Reactions*, **1**, Interscience, New York (1964), pp. 128, 129, 132, 135, 138, 139.

⁶⁰⁵ R. V. Parish, "The Inorganic Chemistry of Tungsten", in *Advances in Inorganic Chemistry and Radiochemistry*, **9**, Academic Press, New York (1966), p. 315.

⁶⁰⁶ R. E. McCarley and T. M. Brown, *Inorg. Chem.* **3** (1964) 1232.

WX_2 (chloride, 300–500°; bromide 450–500°); WI_4 decomposes to WI_2 and I_2 . The tungsten compounds are more stable to thermal decomposition than their molybdenum analogs.

Tungsten tetrachloride and tetrabromide are formed as thin black needles. They are orthorhombic⁶⁰⁶ with unit cells of the following dimensions (a , b , c , respectively, in Å): chloride, 8.07, 8.89, 6.85; bromide, 8.49, 9.29, 7.25. These diamagnetic compounds are isomorphous with their Nb and Ta analogs. The structure of these compounds consists of infinite linear strings of octahedra sharing edges. The metal–metal distances are alternately short and long, implying the existence of direct metal–metal bonding⁶⁰⁷.

Tungsten(V) and -(IV) halides are reduced to W(IV) compounds by N-containing ligands such as pyridine, 2,2-dipyridyl, acetonitrile, etc.⁶⁰⁸. The products have the composition $\text{WX}_4 \cdot \text{L}_2$ and $\text{WX}_4 \cdot \text{B}$ (L = singly coordinating ligand; B = bidentate ligand). The pyridine complexes $\text{WCl}_4 \cdot \text{py}_2$ and $\text{WBr}_4 \cdot \text{py}_2$ can also be prepared by reaction of pyridine with the W(IV) halides⁶⁰⁶.

Complex halides $\text{M}_2[\text{WX}_6]$ ($\text{X} = \text{Cl}, \text{Br}$) may be prepared by heating the higher halides such as WCl_6 with the appropriate metal iodide which is needed for complete reduction (M , complex chloride; Rb, Cs, Tl, 1/2 Ba; complex bromide; K, Rb, Cs). Tungsten(VI) chloride is reduced by reaction with primary and secondary amines with formation of analogous amine salts (M : Me_3NH , Me_2NH_2 , Et_2NH_2). The chloro salts are red; the bromo salts, green. They hydrolyze slowly in moist air. They react with liquid ammonia to form compounds such as $[\text{W}(\text{NH}_2)_3\text{Cl}]$ and with pyridine to produce, for example, $\text{K}[\text{WCl}_5\text{py}]$ and $\text{WX}_4 \cdot \text{py}_2$.

Apparently the only oxyhalide known is the fluoride, WOF_2 , an inert black nonvolatile powder. This is prepared by the reaction of WO_2 with HF at 500°. It is resistant to boiling alkali solutions, concentrated acids and aqua regia. Ignition in air at 700° converts it to WO_3 .

2.7.2. Potassium Cyanotungstate(IV)⁶¹⁰

Potassium octacyanotungstate(IV), $\text{K}_4[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$, is prepared by air oxidation of a W(III)–KCN solution^{610, 611a}. The W(III) solution may be obtained by dissolving $\text{K}_2[\text{W}_2\text{Cl}_9]$ or by reducing a W(VI) solution electrochemically or with Sn⁶⁰⁹. The product consists of orange tetragonal crystals. The $[\text{W}(\text{CN})_8]^{4-}$ ion is dodecahedral and isostructural with the $[\text{Mo}(\text{CN})_8]^{4-}$ ion. It is easily oxidized by MnO_4^- or Ce^{4+} to $[\text{W}(\text{CN})_8]^{3-}$. The standard potential of the $[\text{W}(\text{CN})_8]^{4-}/[\text{W}(\text{CN})_8]^{3-}$ couple is 0.457 V (vs. standard hydrogen electrode, 25°).

An aqueous solution of $\text{K}_4[\text{W}(\text{CN})_8]$ is neutral and stable to acid and alkali. In alkaline solution in sunlight, aquation occurs. Electron exchange between W(IV) and W(V) in the octacyanide ions is very fast but exchange of labeled CN^- with $[\text{W}(\text{CN})_8]^{4-}$ is slow and depends on the light intensity.

The photohydrolysis products of $[\text{W}(\text{CN})_8]^{4-}$ are $[\text{WO}_2(\text{CN})_4]^{4-}$ (yellow–brown) and $[\text{WO}(\text{OH})(\text{CN})_4]^{3-}$ (purple), i.e. 6-coordinate W(IV) complexes and not $[\text{W}(\text{CN})_4(\text{OH})_4]^{4-}$.

⁶⁰⁷ D. L. Kepert and R. Mandyczewsky, *Inorg. Chem.* **7** (1968) 2091.

⁶⁰⁸ T. M. Brown and B. Ruble, *Inorg. Chem.* **6** (1967) 1335.

⁶⁰⁹ E. A. Heintz, *Inorg. Syn.* **7**, McGraw-Hill, New York (1963), p. 142.

⁶¹⁰ B. M. Chadwick and A. G. Sharpe, "Transition Metal Cyanides and Their Complexes", in *Advances in Inorganic Chemistry and Radiochemistry*, **8**, Academic Press, New York (1966), p. 102.

⁶¹¹ F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965): (a) p. 1429; (b) p. 1421.

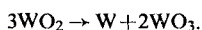
as previously formulated⁶¹². In these ions, two oxygens are *trans* to each other. Single crystal X-ray studies of $K_4[WO_2(CN)_4] \cdot 6H_2O$ show that it has cell constants essentially identical with those of the analogous Mo compound, i.e. space group, monoclinic $P2_1/c$; a , b , c , respectively 7.23, 13.48 and 9.35 Å; β , $113^\circ 45'$; number of formula weights per unit cell, 2.

2.7.3. Tungsten(IV) Oxide⁶¹³

Tungsten(IV) oxide may be prepared by reducing WO_3 with hydrogen containing water vapor, at 800 – 900° , or by heating a mixture of WO_3 and W in the stoichiometric ratio (2:1) in an evacuated sealed tube at 950° . The first method requires about 2 hr, the second 40 hr^{611b}.

Tungsten(IV) oxide is a brown crystalline powder. It has a deformed rutile structure^{605, 614} (C_4) containing WO_6 octahedra linked in chains by common edges. The chains are combined into two-dimensional layers by sharing of apical oxygen atoms. Within the chains, alternate W–W distances are 2.49 and 3.08 Å as compared with 2.74 Å in the metal. This oxide is diamagnetic.

Its melting point is 1500 – 1600° (under N_2); its boiling point is 1730° . It is quite volatile above 1050° . Heated in an inert atmosphere, it undergoes some disproportionation:



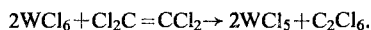
It is stable, however, in an atmosphere of 40–55% H_2 and 45–60% H_2O at 900° .

2.8. OXIDATION STATE V

2.8.1. Tungsten(V) Halides^{615, 616a}

The only W(V) halides reported are the chloride and bromide. The chloride (dark green, m.p. 248°) may be prepared by reduction of WCl_6 with H_2 (380 – 400°)^{617a} or red P (250 – 280°), or by disproportionation of WCl_4 ⁶¹⁸. The bromide (black, green iridescence, m.p. 286°) is obtained by reduction of WCl_6 with HBr ; bromination of W, or bromination of $W(CO)_6$ at low temperature, produces WBr_6 which, when heated, decomposes to WBr_5 .

A recent method⁶¹⁹ for preparing the chloride comprises heating the hexachloride with tetrachloroethylene at 100° in strong light:



The yield is 90–94%. The reaction does not occur at low temperature or in the absence of light. With the same reagent, $MoCl_5$ is converted to $MoCl_4$ (Part II, Section 2.7.1).

⁶¹² S. J. Lippard and B. J. Russ, *Inorg. Chem.* **6** (1967) 1943.

⁶¹³ A. Chretien and W. Freundlich, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959), p. 826.

⁶¹⁴ D. B. Rogers, R. D. Shannon, A. W. Sleight and J. L. Gillson, *Inorg. Chem.* **8** (1964) 841.

⁶¹⁵ J. E. Fergusson, "Halide Chemistry of Chromium, Molybdenum and Tungsten", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 265.

⁶¹⁶ A. D. Beveridge and H. C. Clark, "Pentahalides of the Transition Metals", in *Halogen Chemistry*, **3**, Academic Press, New York (1967): (a) pp. 187, 194, 204, 218; (b) p. 212.

⁶¹⁷ F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965): (a) p. 1419; (b) p. 1430.

⁶¹⁸ T. M. Brown and B. Ruble, *Inorg. Chem.* **6** (1967) 1335.

⁶¹⁹ T. M. Brown and E. L. McCann III, *Inorg. Chem.* **7** (1968) 1227.

Although the structure of the W(V) halides is not known, it may be presumed that it is similar to that of the Mo(V) halides. In the vapor phase, MoCl_5 is monomeric and has a trigonal bipyramidal structure; it dimerizes in the solid state. On the basis of the low magnetic moments (1.12 B and 1.07 B for the chloride and bromide respectively), a trimeric structure has been proposed, i.e. $[\text{W}_3\text{X}_{12}]\text{X}_3$, but the low values might be due to the spin-orbit coupling.

The W(V) halides are more stable than their Mo(V) analogs. They decompose thermally as follows:



Under certain reaction conditions⁶¹⁸, W(VI) and W(V) halides are reduced by various N-containing ligands such as pyridine, 2,2'-dipyridyl and acetonitrile. The products are W(IV) complexes of the types WX_4L_2 and WX_4B (L = singly coordinating ligand; B = bidentate ligand). Fergusson⁶¹⁵, however, has reported the preparation of W(V) complexes by reaction of some of these ligands with WBr_5 and WCl_6 , i.e. in the first case no reduction occurred and in the second W(VI) was reduced to W(V). The reactions were conducted in the absence of oxygen and oxygen-containing solvents. The following complexes were obtained: $\text{WX}_5 \cdot 2\text{py}$, $\text{WCl}_5 \cdot \text{dipy}$, $\text{WBr}_5(o\text{-phen})$ and $\text{WBr}_5(\text{Ph}_3\text{P})_2$ (py, pyridine; dipy, 2,2'-dipyridyl; *o*-phen, *o*-phenanthroline; Ph_3P , triphenylphosphine). Difference in experimental conditions⁶²⁰ accounts for the apparent discrepancy between the two sets of results.

Tungsten(V) complexes⁶¹⁸ are also obtained with 2,4,6-trimethylpyridine and benzonitrile. They are formulated $[\text{WX}_4\text{L}_2]\text{X}$ (X = Cl, Br) on the basis of conductivity measurements of nitromethane solutions. Solution and reflectance spectra indicate that they also exist in this form in the solid state. They are slightly soluble in organic solvents such as acetonitrile, benzene and chloroform. They decompose when exposed to the atmosphere. Reaction of W(V) halides with primary amines leads to formation of amino-basic W(V) halides⁶²¹.

2.8.2. Tungsten(V) Halide and Oxyhalide Complexes^{615, 616b, 622}

Numerous W(V) halide complexes have been described, e.g.:

$\text{M}[\text{WF}_6]$ (white): (M = Li, Na, K, Rb, Cs, NO).

$\text{M}[\text{WCl}_6]$ (green): (M = Na, K, Rb, Cs, Et_4N , Me_4N , Ph_4As) (Ph = C_6H_5).

$\text{M}[\text{WBr}_6]$ (dark green or black): (M = EtNH_3 , Et_2NH_2 , Et_3NH).

The preparative methods are as follows:

$\text{M}[\text{WF}_6]$; reduction of hexafluoride with MI in liquid SO_2 or fluorination with SF_4 or IF_5 of $\text{W}(\text{CO})_6$ in the presence of MF or MI.

$\text{M}[\text{WCl}_6]$; melting mixtures of WCl_6 and MCl (or MI), reaction of MCl with WCl_6 in thionyl chloride, reaction of MCl with WCl_5 in chloroform, reaction of K_2WO_4 with CCl_4 at 400° , reaction of WCl_6 with $\text{K}_2[\text{WCl}_6]$ (room temperature).

$\text{M}[\text{WBr}_6]$; reduction of WBr_6 with MI or reaction of MBr with WBr_5 in an inert solvent.

The compounds $\text{M}_2[\text{WCl}_7]$ (M = K, Rb, Cs) have been reported as formed in the WCl_6 -MCl melts.

⁶²⁰ J. E. Fergusson, private communication.

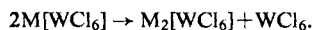
⁶²¹ B. J. Brisdon and G. W. A. Fowles, *J. Less Common Metals*, **7** (1964) 102.

⁶²² G. W. A. Fowles, "Halide and Oxyhalide Complexes", in *Preparative Inorganic Reactions*, **1**, Interscience, New York (1964), pp. 126, 132, 134.

By reaction of W(CO)_6 and KI (2:1 ratio) in IF_5 , the octafluoride $\text{K}_3[\text{WF}_8]$ is obtained. The rubidium and cesium salts have also been prepared.

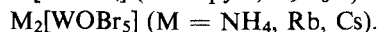
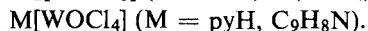
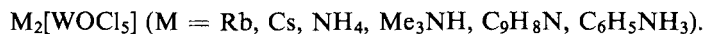
Since the fluoro compounds are isomorphous with the analogous hexafluoroantimonates(V), the anions are octahedral. Presumably the other complex halo anions are also octahedral, with the possible exceptions of $[\text{WF}_8]^{3-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). The magnetic moments are low because of spin-orbit coupling.

The complex halogen-tungsten(V) salts are quite stable when dry even when heated but are susceptible to hydrolysis. When the green salts $\text{M}[\text{WCl}_6]$ ($\text{M} = \text{K}, \text{Cs}$) are heated for a long time *in vacuo* (250–300°), WCl_6 is lost and W(IV) complexes are formed:



Tungsten(V) oxychloride (WOCl_3) is an olive-green product obtained by reduction of WOCl_4 by Al in a sealed tube (100–140°). It is slightly paramagnetic. It may be polymeric with $(\text{WOCl}_3)_2$ units linked in chains via oxy-bridges (analogous to the structure of NbOCl_3). The oxychloride WOCl_4 may be present in the melt of WCl_6 and WO_3 .

Many salts of the W(V) oxyhalo anions have been described, e.g.:



These salts are prepared by adding the cation to an aqueous solution of the anion, obtained by dissolving the pentahalide or potassium oxalatodioxytungstate(V) in HCl or HBr . These complexes are stable in dry air but are rapidly hydrolyzed by moisture; there is a color change from the original green–yellow color to red, then blue.

The magnetic moments of the $[\text{AOX}_5]^{2-}$ complexes ($\text{A} = \text{Mo}, \text{W}$) are close to the spin-only value presumably because tetragonal distortion destroys the spin–orbit coupling. These ions, as well as the corresponding ion $[\text{NbOX}_5]^{2-}$, belong to the point group C_{4v} .⁶²³ The far-infrared spectra of the salts $\text{M}_2[\text{AOX}_5]$ ($\text{M} = \text{Rb}, \text{Cs}$; $\text{A} = \text{Mo}, \text{W}, \text{Nb}$; $\text{X} = \text{Cl}, \text{Br}$) have been compared and the observed bands have been assigned.⁶²³

By reaction of WCl_5 with tetralkylammonium chloride at 0°, at 25°, in neutral alcohol or alcohol saturated with HCl , alkoxide complexes of the following types have been prepared: $\text{M}[\text{W(OR)}_2\text{Cl}_4]$, $\text{M}_2[\text{WORCl}_6]$, $\text{M}[\text{WORCl}_5]$, $[\text{W}_2\text{Cl}_4(\text{OR})_6]$, $[\text{W}_2\text{Cl}_2(\text{OR})_8]$.⁶²⁴ The cations, M , were pyridinium or tetralkylammonium (alkyl group, methyl ethyl, n-propyl); R was CH_3 , C_2H_5 or $n\text{-C}_3\text{H}_7$. By reaction of LiOR or NaOR with WCl_5 in alcohol, dimers are obtained: $[\text{W}_2\text{Cl}_4(\text{OR})_6]$, $[\text{W}_2\text{Cl}_2(\text{OR})_8]$. As the number of alkoxide group increases, the magnetic moments increase; this suggests formation of a strong W-O multiple bond, resulting in lowering the spin–orbit contribution to the magnetic moment. Octahedral or tetragonal symmetry is suggested by the electronic spectra of these compounds.

2.8.3. Tungsten(V) Oxalato Complex, $\text{K}[\text{WO}_2(\text{C}_2\text{O}_4)] \cdot \text{XH}_2\text{O}$ ⁶²⁵

The complex oxalate is prepared by reducing potassium tungstate with tin in a solution containing oxalic acid and potassium oxalate. The color of the solution changes from blue

⁶²³ A. Sabatini and I. Bertini, *Inorg. Chem.* **5** (1966) 204.

⁶²⁴ D. P. Rillema, W. J. Reagan and C. H. Brubaker, Jr., *Inorg. Chem.* **8** (1969) 587.

⁶²⁵ Ref. 622, p. 137.

to green to red. Tin is removed as tin sulfide from the red solution from which red crystals of the oxalato complex are then slowly deposited. This appears to be the only W(V) oxalato complex known.

2.8.4. Potassium Octacyanotungstate(V)

The octacyanotungstate, $K_3[W(CN)_8] \cdot H_2O$ (yellow crystals), is prepared by oxidizing a solution of the octacyanotungstate(IV)—for example, by permanganate^{617b}. The $[W(CN)_8]^{3-}$ ion is stable in the dark to hydrolysis, reduction and CN^- exchange. Exposure to light causes reduction followed by hydrolysis of the W(IV) complex (see Section 2.7.2). The W(V) complex is also reduced to the W(IV) complex by iodide and hydrogen peroxide. The magnetic moment of $K_3[W(CN)_8] \cdot H_2O$ is 1.61 B; its optical spectrum resembles that of the analogous Mo(V) compound. In solution, its structure is the Archimedean antiprism, as indicated by e.p.r. measurements of frozen glycerine solutions⁶²⁶.

2.9. OXIDATION STATE VI

2.9.1. Tungsten(VI) Halides^{627, 628}

The W(VI) halides may be prepared as follows:

WF₆ (pale yellow liquid, m.p., 1.9°, b.p. 17.08°): reaction of F₂⁶²⁹, ClF₃, BrF₃ or ClF (25°)⁶³⁰ with W, reaction of BrF₃, SF₄ or HF with WO₃, reaction of ReF₆ with W(CO)₆ in IF₅, reaction of HF, AsF₃ or SbF₃ with WCl₆.

WCl₆ (blue-black crystals, m.p. 275°, b.p. 346°): reaction of Cl₂^{631, 632a} or S₂Cl₂ with W, reaction of Cl₂, S₂Cl₂, PCl₅, HCl, COCl₂, SOCl₂, CCl₄^{632a}, or hexachloropropene⁶³³ with WO₃, reaction of HCl with WS₃.

WBr₆ (dark blue solid): reaction of Br₂ with W or W(CO)₆.

WF₅Cl (unstable yellow liquid): reaction of TiCl₄ with WF₆.

The molecules of the hexahalides are octahedral (symmetry O_h); they are weakly paramagnetic. The W-X distance (Å) in WF₆ (vapor) is 1.826; in WCl₆, it is 2.26 in the vapor phase and 2.24 in the solid. The hexafluoride exists in a cubic modification near room temperature and in a phase of lower symmetry (probably orthorhombic) at lower temperatures⁶³⁴. The transition temperature is -8.5°. The cell constants (Å) are: $a = 6.28$ (0°); $a = 9.68$, $b = 18.81$, $c = 5.09$ (-30°). The average W-X bond strengths (kcal) are 123 (W-F) and 73.7 (W-Cl). The compounds are monomeric in the vapor state. The solubility of WF₆ in anhydrous HF (room temperature) is 3.14 moles per 1000 g HF⁶³⁵; the con-

⁶²⁶ B. R. McGarvey, *Inorg. Chem.* **5** (1966) 476.

⁶²⁷ J. E. Fergusson, "Halide Chemistry of Chromium, Molybdenum and Tungsten", in *Halogen Chemistry*, **3**, Academic Press, New York (1967), p. 276.

⁶²⁸ E. L. Muetterties and C. W. Tullock, "Binary Fluorides", in *Preparative Inorganic Reactions*, **2**, Interscience, New York (1965), pp. 241, 249, 257, 269, 281.

⁶²⁹ H. F. Priest, *Inorg. Syn.* **3**, McGraw-Hill, New York (1950), p. 181.

⁶³⁰ J. J. Pitts and A. W. Jache, *Inorg. Chem.* **7** (1968) 1661.

⁶³¹ M. H. Lietzke and M. L. Holt, *Inorg. Syn.* **3**, McGraw-Hill, New York (1950), p. 163.

⁶³² F. Hein and S. Herzog, in *Handbook of Preparative Inorganic Chemistry*, **2**, Academic Press, New York, 2nd edn. (1965): (a) p. 1417; (b) p. 1423.

⁶³³ W. W. Porterfield and S. Y. Tyree, Jr., *Inorg. Syn.* **9**, McGraw-Hill, New York (1967), p. 133.

⁶³⁴ S. Siegel and D. A. Northrop, *Inorg. Chem.* **5** (1966) 2187.

⁶³⁵ B. Frlac and H. H. Hyman, *Inorg. Chem.* **6** (1967) 1596.

ductivity of the solution (0°) is $0.35 \text{ ohm}^{-1} \text{ cm}^{-1} \text{ mole}^{-1}$. The free energy of the F^- - Cl^- exchange at 25° ($\Delta G^\circ_{\text{MCl}} - \Delta G^\circ_{\text{MF}}$) is 46.4 kcal per mole.

The hexahalides hydrolyze readily. The chemical reactivity of the highest fluorides of Cr, Mo and W decreases in the order $\text{CrF}_5 > \text{MoF}_6 > \text{WF}_6$ in both oxidation-reduction and halogen exchange reactions; the bond-stretching force constants (from spectral data) are 4.73 and 5.13 respectively for Mo-F and W-F⁶³⁶. Tungsten(VI) fluoride forms adducts such as $\text{WF}_6 \cdot 4.5\text{SO}_3$, $\text{WF}_6(\text{NH}_3)_4$, WF_6py_3 , $\text{WF}_6(\text{CH}_3\text{NH}_2)_3$ (py = pyridine). Ammonia below 0° forms adducts with WCl_6 ; at higher temperatures two, three or four W-Cl bonds are ammonolyzed. The chloride reacts with amines to form products as follows: primary aliphatic, $\text{WCl}_6(\text{NHR})_4$; primary aromatic (ar), $[\text{War}_6]\text{Cl}_6$; secondary, 1:1 adduct followed by reduction to $[\text{R}_2\text{NH}_2]_2\text{WCl}_6$; (tertiary, similar reactions). Alcoholysis also causes reduction to blue paramagnetic alkoxides, $\text{WCl}_3(\text{OR})_2$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$); the ethyl compound reacts further to form the dimer $\text{W}_2\text{Cl}_4(\text{OEt})_6$. Reaction of WCl_6 with phenols leads to phenoxides, $\text{WCl}_6(\text{Oar})_4$ and $\text{W}(\text{Oar})_6$ ^{632a} (ar = aromatic nucleus). The bromide easily decomposes to WBr_5 and Br_2 .

2.9.2. Tungsten(VI) Oxyhalides^{627, 637}

Preparative methods for the W(VI) oxyhalides are as follows:

WOF_4 (white, m.p. 110° , b.p. 190°): reaction of: HF with WOCl_4 ; WO_3 with F_2 or SeF_4 and IF_5 ; WO_2 with CCl_2F_2 ; W with F_2 and O_2 (or HNO_3).

WOCl_4 (red-orange needles, m.p. 211° , b.p. 232°): chlorination of WO_3 with SOCl_2 ^{632a}, HCl , CCl_4 , S_2Cl_2 , S_2Cl_2 - Cl_2 mixture or WCl_6 ; chlorination of WO_3 or a mixture of WO_3 and WO_2 with octachlorocyclopentene⁶³⁸.

WO_2Cl_2 (yellow solid): controlled hydrolysis of WOCl_4 ; chlorination of WO_3 , WS^3 or WO_4^{2-} with, for example, CCl_4 , HCl or NaCl , Cl_2 - O_2 mixtures, S_2Cl_2 - Cl_2 mixtures, CCl_4 - O_2 mixtures; chlorination of metal in air.

WO_2Br_2 (red crystals): reaction of Br_2 - O_2 mixture with W, or bromination of WO_3 with Br_2 or CBr_4 .

WOBr_4 (black): bromination of WO_3 with CBr_4 or WO_3 -carbon mixture with Br_2 or WO_2 -W mixture with Br_2 .

WO_2I_2 : sublimation of product from mixture of W, WO_3 and I_2 in a sealed quartz tube.

The oxyhalides have also been generated as vapors in a cell comprising a stainless steel or mullite tube fitted with end windows for determination of infrared spectra⁶³⁹. The compounds studied were WO_2X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and WOX_4 ($\text{X} = \text{F}, \text{Br}, \text{I}$). The solid and liquid compounds contain polymeric species; the vapors are predominantly monomeric. The structural unit of WOX_4 ($\text{X} = \text{Cl}, \text{Br}$) is an almost square planer WX_4 ; these are linked in chains by the oxygen atoms. The bond lengths ($\text{\AA}$) are: W-Cl, 2.28; W-Br, 2.45; W-O, 2.2 and 1.8. The structure of the W unit is thus a distorted octahedron.

The dioxydihalides disproportionate to WO_3 and the oxytetrahalides at 200 – 300° . The

⁶³⁶ T. A. O'Donnell and D. F. Stewart, *Inorg. Chem.* **5** (1966) 1434.

⁶³⁷ G. W. A. Fowles, "Halide and Oxyhalide Complexes", in *Preparative Inorganic Reactions*, **1**, Interscience, New York (1964), pp. 126, 132.

⁶³⁸ S. E. Feil, S. Y. Tyree, Jr. and F. N. Collier, Jr., *Inorg. Syn.* **9**, McGraw-Hill, New York (1967), p. 123.

⁶³⁹ B. G. Ward and F. E. Stafford, *Inorg. Chem.* **7** (1968) 2569.

chlorine atoms in WOCl_4 can be displaced by alcohols, phenols and acid radicals to form compounds of the type $\text{WO}(\text{OR})_4$ (R = alkyl, aryl or carboxylate). Polytungstates are formed by hydrolysis of the alkoxy compounds. The hexachloride and oxychlorides react with SCN^- in acetone to form $\text{W}(\text{NCS})_6$, $\text{WO}(\text{NCS})_4$ and $\text{WO}_2(\text{NCS})_2$, which usually contain two moles of solvent.

The $\text{W}(\text{VI})$ oxychloro compounds, especially WOCl_4 , form complexes with NH_3 , amines, ether, acetonitrile and 2,2'-dipyridyl; solvolysis of the $\text{W}-\text{Cl}$ bond does not occur as easily as in WCl_6 . Brisdon⁶⁴⁰ used three methods to prepare complexes of the types $\text{WO}_2\text{Cl}_2 \cdot \text{B}$ (B = 2,2'-dipyridyl, 1,10-phenanthroline) and $\text{WO}_2\text{Cl}_2 \cdot 2\text{L}$ (L = dimethylformamide, triphenylphosphine oxide, hexamethylphosphoramide, dimethyl sulfoxide, tetramethylene sulfoxide, acetonitrile); (1) reaction of WO_2Cl_2 with excess pure ligand, above its melting point, in an inert atmosphere; (2) reaction of WCl_6 in acetone with excess ligand; (3) replacement of one ligand by another, e.g. of acetonitrile in $\text{WO}_2\text{Cl}_2 \cdot 2\text{L}$ by dipyridyl or $(\text{C}_6\text{H}_5)_3\text{PO}$, in CH_3CN or CH_2Cl_2 . The complexes have oxygen-bridged polymeric structures in the solid state but are monomeric in the vapor state. They are non-electrolytes in anhydrous acetonitriles.

2.9.3. Tungsten(VI) Halide and Oxyhalide Complexes^{627, 637}

Complexes of the types $\text{M}[\text{WF}_7]$ (M = NO, NO_2 , Rb, Cs, NH_4) and $\text{M}_2[\text{WF}_8]$ (M = Na, K, Rb, Cs) are obtained by reaction of WF_6 with MI or MF in solvents such as IF_5 and ClF_3 . The complex $\text{Na}_2[\text{WF}_7]$ is also formed by reaction of ClF with sodium tungstate at 300° ; when PbWO_4 is used, the products are PbF_4 and WF_6 ⁶³⁰. According to Katz⁶⁴¹, the hexafluorides MF_6 (M = U, Mo, W) react rapidly with NaF when it is formed by decomposition of $\text{UF}_6 \cdot 2\text{NaF}$; the products are $\text{Na}[\text{MF}_7]$. Salts of the ion $[\text{WF}_8]^{2-}$ may be formed by reaction of MF with WF_6 but not if the reaction mixture is absolutely dry. The cubic heptafluoro complexes $\text{M}[\text{WF}_7]$ are obtained when an excess of WF_6 is used. The salt $\text{K}_2[\text{WF}_8]$ has a cubic unit cell indicating octahedral coordination. The $[\text{WF}_7]^-$ ion has a distorted octahedral structure. These compounds are white solids easily hydrolyzed, but stable in dry air.

The oxyhalide complexes (mainly fluoro compounds) are prepared as follows:

$\text{M}_3[\text{WO}_4\text{F}]$ (M = Na, K, Rb, Cs): reaction of MF with M_2WO_4 in melt (Na, K, Rb salts isostructural).

$\text{K}_3[\text{WO}_3\text{F}_3]$ (M = K, Rb, Cs, NH_4): reaction of: MF with WO_3 (molten state); WO_3 with MF and aqueous HF (K, Rb, Cs salts isomorphous).

$\text{K}_2[\text{WO}_3\text{F}_2]$: reaction of KF with WO_3 in aqueous HF.

$\text{NH}_4[\text{WO}_3\text{F}]$: hydrolysis in reaction mixture of WO_3 and NH_4F in H_2O .

$\text{M}_2[\text{WO}_2\text{F}_4]$ (many alkali metal and analogous salts): reaction of WO_3 with MF in aqueous HF.

$\text{NH}_4[\text{WO}_2\text{F}_3]$ (monohydrate).

$\text{M}[\text{WOF}_5]$ (M = Na, K, Rb, Cs, NO, NO_2): reaction of $\text{W}(\text{CO})_6$ with NaI in IF_5 or of WO_3 with MF and SeF_4 .

The oxychloride complexes $\text{M}[\text{WO}_3\text{Cl}]$ (M = Na, K) have been prepared by reaction of MCl with WO_3 .

⁶⁴⁰ B. J. Brisdon, *Inorg. Chem.* **6** (1967) 1791.

⁶⁴¹ S. Katz, *Inorg. Chem.* **5** (1966) 666.

2.9.4. Tungsten(VI) Oxides^{642a, 643}

(a) WO_3

Tungsten trioxide, WO_3 , is the final product of ignition of tungsten or tungsten compounds (e.g. sulfides, lower oxides, etc.) in air. It can be prepared by dehydrating tungstic acid ($WO_3 \cdot aq$)^{644a} obtained by heating an acidified tungstate solution^{632b}. In making tungstic oxide for preparing the pure metal, tungstic acid is dissolved in ammonia; ammonium paratungstate $5(NH_4)_2O \cdot 12NO_3 \cdot aq$ crystallizes and is ignited to WO_3 ^{632b, 644b}. Tungstic oxide is insoluble in water but soluble in alkali solutions; from the solutions, the normal tungstates crystallize.

Several allotropic modifications of WO_3 are known^{644c}, i.e. monoclinic (below -40°); triclinic (-40 to 17°); monoclinic (17 – 320°); orthorhombic (320 – 720°); tetragonal ($> 720^\circ$). At ordinary temperature it has a distorted ReO_3 -type structure built up from chains of WO_6 octahedra, linked by shared corners, infinite in three dimensions⁶⁴⁵. Tungsten trioxide of stoichiometric composition is yellow but the color is changed to gray or blue by slight reduction.

The melting point of WO_3 has been reported as 1470° . It sublimes at about 1100° with a heat of sublimation of about 110 kcal/mole. The vapor contains polymeric species such as W_4O_{12} , W_3O_9 , W_3O_8 and W_2O_6 ⁶⁴⁶.

(b) WO_x ($2 < x < 3$)

When WO_3 is heated (1300 – 1500°) *in vacuo*⁶⁴⁷, heated with metal powders in an inert atmosphere, or reduced with hydrogen, several oxides with formulas intermediate between WO_3 and WO_2 are formed. Their compositions and unit cell formulas are: $WO_{2.98}$ (W_4O_{12-x}); α - $WO_{2.96}$ ($W_{50}O_{148}$); β - $WO_{2.96}$ ($W_{25}O_{74}$); $WO_{2.90}$ ($W_{20}O_{58}$); $WO_{2.72}$ ($W_{18}O_{49}$).

Compounds of this type are nonstoichiometric in the sense that the formal oxidation state number is fractional, but they are not berthollides since they form ordered phases with definite stoichiometry. The berthollides are characterized by disordered phases of variable composition^{645a}. The fractional oxidation state is presumed not to be due to a mixture of tungsten atoms in different oxidation states; the structure is thought to be the WO_3 lattice with delocalized electrons^{645b}.

The structures of these intermediate oxides consist of layers of the basic ReO_3 -type structure separated by shear planes or dislocations⁶⁴⁷. In the homologous series of oxides W_nO_{3n-1} , n is a measure of the layer thickness. Six homologs in the series (Mo, W) $_nO_{3n-1}$ are known ($n = 8, 9, 10, 11, 12, 14$)^{645b}; linking of the octahedra is by shared corners except at the discontinuities where there is edge-sharing.

Gamma tungstic oxide, $W_{18}O_{49}$, can be prepared by heating a mixture of pure tungsten powder and WO_3 (in stoichiometric ratio in an evacuated sealed tube (6 hr, 800°), grinding

⁶⁴² F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 2nd edn. (1966): (a) p. 933; (b) p. 940; (c) p. 937.

⁶⁴³ A. Chretien and W. Freundlich, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959), pp. 825, 835.

⁶⁴⁴ C. D. Rieck, *Tungsten and its Compounds*, Pergamon Press, Oxford (1967): (a) p. 100; (b) p. 38; (c) p. 93.

⁶⁴⁵ (a) L. Kihlberg, "The Crystal Chemistry of Molybdenum Oxides"; (b) A. D. Wadsley, "Non-stoichiometric Metal Oxides. Order and Disorder", in *Nonstoichiometric Compounds*, Advances in Chemistry Series, **39**, American Chemical Society, Washington, DC (1963).

⁶⁴⁶ R. V. Parish, "The Inorganic Chemistry of Tungsten", in *Advances in Inorganic Chemistry and Radiochemistry*, **9**, Academic Press, New York (1966), p. 377.

⁶⁴⁷ E. Gebert and R. J. Ackermann, *Inorg. Chem.* **5** (1966) 136.

the product and heating it again for 24 hr under the same conditions^{632b}. The product is a red-violet crystalline powder of deformed DO_9 type; it is a semi-conductor. This oxide is one of the "tunnel" compounds (see Part II, Section 2.9.6); in such compounds, wide empty tunnels, lined by rings of five or six octahedra, run straight through the structure^{645a}. They are thus related to the tetragonal and hexagonal tungsten and molybdenum bronzes (see Part II, Section 2.9.6); the tunnels in the oxides contain no X-ray scattering atoms while the tunnels in the bronzes contain the alkali (or other) metal atoms.

2.9.5. Tungsten Blues^{642a, 648}

Tungsten blues are obtained by procedures analogous to those used to prepare molybdenum blues (see Part II, Section 2.9.7). They are mixed valence compounds containing different ratios W(VI)/W(V). An example is $H_{0.5}WO_3$ made by reducing (with Zn) a suspension of WO_3 in HCl ^{632b}; other tungsten blues reported are $WO_{2.67}(OH)_{0.33}$ and $WO_{2.7}(OH)_{0.1}$. Wet WO_3 becomes blue on exposure to ultraviolet light as a result of formation of tungsten blue.

2.9.6. Tungsten and Molybdenum Bronzes^{649, 650a-c}

Tungsten bronzes are nonstoichiometric compounds of empirical formula M_xWO_3 in which M is usually one of the alkali metals and x is between 0 and 1. M may also be an alkaline earth metal ion, ammonium ion, rare earth metal ion, etc. The bronzes are characterized by metallic lustre, distinctive colors (golden yellow to bluish-black) and are either electrical conductors or semiconductors depending on M and the value of x . The tungsten bronzes are usually cubic, but phase changes may occur as x is changed; other structures that are found are tetragonal and hexagonal.

A bronze such as M_xWO_3 (M = alkali metal) is a semiconductor with $x < 0.25$ but acquires metallic behavior (becomes conductive) with $x \cong 0.25$. It has been shown that generally the activation energy for electron transfer should become zero when the mean distance between donor centers is 4.5 times their radius which corresponds to $x \approx 0.25$ in M_xWO_3 on the basis of an expanded hydrogenic model⁶⁵¹.

In the conversion of transition metal oxides such as WO_3 and MoO_3 to bronzes, the interstitial dopant such as an alkali metal ion can transfer its valence electron(s) to the host oxide delocalized states; these may originate from direct overlap of the transition metal $d t_{2g}$ orbitals or from indirect overlap of d orbitals through intervening oxygen- $p\pi$ interactions^{651, 652}.

Donor centers can also be introduced by removing oxygen atoms; each oxygen atom removed from WO_3 or MoO_3 corresponds to the addition of two alkali metal atoms⁶⁵¹. The two processes are equivalent as demonstrated by experimental results, showing that the magnetic behavior as a function of x is the same with WO_{3-x} and M_xWO_3 . Cross-over

⁶⁴⁸ M. B. Robin and P. Day, "Mixed Valence Chemistry—A Survey and Classification", in *Advances in Inorganic Chemistry and Radiochemistry*, **10**, Academic Press, New York (1967), p. 339.

⁶⁴⁹ E. Banks and A. Wold, "Oxide Bronzes", in *Preparative Inorganic Reactions*, **4**, Interscience, New York (1968).

⁶⁵⁰ (a) M. J. Sienko, "Electrical and Magnetic Properties of the Tungsten and Vanadium Bronzes"; (b) H. R. Shanks, P. H. Sidles and G. C. Danielson, "Electrical Properties of the Tungsten Bronzes"; (c) A. S. Ribnick, B. Post and E. Banks, "Phase Transitions in Sodium Tungsten Bronzes", in *Nonstoichiometric Compounds*, Advances in Chemistry Series, **39**, American Chemical Society, Washington, DC (1963).

⁶⁵¹ D. R. Kudrak and M. J. Sienko, *Inorg. Chem.* **6** (1967) 880.

⁶⁵² B. L. Crowder and M. J. Sienko, *Inorg. Chem.* **4** (1965) 73.

from semiconductive to metallic behavior occurs when about 1/30 of the oxygen atoms have been removed from the WO_3 structure.

The cubic M_xWO_3 structure is made up of a regular array of WO_6 octahedra connected at all corners and extending in three directions⁶⁵³. Along any cubic axis, strings of octahedra are connected in such a way as to form regular four-membered rings. This results in formation of square channels that can accommodate the alkali metal or other ions. Alternative ways in which the strings of octahedra may be arranged are the formation of five- and six-membered rings. With the former, characteristic of the tetragonal bronzes, there are triangular, rectangular and pentagonal channels along the c -axis. The hexagonal bronzes have triangular and hexagonal channels resulting from the six-membered rings (see also Section 2.9.4 and Part II, Section 2.9.6).

Several methods have been used to prepare tungsten and other bronzes, e.g. reduction of WO_3 by M in the vapor phase^{650a}; reaction of M_2WO_4 , WO_3 and W at high temperature^{650a}; reaction of a metal chloride with WO_3 and WO_2 ⁶⁵⁴. Electrolytic reduction of melts has also been used, e.g. of M_2WO_4 and MO_3 ^{650a}; K_2MoO_3 and MoO_3 ^{655, 656}.

The reaction of a metal chloride with WO_2 and WO_3 is a general method for preparing tungsten bronzes^{654, 657}. The following have been prepared by this procedure: M_xWO_3 ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}, \text{Tl}, \text{Pb}, \text{Nd}$); $\text{Na}_x\text{Ba}_y\text{WO}_3$ ($0 < y < 0.16$; $0 < (x+y) < 0.46$).

Mixed bronzes $\text{K}_x\text{Li}_y\text{WO}_3$ (hexagonal) have been prepared with x as low as 0.13 and $(x+y)$ as high as 0.51⁶⁵⁸. Usually Na and Li bronzes are cubic; by adding Li to the potassium bronze, the range of the hexagonal phase has been increased, which should lead to increased conductivity.

Lithium, ammonium and tin hexagonal bronzes have been synthesized hydrothermally⁶⁵⁹. The reaction mixtures ($\text{WO}_3\text{--W--LiOH}$; $\text{NH}_4\text{OH--WO}_3\text{--W}$; $(\text{NH}_4)_2\text{W}_2\text{O}_7\text{--H}_2\text{O}$; $\text{SnO--WO}_3\text{--W}$) were heated in sealed gold tubes under Ar (3000 atm). The Li and Na tungsten bronzes obtained by the usual methods have perovskite-related or tetragonal-tunnel type structures depending on their composition. Although hexagonal lithium bronze was obtained by the hydrothermal procedure, only cubic (perovskite type) sodium bronze was obtained.

In the cubic rare earth tungsten bronzes, $\text{M}_{0.1}\text{WO}_3$ (blue-violet powders) ($\text{M} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$), the lattice parameter a decreases from 3.828 Å in $\text{Ce}_{0.1}\text{WO}_3$ to 3.788 Å in $\text{Lu}_{0.1}\text{WO}_3$ ⁶⁶⁰. With increase in x from 0.08 to 0.19, the cubic lattice parameter of La_xWO_3 increases from 3.829 to 3.845 Å. Below $x = 0.08$, a tetragonal phase appears⁶⁶¹. The yttrium bronze Y_xWO_3 also occurs in cubic and tetragonal forms; the latter appears at $x < 0.09$. Scandium does not form a bronze under the experimental conditions used to make the lanthanum and yttrium bronzes (reaction of metal oxide, WO_3 and W at high temperature *in vacuo*).

Nearly isotropic behavior of single crystals of hexagonal In_xWO_3 ($x = 0.21\text{--}0.27$) was

⁶⁵³ R. J. Bouchard and J. L. Gillson, *Inorg. Chem.* **7** (1968) 969.

⁶⁵⁴ L. E. Conroy and T. Yokokawa, *Inorg. Chem.* **4** (1963) 994.

⁶⁵⁵ G. H. Bouchard, Jr., J. Perlstein and M. J. Sienko, *Inorg. Chem.* **6** (1967) 1682.

⁶⁵⁶ A. Wold, W. Kunmann, R. J. Arnott and A. Ferretti, *Inorg. Chem.* **3** (1964) 545.

⁶⁵⁷ L. E. Conroy and G. Podolsky, *Inorg. Chem.* **7** (1968) 614.

⁶⁵⁸ E. Banks and A. Goldstein, *Inorg. Chem.* **7** (1968) 966.

⁶⁵⁹ T. E. Gier, D. C. Pease, A. W. Sleight and T. A. Bither, *Inorg. Chem.* **7** (1968) 1646.

⁶⁶⁰ W. Ostertag, *Inorg. Chem.* **5** (1966) 758.

⁶⁶¹ B. Broyde, *Inorg. Chem.* **6** (1967) 1588.

observed in measurements of electrical resistance perpendicular and parallel to the c -axis. These results are consistent with formation of a π conduction band from cation t_{2g} and anion $p\pi$ covalent interactions⁶⁶².

The first authentic molybdenum bronzes were prepared by Wold *et al.*⁶⁵⁶ by electrolytic reduction of $\text{MoO}_3\text{--M}_2\text{MoO}_4$ ($\text{M} = \text{Na, K}$) melts at $550\text{--}675^\circ$. The structure of these bronzes (M_xWO_3 ; $x < 0.3$) was not related to those of the analogous tungsten bronzes; bronzes with $x \cong 1$ were also obtained.

The blue bronze $\text{K}_{0.30}\text{MoO}_3$ has metallic properties above 180°K ; the red bronze $\text{K}_{0.33}\text{MoO}_3$ is practically an insulator at room temperature. The difference is attributed to molecular orbital population and electron delocalization over the M_6O_{18} and $\text{M}_{16}\text{O}_{30}$ clusters that make up the structures of the host oxides of the red and blue bronzes respectively⁶⁵⁵.

Molybdenum bronzes isotypic with known tungsten bronzes have been prepared at high pressure (65 kbar) in the tetrahedral anvil press⁶⁶³. The following were obtained: Na_xMoO_3 cubic ($x = 0.90\text{--}0.97$); K_xMoO_3 , cubic ($x = 0.89\text{--}0.92$); $\text{K}_{0.5}\text{MoO}_3$, tetragonal; $\text{Rb}_{0.27}\text{MoO}_3$, hexagonal. The cubic and tetragonal phases are metallic conductors like the tungsten analogs; the hexagonal bronze is a semiconductor. Orthorhombic Rb_xMoO_3 ($x = 0.41\text{--}0.44$) prepared by this procedure is also a semiconductor. This method was also used to make the already known Ba_xWO_3 and Sr_xWO_3 (tetragonal I)⁶⁵⁴.

For further information, see the chapter on tungsten bronzes.

2.9.7. Tungstates^{642c, 643b}

Normal tungstates M_2WO_4 can be crystallized from solutions made by dissolving tungsten trioxide in alkali metal hydroxide or carbonate solutions. Other tungstates can be made from the alkali metal tungstate solutions by metathetical reactions. Other procedures include fusion of WO_3 with a metal oxide or carbonate and fusion of metal chloride with Na_2WO_4 . The mineral *scheelite* (CaWO_4) is one of the principal tungsten ores.

Most metal tungstates are insoluble in water; exceptions are those of the alkali metals, ammonium, magnesium and thallium(I). Tungstates, like molybdates, are easily reduced but are not powerful oxidizing agents. Tungstate ion in acid solution polymerizes to isopolyanions and condenses with other anions to form heteropolyanions; in this behavior, tungstates closely resemble molybdates (see Section 2.9.8).

In a solution of Na_2WO_4 in water labeled with ^{18}O , there is complete exchange of oxygen between H_2O and WO_4^{2-} in the time required for mixing reagents and separating BaWO_4 ⁶⁶⁴.

The tungstates MWO_4 ($\text{M} = \text{Sr, Ba, Pb}$) have the scheelite (CaWO_4) structure. Sodium tungstate, Na_2WO_4 , like Na_2MoO_4 and Ag_2MoO_4 , has the spinel structure. Lithium tungstate and lithium molybdate are isostructural with beryllium silicate. All of these contain WO_4 tetrahedra. The tungstates MWO_4 ($\text{M} = \text{Ni, Mn, Co, Mg, Zn}$) are isostructural (space group C_{2h}^4) and are characterized by WO_6 octahedra⁶⁶⁵.

Enthalpies of formation (from $\text{MO} + \text{WO}_3$) have been determined for the isostructural tungstates MWO_4 ($\text{M} = \text{Mg, Co, Ni, Cu, Zn, Cd}$). The structure of these crystals is a distorted hexagonal close-packed array of oxide ions with tungsten ions in octahedral holes;

⁶⁶² R. J. Bouchard and J. L. Gillson, *Inorg. Chem.* **7** (1968) 969.

⁶⁶³ T. A. Bither, J. L. Gillson and H. S. Young, *Inorg. Chem.* **5** (1966) 1559.

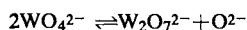
⁶⁶⁴ G. C. Geier and C. H. Brubaker, Jr., *Inorg. Chem.* **5** (1966) 321.

⁶⁶⁵ G. M. Clark and W. P. Doyle, *Spectrochim. Acta* **22** (1966) 1441.

the divalent cations are located in two sets of nonequivalent distorted octahedral sites⁶⁶⁶.

Several tungstates of the type $\text{XR}_2\text{O}_3 \cdot \text{WO}_3$ have been identified by X-ray diffraction and microscopy in solid-state reaction mixtures heated to 1400–1600° ($\text{R} = \text{Sm}, \text{Y}, \text{La}$); $3\text{Sm}_2\text{O}_3 \cdot \text{WO}_3$ (light yellow) and $3\text{La}_2\text{O}_3 \cdot \text{WO}_3$ (white) are refractory compounds with melting points $\sim 2240^\circ$ and $\sim 2050^\circ$ respectively. X-ray powder patterns indicated that these compounds have a disordered pyrochlore (or ordered defect fluorite) structure (face-centred cubic) with $a = 10.80 \text{ \AA}$ ($3\text{Sm}_2\text{O}_3 \cdot \text{WO}_3$) and $11.18 \text{ \AA}$ ($\text{La}_2\text{O}_3 \cdot \text{WO}_3$)⁶⁶⁷. The rhombohedral mixed oxides $3\text{R}_2\text{O}_3 \cdot \text{WO}_3$ ($\text{R} = \text{Tm}, \text{Yb}, \text{Y}, \text{Lu}$) are formed in the reactions of R_2O_3 and WO_3 at high temperature⁶⁶⁸.

An electrochemical study⁶⁶⁹ of solutions of Na_2WO_4 in an equimolar NaNO_3 – KNO_3 melt indicated existence of the equilibrium



(see Part I, Section 2.9.2(d)).

If H_2S is passed into a tungstate solution, oxythiotungstates and, finally, the thio-tungstate are produced:

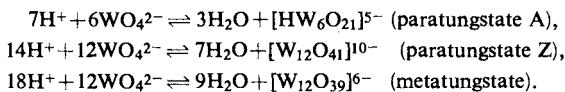


Acidification of the thiotungstate solution causes precipitation of WS_3 .

2.9.8. Iso- and Heteropolyanions of Tungsten(VI)

Tungstate solutions can absorb considerable quantities of strong acid by mechanisms leading to formation of isopolytungstates⁶⁷⁰. As indicated in the discussion of isopoly-molybdates (p. 739), despite extensive investigations, the problem of the isopolyanions (i.e. number and composition of polymeric species) has not been completely solved. A major difficulty is the low rate of attainment of equilibrium in the acidified solutions⁶⁷¹.

On the basis of ultracentrifugation results, acidity measurements and Raman spectra, Aveston⁶⁷² has concluded that the following are the main equilibria:



The logarithms of the three equilibrium constants are 53.98 ± 0.02 , 110.03 ± 0.05 , and 132.51 ± 0.03 respectively.

In a freshly prepared $\text{Na}_{10}\text{W}_{12}\text{O}_{41} \cdot 28\text{H}_2\text{O}$ (sodium paratungstate) solution, the principal species is $[\text{W}_{12}\text{O}_{41}]^{10-}$; slow hydrolysis produces a mixture of this ion and $[\text{HW}_6\text{O}_{21}]^{5-}$. At higher acidities, $[\text{W}_{12}\text{O}_{39}]^{6-}$ is formed.

Heteropoly tungstates are produced by heating and acidifying solutions of a tungstate and a salt of the central atom⁶⁷³. About thirty-eight ions can function as central atoms, e.g.

⁶⁶⁶ A. Navrotsky and O. J. Kleppa, *Inorg. Chem.* **8** (1969) 756.

⁶⁶⁷ L. L. Y. Chang and B. Phillips, *Inorg. Chem.* **3** (1964) 1792.

⁶⁶⁸ E. A. Aitken, S. F. Bartram and E. F. Juenke, *Inorg. Chem.* **3** (1964) 949.

⁶⁶⁹ R. N. Kust, *Inorg. Chem.* **6** (1967) 157.

⁶⁷⁰ D. L. Kepert, "Isopolytungstates", in *Progress in Inorganic Chemistry*, **4**, Interscience, New York (1967), p. 199.

⁶⁷¹ H. R. Craig and S. Y. Tyree, Jr., *Inorg. Chem.* **4** (1965) 997.

⁶⁷² J. Aveston, *Inorg. Chem.* **3** (1964) 981.

⁶⁷³ G. A. Tsigdinos, *Heteropoly Compounds of Molybdenum and Tungsten*, bulletin Cdb-12a, Climax Molybdenum Company, New York (September, 1966).

Cu^{2+} , Zn^{2+} , Fe^{3+} , Al^{3+} , Si^{4+} , Ge^{4+} , P^{3+} , P^{5+} , V^{5+} , Cr^{3+} , Te^{6+} , Mn^{4+} , I^{7+} . Examples of the principal types of heteropolytungstates are:

1:6 series: $[\text{Te}^{\text{VI}}\text{W}_6\text{O}_{24}]^{6-}$, $[\text{I}^{\text{VII}}\text{W}_6\text{O}_{24}]^{5-}$ (isomorphous with 1:6 molybdates), $[\text{Ga}^{\text{III}}\text{W}_6\text{O}_{24}\text{H}_6]^{3-}$.

1:9 series: $[\text{Be}^{\text{II}}\text{W}_9\text{O}_{31}]^{6-}$.

1:12 series: $[\text{P}^{\text{V}}\text{W}_{12}\text{O}_{40}]^{3-}$, $[\text{S}^{\text{IV}}\text{W}_{12}\text{O}_{40}]^{4-}$ ⁶⁷⁴, $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ ⁶⁶⁴.

2:18 series: $[\text{P}_2^{\text{V}}\text{W}_{18}\text{O}_{62}]^{7-}$.

Compounds of 1:10 and 2:17 series are also known.

The structures of the iso- and heteropolyanions of molybdenum and tungsten are built up from MO_6 octahedra sharing corners and edges but not faces^{642b}. In the heteropolyanions, the hetero (central) atom may be coordinated in three different ways^{642b}, ⁶⁷⁶. For example, in the 12-heteropolyanions such as $[\text{PW}_{12}\text{O}_{40}]^{3-}$ there are four groups of three WO_6 octahedra sharing corners (oxygen atoms); these four groups share corners to form a tetrahedral cage holding the phosphorus atom (Fig. 17, p. 741); the metatungstate ion $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ (or $[\text{W}_{12}\text{O}_{38}(\text{OH})_2]^{6-}$) and the 2:18 heteropolytungstates have the same structure⁶⁷⁵. Octahedral and icosahedral coordination of the central atom is also found in some heteropolyanions.

In a definitive analysis of the factors determining which iso- and heteropolyanions can form, Kepert⁶⁷⁵ has shown how their structures can be predicted on the basis of the size and charge of the metal atoms. In structures composed of MO_6 octahedra sharing edges, the coulombic repulsion among the highly charged metal atoms can be reduced if they move away from the centres of the octahedra. With increasing size of the anion, such distortion becomes increasingly ineffective and ultimately sharing of edges ceases. This point will be reached later for the smaller ions, i.e. in the order $\text{V}^{5+} < \text{Mo}^{6+} < \text{W}^{6+} < \text{Nb}^{5+} < \text{Ta}^{5+}$, a conclusion in accord with experimental evidence. According to Lipscomb⁶⁷⁶, the tendency is toward formation of stable iso- and heteropolyanions in which no octahedron terminates in three or more unshared O^{2-} ions.

While oxygen exchange is almost instantaneous between H_2^{18}O and WO_4^{2-} , there is no appreciable oxygen exchange between water and the heteropolytungstate $[\text{CoW}_{12}\text{O}_{40}]^{4-}$ ⁶⁶⁴; these results have been interpreted as supporting an outer-sphere mechanism for the electron exchange between 12-tungstocobaltate(III) and -(II).

Each of the five isostructural polytungstates $[\text{M}_2\text{W}_{12}\text{O}_{40}]^{x-}$ (M and x : P, 3-; Si, 4-; Fe^{III}, 5-; Co^{II}, 6-; H, 6-) can accept two electrons without decomposition^{677a} in neutral solution; in acid solution in which protonation can occur (which keeps the overall ionic charge low) more electrons can be added. In neutral solution, reduction can continue until the charge on the reduced species is 8- (heteropoly blues⁶⁴⁸). With the two forms of $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ and $[\text{As}_2\text{W}_{18}\text{O}_{62}]^{6-}$, the initial reduction steps correspond to addition of up to six electrons per anion^{677b}. The analogous heteropoly molybdates undergo three successive two-electron steps in acid solution^{677c}. The 18-molybdo- and tungsto-diphosphate anions are more readily reduced than the 12-anions.

For further details, see the chapter on isopolyanions and heteropolyanions.

⁶⁷⁴ E. O. North, *Inorg. Syn.* **1**, McGraw-Hill, New York (1939), p. 129.

⁶⁷⁵ D. L. Kepert, *Inorg. Chem.* **8** (1969) 1556.

⁶⁷⁶ W. N. Lipscomb, *Inorg. Chem.* **4** (1965) 132.

⁶⁷⁷ (a) M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.* **5** (1966) 1249; (b) M. T. Pope and E. Papoconstantinou, *ibid.* **6** (1967) 1147; (c) E. Papoconstantinou and M. T. Pope, *ibid.* 1152.

2.10. PEROXYTUNGSTEN COMPOUNDS^{678, 679}

Like Mo(VI), W(VI) forms peroxy compounds in which the ratio of peroxy groups to metal is 4:1, 3:1, 2:1 and 1:1. Other peroxy compounds of intermediate ratios are also known. Preparative methods are similar to those used for the peroxymolybdenum compounds.

Reaction of excess H_2O_2 with tungstates in neutral or slightly alkaline solution gives rise to red salts whose composition appears to be $\text{M}[\text{W}(\text{O}_2)_4]$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Co}, \text{Zn}(\text{NH}_3)_4, 2\text{Na}, 2\text{K}$). Some investigators, however, have concluded that part of the peroxide oxygen is bound as H_2O_2 since some of it is lost when the calcium salt is dehydrated.

These compounds are extremely unstable. They decompose to tungstates, perhaps via a series of intermediates containing 3, 2 and 1 (O_2) per W.

By the same methods used to prepare the Mo compounds, peroxytungstates containing three (O_2) per W atom have been obtained. These may be $\text{M}[\text{WO}(\text{O}_2)_3]$ ($\text{M} = \text{Ca}, \text{Sr}$) or mixtures of salts of $[\text{W}(\text{O}_2)_4]^{2-}$ and $[(\text{O}_2)_2\text{OWOWO}(\text{O}_2)_2]^{2-}$.

The 2:1 peroxytungstates are prepared by reaction of a high concentration of H_2O_2 with alkali metal tungstates in acid solution. They appear to be dimers. The salt $\text{K}_2[(\text{O}_2)_2\text{OWOWO}(\text{O}_2)_2] \cdot 4\text{H}_2\text{O}$ can be dehydrated at 100° without loss of peroxide oxygen.

The crystal structure of the potassium salt has been determined. The interatomic distances ($\text{\AA}$) are as follows: W–O, peroxy, 1.91; W–O, apical, 1.68; W–O, bridge, 1.93; W–O, water, 2.36; O–O, peroxy group, 1.50. The OWO (peroxy group) angle is about 46° and the WOW (bridge) angle is 138° . The planes containing the two O–W– H_2O axes are at right angles to each other.

The 2:1 peroxy compounds are thermally more stable than the tetraperoxy compounds. At room temperature, the tungsten compounds are more stable than the molybdenum compounds. The products of decomposition are tungstates.

Monoperoxy compounds can be obtained by decomposing tungstates of higher (O_2):W ratio, by reaction of H_2O_2 with tungstates and by neutralizing H_2O_2 –tungstic acid solutions. These are formulated as $\text{M}_2'[\text{WO}_3(\text{O}_2)] \cdot \text{aq.}$ and $\text{M}''[\text{WO}_3(\text{O}_2)] \cdot \text{aq.}$

Other peroxytungstates with (O_2):W ratios between 0 and 1 have been obtained by reaction of H_2O_2 with tungstates and polytungstates. These lower peroxy compounds may be peroxypolytungstates.

Several complex peroxytungstates have been described, e.g. peroxyfluorides, peroxyoxalates and peroxytartrates.

⁶⁷⁸ P. Pascal, p. 24; A. Chretien and W. Freundlich, p. 859, in *Nouveau Traité de Chimie Minérale*, **14**, Masson et Cie, Paris (1959).

⁶⁷⁹ J. A. Connor and E. A. V. Ebsworth, "Peroxy Compounds of Transition Metals", in *Advances in Inorganic Chemistry and Radiochemistry*, **6**, Academic Press, New York (1964), p. 313.

INDEX

- Bronze 764
- Chromates 692
 di- 692
 halo- 694
 poly- 694
 substituted 695
- Chromates(IV) 688
- Chromic acid, *see under* Chromium(VI) oxide
- Chromium
 allotropes 629
 alloys 639
 analysis 637
 carbonyls 647
 derivatives 648
 complexes
 cyano 650
 dipyridyl 650
 isonitrile 650
 nitrosyl 650
 olefin dithiol 651
 organometallic 652
 discovery 624
 electron transfer reactions 660
 non-metal compounds 642
 occurrence 625
 π -acceptor ligand compounds 645
 preparation 629
 production 626
 properties
 biological 636
 chemical 633
 nuclear 629
 physical 631
 uses 626
- Chromium(II) 655
 complexes 657
 halide 657
 hydroxide 660
 oxide 660
 salts 657
- Chromium(III)
 biological ligand reactions 680
 competitive reactions 680
 complexes
 halide 665
- Chromium(III) (*cont.*)
 preparation 675
 stability 688
 coordination chemistry 666
 stereoisomerism 670
 electrodeposition 679
 halides, anhydrous 664
 hydrolysis 676
 hydroxide 665
 ligand substitution reactions 683
 acid hydrolysis 684
 anation 687
 base hydrolysis 686
 exchange reactions 686
 olation 677
 oxide 665
 oxolation 677
 oxochloride 665
- Chromium(IV)
 alkoxides 690
 complex halides 688
 halides, anhydrous 688
 oxide 689
 reaction intermediates 690
- Chromium(V)
 halogen compounds, anhydrous 690
 oxygen compounds 691
 reaction intermediates 691
- Chromium(VI)
 condensation in anhydrous melts 694
 fluoride 694
 oxide 692
 oxycompounds 691
 redox reactions 696
 induced oxidation 696
 organic substances oxidation 698
 with inorganic substances 697
- Chromyl compounds 695
 halides 694
- Hagg's rule 644
- Molybdates 738
 cyano- 729
 potassium cyano-(II) 717
- Molybdates(IV) 723

Molybdenum

- allotropes 703
- alloys 708
- analysis 707
- Blues 737
- bronzes 738
- complexes, organometallic 711
- discovery 700
- non-metal compounds 709
- occurrence 701
- π -acceptor compounds 710
- preparation 703
- production 701
- properties
 - biological 706
 - chemical 706
 - nuclear 703
 - physical 705
- uses 701

Molybdenum(II)

- acetate 717
- halogen compounds 715
- oxide 717

Molybdenum(III)

- chelate compounds 719
- coordination compounds 719
- halides 718
- hydroxide 720
- oxide 720

Molybdenum(IV)

- chelate compounds 721
- coordination compounds 721
- halogen compounds 720
- oxide 723

Molybdenum(V)

- bioinorganic chemistry 730
- chelate compounds 727
- complexes
 - acetylacetone 727
 - amino acetate 729
 - cysteine 729
 - cysteine ester 729
 - dialkyl dithio carbamate 728
 - halide 725
 - histidine 729
 - oxalato 728
 - oxyhalide 725, 726
 - 2,4,6-trimethylpyridine 727
 - xanthate 728
- halides 724
- hydroxide 731
- oxide 731

Molybdenum(VI)

- anions
 - heteropoly- 739
 - isopoly- 739
- chelate compounds 734

Molybdenum(IV) (cont.)

- complexes 734
- halides 733
- oxyhalides 733
- halides 731
- oxides 735
- oxyhalides 732

Racemic mixture 674**Rare gas rule 646, 653****Stereoisomerism 670****Tungstates 766**

- potassium cyano(II) 754
- potassium cyano(III) 755
- potassium cyano(IV) 756
- potassium octacyano(V) 760

Tungsten

- allotropes 745
- alloys 749
- analysis 749
- Blues 764
- bronzes with molybdenum 764
- discovery 742
- non-metal compounds 750
- occurrence 743
- organometallic compounds 752
- π -acceptor ligands 751
- preparation 745
- production 744
- properties
 - biological 748
 - chemical 748
 - nuclear 745
 - physical 746
- uses 744

Tungsten(II), halogen compounds 753**Tungsten(III), halogen compounds 754****Tungsten(IV)**

- halogen compounds 755
- oxide 757

Tungsten(V)

- complexes
 - halide 758
 - oxalate 759
 - oxyhalide 758
- halides 757

Tungsten(VI)

- anions
 - heteropoly- 767
 - isopoly- 767
- complexes
 - halide 762
 - oxyhalide 762
- halides 760
- oxides 763
- oxyhalides 761

VOLUME 1

The element Hydrogen, ortho- and para-Hydrogen, atomic Hydrogen

K M MACKAY *University of Waikato*

Hydrides

K M MACKAY *University of Waikato*

Deuterium and Tritium

K M MACKAY *University of Waikato* & M F A DOVE *University of Nottingham*

Proton, protonic acids and hydrogen bond

J E PRUE *University of Reading*

The monatomic gases: physical properties and production
A H COCKETT & K C SMITH *British Oxygen Co Ltd, London*

The chemistry of Krypton, Xenon and Radon

N BARTLETT *University of California, Berkeley* &

F O SLADKY *University of Innsbruck*

Lithium and its compounds

W A HART & O F BEUMEL Jr *Foote Mineral Co, Pennsylvania*

Sodium, Potassium, Rubidium, Cesium and Francium

T P WHALEY *International Minerals and Chemical Corp, Illinois*

Beryllium

D A EVEREST *National Physical Laboratory, Teddington*

Magnesium, Calcium, Strontium, Barium and Radium

R D GOODENOUGH & V A STENGER *The Dow Chemical Co, Michigan*

Boron

N N GREENWOOD *University of Leeds*

Aluminium, Gallium, Indium and Thallium

K WADE & A J BANISTER *University of Durham*

Carbon

A K HOLLIDAY, G HUGHES & S M WALKER

University of Liverpool

An introduction to the organic chemistry of the metallic elements

M L H GREEN *University of Oxford* & P POWELL *Royal Holloway College*

Silicon

E G ROCHOW *Harvard University*

Index

VOLUME 2

Germanium

E G ROCHOW, *Harvard University*

Tin

E W ABEL *University of Exeter*

Lead

E W ABEL *University of Exeter*

Nitrogen

K JONES *University of Manchester Inst. of Science & Technology*

Phosphorus

A D F TOY *Stauffer Chemical Co, New York*

Arsenic, Antimony and Bismuth

J D SMITH *University of Sussex*

Oxygen

E A V EBSWORTH *University of Edinburgh*,

J A CONNOR *University of Manchester*, &

J J TURNER *Newcastle on Tyne University*

Sulphur

M SCHMIDT & W SIEBERT *University of Wurzburg*

Selenium, Tellurium and Polonium

K W BAGNALL *University of Manchester*

Fluorine

T A O'DONNELL *University of Melbourne*

Chlorine, Bromine, Iodine and Astatine

A J DOWNS & C J ADAMS *University of Oxford*

Index

VOLUME 3

Copper

A G MASSEY *University of Technology, Loughborough*

Silver

N R THOMPSON *ICI, Runcorn Heath Laboratory, Cheshire*

INDEPENDENT OPINION

"These books are attractively bound and have clear print. Since the length and cost are not prohibitive, this set of books should be well within the budget of most libraries. Not only will the professional chemist find these books useful, but students and other readers will find them a valuable reference source. (Comprehensive Inorganic Chemistry) should be found in every undergraduate and graduate library, as well as industrial libraries. Many professional chemists may even consider them for personal libraries. Highly recommended."

Choice—A publication of the Association of College and Research Libraries.

Gold

B F G JOHNSON *University of Cambridge*

& R DAVIS *Kingston Polytechnic*

Group IIB

B J AYLETT *Westfield College, London*

Scandium, Yttrium and Lanthanum

R C VICKERY *Hudson, Florida*

Titanium

R J H CLARK *University College, London*

Zirconium and Hafnium

D C BRADLEY & P THORNTON *Queen Mary College, London*

Vanadium

R J H CLARK, *University College, London*

The chemistry of Niobium and Tantalum

D BROWN *Atomic Energy Research Establishment, Harwell*

Chromium, Molybdenum and Tungsten

C L ROLLINSON *University of Maryland*

Manganese

R D W KEMMITT *University of Leicester*

Technetium

R D PEACOCK *University of Leicester*

Rhenium

R D PEACOCK *University of Leicester*

Iron

D NICHOLLS *University of Liverpool*

Cobalt

D NICHOLLS *University of Liverpool*

Nickel

D NICHOLLS *University of Liverpool*

The 2nd and 3rd row elements of group

VIII A, B and C

S E LIVINGSTONE *University of New South Wales*

Index

VOLUME 4

The Lanthanides

T MOELLER *Arizona State University*

Carbonyls, Cyanides, Isocyanides and Nitrosyls

W P GRIFFITH *Imperial College of Science & Technology London*

Compounds of the transition elements involving metal-metal bonds

D L KEPERT *University of Western Australia*

& K VRIEZE *University of Amsterdam*

Transition metal hydrogen compounds

J C GREEN & M L H GREEN *University of Oxford*

Non-stoichiometric compounds: an introductory essay

D J M BEVAN *The Flinders University of South Australia*

Tungsten bronzes, Vanadium bronzes and related compounds

P HAGENMULLER *University of Bordeaux*

Isopolyanions and heteropolyanions

D L KEPERT *University of Western Australia*

Transition metal chemistry

B F G JOHNSON *University of Cambridge*

Organo-transition metal compounds and related aspects of homogeneous catalysis

B L SHAW & N I TUCKER *University of Leeds*

Index

VOLUME 5

The Actinides

J A LEE & J A MARPLES

G W C MILNER & G PHILLIPS

P G MARDON

Atomic Energy Research Establishment, Harwell

C KELLER *Kernforschungszentrum, Karlsruhe*

S H EBERLE *Universität Karlsruhe*

D BROWN, R M DELL & P E POTTER *AERE, Harwell*

K W BAGNALL *University of Manchester*

J RYDBERG & J O LILJENZIN *Chalmers University of Technology*

S ÅHRLAND *University of Lund*

Master Index

INDEPENDENT OPINION

Volume 1 1467 pp + index

"This covers the chemistry of hydrogen, the noble gases, and of the elements of Groups IA, IIA, IIIB, carbon and silicon. The first three chapters deal with hydrogen, hydrides, deuterium and tritium and the fourth is an interesting discussion of the proton, protonic acids and the hydrogen bond. Two chapters follow on the inert gases, including interesting and extensive recent knowledge about their compounds set out by N. Bartlett and F. O. Sladky. Four chapters on the alkalis and alkaline earths contain a wealth of detail, although perhaps along traditional lines. N. N. Greenwood has written an excellent account on boron chemistry of book length in itself, and another chapter deals at length with much new information about aluminium, gallium, indium and thallium. Chapters 13 and 15 deal with carbon and silicon. Here it might have been expected that more would have been included on the high pressure chemistry of carbon and silicates, and mineral chemistry. Chapter 14 by M. L. H. Green and P. Powell is a useful introduction to the organic chemistry of the metallic elements, along modern lines of ligand field theory and ideas about metal complexes.

Throughout this volume, with its different authors, it is perhaps inevitable that there is some lack of uniformity in the extent of detail given. There are also a few lapses in symbolism, notation, and uniformity of units. Yet the whole must be regarded as a highly commendable collection of material which will be valuable to chemists of all kinds."

Professor Sir Harold Thompson FRS
Oxford

Volume 2 1594 pp + index

"Volume 2 is concerned with the chemistry of the elements of Groups IV, V, VI, VII. The general impression on reading the various chapters of this volume is the great effectiveness in reporting a considerable amount of chemistry in a very digestible form. The systematic presentation applied to each chapter allows a rapid assessment of the appropriate chemical information, and the text is well documented with reference to the original literature plus good review articles for a more detailed coverage. Perhaps a minor criticism of this work lies in the indexing; the subject index is relatively sparse for a text of such magnitude and it would have been of considerable utility to have a formulae index to the text.

The area of chemistry covered by this work is obviously very great, but it does appear to have

dealt with it in a very succinct manner for the majority of the text, which extends to approximately 1500 pages. The two major chapters in the book are associated with the chemistry of nitrogen, approximately 240 pages, and the chemistry of the halogens (excepting fluorine), approximately 500 pages. The book thus encompasses in one volume what would normally be a series of books. Both of the above mentioned chapters are admirable and the authors, K. Jones on nitrogen with A. J. Downs and C. J. Adams on the halogens, are to be commended on both the presentation and coverage. The chapter on the halogens illustrates the real strength of the series, in that detailed chemical information is not only presented but discussed in physico-chemical theoretical terms. A scientific compendium of this size often suffers from the "catalogue" approach, but the present text presents the chemistry in critical mode with a realistic assessment of the various physical methods used in property determination. Thus the properties of the halogens are discussed in terms of bond energies, bond lengths, vibrational properties, e.s.r., n.m.r., n.q.r. and Mossbauer spectroscopy, electronic and magnetic properties and dipole moments allowing a detailed appraisal of the use of various modern methods in studying the chemical properties reviewed.

Considering the magnitude of the task undertaken, it is extremely pleasing to note the number of chapters referring to papers in the 1971 period—a truly great commendation on the overall editorship of these volumes. Perhaps a general note in each volume stating the period covered by the references would have been of help. In general this work provides a welcome and unique addition to the inorganic literature."

Professor J. Lewis FRS
Cambridge

Volume 3 1370 pp + index

"This volume covers the chemistry of the elements of the d-block of the Periodic Table (the transition elements), with the exception of the Lanthanide elements (Vol. 4), the Actinide elements (Vol. 5) and some special aspects which are common to many of the transition elements (Vol. 4). The volume is therefore concerned specifically with the three elements which characterize each of the ten transition groups, and the chapters are mostly grouped in this way. However, the six platinum metals are treated in one chapter which is the best way to fit these similar elements into the overall scheme which is standard for all five volumes. There are altogether 17 chapters, written by 14 authors who are internationally

recognized 1370 pages of text and a useful 17 page index.

The five volumes are quite remarkable, in that they can justifiably claim to be comprehensive, yet at the same time remain interesting and readable; they are probably unique in this respect. Volume 3 serves as an excellent source-book for the essential physical constants of all important compounds (simple and complex) of the transition metals. These are arranged so that significant comparisons are made wherever possible, and there are extensive references. It says much for the ingenuity of the editors, authors, and particularly the printers that the presentation of such an amount of information has been possible, while still maintaining the readability of the text. Throughout the volume chemical properties and reactions are discussed and interpreted rather than listed. The need for skilled correlation of data is particularly important in Volume 3, since it is in the area of the transition elements that a major part of the research work in inorganic chemistry has been published in recent years, and in this area also there has been a major interaction of inorganic with theoretical chemistry.

This volume must surely become the first point of reference for research workers and teachers alike. The transition elements play an important role in Pure and Applied Chemistry, Physics, Materials Science and Biology, and the authors clearly intend their chapters to be of value to this wide audience. Teachers at any level will also appreciate the very high quality of the general presentation, discussion, formulae and diagrams. Apart from reference to the original literature, few scientists will find it necessary to look outside this volume for their material."

Professor C. C. Addison FRS
Nottingham

Volume 4 994 pp + index

"Volume 4 is concerned with the general chemistry of the lanthanides and some special topics in transition metal chemistry.

Therold Moeller has packed a great amount of the fundamental chemistry of the lanthanides into his 101 pages in an interesting and scholarly manner with tables of essential data. Important recent developments in their organometallic chemistry have come too late to be included, but the chapter provides a useful fairly detailed first reference to their inorganic chemistry.

The subjects of the surveys are topical and obviously bear the mark of the late Sir Ronald Nyholm. They vary considerably in detail of treatment, interest and authority. Generally they emphasize recent work until about 1969-70 but rarely show a sense of history. They vary in length from 60 to 200 pages, mostly around 100 pages. They are authoritative and useful surveys all giving numerous references to recent reviews and

original work. The authors are well known chemists whose style and subject matter are familiar to most inorganic chemists. There are eight surveys as follows:—

Carbonyls, cyanides, isocyanides and nitrosyls by W. Griffith. Compounds of the transition elements involving metal-metal bonds by D. L. Kepert and K. Vrieze. Transition metal hydrogen compounds by J. C. Green and M. L. H. Green. Non-stoichiometric compounds: an introductory essay by D. J. M. Bevan. Tungsten bronzes, vanadium bronzes and related compounds by P. Hagenmuller. Isopolyanions and heteropolyanions by D. L. Kepert. Transition metal chemistry by B. F. G. Johnson. Organo-transition metal compounds and related aspects of homogeneous catalysis by B. L. Shaw and N. I. Tucker.

This volume has its own subject index of sixteen and a half pages, and is well produced with numerous tables of data and references provided at the foot of each page."

Professor J. Chatt FRS
Sussex

Volume 5 635 pp + Master index

"Volume 5 is devoted to the Actinides (635 pp) and the Master Index (78 pp). The latter serves little purpose since it merely indicates the sub-sections of CIC, and thus repeats the indexes in each individual volume. Indeed, as the treatment of each element or series of elements follows a standard pattern, the volumes are essentially self-indexing anyway. A one-page table of contents at the beginning of Volume 5 would have been more helpful and is a curious omission. The running headings at the top of each double page are also singularly uninformative, only three being used: 'The Elements' for 102 pages, 'Compounds' for 361 pages and 'Solution Chemistry' for the remaining 171 pages.

The treatment of actinium and the actinides (elements 89-103) is both readable and authoritative. Nine of the contributors are from AERE, Harwell, and the other five (with one exception) are from nuclear chemistry institutes in Sweden and Germany. In reviewing these 5f elements it is salutary to recall that the majority have been synthesized for the first time within the last 30 years—yet the number of compounds known and the amount of information on them has already outstripped the more limited chemistry of their 4f congeners, the lanthanides. The authors have done a magnificent job in assembling, collating, assessing, and systematizing a vast amount of data on the physical and chemical properties of these elements and their numerous compounds. The work, which is extensively referenced, will undoubtedly remain the standard first source of information in this area for many years to come."

Professor N. N. Greenwood FRIC
Leeds