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

MANGANESE

R. D. W. Kemmitt

TECHNETIUM AND RHENIUM

R. D. Peacock

Chapters 37, 38 and 39 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 018870 2 (Hard cover)
ISBN 0 08 018869 9 (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

37. MANGANESE

R. D. W. KEMMITT

The University, Leicester

HISTORY

Although manganese was not identified as an element until 1774 by Scheele, some of the ores of manganese have been known from times of antiquity and the history and recognition of the different types of ore have been described in detail[1,2]. The commonest mineral, pyrolusite (MnO_2), when added to glass bleaches the green or yellow colour produced by iron oxide impurities, and it is the references in ancient writings to this use of the ore which enable it to be traced from the first century to the present time.

In 1770 J. G. Kaim heated pyrolusite with black flux and obtained a regulus, but it was not until 1774 that the great Swedish chemist, C. W. Scheele, realized that the ore and its extracts contained a new element[3]. Although Scheele made this discovery he did not succeed in isolating the metal, and this was achieved by J. G. Gahn in the same year. Scheele supplied Gahn with samples of pyrolusite (Braunstein) ore and Gahn mixed the ore with oil and heated it in a charcoal-lined crucible to obtain the metal. Pyrolusite was first described as a variety of the magnetic oxide of iron, lodestone or *lapis magnes*. However, although pyrolusite is non-magnetic it was still classified as a *lapis magnes* in early times on the grounds of its similar external appearance. Hence the name of the metal was derived from the Latin *magnes*, or magnet; the German equivalent is *Mangan* and the French *manganèse*.

The use of manganese in steel was first introduced around 1839 when Heath used "carburet" of manganese in making steel crucibles. The addition of manganese as spiegeleisen (20% manganese–iron alloy) was initiated by Mushet in 1856 and made the Bessemer process successful. The use of ferromanganese as an additive to control the sulphur content of steel was patented by Siemens, and in 1888 Hadfield introduced the high-manganese steel which still bears his name[4]. Today the major use of manganese is as an alloying and cleansing agent for steels, iron and non-ferrous metals. It has been estimated that about 14 lb of manganese mainly in the form of ferromanganese has been used for each ton of steel produced[3].

OCCURRENCE OF MANGANESE

Manganese is widely distributed in the combined state. It is the twelfth most abundant element and constitutes about 0.085% of the earth's crust. Of the heavy metals, only iron is

---

[1] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, Vol. XII (1932).

[2] R. Hadfield, *J. Iron Steel Inst.* **115** (1927) 211.

[3] A. H. Sully, *Metallurgy of the Rarer Metals: 3, Manganese*, Butterworths (1955).

[4] F. E. Bacon, *Manganese and Manganese Alloys*, in *Kirk–Othmer Encyclopaedia of Chemical Technology*, 2nd edn., Interscience, Vol. 12 (1967), p. 887.

more abundant. It is one of the trace elements essential to the life of plants and animals[5]. The cells of all living things contain minute concentrations of manganese (microgram per gram) and a deficiency of this metal in all organisms studied, ranging from bacteria through plants to mammals, inhibits growth and diminishes life expectancy[6]. Manganese deficiency in higher plants causes mottled chlorosis (lack of chlorophyll) in which the leaves become pale or yellow while the veins remain green. In man it has been suggested that "apresoline disease" may well be a manganese deficiency[6]. The normal requirement of the human diet has been estimated to be about 4 mg per day, and the consumption of tea and coffee provides a large source of the metal. Seeds, nuts and cereals also have high manganese contents, but milk products and sea foods are low.

In some areas of the world, e.g. parts of the United States, the soil is deficient in manganese, and in these areas manganous sulphate or oxide is added to fertilizers. Small concentrations of manganese compounds are also added to many animal and chicken foods, and some vitamin–mineral formulations contain manganese glycerophosphate and manganese hypophosphite as nutriments[7].

An unknown manganese complex is involved in photosynthesis and the element is essential in the energy-converting unit of the plant. The smallest energy-converting unit appears to contain two Mn atoms, two Cu atoms, ten Fe atoms and 300 chlorophylls, and the manganese is an essential element for the oxygen-evolving step in photosynthesis. A scheme for this process has been suggested from a knowledge of some redox potentials of porphyrin complexes of manganese[8].

Manganese is not only important in photosynthesis but it can activate other enzymatic processes. Thus it is thought to be involved in oxidative phosphorylation, and it activates enzymes such as arginase, enolase and peroxidases. It also seems to be involved in the structures of the nucleic acids and it promotes the synthesis of cholesterol[6, 9]. Some manganese metalloenzymes and manganese activated enzymes are given in ref. 8.

Many of the iron-depositing bacteria form deposits of both manganese and iron oxides, and these bacteria may well account for the occurrence of manganese in some iron ores as well as the manganese nodules found on ocean floors[7].

An extremely useful property of the paramagnetic manganous ion present in biological systems is that not only can it be studied by e.s.r. techniques but it can also be used as a n.m.r. relaxation probe. Also, since zinc and magnesium can be substituted by manganese in certain enzymes, it is possible to use manganese(II) as a probe in other systems[10].

Although manganese is essential to man, in high concentrations it becomes quite poisonous[5, 6]. Chronic manganese poisoning has chiefly been found in miners who are either in manganese mines or in ore-crushing mills. The manganese enters the body via the lungs by

---

[5] G. C. Cotzias, *The Encyclopaedia of Biochemistry* (edited by R. J. Williams and E. M. Lansford, Jr.), Reinhold, New York (1967), p. 506.

[6] G. C. Cotzias, *Manganese in Mineral Metabolism: An Advanced Treatise* (edited by C. L. Comar and F. Bronner), Academic Press, New York, Vol. 2, pt. B (1962), p. 403.

[7] C. A. Hampel, in *The Encyclopaedia of the Chemical Elements* (edited by C. A. Hampel), Reinhold, New York (1968), p. 389.

[8] M. Calvin, *Revs. Pure Appl. Chem.* **15** (1965) 1; J. E. Coleman and B. L. Vallee, *Comprehensive Biochemistry* (edited by M. Florkin and E. H. Stotz), Elsevier, Vol. 16 (1965), p. 165.

[9] U. Weser, *Structure and Bonding* **5** (1968) 41.

[10] B. L. Vallee and R. J. P. Williams, *Chemistry in Britain* 4 (1968) 397; M. Cohn, *Magnetic Resonance in Biological Systems* (edited by A. Ehrenberg, B. G. Malmstrom and T. Vanngard), Pergamon Press (1967), p. 101.

inhalation of the dust, and chronic manganese poisoning usually results after one to three years' exposure to large amounts of dust. Some people seem to be more prone to attack than others. The first symptoms are of a psychic nature and can take the form of fits of laughter or crying and even homicide. Later, neurological changes occur and the patient suffers from trembling, rigidity and the general symptoms of Parkinson's disease. Chronic manganese poisoning is incurable once the symptoms have passed the early stages[5,6].

From 1837, when the first case of manganese poisoning was reported, until 1940, there were only 353 known cases[11]. Today manganese poisoning is not a great industrial problem since the enforcement of modern safety practices can so easily prevent it.

Manganese salts taken into the body either by injection or orally are not so dangerous since most is excreted.

Manganese ores are found in many parts of the world[3]. The most common ones are pyrolusite and psilomelane and some properties of these and other ores are listed in Table 1.

TABLE 1. IMPORTANT MANGANESE ORES [a]

Ore	Formula	Specific gravity	% manganese
Pyrolusite	MnO_2	4.8	63.2
Psilomelane	b	3.7–4.7	45–60
Manganite	$Mn_2O_3 \cdot H_2O$	4.2–4.4	62.4
Braunite	$3Mn_2O_3 \cdot MnSiO_3$	4.8	62
Hausmannite	Mn_3O_4	4.8	72 [c]
Rhodochrosite (or dialogite)	$MnCO_3$ [d]		47
Rhodonite	$MnSiO_3$		42
Bementite	e		31

[a] A. H. Sully, *Metallurgy of the Rarer Metals—Manganese*, Butterworths (1955), p. 3.
[b] Thought to be colloidal MnO_2 containing adsorbed water and oxides of sodium, potassium, and barium.
[c] Of primary origin and occurs as veins in igneous rocks.
[d] Contains iron, calcium, and magnesium carbonates.
[e] Hydrated silicate.

The USSR is easily the largest single producer of manganese ore (about 8 million short tons in 1969), and about 7.5 million short tons are produced annually by the Republic of South Africa, Brazil, India and China[4].

Most manganese ore occurs as secondary deposits since over the course of time the manganese has been dissolved out and redeposited as the carbonate, oxide or hydroxide. There are also some primary sources of manganese ore occurring as silicate minerals, and these become of commercial importance when surface water decomposes the silicates during tropical weathering. This happens in India, Brazil and Ghana.

The ores are usually mined by open-cast methods, but in India and Brazil there is some underground mining, and in the Caucasus the ore is obtained from adits in hill-sides. The ore is usually sold in the crude state, although some has to be crushed and classified. If necessary it is then washed to remove earthy material. In the United States, where there is no high-grade ore, low-grade oxide and carbonate ores are concentrated by flotation methods.

---

[11] L. T. Fairhall and P. A. Neal, *Industrial Manganese Poisoning*, Nat. Inst. Health Bull. 182 (1943).

METALLURGY OF MANGANESE

There are four types of impurities usually found in manganese ores[3]: (a) metallic impurities of iron (which is the most common), lead, zinc and silver, and in some ores nickel, tungsten and copper; (b) gangue impurities which are slag forming such as silica, alumina, lime, magnesia or baryta; (c) volatile impurities such as water, carbon dioxide and organic matter; (d) non-metallic impurities such as sulphur and phosphorus.

(a) *Metallic impurities.* Any zinc present in the ore is volatilized off during smelting and can be recovered and sold. The other metallic impurities, however, are reduced during smelting and are retained in the manganese, and although these are undesirable when the ore is used for metallurgical purposes, small amounts are not harmful. For the production of ferromanganese the iron to manganese ratio should not be more than 1:9. The presence of iron, however, is undesirable if the ore is to be used in glass or battery production (see later).

(b) *Gangue impurities.* Although a certain amount of slag is useful in smelting as an impurity remover, an excessive amount is harmful since (i) manganese is always lost in the slag, (ii) too big a volume of slag requires the use of more coke, and (iii) the additional weight in the ore increases transportation costs.

(c) *Volatile impurities.* Although water and carbon dioxide would be driven off in the blast furnace, this is not desirable since extra heat is required and would increase the loss of manganese by volatilization. Hence the ores are frequently calcined before smelting. This applies particularly to the rhodochrosite ores which can have up to 38.3% carbon dioxide present as carbonate.

(d) *Non-metallic impurities.* Since phosphorus is retained in the manganese during smelting and it is impracticable to remove it, ores containing large amounts of phosphorus cannot be used for producing ferromanganese. The maximum permissible phosphorus content in ferromanganese ore is 0.20–0.25% while in steel the specification is usually less than 0.05% [3]. Any sulphur present is not so harmful since it combines with the manganese or lime and passes into the slag.

Ferromanganese which contains mainly manganese (80%) and iron is the principal metallurgical form of manganese[3]. It is produced either in a blast furnace or electric arc furnace in several forms. Spiegeleisen, which contains 5–20% of manganese and 3.5–5.5% carbon, is prepared in a blast furnace and silicomanganese which contains 65–70% of manganese and 15–20% of silicon, is made in an electric arc furnace. The pure metal is prepared either electrolytically or by the reduction of the ore with silicon or aluminium in an electric arc furnace[3, 4].

Blast-furnace preparation of ferromanganese. The furnace used in this process is very similar to that used for iron. Although any ore can be used for the production of ferromanganese, the charge usually contains a mixture of ores in a proportion which will ensure that the final product has the correct specification. The coke used for the reduction must have a low ash content in order to keep the bulk of the slag low and hence prevent losses of manganese and heat. The amount of iron oxide which might be present in the coke must also be taken into consideration since this could effect the ratio of manganese to iron in the final product. Low silica-containing ores are also preferred so that the volume of slag can be kept to a minimum. A certain amount of dolomite or limestone is added to the charge to combine with the silica, and this also helps to keep the amount of manganese lost to the slag to a minimum. To keep dust losses to a minimum, coarse ores are mixed with fine ores.

There are important differences between the operation of the blast furnace for the production of ferromanganese and pig iron. Manganese has a much higher affinity for oxygen than iron, and whereas the reduction of MnO by carbon monoxide is endothermic, the corresponding reduction of FeO is exothermic. This means that more coke is required in producing ferromanganese.

The other important difference between pig-iron and ferromanganese production is that MnO reduction is inhibited by carbon dioxide even when the gas is in low concentration. This is not the case with FeO which can be reduced in the presence of mixtures of carbon monoxide and carbon dioxide even when the latter is in high concentration. In view of this property of manganese the reduction of the ore takes place mainly where the carbon monoxide concentration is greatest. This is at the hearth of the furnace in contact with the solid carbon.

Since the volume of coke used in ferromanganese smelting is high, the volume of blast-furnace gases is also much higher than is the case for pig-iron production. Thus in the ferromanganese process the exit gases leave the furnace at a much higher temperature and velocity and this results in losses of manganese through the stack in addition to that lost in the slag.

This process gives ferromanganese with a high carbon content. Low carbon ferromanganese is produced by reducing manganese ore with silicomanganese in an electric arc furnace.

Production of spiegeleisen. Spiegeleisen is produced in a modified ferromanganese blast furnace. Due to the much higher silica content of the spiegel ores used in this process, more carbon fuel is needed than in the production of ferromanganese. In general the production of spiegeleisen is metallurgically uneconomic and the demand for spiegeleisen is much less than that for high-grade ferromanganese[3, 4].

Electric-arc-furnace production of ferromanganese and silicomanganese. If cheap electric power is available, the smelting of manganese ore with coke and limestone in an electric arc furnace to give ferromanganese can be economical. The composition of the slag in this process is very similar to that in the blast furnace and the same considerations involving losses of manganese apply. In the furnace the ore breaks down to a dust, and dust losses as well as losses due to volatilization are encountered. Usually about 85% of the manganese is recovered from the ore and about 3000 kWh are required to produce one ton of ferromanganese.

Silicomanganese is manufactured by a similar method except that the charge contains more quartzite.

Preparation of the pure metal. The electrolysis of manganous sulphate solutions forms the basis of the only commercial source of high-purity manganese metal. The process was developed in the 1930's by the United States Bureau of Mines, and a full-scale plant was operated commercially by the Electro Manganese Corporation which is now owned by the Foote Mineral Co.[7]

Some of the important points which must be taken into consideration in this process are[3, 4, 12]: (a) the manganese present in the ore must be converted to its divalent form so that it will dissolve in acids; (b) the impurities in the electrolyte must be kept to a minimum since most metallic impurities will deposit before manganese; (c) the anode and cathode compartments must be separated by a diaphragm since manganese will not deposit in acid

---

[12] T. W. Clapper, in *Encyclopaedia of Electrochemistry* (edited by C. A. Hampel), Reinhold, New York (1964).

solution and the anolyte is an acid solution which when spent can be used to leach manganese from the ore; (d) the electrolyte must be saturated with ammonium sulphate which can act as a buffer and prevent deposition of manganese dioxide. Thus in the electrolytic process the ore is first roasted in the presence of reducing gases to convert the higher oxides of manganese to manganous oxide. The ore is then leached with sulphuric acid of pH 3, and the solution is neutralized with ammonia or calcined ore to precipitate iron and aluminium oxides which can be removed by filtration. The solution is then saturated with hydrogen sulphide gas to precipitate the sulphides of arsenic, copper, cobalt, lead, molybdenum and zinc, and, finally, the solution is treated with ferrous sulphide and air to remove organic matter and colloidal metal sulphides and sulphur. In some processes manganese silicate slag is leached with sulphuric acid to provide a solution of manganous sulphate which is then purified as described above.

The manganese sulphate solution is electrolysed using a lead anode containing about 1% of silver and a cathode of Hastelloy or stainless steel containing 18% chromium, 12% nickel and 2% molybdenum. The presence of silver alloyed in the lead anode greatly reduces the amount of manganese dioxide which is deposited at the anode. The anolyte which is also used to leach the ore has a pH of about 1 and the catholyte has a pH of about 6 to 7.2.

If a pure manganous sulphate solution is electrolysed, the manganese deposits in the ductile gamma form and the current efficiency drops. However, if sulphur in some form is present (usually as sulphur dioxide), then the first few thousandths of an inch of manganese deposited is in the γ-form. This then changes to the brittle α-form, and the remaining manganese deposits in this form. The current efficiency is maintained when this allotrope of manganese is present. When the deposit of manganese is about one-eighth of an inch thick, the manganese is removed as chips by flexing and hammering the deposit. Removal of the manganese is made easier by the deposit being in the brittle α-form. The manganese obtained has a purity of 99.94%. The main impurity is sulphur. Hydrogen is also present but this can be removed by heating the product to 500°C.

Manganese metal can also be obtained by reduction of its ores with silicon or aluminium in an electric furnace. Electrolytic manganese, however, is a cheaper and purer product and can be produced at about the same cost as low-carbon ferromanganese[4, 7].

Manganese can be further purified by distillation[3, 13].

MANGANESE ALLOYS AND THE USE OF MANGANESE IN STEEL

Manganese forms numerous alloys many of which are extremely important in the manufacture of steel. There is, however, insufficient space to mention all the alloys of manganese here. They have been reviewed in refs. 3, 4, 14, and 15.

The pure metal forms numerous binary and ternary alloys. In non-ferrous metals it improves their strength, ductility and hot-rolling properties. It is used as an alloying agent and cleanser in aluminium alloys, aluminium–bronzes, constantan, manganese–bronze, Monel, nickel–silver and nickel–chromium resistance alloys. A nitrogen containing electrolytic manganese is also available for adding nitrogen to alloys[3, 4].

One of the most important uses of manganese is in the production of steel[3,4]. The manganese when added to the molten iron serves three functions. First it acts as a scavenger

---

[13] G. Brauer, *Handbook of Preparative Inorganic Chemistry*, 2nd edn., Academic Press, Vols. 1, 2 (1963).

for sulphur and the manganese sulphides formed pass into the slag of the steel-making process. The removal of sulphur eliminates the main cause of "hot shortness", a phenomenon in which the steel tends to rupture in rolling or forging operations. Second, it deoxidizes and cleanses the steel by reacting with iron oxide and oxygen present to form manganous oxide. Removal of the oxygen prevents it forming small bubbles in the steel as it solidifies. Given enough time the manganous oxide can be removed from the surface of the molten steel with the slag; however, some manganous oxide can remain and can affect the properties of the steel. Third, the addition of manganese to unalloyed steel is the cheapest way to increase the hardness of the product, and all steels contain manganese.

Electrolytic manganese. The use of the pure metal in the manufacture of certain steels not only has the advantage over other manganese alloys that the specifications of low carbon and phosphorus contents become easier to meet, but it occupies less space, is easier to weigh and does not lower the temperature of the molten iron as much. Electrolytic manganese is used in a number of free-machining steels and flat-rolled low-carbon sheet steels.

Standard ferromanganese. This alloy, which contains up to 7% carbon and 74–76% manganese, is commonly used in steel for deoxidation or alloying. It is used to make Bessemer, open-hearth, and electric furnace steels for forgings, rolled products and castings.

Medium-carbon ferromanganese. This alloy, which contains 80–85% manganese, 1.25–1.50% carbon and a maximum of 1.50% silicon, is used in making steels where the carbon content is too low for standard ferromanganese to be used.

Low-carbon ferromanganese. This alloy is used in the preparation of steels in which the carbon content is very important. Three grades are produced which have carbon contents ranging from 0.07 to 0.75% carbon.

Silicomanganese. This alloy, which contains 65–70% manganese and 15–20% silicon, is used in the open-hearth manufacture of steel. In this process the alloy acts as a blocking agent which stops the reaction between carbon and oxygen in the steel by reducing the amount of oxygen present in the molten steel. The combined effect of the manganese and silicon is to produce a steel with a minimum of non-metallic inclusions.

Hadfield manganese steel. This steel, which contains about 13% manganese and about 1.25% carbon, has remarkable properties. It is very hard, non-magnetic, and has great strength and wear resistance. It is used for parts of excavators, dredgers, rail crossings and other parts which are subjected to severe mechanical conditions of service. The steel is substantially austenitic since the hardening transformation temperature is suppressed by manganese. When the steel is cast or rolled it contains continuous carbides and other transformation products causing brittleness. Hence heat treatment is necessary before the steel is put into surface. Hadfield steel cannot be used at temperatures above 250°C since, unlike ordinary steels which soften and become ductile on heating, transformations take place that cause brittleness. The steel also work-hardens by a considerable amount, and this makes it difficult to machine. Hence when the steel is not subject to shock and impact the steel may not work-harden sufficiently to give it adequate wear resistance. Since it is non-magnetic it is also used as cover plates for magnets and in motor and generator parts. However, it is not rust resistant[4].

NON-METALLURGICAL USES OF MANGANESE

One of the most important non-metallurgical uses of manganese is in electrical batteries in which manganese dioxide acts as a depolarizer in the Leclanché type of electric cell[3].

The ore must have a high oxide content and must be free from impurities which would affect the function of the battery. Only certain ores meet the necessary requirements and manganese dioxide for use in batteries is also made by electrolysis of manganese(II) sulphate solutions[12].

Manganese dioxide is also used in the manufacture of glass to bleach the colour of any iron present. If excess manganese dioxide is added, a pink coloration can be produced in the glass and if a large excess is present it will appear black[3]. Other uses of manganese compounds include the use of manganese(II) sulphate or oxide in fertilizers, ethylenebis (dithiocarbamate) manganese(II) (Maneb) as a pesticide and fungicide, and methylcyclopentadienylmanganese-tricarbonyl as an anti-knock in petrol.

THE ELEMENT

Allotropes

Four allotropes of manganese have been described[3]. Their physical properties are given in Table 2.

TABLE 2. PHYSICAL PROPERTIES OF MANGANESE

Atomic weight	54.9380 [a]
Melting point (°C)	1244±3 [a]
Volume contraction on solidification	4.5% [b]
ΔH_f (kcal gm^{-1})	3.5 [c]
Boiling point, 760 mm (°C)	2095 [b]
Vapour pressure equations:	
From m.p. to b.p. [c]	$\log_{10} P_{\mathrm{mm}} = \frac{-14{,}850}{T} - 2.52 \log T + 17.88$
From 1043–1158°K [d]	$\log_{10} P_{\mathrm{mm}} = \frac{-13{,}625}{T} + 8.7587$
ΔH_s at 0°K (kcal gm^{-1})[d]	63.681
Transition temperatures and heats of transitions[b]:	
Alpha to beta (700±3°C)	535 cal g atom^{-1}
Beta to gamma (1079±3°C)	545 cal g atom^{-1}
Gamma to delta (1140±3°C)	430 cal g atom^{-1}
Specific heats[b]:	
Mn (alpha) (298–1000°K)	$C_p = 5.70 + 3.38 \times 10^{-3}T - 0.375 \times 10^{5}T^{-2}$
Mn (beta) (1000–1374°K)	$C_p = 8.33 + 0.66 \times 10^{-3}T$
Mn (gamma) (1374–1410°K)	$C_p = 10.7$
Mn (delta) (1410–1450°K)	$C_p = 11.30$
Mn (liquid)	$C_p = 11.0$
Entropy (cal mole^{-1} deg^{-1}) [b] at 25°C:	
Mn (alpha)	7.59±0.04
Mn (gamma)	7.72±0.04
Dissociation energy of Mn_2 molecule (kcal) [e] (upper limit)	$D_0^{\circ} < 21$
Crystal structures:	
Alpha [f]	Body-centred cubic $a = 8.9125$ Å
Beta [b]	Body-centred cubic $a = 6.300$ Å
Gamma [b]	Face-centred tetragonal at room temperature $a = 3.774$ Å; $c/a = 0.934$ Å Face-centred cubic at high temperature $a = 3.855$–3.860 Å

TABLE 2 (*cont.*)

Delta	Body-centred cubic at high temperature $a = 3.075$–3.087 Å
Specific gravity at room temperature[b]:	
Alpha	7.44
Beta	7.29
Gamma	7.21
Electrical resistivity (ohm cm^{-1}) [b]	
Alpha	150–260×10^{-6}
Beta	90×10^{-6}
Gamma	40×10^{-6}
Linear coefficient of expansion at 20°C[b]	
Alpha	22.3×10^{-6}
Beta	24.9×10^{-6}
Gamma	14.8×10^{-6}
Thermal conductivity [b] (c.g.s.), Beta	0.05 at −190°C
Ionization potentials [g] (eV):	
1st	7.432
2nd	15.636
3rd	33.690
4th	—
5th	*ca.* 76.006
6th	—
7th	119.240
Néel temperature [b], Alpha	100°K
Magnetic susceptibility [b] (e.m.u.):	
Alpha (at 293°K)	9.6×10^{-6}
Beta (at 293°K)	8.8×10^{-6}

[a] *Handbook of Chemistry and Physics*, 46th edn. (1965), Chemical Rubber Co.

[b] A. H. Sully, *Metallurgy of the Rarer Metals: 3, Manganese*, Butterworths, London (1955).

[c] *Metals Reference Book*, 4th edn. (ed. by C. J. Smithells), Butterworths, London (1967).

[d] V. L. Bogatyrev and I. V. Golubtsov, *Zhur. Fiz. Khim.* 40 (1966) 938.

[e] A. Kant and B. Strauss, *J. Chem. Phys.* 41 (1964) 3806.

[f] C. P. Gazzara, E. O. Hall, R. M. Middleton and R. J. Weiss, *Acta Cryst.* **22** (1967) 859.

[g] B. Lakatos, J. Bohus and Gy. Medgyesi, *Acta Chim. Hung. Tomus* **20** (1959) 1.

Alpha manganese, which is the stable form at room temperature, is hard and brittle and will scratch glass. It has a body-centred cubic lattice and there are four kinds of manganese atom present with coordination numbers 16, 16, 13 and 12. The Mn–Mn distances range from 2.24 to 2.91 Å. Although for a long time it was thought that the complex structure was due to the presence of manganese in different valency states, there is no generally accepted explanation for the structure[16].

Beta manganese can be readily isolated at room temperature by simply quenching manganese from above the alpha–beta transformation temperature[3]. Like the alpha form, it is hard and brittle and will scratch glass. It has a body-centred cubic lattice and there are two types of manganese present with different environments. Each type has a coordination number of 12 with Mn–Mn distances varying from 2.36 to 2.67 Å [3].

Electrodeposited manganese commonly exists as the γ-form. It cannot be obtained completely pure by quenching since during this process it decomposes to the α-form[3]. The

[14] M. Hansen and K. Anderko, *Constitution of Binary Alloys*, 2nd edn., McGraw-Hill, New York (1958); R. P. Elliot, *Constitution of Binary Alloys*, First Supplement, McGraw-Hill, New York (1965); F. A. Shunk, *Constitution of Binary Alloys*, Second Supplement, McGraw-Hill, New York (1969).

[15] R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys*, Wiley (1963).

[16] A. F. Wells, *Structural Inorganic Chemistry*, 3rd edn., Oxford University Press (1962).

γ-form obtained by electrodeposition is unstable at room temperature and decomposes to the α-form particularly if the temperature of the sample is increased. At low temperatures, however, it can be retained[3]. Gamma manganese is ductile and can be stabilized by the addition of copper. At room temperature it has a face-centred tetragonal lattice. At high temperatures, gamma manganese has a face-centred cubic lattice[3].

Delta manganese cannot be retained by quenching. However, high temperature (1140–1240°C) X-ray work has clearly identified this fourth allotrope which has a body-centred cubic lattice[3].

Isotopes

The isotopes of manganese together with their preparations and properties are summarized in Table 3. The only stable and naturally occurring isotope is ^{55}Mn. All the radioisotopes except ^{53}Mn are short-lived. ^{54}Mn has been observed in radioactive fallout, and it has been suggested that the amount of cosmogenic ^{53}Mn produced in iron meteorites in space principally by the reaction, ^{56}Fe (p, α) ^{53}Mn, should be measurable in newly fallen meteorites for dating determinations[17]. Both ^{54}Mn and ^{56}Mn have been used in tracer studies and are useful in studying manganese in biological systems[6]. Compounds containing manganese can be conveniently activated in a flux of neutrons by the reaction, ^{55}Mn (n, γ).

It is possible to investigate the ^{55}Mn nucleus in diamagnetic compounds by nuclear magnetic resonance spectroscopy, and recently the spectra of a variety of diamagnetic manganese carbonyl derivatives have been examined at a frequency of 14.858 Mc/s [18]. The line widths are in general large owing to quadrupole relaxation by the ^{55}Mn nucleus which has a spin of 5/2.

THE CHEMISTRY OF MANGANESE

Manganese is the twenty-fifth element in the Periodic Table and in the ground state has the electronic configuration $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^2$. It is the first member of the subgroup VIIA and it is only in its highest oxidation that it shows any similarity with the halogens in subgroup VIIB. Thus Mn_2O_7 is analogous to Cl_2O_7 and the salts of permanganic acid, $HMnO_4$, are isomorphous with the salts of perchloric acid, $HClO_4$. However, in general, manganese is much more similar to iron in both its physical and chemical properties.

Manganese is fairly electro-positive and the metal oxidizes superficially in air. It reacts with water slowly at room temperature but rapidly on heating liberating hydrogen[19]. It readily dissolves in dilute mineral acids to give the divalent ion and hydrogen. At room temperature it is not particularly reactive towards non-metals but at high temperatures it combines directly with boron, carbon, silicon, phosphorus, arsenic, sulphur and selenium. Although it does not combine with hydrogen it will burn in nitrogen to give a nitride. It will combine with oxygen to give Mn_3O_4, and with chlorine and fluorine to give $MnCl_2$ and MnF_2 and MnF_3 respectively.

Compounds of manganese are known in which the manganese has a formal oxidation state of −(III), −(II), −(I), (0), +(I), +(II), +(III), +(IV), +(V), +(VI) and +(VII), and some oxidation potentials of the element are given in Table 4. Manganese(II) is the most

---

[17] K. Rankama, *Progress in Isotope Geology*, Interscience, New York (1963), p. 391.

[18] F. Calderazzo, E. A. C. Lucken and D. F. Williams, *J. Chem. Soc.* A (1967) 154.

[19] N. V. Sidgwick, *The Chemical Elements and their Compounds*, Oxford, Vol. II (1950).

TABLE 3. ISOTOPES OF MANGANESE [a, b]

e	Nuclear spin ($h/2\pi$)	Magnetic moment (μ_n)	Half-life	Mode of decay	Thermal neutron cross-section (barns)	Class [c] and genetic relationships	Energies of major radiations (MeV) [d]	Sy
			0.4 s			Class 4		Prot
			0.286 s	β^+		Class 2	β^+, 6.61 max., γ, 0.511 [e]	^{50}Cr
n			2 m	β^+, EC [f]		Class 3	γ, 0.511 [e], 0.66, 0.783, 1.11, 1.28, 1.45	^{50}Cr
			45.2 m	β^+, EC [f]		Class 1, parent ^{51}Cr	β^+, 2.17 max., γ, 0.511 [e], 1.56, 2.03	^{50}Cr ^{50}Cr
	6 [h]		5.60 d	β^+, EC		Class 1	β^+, 0.575 max., γ, Cr X-rays, 0.511 [e], 0.744, 0.935, 1.434	^{52}Cr ^{52}Cr
n			21.1 m	β^+, IT 2%, EC [f]		Class 1, daughter ^{52}Fe	β^+, 1.63 max., γ, 0.383, 0.511 [e], 1.434	Dau
	7/2 [b]	5.050 [b]	1.9×10^6 y	EC	170	Class 2	γ, Cr X-rays	^{53}Cr ^{52}Cr
			303 d	EC, no β^+, no β^-		Class 1	γ, Cr X-rays, 0.835, e^-, 0.829	^{56}Fe ^{51}V ^{53}Cr ^{54}Cr
	5/2 [b]	3.4438 ± 0.0020 [g]	Stable		13.3			
			2.576 d	β^-		Class 1, daughter ^{56}Cr	β^-, 2.85 max., γ, 0.847, 1.811, 2.110	^{55}M
			1.7 m	β^-		Class 2	β^-, 2.55 max., γ[Fe X-rays, 0.014], 0.122, 0.136, 0.22, 0.353, 0.692	^{54}Cr ^{57}Fe
			7 d	β^-		Class 5		Alph M
			1.1 m	β^-		Class 2	γ, 0.36, 0.41, 0.52, 0.57, 0.82, 1.0, 1.25, 1.4, 1.6, 2.2, 2.8	^{58}Fe

M. Lederer, J. M. Hollander and I. Perlman, *Table of Isotopes*, 6th edn., Wiley, New York. This reference contains references to original literat
ormation on the means by which isotopic assignments were established.
ndbook of Chemistry and Physics, 46th edn., Chemical Rubber Co. (1965).
ss 1, element and mass number certain. Class 2, element certain and mass number probable. Class 3, element probable and mass num
ed. Class 4, insufficient evidence for definite isotopic assignment. Class 5, probably in error.
most prominent radiations are listed. Continuous β^+ or β^- spectra are followed by notation max.
11 implies all decays proceed by positron emission (see ref. a).
ay inferred or assumed and not directly measured.
B. Mims, G. E. Devlin, S. Geschwind and J. Jaccarino, *Phys. Letters* **24A** (1967) 481.
E. Adelroth, I. Lindgren, R. Djaj and A. Rosen, *Arkiv Fysick* **31** (1966) 549.

TABLE 4. SOME OXIDATION POTENTIALS OF MANGANESE[a]

	$E°$ (V)
$Mn(c) = Mn^{2+}(aq) + 2e^-$	1.20
$Mn^{2+}(aq) = Mn^{3+}(aq) + e^-$	*ca.* −1.5
$Mn^{2+}(aq) + 2H_2O(liq) = MnO_2(c) + 4H^+(aq) + 2e^-$	−1.239
$MnO_2(c) + 4OH^-(aq) = MnO_4^-(aq) + 2H_2O(liq) + 3e^-$	−0.588
$MnO_4^{3-}(aq) = MnO_4^{2-}(aq) + e^-$	*ca.* −0.3
$Mn^{2+}(aq) + 4H_2O(liq) = MnO_4^-(aq) + 8H^+(aq) + 5e^-$	−1.51
$MnO_2(c) + 2H_2O(liq) = MnO_4^-(aq) + 4H^+(aq) + 3e^-$	−1.69
$MnO_2(c) + 2H_2O(liq) = MnO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	−2.26
$Mn(c) + 2OH^-(aq) = Mn(OH)_2(c) + 2e^-$	1.58
$Mn(OH)_2(c) + OH^-(aq) = Mn(OH)_3(c) + e^-$	*ca.* 0.2
$Mn(OH)_3(c) + OH^-(aq) = MnO_2(c) + 2H_2O(liq) + e^-$	*ca.* −0.1
$Mn(OH)_2(c) + 2OH^-(aq) = MnO_2(c) + 2H_2O(liq) + 2e^-$	*ca.* 0.03
$Mn(OH)_2(c) + 6OH^-(aq) = MnO_4^-(aq) + 4H_2O(liq) + 5e^-$	−0.34
$MnO_2(c) + 4OH^-(aq) = MnO_4^{3-}(aq) + 2H_2O(liq) + e^-$	*ca.* −0.9
$MnO_2(c) + 4OH^-(aq) = MnO_4^{2-}(aq) + 2H_2O(liq) + 2e^-$	−0.603

[a] T. A. Zordan and L. G. Hepler, *Chem. Rev.* **68** (1968) 737.

important and, under normal conditions, the most stable oxidation state. In acid or neutral aqueous solution the manganese(II) ion exists as the pale pink hexaquo ion, $Mn(H_2O)_6^{2+}$, which is quite stable to oxidation. However, in basic solution the hydroxide, $Mn(OH)_2$, is precipitated, and this is sensitive to oxidation by atmospheric oxygen (Table 4). Most compounds and complexes of manganese(II) are high spin with five unpaired electrons, and their magnetic properties have been extensively studied. Electron spin resonance spectra may also be obtained[20].

The chemistry of manganese(III) is not extensive, and in the higher oxidation states manganese dioxide and potassium permanganate are the most important compounds. The lowest oxidation states are usually found in the carbonyl, nitrosyl and organometallic derivatives of manganese.

ANALYSIS OF MANGANESE[21]

The production of an intense red–violet colour when a manganese containing solution is added to an alkaline solution of formaldoxime provides a very sensitive and fairly specific test for manganese. A rapid, sensitive and specific test suitable for fieldwork in detecting manganese in minerals and rocks consists of adding one drop of the test solution to a piece of filter paper previously impregnated with 8-hydroxyquinoline, and then exposing it to ammonia fumes. Formation of a brown stain indicates the presence of manganese.

Probably the simplest method for the rapid determination of manganese in solution is oxidation of the metal to permanganate followed by estimation of the permanganate either spectrophotometrically or by titration with a suitable reductant[22]. In the photometric

---

[20] R. D. Dowsing, J. F. Gibson, M. Goodgame and P. J. Haywood, *J. Chem. Soc.* A (1970) 1133.

[21] M. D. Cooper and P. K. Winter, in *Treatise on Analytical Chemistry* (edited by I. M. Kolthoff and P. J. Elving), Interscience, Part II, Volume 7 (1961), p. 425.

[22] R. T. Oliver and E. P. Cox. *Anal. Chem.* **39** (1967) 102R.

method, oxidation to permanganate is conveniently achieved by treating the sample with an excess of potassium periodate in a nitric acid–phosphoric acid medium. Other methods which are used for determining manganese are given in refs. 21 and 22.

MANGANESE HYDRIDES

Although hydrogen dissolves in manganese and hydrogen contents of up to 60 c.c. per 100 g of manganese have been observed, there is no definite evidence for any solid binary hydride of manganese[3, 23]. A spectroscopic hydride, MnH, however, is known. The bond distances in MnH and the corresponding deuteride, MnD, are 1.7307_5 and 1.7234 Å respectively[24].

MANGANESE HALIDES

The halides of manganese and their complexes have been recently reviewed in detail[25]. All the halides of manganese(II) are known and numerous complexes of these compounds have been described. There is considerably less data on the higher halides.

MANGANESE FLUORIDES

Manganese(II) Fluoride

Manganese difluoride, MnF_2, is sparingly soluble in water and is simply prepared by addition of hydrofluoric acid to manganese(II) carbonate[13]. Manganese difluoride can also be obtained by the action of anhydrous hydrogen fluoride on manganese powder at 180° under autogenous pressure[26], passage of anhydrous hydrogen fluoride over heated manganese dichloride[27], and the action of heat on ammonium trifluoromanganate(II) in a stream of carbon monoxide[28]. The preparation of single crystals of MnF_2 suitable for magnetic and spectral studies have also been described[29–32]. Some properties of MnF_2 are given in Table 5.

Manganese difluoride is pale pink and its structure has been investigated by a number of workers[25]. Single crystal studies show that the compound has a distorted rutile structure of space group $P/4mnm$, the unit cell containing two formulae units. The structure consists of tetragonally distorted MnF_6 octahedra with four Mn–F bands 2.11 Å in length and two Mn–F bands 2.14 Å in length[25, 32]. The variation of the lattice parameters with temperature have been investigated[33, 34]. There is a slight variation of a with temperature, but c decreases noticeably, particularly below the Néel temperature.

---

[23] K. M. Mackay, *Hydrogen Compounds of the Metallic Elements*, Spon, London (1966).

[24] L. E. Sutton, (ed.), *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Chemical Society Special Publication No. 11 (1958).

[25] R. Colton and J. H. Canterford, *Halides of the First Row Transition Metals*, Wiley (1969), p. 212.

[26] J. E. Castle and E. L. Muetterties, *J. Inorg. Nucl. Chem.* **18** (1961) 148.

[27] H. C. Anderson, W. B. Burford, S. B. Bitterlick, R. D. Fowler, J. M. Hamilton, I. Litant and A. Spadetti, *Ind. Engng. Chem.* **39** (1947) 343.

[28] P. Nuka, *Z. anorg. allgem. Chem.* **180** (1929) 235.

[29] N. N. Mikhailova and S. V. Petrov, *Kristallografiya* **11** (1966) 433.

[30] S. Legrend and M. Binard, *Bull. Soc. Chim. France* (1964) 1900.

[31] K. Nassau, *J. Appl. Phys.* **32** (1961) 1820.

[32] M. Griffel and J. W. Stout, *J. Am. Chem. Soc.* **72** (1950) 4351.

[33] D. F. Gibbon, *Phys. Rev.* **115** (1959) 1194.

[34] S. L. Strong, *J. Phys. Chem. Solids* **19** (1961) 51.

TABLE 5. SOME PROPERTIES OF MANGANESE(II) HALIDES

	MnF_2	$MnCl_2$	$MnBr_2$	MnI_2
Melting point (°C) [a]	920	652±2	695	613
Boiling point (°C) [a]		1190 or 1225		
$\triangle H_f^\circ$ [b] (kcal $mole^{-1}$)	*ca.* −190	−115.6	−92.6	−64.2
$\triangle G_f^\circ$ [b] (kcal $mole^{-1}$)	*ca.* −179	−105.9	−89	−65
S° [b] (cal $mole^{-1}$ deg^{-1})	22.25	28.26		
$\triangle H_{sub}$ [a] (kcal $mole^{-1}$)	76.1 [c, d]	e, d	f	
Structure [a]	Tetragonal [g] $a = 4.8734$ Å $c = 3.3099$ Å	Hexagonal $a = 3.711$ Å $c = 17.59$ Å	Hexagonal $a = 3.820$ Å $c = 6.188$ Å	Hexagonal $a = 4.146$ Å $c = 6.289$ Å

[a] Ref. 25.
[b] T. A. Zordon and L. G. Hepler, *Chem. Rev.* **68** (1968) 737.
[c] Vapour pressure equation (881–920°C), $\log P_{mm} = -15{,}960/T + 8.70$.
[d] Vaporizes as linear monomers.
[e] Vapour pressure equation (725–950°C), $\log P_{mm} = -8448/T + 8.559$.
[f] Vaporizes as linear monomers with some dimers present.
[g] For other determinations of structure, see ref. 25.

The magnetic properties of MnF_2 have been extensively studied and they have been reviewed recently[25]. Above 80°K the Curie–Weiss law is obeyed and the spectroscopic splitting factor is close to the free electron value. At low temperatures it becomes antiferromagnetic; the reported values of the Néel temperature range from 66° to 75°K [25]. The magnetic structure of MnF_2 has been discussed by several workers (see ref. 35).

The electronic absorption spectrum of manganese difluoride has been extensively studied[25]. Although there is much disagreement concerning the assignment of the bands above 35,000 cm^{-1}, below this frequency agreement is good. The observed antisymmetric stretching and bending frequencies for linear MnF_2 in (a) an argon matrix are 700.1 and 124.8 cm^{-1} respectively, and in (b) a neon matrix are 722.1 and 132.0 cm^{-1} respectively[36].

Complex Fluorides of Manganese(II)

Both tetrafluoromanganates(II) and trifluoromanganates(II) are known. The salts, A_2MnF_4 (A = alkali metal), are generally prepared in a melt of manganese difluoride and the alkali metal fluoride[25]. This method has been used to prepare $BaMnF_6$ [37] and single crystals of K_2MnF_4 have been prepared by fusing $KMnF_3$ with KHF_2 at 900°C [38]. Stoichiometric amounts of the fluoride must be used in all these preparations since the trifluoromanganates are formed by this method. Also $K_3Mn_2F_7$, which has a tetragonal unit cell ($a = 4.19$, $c = 21.66$ Å), can be isolated from a KF–MnF_2 mixture[39]. Properties of these complexes are given in Table 6. Magnetic and heat capacity data on K_2MnF_4 are available[25].

The trifluoromanganates, $AMnF_3$, have generally been prepared either by mixing solutions of alkali metal fluorides with manganese difluoride or fusing the constituents in a melt[25]. Methods for preparing single crystals are also reported[31, 40].

---

[35] P. Heller, *Phys. Rev.* **146** (1966) 403.
[36] J. W. Hastie, R. Hauge and J. L. Margrave, *Chem. Communs.* (1969) 1452.
[37] J. C. Cousseins and M. Samouel, *Compt. rend.* **265c** (1967) 1121.
[38] D. J. Breed, *Phys. Letters* **23** (1966) 181.
[39] A. Chretien and J. C. Cousseins, *Compt. rend.* **259** (1964) 4696.
[40] K. Knox, *Acta Cryst.* **14** (1959) 1115.

TABLE 6. PROPERTIES OF SOME TETRAFLUOROMANGANATES(II)[a]

	M.p. (°C)	Structure[b]
K_2MnF_4[c]	795°[d]	Tetragonal: $a = 4.171$; $c = 13.259$ Å
Rb_2MnF_4	796°	Tetragonal: $a = 4.25$; $c = 13.92$ Å
Cs_2MnF_4[e]	725°	Tetragonal:[f] $a = 4.31$; $c = 14.63$ Å
$BaMnF_4$		Orthorhombic: $a = 15.08$; $b=4.22$; $c = 5.99$ Å

[a] Ref. 25.

[b] From X-ray powder methods.

[c] Becomes antiferromagnetic at *ca.* 75°K. Magnetically anisotropic at room temperature (ref. 38).

[d] Polymorphic transition occurs at 787°.

[e] Reported to be dimorphic.

[f] High temperature form.

The crystal structures and magnetic properties of the trifluoromanganates have been studied extensively[25], and some properties are summarized in Table 7. Except for the sodium and caesium salts, the trifluoromanganates have the cubic perovskite structure and their structures (particularly $KMnF_3$) have been investigated at low temperatures. The structure of $CsMnF_3$ has been described in detail[41,42]. It contains two types of manganese. One third of the manganese atoms occupy centres of fluorine octahedra that share their corners with other octahedra as in the perovskite structure, and the remaining are in distorted fluorine octahedra which share one face and three corners with other octahedra. All the Mn–F bond distances average at 2.13 Å.

TABLE 7. PROPERTIES OF SOME TRIFLUOROMANGANATES(II)[a]

	M.p. (°C)	Structure	Magnetic properties	
			μ, BM	T_N (°K)
$NaMnF_3$	762°			
$KMnF_3$	1032°	Cubic[b]	5.94	89
		$a = 4.182$–4.194 Å	6.04	95
			6.15	88
$RbMnF_3$	986°	Cubic		82
		$a = 4.241$–4.25 Å		
$CsMnF_3$	780°	Hexagonal		
		$a = 6.213$; $c = 15.074$ Å		
$TlMnF_3$	820°	Cubic		85
		$a = 4.250$ Å		76
NH_4MnF_3		Cubic		
		$a = 4.238$–4.250 Å		

[a] Ref. 25.

[b] Becomes orthorhombic at 184°K.

---

[41] A. Zalkin, K. Lee and D. H. Templeton, *J. Chem. Phys.* **37** (1962) 697.

[42] K. Lee, A. M. Portis and G. L. Witt, *Phys. Rev.* **132** (1963) 144.

The electronic absorption spectra of the trifluoromanganates are almost identical to MnF_2 and have been studied in great detail[25]. $KMnF_3$ is reported to have a Mn–F stretching frequency at 407 cm^{-1} [43].

In common with other metal fluorides complexes of MnF_2 with nitrogen, oxygen, etc., donor ligands do not appear to have been investigated in any detail[1].

Manganese(III) Fluoride

Manganese trifluoride has been prepared by treating MnF_2 [13, 27], $MnCl_2$ [44], MnI_2 [13], or manganese oxides[45] with fluorine or by the action of bromine trifluoride on $Mn(IO_3)_2$ [46, 47] and fluorinating the product at 500°C to remove traces of bromine trifluoride[47].

Manganese trifluoride, a red–purple solid, is instantly hydrolysed by water but is thermally stable. One hundred millilitres of anhydrous hydrogen fluoride at 11.5°C will dissolve 0.164 g of the solid[25]. It has been used as a fluorinating agent in organic chemistry both on a laboratory and on an industrial scale[25,48]. Properties of MnF_3 are summarized in Table 8. The diffuse reflectance spectrum has been recorded[25]. The structure consists of distorted MnF_6 octahedra in which there are two (Mn–F) distances of 2.1 Å, a second pair of 1.9 Å and a third pair of 1.8 Å in length[47, 49].

TABLE 8. SOME PROPERTIES OF MANGANESE TRIFLUORIDE [a]

ΔH_f°	-238 ± 5 kcal mole^{-1}
ΔH_{sub}°	68 ± 3 kcal mole^{-1}
Vapour pressure equation	$\log P_{atm} = -14{,}250/T + 7.68$
Structure (single crystal)	Monoclinic $a = 8.509$; $b = 5.037$; $c = 13.448$ Å; $\beta = 92.74°$

[a] Ref. 25.

Complex Fluorides of Manganese(III)

Hexafluoromanganates(III), pentafluoromanganates(III), and tetrafluoromanganates(III) are known. Potassium hexafluoromanganate K_3MnF_6, a purple–blue complex, is prepared by fusing a mixture of potassium hydrogen fluoride with $K_2MnF_5(H_2O)$ in an inert atmosphere and removing excess potassium fluoride by washing with dimethylformamide[50]. The complex is reported to have a tetragonal unit cell and a room temperature magnetic moment of 4.95 BM [50]. Manganese–fluorine stretching frequencies have been observed at 560 s and 617 w cm^{-1} [43].

Pink potassium pentafluoroaquomanganate(III), $K_2MnF_5 \cdot H_2O$, has been prepared from manganese dioxide and potassium hydrogen fluoride in hydrofluoric acid[51], from electrolytic

---

[43] R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.* (1959) 2762.

[44] H. J. Emeléus and G. L. Hurst, *J. Chem. Soc.* (1964) 396.

[45] E. E. Aynsley, R. D. Peacock and P. L. Robinson, *J. Chem. Soc.* (1950) 1622.

[46] A. G. Sharpe and A. A. Woolf, *J. Chem. Soc.* (1951) 798.

[47] M. A. Hepworth and K. H. Jack, *Acta Cryst.* **10** (1957) 345.

[48] M. Stacey and J. C. Tatlow, *Advances in Fluorine Chemistry* (edited by A. G. Sharpe, M. Stacey and J. C. Tatlow), Butterworths, Vol. 1 (1960), p. 166.

[49] M. A. Hepworth, K. H. Jack and R. S. Nyholm, *Nature* **179** (1957) 211.

[50] R. D. Peacock, *J. Chem. Soc.* (1957) 4684.

[51] W. G. Palmer, *Experimental Inorganic Chemistry*, Cambridge, London (1954).

oxidation of MnF_2 in 40% hydrofluoric acid followed by addition of a saturated solution of KHF_2 in hydrofluoric acid[52] and from the oxidation of manganese sulphate with potassium permanganate in hydrofluoric acid containing potassium fluoride[53]. $K_2MnF_5{\cdot}H_2O$ has a room temperature magnetic moment of 3.32 BM [54].

$Cs_2MnF_5{\cdot}H_2O$ has been prepared by addition of manganese trifluoride to a solution of caesium fluoride in hydrofluoric acid[55].

Ammonium pentafluoromanganate(III) is reported to have an orthorhombic cell[56] ($a = 6.20$, $b = 7.94$, $c = 10.72$ Å). The structure apparently consists of chains of tetragonally elongated octahedra linked by the long bonds into infinite kinked chains. The bridging Mn–F bond length is 2.12 Å and the in-plane Mn–F bond lengths are 1.84 and 1.85 Å. The bridging FMnF angle appears to be 139°. The electronic absorption spectrum of a single crystal has also been reported[56]. However, since the infrared spectra of the crystals used in these studies showed some evidence for O–H bonds it has been suggested[57] that the compound studied might be $(NH_4)_2MnF_4OH$ and that the Mn^{3+} ion is surrounded by four fluoride ions and two shared hydroxide ions. On this basis a more satisfactory interpretation of the electronic spectrum results[57].

The dark brown to violet tetrafluoromanganates, $LiMnF_4$, $KMnF_4$ and $RbMnF_4$, have been prepared by hydrogen reduction of the corresponding pentafluoromanganates(IV). They obey the Curie–Weiss law[58, 59].

Manganese(IV) Fluoride

Manganese tetrafluoride may be prepared by fluorinating manganese powder in a fluidized bed at 600–700°C [60], manganese trifluoride at 550°C [58] or Li_2MnF_6 at 550°C [61]. It is a very hygroscopic blue solid which slowly decomposes to manganese trifluoride and fluorine at room temperature[58, 60]. It obeys the Curie–Weiss law and has a Weiss constant of 10° and magnetic moment of 3.84 BM [58, 61].

Complex Fluorides of Manganese(IV)

Hexafluoromanganates(IV) and pentafluoromanganates(IV) are known. The hexafluoromanganates have been prepared by high temperature (300–500°C) fluorination of mixtures of manganese salts with both alkali and alkaline earth metal salts[25], electrolytic oxidation of a mixture of manganese difluoride and an alkali metal fluoride in 40% hydrofluoric acid[52, 62], reduction of a mixture of potassium permanganate and KHF_2 in 40% hydrofluoric acid by hydrogen peroxide or ether[51, 63], and fluorination of a mixture of potassium permanganate and potassium chloride in refluxing bromine trifluoride[64].

---

[52] B. Cox and A. G. Sharpe, *J. Chem. Soc.* (1954) 1798.

[53] J. T. Grey, *J. Am. Chem. Soc.* **68** (1946) 605.

[54] R. S. Nyholm and A. G. Sharpe, *J. Chem. Soc.* (1952) 3579.

[55] I. G. Ryss and B. S. Vitokhnovskaya, *Zh. Neorg. Khim.* 3 (1958) 1185.

[56] R. Dingle, *Inorg. Chem.* **4** (1965) 1287.

[57] N. S. Hush and R. J. M. Hobbs, *Progress in Inorganic Chemistry* (edited by F. A. Cotton), Vol. 10 (1968), p. 259.

[58] R. Hoppe, W. Dahne and W. Klemm, *Ann. chim. (Paris)* **658** (1962) 1.

[59] R. Hoppe, W. Liebe and W. Dahne, *Z. anorg. allgem. Chem.* **307** (1961) 276.

[60] H. W. Roesky, O. Glemser and K. H. Hellberg, *Chem. Ber.* **98** (1965) 2046.

[61] R. Hoppe, W. Dahne and W. Klemm, *Naturwissenschaften* **48** (1961) 429.

[62] B. Cox, *J. Chem. Soc.* (1954) 3251.

[63] H. Bode, H. Jenssen and F. Bandte, *Angew. Chem.* **65** (1953) 304.

[64] A. G. Sharpe and A. A. Woolf, *J. Chem. Soc.* (1951) 798.

The MnF_6^{2-} ion does exist in aqueous solution but eventually undergoes a slow irreversible decomposition[65]. There is no single crystal X-ray data available for any of the salts but X-ray powder data is available. The salts A_2MnF_6 (A = Li, Na, K; A_2 = Ca, Sr, Ba) are all hexagonal. Cs_2MnF_6 is cubic and Rb_2MnF_6 exists in three modifications—trigonal, cubic and hexagonal[25]. Mn–F bond distances have been obtained from X-ray powder data[24]. The magnetic moments of complexes vary from 3.80 to 3.95 BM [2], and K_2MnF_6 has a Mn–F stretching frequency at 625 cm^{-1} [43].

The pentafluoromanganates(IV), $AMnF_5$, have been prepared by fluorination of the trifluoromanganate at 450–500°C [58, 59]. $KMnF_5$ has also been obtained by refluxing potassium permanganate in selenium tetrafluoride[66]. The pentafluoromanganates(IV) are moisture sensitive. Their magnetic moments are close to the spin-only value[59]. Their structures are unknown.

MANGANESE CHLORIDES

Manganese(II) Chloride

Anhydrous manganese dichloride, a pink crystalline solid, can be prepared by a variety of methods[25]. These include treatment of manganese(II) acetate with acetyl chloride in benzene[67], treatment of manganese(II) nitrate, carbonate or acetate with refluxing thionyl chloride[25], or dissolving manganese metal in concentrated hydrochloric acid followed by dehydration of the product in a stream of hydrogen chloride gas at 580°C [68]. Some properties of $MnCl_2$ are given in Table 5. The vapours of $MnCl_2$ monomers exhibit a Mn–Cl asymmetric stretching frequency[69] at 467 cm^{-1}. The magnetic moment of $MnCl_2$ is 5.73 BM and it has a θ value of 3.3°. It has been suggested that at 1.96°K and in the absence of a magnetic field, $MnCl_2$ becomes antiferromagnetic (see ref. 25). Manganese dichloride is very soluble in water.

Hydrates of Manganese(II) Chloride

Three hydrates, $MnCl_2{\cdot}6H_2O$, $MnCl_4{\cdot}4H_2O$ and $MnCl_2{\cdot}2H_2O$, can be isolated from aqueous solution. Little is known about the hexahydrate which can be isolated from solutions of $MnCl_2$ at low temperatures[1, 70]. At −2°C it rapidly decomposes to the tetrahydrate.

The tetrahydrate is easily prepared from a saturated aqueous solution of manganese dichloride. $MnCl_2{\cdot}4H_2O$ is monoclinic; $a = 11.186$, $b = 9.513$, $c = 6.186$ Å and $\beta = 99.74°$; space group $P2_1/n$. Discrete octahedral molecules are present with the central manganese atom coordinated to two *cis*-chlorine atoms and four water molecules. Average Mn–Cl and Mn–O distances are 2.488 and 2.206 Å respectively[71, 72]. The heat of formation is −404 kcal $mole^{-1}$ [25]. The room temperature magnetic moment is 5.94 BM, and at very low temperatures it becomes antiferromagnetic[25]. The Néel temperature is 1.6°K; a specific heat anomaly occurs at this temperature[25] and at 1.622°K an anomaly occurs in the thermal expansion

---

[65] R. D. Peacock, *Progress in Inorganic Chemistry* (edited by F. A. Cotton), Interscience, Vol. 2 (1960), p. 193.

[66] R. D. Peacock, *J. Chem. Soc.* (1953) 3617.

[67] G. W. Watt, P. S. Gentile and E. P. Helvenston, *J. Am. Chem. Soc.* **77** (1955) 2752.

[68] R. A. Butera and W. F. Giauque, *J. Chem. Phys.* **40** (1964) 2379.

[69] G. E. Leroi, T. C. James, J. T. Hougen and W. Klemperer, *J. Chem. Phys.* **36** (1962) 2879.

[70] L. A. Ozerov, *Trudy Voronezh. Univ.* **28** (1953) 24.

[71] A. Zalkin, J. D. Forrester and D. H. Templeton, *Inorg. Chem.* **3** (1964) 529.

[72] W. H. Baur, *Inorg. Chem.* **4** (1965) 1840.

coefficient due to antiferromagnetic ordering[73]. The electronic absorption spectra has been studied[74] and an Mn–O stretching frequency is observed at 395 cm^{-1} [75]. The thermal decomposition of $MnCl_2 \cdot 4H_2O$ has been studied by a number of techniques. The data is summarized in Table 9.

TABLE 9. THERMAL DECOMPOSITION OF MANGANESE(II) HALIDE HYDRATES [a]

$$MnCl_2 \cdot 6H_2O \xrightarrow{-2^\circ} MnCl_2 \cdot 4H_2O + 2H_2O\ ^{a}$$

$$MnCl_2 \cdot 4H_2O \xrightarrow{55^\circ} MnCl_2 \cdot 2H_2O + 2H_2O\ ^{a}$$

$$MnCl_2 \cdot 2H_2O \xrightarrow{135^\circ} MnCl_2 \cdot H_2O + H_2O\ ^{a}$$

$$MnCl_2 \cdot H_2O \xrightarrow[(191\text{–}228^\circ)\ ^{b}]{210^\circ} MnCl_2 + H_2O\ ^{a}$$

$$MnCl_2 \xrightarrow[(650\text{–}950^\circ)\ ^{b}]{} Mn + Cl_2$$

$$MnBr_2 \cdot 2H_2O \xrightarrow[(60\text{–}146^\circ)\ ^{b}]{} MnBr_2 \cdot H_2O + H_2O$$

$$MnBr_2 \cdot H_2O \xrightarrow[(146\text{–}197^\circ)\ ^{b}]{} MnBr_2 + H_2O$$

$$MnI_2 \cdot H_2O \xrightarrow[(86\text{–}160^\circ)\ ^{b}]{} MnI_2 + H_2O$$

$$MnI_2 \xrightarrow[(590\text{–}943^\circ)\ ^{b}]{} Mn + I_2$$

[a] H. J. Borchardt and F. Daniels, *J. Phys. Chem.* **61** (1957) 917; Ref. 25.
[b] P. Lumme and M. T. Raivio, *Suomen Kemiistilehti* **41B** (1968) 194.

Manganese dichloride dihydrate, $MnCl_2 \cdot 2H_2O$, can be obtained from a saturated aqueous solution of $MnCl_2$ at about 65°C [25]. At room temperature it readily absorbs water. It is monoclinic ($a = 7.409$, $b = 8.800$, $c = 3.691$ Å; $\beta = 98.67^\circ$; space group $C2/m$). The structure consists of polymeric chains of manganese and chlorine atoms in a nearly square planar arrangement. The water molecules complete the octahedron and the chains are held together by hydrogen bonds[76]. The Mn–O distance is 2.150 Å, the Mn–Cl distances are 2.515 and 2.592 Å. $MnCl_2 \cdot 2H_2O$ becomes magnetically ordered at low temperatures[77] (no details are reported) and the electronic absorption spectrum has been examined[78].

Complex Chlorides of Manganese(II)

Hexachloromanganates(II), tetrachloromanganates(II), trichloromanganates(II) and hydrated tetra- and tri-chloromanganates are known. The salts, A_2MnCl_4 (A = alkali metal), are prepared by fusing stoichiometric amounts of the appropriate chlorides in a melt[79, 80]. The correct proportions must be used since other chloro complexes can be formed. The salts, $(MR_4)_2MnCl_4$ (M = N, P or As; R = alkyl or aryl), have been prepared by mixing the

---

[73] R. Gonano, F. Ono and Hirooka, *J. Appl. Phys.* **39** (1968) 710.
[74] I. Tsujikawa and E. Kanda, *J. Phys. Soc. Japan* **18** (1963) 1382.
[75] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta* **20** (1964) 429.
[76] B. Morosin and E. J. Graeber, *J. Chem. Phys.* **42** (1965) 898; B. K. Vainshtein, *Dokl. Akad. Nauk SSSR* **83** (1952) 227.
[77] A. Narath, *Phys. Rev.* **136** (1964) 766.
[78] K. E. Lawson, *J. Chem. Phys.* **44** (1966) 4149; D. H. Goode, *J. Chem. Phys.* **43** (1965) 2830.
[79] H. J. Seifert and F. W. Koknat, *Z. anorg. allgem. Chem.* **341** (1965) 269.
[80] B. F. Markov and R. V. Chernov, *Ukrain. Khim. Zh.* **24** (1958) 139.

appropriate amounts of the chlorides in ethanol or acetone[81, 89, 97]. Other preparations include refluxing a mixture of Et_4NCl with $MnCl_2 \cdot 4H_2O$ in thionyl chloride[90] and the interaction of pyridinium chloride[91] or Et_4NCl[92] with $MnCl_2$ in concentrated hydrochloric acid. The complex $MnCl_2(DMSO)_3$, formed from manganese dichloride and dimethylsulphoxide, DMSO, is correctly formulated as $Mn(DMSO)_6^{2+}MnCl_4^{2-}$ [25]. The compound, $Mn(C_5H_7S_2)_2Cl_4$, prepared by treating an ethanolic solution of acetylacetone and manganese dichloride with hydrogen sulphide and hydrogen chloride, has now been formulated as 3,5-dimethyldithiolium tetrachloromanganate(II)[93]. Heat of solution measurements have allowed calculation of $\triangle H^\circ_{298}$ for the reactions

$$2MCl(c) + MnCl_2(c) = M_2MnCl_4(c)$$

The values are -11.21, -7.92 and -14.07 kcal mole^{-1} when M is Cs^+, Me_4N^+ and Et_4N^+ respectively[83,94]. Using this and other data, a value of -333.8 kcal mole^{-1} for $\triangle H^\circ_f$ of Cs_2MnCl_4 is obtained[95]. Compounds containing the MnX_4^{2-} anion are usually tetrahedral, but in $(MeNH_3)_2MnCl_4$ and α-Cs_2MnCl_4 the manganese is in an octahedral environment[97]. Crystallographic structural data is available for Rb_2MnCl_4[79], $(MeNH_3)_2MnCl_4$[97, 98], $(EtNH_3)_2MnCl_4$[98], $(Me_4N)_2MnCl_4$[99], $(MePh_3As)_2MnCl_4$[81] and α-Cs_2MnCl_4[97]. The magnetic moments of the tetrachloromanganates fall in the range 5.8–5.95 BM[85, 88, 89]. The electronic absorption spectra of solutions and single crystals are available[25, 97]. There are also detailed infrared and Raman studies[96].

The tetrachloromanganate(II) dihydrates, $MnCl_4^{2-} \cdot 2H_2O$, are prepared by the interaction of stoichiometric amounts of the appropriate chlorides in water[100, 101, 102].

From a study of the $NH_4Cl/MnCl_2/H_2O$ system the compounds $6NH_4Cl \cdot MnCl_2 \cdot 2H_2O$ and $2NH_4Cl \cdot MnCl_2 \cdot 2H_2O$ have been isolated and a range of solid solutions exist between these two compounds[100]. The compound has a tetragonal unit cell, $a = 7.514$, $c = 8.245$ Å and the structure has been related to that of NH_4Cl. The salts $M_2MnCl_4 \cdot 2H_2O$ (M = K, Rb, or Cs) all contain *trans*-$MnCl_4(H_2O)_2$ octahedra. Structural data is given in Table 10.

---

[81] P. Pauling, *Inorg. Chem.* **5** (1966) 1498.

[82] H.B. Jonassen, L.J.Theriot, E. A. Boudreaux and W. A. Ayres, *J. Inorg. Nucl. Chem.* **26** (1964) 595.

[83] P. Paoletti and A. Vacca, *Trans. Faraday Soc.* **60** (1964) 50.

[84] A. B. Blake and F. A. Cotton, *Inorg. Chem.* **3** (1964) 5.

[85] D. V. R. Rao and S. K. Naik, *Current Sci.* (*India*) **33** (1964) 109.

[86] C. Furlani and A. Furlani, *J. Inorg. Nucl. Chem.* **19** (1961) 51.

[87] E. A. Boudreaux, H. B. Jonassen and L J. Theriot, *J. Am. Chem. Soc.* **85** (1963) 2039.

[88] L. Naldini and A. Sacco, *Gazz. chim. ital.* **89** (1959) 2258.

[89] N. S. Gill and R. S. Nyholm, *J. Chem. Soc.* (1959) 3997.

[90] D. M. Adams, J. Chatt, J. M. Davidson and J. Gerrett, *J. Chem. Soc.* (1963) 2189.

[91] H. P. de la Garanderie, *Compt. rend.* **255** (1962) 2585.

[92] N. S. Gill and F. B. Taylor, *Inorg. Synthesis* **9** (1967) 136.

[93] G. A. Heath, R. L. Martin and I. M. Stewart, *Australian J. Chem.* **22** (1969) 83.

[94] P. Ehrlich, F. W. Koknat and H. J. Seifert, *Z. anorg. allgem. Chem.* **341** (1965) 281.

[95] T. A. Zordon and L. G. Hepler, *Chem. Revs.* **68** (1968) 737.

[96] H. G. M. Edwards, M. J. Ware and L. A. Woodward, *Chem. Communs.* (1968) 540; J. S. Avery, C. D. Burbridge and D. M. L. Goodgame, *Spectrochim. Acta* **24A** (1968) 1721.

[97] J. J. Foster and N. S. Gill, *J. Chem. Soc.* A, (1968) 2625.

[98] Y. Okaya, R. Pepincky, Y. Takeuchi, H. Kuroya, A. Shimada, P. Galletelli, N. Stemple and A. Beevers, *Acta Cryst.* **10** (1957) 798.

[99] B. Morosin and E. J. Graebner, *Acta Cryst.* **23** (1967) 766.

[100] A. L. Greenberg and G. H. Walden, *J. Chem. Phys.* **8** (1940) 645.

[101] S. J. Jensen, *Acta Chem. Scand.* **18** (1964) 2085.

[102] H. Forstat, N. D. Love and J. N. McElearney, *Phys. Letters* **25A** (1967) 253.

TABLE 10. STRUCTURES OF SOME TETRACHLOROMANGANATE(II) DIHYDRATES

$K_2MnCl_4(H_2O)_2$	$Rb_2MnCl_4(H_2O)_2$	$Cs_2MnCl_4(H_2O)_2$
Tetragonal [a]	Triclinic [b]	Triclinic [b]
$I4/mmm$	$P\bar{1}$	$P\bar{1}$
$a = 7.415$ Å	$a = 5.66$ Å	$a = 5.74$ Å
$c = 8.220$ Å	$b = 6.48$ Å	$b = 6.66$ Å
	$c = 7.01$ Å	$c = 7.27$ Å
	$\alpha = 66.7°$; $\beta = 87.8°$; $\gamma = 84.8°$	$\alpha = 67.0°$; $\beta = 87.8°$; $\gamma = 84.3°$
Mn–Cl dist. 2.531 Å	2.54, 2.58 Å	2.54 Å
Mn–O dist. 2.175 Å	2.08 Å	2.13 Å

[a] S. J. Jensen, *Acta Chem. Scand.* **22** (1968) 647.
[b] S. J. Jensen, *Acta Chem. Scand.* **18** (1964) 2085.

$Rb_2MnCl_4(H_2O)_2$ becomes antiferromagnetic below 2.24°K [25] and the electronic absorption spectrum of $(NH_4)_2MnCl_4 \cdot 2H_2O$ has been recorded at several temperatures[103].

The trichloromanganates(II), $AMnCl_3$, have been prepared either by fusing stoichiometric amounts of the appropriate chlorides[79, 80] or by heating 1:1 mixtures of an alkali metal chloride and $MnCl_2 \cdot 4H_2O$ in an atmosphere of anhydrous hydrogen chloride[104,105]. $Me_4N \cdot MnCl_3$ has been prepared from an aqueous solution[99]. Heat of solution measurements have allowed calculation of ΔH°_{298} for the reactions

$$MCl(c) + MnCl_2(c) = MMnCl_3(c)$$

The values[94] are -0.71, -3.63, -6.21 and -9.78 kcal mole^{-1} when M is Na^+, K^+, Rb^+ and Cs^+ respectively. A value of -4.4 has also been given for $KMnCl_3$ [106]. From the former data the ΔH°_f (-228.8 kcal mole^{-1}) of $CsMnCl_3$ has been calculated[95]. Only the structure of Me_4NMnCl_3 is known[99]. The structure contains chains of $MnCl_6$ octahedra joined at their faces. There is a slight trigonal elongation of the octahedra and there is some distortion of the discrete Me_4N^+ ions. The Mn–Cl distance is 2.560 Å. Lattice constants of other salts are given in Table 11. Some of the salts $AMnCl_3$ become antiferromagnetic at low temperatures. When $A = K^+$, Rb^+ and Cs^+, the Néel temperatures are 100°, 86° and 69°K respectively[107]. The polarized optical absorption spectrum of Me_4NMnCl_3 is consistent with a trigonal distortion of the $MnCl_6$ octahedra, and in this complex there is no paramagnetic–antiferromagnetic transition[108].

Alkali metal trichloromanganate(II) dihydrates, $AMnCl_3 \cdot 2H_2O$, are usually obtained from aqueous solutions of stoichiometric quantities of the chlorides[79, 101, 104, 109, 110]. The salt $RbMnCl_3 \cdot 2H_2O$ exists in two modifications[111]. A mixture of the α- and β-forms is precipitated when a saturated solution of RbCl and $MnCl_2 \cdot 4H_2O$ in a 1:5 ratio is cooled from 80°

---

[103] D. H. Goode, *J. Chem. Phys.* **43** (1965) 2830.
[104] W. J. Croft, M. Kestigian and F. D. Leipziger, *Inorg. Chem.* **4** (1965) 423.
[105] M. Kestigian, W. J. Croft, F. D. Leipziger and R. J. Carter, *J. Chem. Engng. Data* **12** (1967) 97.
[106] S. A. Shchukarev, I. V. Vasil'kova and G. M. Barvenok, *Vestn. Leningrad Univ., Ser. Fiz. i Khim.* **20** (1965) 145.
[107] R. W. Kedzie, J. R. Shane, M. Kestigian and W. J. Croft, *J. Appl. Phys.* **36** (1965) 1195.
[108] K. E. Lawson, *J. Chem. Phys.* **47** (1967) 3627.
[109] S. J. Jensen, P. Andersen and S. E. Rasmussen, *Acta Chem. Scand.* **16** (1962) 1890.
[110] J. Suss, *Z. Krist.* **51** (1912) 248.
[111] S. J. Jensen, *Acta Chem. Scand.* **21** (1967) 889.

TABLE 11. STRUCTURES OF ANHYDROUS AND HYDRATED TRICHLOROMANGANATES(II)

$KMnCl_3$	—	Tetragonal[a]	$a = 10.024$;	$c = 9.972$ Å	
$RbMnCl_3$	$P6_3/mmc$	Hexagonal[b]	$a = 7.165$;	$c = 17.815$ Å	
$CsMnCl_3$	—	Hexagonal[c]	$a = 7.288$;	$c = 27.44$ Å	
Me_4NMnCl_3	$P6_3/m$	Hexagonal[d]	$a = 9.151$;	$c = 6.494$ Å	
$KMnCl_3 \cdot 2H_2O$	$P\bar{1}$	Triclinic[e]	$a = 6.49$;	$b = 6.91$;	$c = 9.91$ Å
			$\alpha = 96.8$;	$\beta = 114.1°$;	$\gamma = 112.6°$
α-$RbMnCl_3 \cdot 2H_2O$	$Pcca$	Orthorhombic[f]	$a = 9.005$;	$b = 7.055$;	$c = 11.34$ Å
β-$RbMnCl_3 \cdot 2H_2O$	$P\bar{1}$	Triclinic[f]	$a = 6.65$;	$b = 7.01$;	$c = 9.03$ Å
			$\alpha = 92.3°$;	$\beta = 109.4°$;	$\gamma = 112.9°$
$CsMnCl_3 \cdot 2H_2O$	$Pcca$	Orthorhombic[g]	$a = 9.060$;	$b = 7.285$;	$c = 11.455$ Å

[a] W. J. Croft, M. Kestigian and F. D. Leipziger, *Inorg. Chem.* **4** (1965) 423.
[b] H. J. Seifert and F. W. Koknat, *Z. anorg. allgem. Chem.* **341** (1965) 269.
[c] M. Kestigian, W. J. Croft, and F. D. Leipziger, *J. Chem. Eng. Data* **12** (1967) 97.
[d] B. Morosin and E. J. Graebner, *Acta Cryst.* **23** (1967) 766.
[e] S. J. Jensen, *Acta Chem. Scand.* **22** (1968) 641.
[f] S. J. Jensen, *Acta Chem. Scand.* **21** (1967) 889.
[g] S. J. Jensen, S. E. Rasmussen and P. Anderson, *Acta Chem. Scand.* **16** (1962) 1890.

to 50°C. If this mixture is allowed to stand in the mother liquor at 25° for several months, the transformation α to β occurs. At 0°C the β-form transforms to the α-phase. Structural data on some $AMnCl_3 \cdot 2H_2O$ salts are given in Table 11. $KMnCl_3 \cdot 2H_2O$ and β-$RbMnCl_3 \cdot 2H_2O$ contain $Mn_2Cl_6(H_2O)_4$ anions. The octahedra are joined at an edge by bridging chlorines and the water molecules are in a *trans*-configuration. α-$RbMnCl_3 \cdot 2H_2O$ and $CsMnCl_3 \cdot 2H_2O$, however, contain *cis*-$MnCl_4(H_2O)_2$ octahedra and the octahedra are joined into zigzag chains by sharing corners. The single crystal optical absorption spectrum of $KMnCl_3 \cdot 2H_2O$ has been investigated[103] and the compound has a magnetic transition at 2.70°K[112]. There is also data on the electronic absorption spectrum of $CsMnCl_3 \cdot 2H_2O$ [113].

The complex chloromanganates $NaMn_2Cl_5$, Na_4MnCl_6, $K_3Mn_2Cl_7$, K_4MnCl_6, $Rb_3Mn_2Cl_7$, $CsMn_4Cl_9$ and Cs_3MnCl_5, have been isolated from mixtures of manganese dichloride and an alkali metal chloride[79, 80, 94, 97]. $K_3Mn_2Cl_7$ is tetragonal[79], $a = 5.027$, $c = 25.325$ Å. The heat of the reaction[94]

$$3CsCl(c) + MnCl_2(c) = Cs_3MnCl_5$$

has been calculated as $\triangle H^\circ_{298} = -9.81$ kcal mole^{-1} from heat of solution data. This gives a value of -435.9 kcal mole^{-1} for $\triangle H^\circ_f$ of Cs_3MnCl_5 [95].

Manganese(III) Chloride

Manganese trichloride is reported to result from the action of hydrogen chloride[114] on manganese(III) acetate at $-100°$ or by treating manganese dioxide with hydrogen chloride in anhydrous ethanol at $-63°$ followed by precipitation of the product with carbon tetrachloride or petrol[115]. $MnCl_3$ is a black compound which decomposes above $-40°$. Several complexes of $MnCl_3$ have recently been isolated[116, 117] (see section on manganese(III) complexes).

---

[112] H. Forstat, J. N. McElearney and B. T. Bailey, *Phys. Letters* **27A** (1968) 549.
[113] A. Le Paillier-Malecot, *Compt. rend.* **265B** (1967) 657.
[114] A. Chretien and G. Varga, *Bull. soc. chim. France* **3** (1936) 2385.
[115] J. H. Krepelka, *Collection Czechoslav. Chem. Communs.* **7** (1935) 105.
[116] H. Funk and H. Kreis, *Z. anorg. allgem. Chem.* **349** (1967) 45.
[117] H. A. Goodwin and R. N. Sylva, *Australian J. Chem.* **20** (1967) 629.

Complex Chlorides of Manganese(III)

Hexachloromanganates, $MnCl_6^{3-}$, and pentachloromanganates, $MnCl_5^{2-}$, are known. *Tris*(1,2-propenediamine)M^{3+}:$MnCl_6^{3-}$ (M = Cs or Rh) is prepared by the interaction of $MnSO_4 \cdot H_2O$ with the cobalt or rhodium complex, *tris*(1,2-propenediamine)M·Cl in the minimum of hydrochloric acid followed by addition of small amounts of sodium chlorate. The compounds slowly decompose on standing[118, 119]. $[Co(C_3H_{10}N_3)_3] \cdot [MnCl_6]$ obeys the Curie law and has a magnetic moment of 4.91 BM [118] and Mn–Cl stretching frequencies at 342 and 183 cm^{-1} [120]. The electronic absorption spectra of the complexes and the influence of the Jahn–Teller effect has been discussed[118, 119].

The pentachloromanganate(III) complexes, $(Et_4N)_2MnCl_5$, $(dipy)H_2 \cdot MnCl_5$ and $(phen)H_2 \cdot MnCl_5$ have been prepared either via manganese dioxide or potassium permanganate in the presence of hydrogen chloride or hydrochloric acid[117, 119, 121]. The electronic spectra[117, 119] and magnetic properties have been studied[121].

The $MnCl_5^{2-}$ anion, in the salt $(dipy)H_2 \cdot MnCl_5$, is 5-coordinate with a distorted square based pyramidal geometry[122].

The preparation of K_2MnCl_5 has also been described but the compound has not been studied[25].

Complex Chlorides of Manganese(IV)

Hexachloromanganates(IV), $MnCl_6^{2-}$, have been prepared by adding a permanganate to a solution of the appropriate chloride in hydrochloric acid saturated with hydrogen chloride gas[123]. K_2MnCl_6 has also been prepared from manganese(III) acetate and potassium acetate in a large excess of acetyl chloride[124]. The salts K_2MnCl_6, Rb_2MnCl_6, Cs_2MnCl_6, $(NH_4)_2MnCl_6$ and $(Me_4N)_2MnCl_6$ have face-centred cubic lattices of the K_2PtCl_6 type. The cell dimensions are 9.645, 9.82, 10.17, 9.80 and 12.70 Å respectively[123]. K_2MnCl_6 has a reported[123] Mn–Cl distance of 2.28 Å and Mn–Cl stretching frequencies[123] at 358 and 200 cm^{-1}. The complex obeys the Curie–Weiss law and has a magnetic moment of 3.90 BM and a Weiss constant of 30°. The initial results of the electronic absorption spectrum[123] of K_2MnCl_6 have been questioned[125].

MANGANESE BROMIDES

Manganese(II) Bromide

Anhydrous manganese dibromide has been prepared[126] by the action of hydrobromic acid on manganese carbonate followed by dehydration of the product first at 100°C and finally in hydrogen bromide gas at 725°C. $MnBr_2$ can also be obtained by treating manganese(II) acetate with acetyl bromide in benzene[67] and drying the product in a

---

[118] W. E. Hatfield, R. C. Fay, C. E. Pfluger and T. S. Piper, *J. Am. Chem. Soc.* **85** (1963) 265.

[119] T. S. Davis, J. P. Fackler and M. J. Weeks, *Inorg. Chem.* 7 (1968) 1994.

[120] D. M. Adams and D. M. Morris, *J. Chem. Soc.* A (1968) 694.

[121] N. S. Gill, *Chem. and Ind.* (*London*) (1961) 989.

[122] I. Bernal, N. Elliott and R. A. Lalancette, quoted by G. Davies, *Coord. Chem. Revs.* **4** (1969) 199.

[123] P. C. Moews, *Inorg. Chem.* **5** (1966) 5.

[124] H. D. Hartd and M. Fleischer, *Z. anorg. allgem. Chem.* **357** (1968) 113.

[125] B. Jezowska-Trzebiatowska, S. Wajda, M. Baluka, L. Natkaniec and W. Wojciechowski, *Inorg. Chim. Acta* **1** (1967) 205.

[126] W. B. Hadley and J. W. Stout, *J. Chem. Phys.* **39** (1963) 2205.

nitrogen atmosphere at 200°C. Some properties of manganese dibromide are given in Table 5. It is hygroscopic. Manganese dibromide has a room temperature magnetic moment of 5.82 BM. It does not obey the Curie or the Curie–Weiss laws at normal temperatures. From 46.4° to 77.3°K the magnetic susceptibility is given by the expression

$$\chi_m = 4.38/T+4.7$$

The Néel temperature is 2.16°K [25]. The electronic absorption spectrum has been recorded but there is some disagreement over calculation of various parameters[25].

Hydrates of Manganese(II) Bromide

The hydrates $MnBr_2 \cdot 4H_2O$ and $MnBr_2 \cdot 2H_2O$ are known. Data on their thermal decomposition is given in Table 9. The tetrahydrate is obtained by evaporation of a saturated solution of manganese dibromide at room temperature[1]. It has a magnetic moment of 5.93 BM, a Weiss constant of 2° and a Néel temperature of 2.13°K [25].

Manganese dibromide dihydrate can be isolated[1] by evaporation of a saturated aqueous solution of manganese dibromide at about 65°C. It has also been prepared by mixing stoichiometric amounts of manganese carbonate and hydrobromic acid[127]. The structure is monoclinic, $a = 7.763$, $b = 8.990$, $c = 3.881$ Å, $\beta = 97.62°$, space group $C2/m$. The manganese is coordinated to four bromines in a nearly square planar environment, and each bromine is shared by two metal atoms. The water molecules fill the *trans*-positions of the octahedron, and the structure[128] is analogous to $MnCl_2 \cdot 2H_2O$.

Complex Bromides of Manganese(II)

Tetrabromomanganates(II) and tribromomanganates are known. Substituted ammonium, phosphonium and arsonium salts have been prepared by mixing appropriate amounts of the bromides in ethanol or acetone[81, 86, 88, 89, 97, 129]. The heat of the reaction

$$2Et_4NBr + MnBr_2 = (Et_4N)_2MnBr_4$$

is -10.12 kcal mole^{-1}. The magnetic moments of the complexes are in the range 5.8–5.9 BM[88, 89]. The electronic absorption spectrum of the $MnBr_4^{2-}$ ion has been recorded[86, 89, 97, 129, 131]. The infrared and Raman spectra have been investigated in detail[96].

Some tribromomanganates have recently been prepared. $Me_4N \cdot MnBr_3$ is hexagonal, $a = 9.44$, $c = 6.76$ Å[97].

Manganese(III) Bromide

Manganese(III) bromide, $MnBr_3$, is not known. Some years ago it was claimed that addition of bromine to manganese metal in ether resulted in the formation of the adduct $MnBr_3 \cdot 3Et_2O$, but other workers have not been able to repeat this work[132]. It is possible, however, that adducts of $MnBr_3$ might be isolated using ligands which are more basic than diethyl ether.

---

[127] P. Lumme and M. T. Raivio, *Soumen Kemiistilehti* **41B** (1968) 194.

[128] B. Morosin, *J. Chem. Phys.* **47** (1967) 417.

[129] F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc.* **84** (1962) 167.

[130] P. Paoletti, *Trans. Faraday Soc.* **61** (1965) 219.

[131] B. D. Bird and P. Day, *Chem. Communs.* (1967) 741.

[132] J. G. F. Druce, *J. Chem. Soc.* (1937) 1407.

MANGANESE IODIDES

Manganese(II) Iodide

Anhydrous manganese di-iodide can be prepared by direct interaction of the constituents in ether[1] or the interaction of MnO_2 or MnS_2 with aluminium tri-iodide in a sealed tube at 230° [133, 134]. It is very soluble in water and properties are given in Table 5. It has a magnetic moment of 5.88 BM, and from room temperature to 60°K deviates only slightly from the Curie law. The Néel temperature is 3.4°K [25].

Hydrates of Manganese(II) Iodide

$MnI_2 \cdot H_2O$ has been prepared from stoichiometric amounts of manganese carbonate in hydroiodic acid[127]. Data on its thermal decomposition is given in Table 9.

Complex Iodides of Manganese(II)

Tetraiodomanganates(II), MnI_4^{2-}, are known. Substituted ammonium, phosphonium and arsonium salts have been prepared from the constituent iodides in acetone or ethanol and their magnetic and electronic spectra have been studied[88,89,97,129]. The adduct, $MnI_2(MeCN)_3$, is correctly formulated[25] as $Mn(MeCN)_6^{2+}MnI_4^{2-}$. The infrared and Raman spectra of the tetraiodomanganates have been studied in detail[96].

OXIDE HALIDES

Oxide Fluorides

At the present time only MnO_3F is known. It has been prepared by treating potassium permanganate with anhydrous hydrogen fluoride[135, 139], iodine pentafluoride[137] at 40° or with fluorosulphuric acid[135]. The dark green solid can be purified by distillation *in vacuo*. Manganese trioxide fluoride melts[135, 136] at $-78°$ and the extrapolated b.p. is 60°. From $-15°$ to 10° the vapour pressure equation is $\log P_{mm} = -1007/T + 8.2$. The calculated[135] heat of vaporization is 8.1 kcal mole^{-1}. MnO_3F is very moisture sensitive and decomposes explosively at room temperature to give oxygen, manganese dioxide and manganese difluoride[135]. The microwave spectrum[138] shows that the molecule is very nearly tetrahedral. Mn–F = 1.724 Å, Mn–O = 1.586 Å, and the OMnF angle is 108.45°. At present this is the only oxyfluoride of manganese known but the recent isolation of a number of oxychloride compounds suggests that analogous fluorine compounds should exist.

Oxide Chlorides

Manganese trioxide chloride, MnO_3Cl, has recently been prepared by passage of dry hydrogen chloride gas through a solution of potassium permanganate in concentrated sulphuric acid[139]. The action of chlorosulphuric acid on Mn_2O_7 also gives MnO_3Cl, but

---

[133] M. Chaigneau, *Bull. Soc. chim. France* (1957) 886.
[134] M. Chaigneau and M. Chastagnier, *Bull. soc. chim. France* (1958) 1192.
[135] A. Engelbrecht and A. V. Grosse, *J. Am. Chem. Soc.* **76** (1954) 2042.
[136] K. Wiechert, *Z. anorg. allgem. Chem.* **261** (1950) 310.
[137] E. E. Aynsley, *J. Chem. Soc.* (1958) 2425.
[138] A. Javan and A. Engelbrecht, *Phys. Rev.* **96** (1954) 649.
[139] D. Michel and A. Doiwa, *Naturwissenschaften* **53** (1966) 129.

from this reaction MnO_2Cl_2 and $MnOCl_3$ have also been isolated[140]. It is possible that MnO_3Cl was isolated some years ago[1]. All three oxychlorides are volatile liquids at 0°C and are solids at -68°C. They are explosively unstable at room temperature but are soluble in CCl_4 in which they can be handled more safely.

MANGANESE CYANIDES

The cyanide derivatives of manganese, which only exist as complexes, have recently been reviewed[141]. Complexes of Mn(I), Mn(II), Mn(III) and Mn(IV) exist and there is some evidence for a derivative of Mn(0). Nitrosyl cyanide complexes are also dealt with here.

Manganese(0)

A yellow product of approximate composition, $K_5Mn(CN)_6 \cdot K_6Mn(CN)_6 \cdot 2NH_3$ has been obtained by reduction of $K_3Mn(CN)_6$ with potassium in liquid ammonia[142]. The compound has a magnetic moment of 1.25 BM and this together with its reducing power suggest that 30–40% of the product contains a manganese(0) compound with one unpaired electron[141].

Manganese(I)

The salts of the $Mn(CN)_6^{5-}$ ion are obtained by reduction of the $Mn(CN)_6^{4-}$ ion electrolytically[141], with Devarda's alloy[144] or with metal amalgams[145, 146]. The salts are colourless and diamagnetic[143] and are very easily oxidized in air. In 1.5 M NaCN the potential of the system

$$Mn(CN)_6^{4-} + e = Mn(CN)_6^{5-}$$

is -1.06 V [143] and the soluble $Na_5Mn(CN)_6$ liberates hydrogen from hot water. There are conflicting reports on the values of the lattice constants of $K_5Mn(CN)_6$. One paper[143] gives a tetragonal cell, $a = 16.35$, $c = 13.11$ Å; the other[147] describes it as cubic, $a = 11.89$ Å. It has been suggested that the latter result refers to a hydrate[141]. The $C{\equiv}N$ stretching frequency of $K_5Mn(CN)_6$ has been reported and is unusual in being notably higher than the corresponding technetium and rhenium anions[141].

Manganese(I) carbonyl cyanide complexes $K_2[Mn(CO)_3(CN)_3]$ and $K_3[Mn(CO)_2(CN)_4]$ have been obtained from KCN and $MnCl(CO)_5$. Their infrared spectra have also been studied[150].

A manganese(I) nitrosyl cyanide complex, $K_3[Mn(CN)_5NO]2H_2O$, can be prepared from $K_3Mn(CN)_6$, KCN and hydroxylamine[148]. The complex may be dehydrated by storing

---

[140] T. S. Briggs, *J. Inorg. Nuclear Chem.* **30** (1968) 2866.

[141] B. M. Chadwick and A. G. Sharpe, *Advances in Inorganic and Radiochemistry* (edited by H. J. Emeléus and A. G. Sharpe), Vol. 8 (1966), p. 83.

[142] V. J. Christensen, J. Kleinberg and A. W. Davidson, *J. Am. Chem. Soc.* **75** (1953) 2495.

[143] W. D. Treadwall and W. E. Raths, *Helv. Chim. Acta* **35** (1952) 2259.

[144] W. Manchot and H. Gall, *Ber. deut. chem. Ges.* **61** (1928) 1135.

[145] W. D. Treadwall and W. E. Raths, *Helv. Chim. Acta* **35** (1952) 2275.

[146] D. Clauss and A. Lissner, *Z. anorg. allgem. Chem.* **297** (1958) 300.

[147] K. Schwochau and W. Herr, *Z. anorg. allgem. Chem.* **319** (1962) 148.

[148] F. A. Cotton, R. R. Monchamp, R. J. M. Henry and R. C. Young, *J. Inorg. Nucl. Chem.* **10** (1959) 28.

[149] P. Gans, A. Sabatini and L. Sacconi, *Inorg. Chem.* **5** (1966) 1877.

[150] H. Behrens, E. Ruyter and E. Lindner, *Z. anorg. allgem. Chem.* **349** (1967) 251.

over P_2O_5 *in vacuo*. The purple complex dissolves in water to give a permanganate-like coloured solution which slowly decomposes in acid, neutral, or alkaline solution. $K_3[Mn(CN)_5NO]$ is diamagnetic[141] and has a N–O stretching frequency[149] at 1700 cm^{-1}. $K_3[Mn(CN)_5NO]\cdot 2H_2O$ has a monoclinic unit cell. The central manganese is in a distorted octahedral environment of point symmetry C_{4v} in which the Mn–C distances vary between 1.97 and 2.01 Å and the Mn–N distance is 1.66 Å [151]. The electronic spectrum of $K_3[Mn(CN)_5NO]\cdot 2H_2O$ has been reported[152]. $E°$ for the system

$$[Mn(CN)_5NO]^{2-} + e = [Mn(CN)_5NO]^{3-}$$

is +0.6 V [141].

Manganese(II)

Manganese(II) cyanide does not appear to be known[141]. When a limited quantity of potassium cyanide solution is added to manganese(II) chloride a rose-coloured precipitate is first formed which then becomes green and very insoluble. The stoichiometry of the green product is $KMn(CN)_3$ and it has recently been confirmed by infrared, magnetic and X-ray powder techniques that the complex should be formulated as $K_2Mn[Mn(CN)_6]$ [153]. It is very sensitive to water and oxygen.

The addition of excess potassium cyanide solution to manganese(II) acetate or carbonate in an inert atmosphere produces a yellow solution from which the blue violet complex $K_4[Mn(CN)_6]\cdot 3H_2O$ can be obtained. The more soluble sodium salt can be prepared similarly[13]. The complex is only stable in cyanide solutions of concentration greater than 1.5 M; at lower concentrations green $K_2Mn[Mn(CN)_6]$ is deposited. $K_4[Mn(CN)_6]\cdot 3H_2O$ can be dehydrated over concentrated sulphuric acid. The magnetic moment[154] of $K_4[Mn(CN)_6]\cdot 3H_2O$ is 2.18 BM and electron delocalization determinations agree with e.s.r. data[155]. Solutions of $Mn(CN)_6^{4-}$ absorb carbon monoxide but no carbonyl complex has been isolated[156]. Labelled cyanide exchanges with $Mn(CN)_6^{4-}$ at a measurable rate[157], and polarographic studies suggest that another unidentified ion can exist in aqueous solution[158]. The ^{13}C and ^{14}N n.m.r. spectra of $Mn(CN)_6^{4-}$ have been studied[159, 160].

The yellow paramagnetic nitrosyl cyanide $K_2[Mn(CN)_5NO]$ is prepared by oxidation of the corresponding Mn(I) complex with nitric acid[148]. The magnetic moment is 1.73 BM. The infrared, electronic and electron spin resonance spectra have been studied[141, 161].

Manganese(III)

Potassium hexacyanomanganate(III), $K_3Mn(CN)_6$, is best prepared by the action of aqueous potassium cyanide on manganese(III) orthophosphate, the latter being obtained

---

[151] A. Tullberg and N. G. Vannerberg, *Acta Chem. Scand.* **21** (1967) 1462.

[152] P. T. Manoharan and H. B. Gray, *Inorg. Chem.* **5** (1966) 823; *J. Am. Chem. Soc.* **87** (1965) 3340.

[153] A. M. Qureshi and A. G. Sharpe, *J. Inorg. Nucl. Chem.* **30** (1968) 2269.

[154] B. N. Figgis, *Trans. Faraday Soc.* **57** (1961) 198, 204.

[155] J. M. Baker, B. Bleaney and K. D. Bowers, *Proc. Phys. Soc.* **B69** (1956) 1205.

[156] J. Müller, *Bull. soc. chim. France* **29** (1903) 27.

[157] A. G. MacDiarmid and N. F. Hall, *J. Am. Chem. Soc.* **76** (1954) 4222.

[158] W. Kemula, S. Siekierski and K. E. Siekerski, *Roczniki Chem.* **29** (1955) 966.

[159] D. G. Davis and R. J. Kurland, *J. Chem. Phys.* **46** (1967) 388.

[160] A. Loewenstein, *Chem. Abs.* **66** (1967) 6870v.

[161] W. P. Griffith, *Advances in Organometallic Chemistry* (edited by F. G. A. Stone and R. West), Academic Press, Vol. 7 (1968), p. 211.

by oxidation of a Mn(II) salt with nitric acid in the presence of phosphoric acid[162]. It can also be obtained by the oxidation of freshly prepared $MnCO_3$ with hydrogen peroxide in the presence of potassium cyanide[13] or the action [51] of KCN on $K_2MnF_5 \cdot H_2O$. The salt is stable in air but is hydrolysed in aqueous solution to hydrated Mn_2O_3. It is best recrystallized from a solution of KCN. Potassium hexacyanomanganate(III) is isomorphous with $K_3Fe(CN)_6$. The lattice constants[141] are $a = 13.59$, $b = 10.62$, $c = 8.52$ Å. The magnetic moment at room temperature is 3.50 BM, and $Mn(CN)_6^{3-}$ is one of the few examples of a low-spin manganese(III) complex[141]. The exchange reaction[162] of aqueous cyanide with $Mn(CN)_6^{3-}$ is very fast and it is thought to involve the intermediate $[Mn(CN)_6 \cdot H_2O]^{3-}$. The electron exchange reaction between $Mn(CN)_6^{4-}$ and $Mn(CN)_6^{3-}$ is rapid and the rate has not been measured[163]. The electronic and infrared spectra have been studied[141]. The standard potential[141] of the system

$$Mn(CN)_6^{3-} + e = Mn(CN)_6^{4-}$$

is −0.24 V. The ^{13}C and ^{14}N n.m.r. spectra have been studied[159, 160]. A rose-red hydroxy complex $K_3[Mn(CN)_5OH]$ has been described. It has a room temperature magnetic moment of 2.92 BM [164].

Manganese(IV)

Canary yellow $K_2Mn(CN)_6$ has been prepared by the oxidation of $K_3Mn(CN)_6$ with NOCl [166a]. Its magnetic moment is very close to the spin-only moment expected for a d^3 configuration.

Red crystals of $K_4Mn(CN)_8$ are reported to result from the action of potassium cyanide on an aqueous solution of potassium permanganate[165], but a later worker could not repeat this preparation[166].

It seems likely[141] that either electrolytic oxidation of $K_3Mn(CN)_6$ or the action of KCN on K_2MnF_6 could yield manganese(IV) cyanide complexes[141].

OXIDES

Six stoichiometric oxides of manganese are known: MnO, Mn_3O_4, Mn_5O_8, Mn_2O_3, MnO_2 and Mn_2O_7. The last is the anhydride of permanganic acid and is a dangerously explosive compound. Some properties of the oxides are given in Table 12. Manganese trioxide, MnO_3, is described in the earlier literature, but it seems unlikely that this compound has any existence[1]. It is said to result from the action of concentrated sulphuric acid on potassium permanganate. In this context it is interesting to note that the MnO_3^+ ion is present in a solution of $KMnO_4$ in concentrated sulphuric acid[167]. All oxides and hydroxides of manganese when heated in air to about 1000°C form Mn_3O_4. Some data on the surface reactions between metallic manganese and oxygen is given in ref. 3.

---

[162] A. W. Adamson, J. P. Welker and W. B. Wright, *J. Am. Chem. Soc.* **73** (1951) 4786.
[163] A. W. Adamson, *J. Phys. Chem.* **56** (1952) 858.
[164] H. K. Saha, *Sci. Cult.* **27** (1961) 582.
[165] A. Yakimach, *Compt. rend.* **190** (1930) 681.
[166] N. Goldenberg, *Trans. Faraday Soc.* **36** (1940) 847.
[166a] J. R. Fowler and J. Kleinberg, *Inorg. Chem.* **9** (1970) 1005.
[167] A. Carrington and M. C. R. Symons, *Chem. Revs.* **63** (1963) 443.

TABLE 12. SOME PROPERTIES OF MANGANESE OXIDES

	MnO	Mn_3O_4	Mn_2O_3	MnO_2	Mn_2O_7
Melting point (°C)	1785 [a]	1560 [b]			5.9 [a]
Density	5.18 [a]	4.8 [b]		4.83 [b]	2.396 [a, d]
ΔH_f° (kcal mole^{-1})	−92.0	−331.3	−228.7	−124.4	−177.4 [a, d]
ΔG_f° (kcal mole^{-1}) [c]	−86.7	−306.2	−210.1	−111.3	
S° (cal mole^{-1} deg^{-1}) [c]	14.3	36.8	26.4	12.68	

[a] Ref. 13. [b] Ref. 181. [c] Ref. 95. [d] At 20°C.

Manganese(II) Oxide

Manganese(II) oxide, a grey–green to dark green powder can be prepared[13, 168] from any suitable manganese oxide or salt, e.g. $MnCO_3$, $Mn(NO_3)_2 \cdot 6H_2O$ by heating with hydrogen at temperatures below 1200°C. It occurs naturally as the mineral manganosite. Above 1200°C MnO is reduced by hydrogen to the metal. It is insoluble in water and is a wholly basic oxide[19, 51]. Manganese(II) oxide is moderately stable in air, but will take up oxygen if left to stand in air and becomes brown especially when finely divided. However, its stability to air depends markedly on its mode of preparation. Samples heated for long periods are the most stable[168]. MnO has a sodium chloride lattice[168], $a = 4.436$ Å, but at the Néel temperature and below it, a distorted rhombohedral form is observed due to antiferromagnetic ordering[169, 170, 171]. The lattice constants from 100° to 310°K have been recorded[172] and the effect of pressure[173] on the lattice constant has also been investigated. Manganese(II) oxide is one of the classic examples of a compound which becomes antiferromagnetic at low temperatures, and the properties of the compound around the Néel temperature have been investigated in some detail. Thus the electronic spectrum above and below the Néel temperature[57], the effect of pressure on the Néel temperature[174], and the heat capacity and thermal expansion at the Néel temperature[175] have all been studied.

Manganese(II) oxide exhibits non-stoichiometry and it has been found that the composition of the oxide ranges from $MnO_{1.00}$ to $MnO_{1.045}$ as the partial pressure of oxygen is raised from 10^{-10} or 10^{-11} to 10^{-2} atm in the temperature range 1500–1650°C [176].

The compound $Mn(PO_2Cl_2)_2 \cdot (CH_3CO_2Et)_2$ is readily formed in a most unusual reaction when MnO is added to a solution of $POCl_3$ in ethylacetate. Single crystal X-ray studies show that the Mn^{2+} ion present is in an octahedral environment. The manganese ions are joined together by bridging PO_2Cl_2 groups to form chains and the octahedron about each manganese is completed by coordinating to the keto groups of two ethylacetates[177].

[168] T. E. Moore, M. Ellis and P. W. Selwood, *J. Am. Chem. Soc.* **72** (1950) 856.
[169] C. G. Shull, W. A. Strauser and E. O. Wollam, *Phys. Rev.* **83** (1951) 33.
[170] D. B. Bloch, P. Charbit and R. Georges, *Compt. rend.* **266B** (1968) 430.
[171] J. S. Smart and S. Greenwald, *Phys. Rev.* **82** (1951) 113.
[172] C. P. Gazzara and R. M. Middleton, *Adv. X-ray Anal.* **9** (1966) 152.
[173] R. L. Clendenen and H. G. Drickamer, *J. Chem. Phys.* **44** (1966) 4223.
[174] H. Bartholin, D. Bloch and R. Georges, *Compt. rend.* **264B** (1967) 360.
[175] R. D. Gamblir, S. N. Vaidya and E. S. R. Gopal, *J. Indian Inst. Sci.* **49** (1967) 48.
[176] M. W. Davies and F. D. Richardson, *Trans. Faraday Soc.* **55** (1959) 604.
[177] J. Danielsen and S. E. Rasmussen, *Acta Chem. Scand.* **17** (1963) 1971.

Mass spectrometric studies have shown that the heat of the reaction

$$MnO(s)+TaF_5(g) = MnF_2(g)+TaOF_3(g)$$

is 75 ± 10 kcal $mole^{-1}$ [178].

Mn_3O_4

All oxides and oxyhydroxides of manganese on heating in air to about 1000° form Mn_3O_4. It is best prepared by heating specially prepared electrolytic manganese dioxide to 1050°. A product almost as pure has been obtained by prolonged ignition of pure $MnSO_4$ in air at about 1000° [168]. The oxide either appears as black crystals with a metallic sheen or as a dark purple–red powder when finely divided. It occurs naturally as the mineral hausmannite. Mn_3O_4 has a distorted normal spinel structure[179,180] with a tetragonal unit cell[181] ($a = 8.140$, $c = 9.435$ Å). A recent X-ray determination gives the Mn–O bond distances as 2.29 and 1.93 Å [182]. At high temperatures it changes to the cubic spinel structure[183]. Disagreement continues as to whether the compound should be formulated as $Mn^{II}Mn_2^{III}O_4$ or $Mn^{IV}Mn_2^{II}O_4$. Neutron diffraction data, however, suggests that $Mn^{II}Mn_2^{III}O_4$ is the correct structure[180]. Single crystals of Mn_3O_4 have been prepared[164]. The magnetic properties of Mn_3O_4 have been studied above and below the Curie point[180, 185]. Gaseous Mn_3O_4 is reported to exist in a polynuclear state[186].

Mn_5O_8

The stoichiometric oxide of manganese $MnO_{1.6}$ or Mn_5O_8 has been prepared[187,188] by the oxidation of Mn_3O_4 in nitrogen–oxygen mixtures at 250–550°C, by the decomposition of β-MnOOH at similar temperatures or by the topotactic decomposition of γ-MnOOH at low oxygen pressure at 400°C. The crystal structure[188] of Mn_5O_8 has been determined and is isotypic with $Cd_2Mn_3O_8$. The valence structure is $Mn_2^{II}Mn_3^{IV}O_8$. The structure consists of pseudohexagonal manganese(IV) sheets with similar oxygen sheets on either side, to give a distorted octahedrally coordinated manganese(IV). As every fourth manganese(IV) ion is missing in these main layers, their composition becomes Mn_3O_8, and chains of coordination octahedra linked by common edges are found. Manganese(II) ions are above and below the empty manganese(IV) sites completing the composition $Mn_2^{II}Mn_3^{IV}O_8$.

Mn_2O_3

Manganese(III) oxide exists in two forms referred to as α-Mn_2O_3 and γ-Mn_2O_3. The α-form has been prepared by the decomposition of commercial MnO_2 in air at 800°C [189] or

---

[178] K. F. Zmbov and J. L. Margrave, *J. Phys. Chem.* **72** (1968) 1099.

[179] R. Ward, *Progress in Inorganic Chemistry* (edited by F. A. Cotton), Interscience, Vol. 1 (1959), p. 465.

[180] M. B. Robin and P. Day, *Advances in Inorganic and Radiochemistry* (edited by H. J. Emeléus and A. G. Sharpe), Academic Press, Vol. 10 (1967), p. 248.

[181] H. J. Goldschmidt, *Interstitial Alloys*, Butterworths (1967).

[182] S. Åsbrink,, unpublished result quoted in R. Norrestam, *Acta Chem. Scand.* **21** (1967) 2871.

[183] K. S. Irani, A. P. B. Sinha and A. B. Biswas, *J. Phys. Chem. Solids* **23** (1962) 711.

[184] E. J. Scott, *J. Chem. Phys.* **23** (1955) 2459.

[185] D. G. Wickham and W. J. Croft, *J. Phys. Chem. Solids* **7** (1958) 351.

[186] O. Glemser and H. Weizenkorn, *Z. anorg. allgem. Chem.* **319** (1963) 266.

[187] H. R. Oswald, W. Feitnecht and M. J. Wampetich, *Nature* **207** (1965) 72.

[188] H. R. Oswald and M. J. Wampetich, *Helv. Chim. Acta* **50** (1967) 2023.

[189] R. Norrestam, *Acta Chem. Scand.* **21** (1967) 2871.

by the decomposition of the nitrate, carbonate, oxalate or chloride hydrate of manganese(II) in air between 600–800°C. The action of heat on the pure hydrated manganese(II) nitrate results in a good preparation of α-Mn_2O_3, but the temperature must not rise much above 600°C if stoichiometric Mn_2O_3 is to result[168]. In all preparations the temperature must not rise above 800°C since α-Mn_2O_3 decomposes into tetragonal Mn_3O_4 at 850–900°C in air[168, 189]. When α-Mn_2O_3 is heated in vacuum from 300° to 500°C, Mn_3O_4 is formed, and it appears to be impossible to pump oxygen off the oxide without converting it to Mn_3O_4[168]. α-Mn_2O_3 is black. Almost pure α-Mn_2O_3 is said to occur in the mineral bixbyite which more often occurs as a solid solution of Fe_2O_3 in Mn_2O_3[168].

γ-Mn_2O_3 has been prepared by heating the so-called γ-MnO_2 in vacuum at 500°C for about 78 hr[168] or by careful dehydration of γ-MnOOH[13]. The product has been described as brown or black. Prolonged heating of γ-MnO_2 in vacuum at 500°C gives, successively, γ-Mn_2O_3, Mn_3O_4 and finally MnO[168].

A single crystal X-ray study of α-Mn_2O_3 shows that the structure clearly deviates from the body-centred cubic symmetry of bixbyite[189]. α-Mn_2O_3 has an orthorhombic unit cell ($a = 9.412$, $b = 9.418$, $c = 9.423$ Å). The manganese atoms are in two different octahedral environments and four shorter and two longer manganese–oxygen bond lengths are found. The distortion is probably a consequence of the Jahn–Teller effect of the high spin d^4 manganese(III) ion. The Néel temperature of α-Mn_2O_3 is about 82°K[190], and the magnetic properties of α-Mn_2O_3–Fe_2O_3 mixtures have been studied[191]. The magnetic susceptibility of α-Mn_2O_3 has been measured at 25°, −80° and −185°C[168]. The action of hydrogen on α-Mn_2O_3 has been investigated[168].

γ-Mn_2O_3 is reported to have a tetragonal unit cell[192] ($a = 8.1$, $c = 9.4$ Å). Numerical data on the interplanar spacings have also been reported[168]. The X-ray patterns of γ-Mn_2O_3 and Mn_3O_4 are nearly identical[168], and the structure of γ-Mn_2O_3 is related to Mn_3O_4 in the same way as γ-Fe_2O_3 is to Fe_3O_4[16]. Hydrogen ions, however, may be present[193] in γ-Mn_2O_3. The magnetic susceptibility of γ-Mn_2O_3 has been measured at 25°, −80° and −185°C[168], and an appraisal of magnetic susceptibility measurements led to the conclusion that the vacant octahedral sites are disordered[194]. The magnetic moments of α-Mn_2O_3 and γ-Mn_2O_3 at 293°K are 3.5 and 4.1 BM respectively[195]. When heated in vacuum at 500° for 48 hr, γ-Mn_2O_3 transforms to α-Mn_2O_3. This transformation also occurred spontaneously in a sample which had been standing at room temperature for one year[168]. The optical spectrum of Mn^{3+} in an Al_2O_3 host lattice has been studied[57].

MnO_2

In addition to the dioxide which occurs naturally as pyrolusite there are many materials which have either been prepared in the laboratory or have been found in the mineral world with compositions approximating to MnO_2. The various forms have often been described as polymorphs of MnO_2. X-ray studies, however, have now indicated why the manganese dioxide system is so complex and why different structures appear when the oxide is obtained from solutions containing various ions[16, 196].

[190] R. G. Meisenheimer and D. L. Cook, *J. Chem. Phys.* **30** (1959) 605.

[191] J. A. Cape, G. P. Espinosa, S. Geller and R. W. Grant, *J. Appl. Phys.* **38** (1967) 1457.

[192] E. J. W. Verwey and J. H. de Boer, *Rec. trav. chim.* **55** (1936) 531.

[193] A. D. Wadsley, *Non-Stoichiometric Compounds* (edited by L. Mandelcorn), Academic Press (1964).

[194] K. P. Sinha and A. P. B. Sinha, *J. Phys. Chem.* **61** (1957) 758.

[195] B.N. Figgis and J. Lewis, *Progress in Inorganic Chemistry* (edited by F. A. Cotton), Vol. 6 (1964), p. 37.

[196] A. D. Wadsley and A. Walkley, *Rev. Pure Appl. Chem.* **1** (1951) 203.

β-MnO_2, with the same crystal structure as the mineral pyrolusite, is the only stoichiometric form. It has been prepared in a number of ways, but one of the best methods is the action of heat on recrystallized manganese nitrate[168, 197]. The nitrate is decomposed at 145–160° in a stream of oxygen or air to remove oxides of nitrogen and water vapour. When decomposition is almost complete, the mass is poured into excess hot water, stirred and filtered off. The oxide is dried at 110°, ground in an agate mortar, boiled first with 1:1 nitric acid and then with water and finally re-dried at 110–120°C [197]. The β-MnO_2 produced has a dark grey colour.

β-MnO_2 has a tetragonal (rutile type) lattice with $a = 4.398, b = 2.873$ Å, and the structure consists of a framework built up of infinite single chains of MnO_6 octahedra[198]. Each octahedron shares two opposite edges with its neighbours, while neighbouring chains merely share corners. The effect of pressure on the lattice constants has been examined[173]. The c-axis expands with increasing pressure in the low-pressure region, then passes through a maximum and contracts. The a-axis decreases smoothly.

β-MnO_2 exhibits non-stoichiometry and the possible composition range of MnO_x is $1.93 < x < 2.0$ [196]. There is also evidence that some samples loose oxygen on standing for long periods, and this appears to apply to samples which have been heated in oxygen during their preparation in order to increase their stoichiometry[199]. The mechanism of formation of β-MnO_2 from manganous nitrate or perchlorate has been considered, and on the basis of X-ray powder data there is evidence that manganese dioxide crystallites are finally built up in a direction at right angles to the c-axis[199]. It is also possible that ε$_1$-MnO_2 (see later), whose structure is unknown, is an intermediate phase in the formation of β-MnO_2 [199]. Thermogravimetric experiments [199] on β-MnO_2 show that the reactions

$$4MnO_2 \rightarrow 2Mn_2O_3 + O_2$$
$$6Mn_2O_3 \rightarrow 4Mn_3O_4 + O_2$$

occur at 600° and 1000°C respectively.

β-MnO_2 is antiferromagnetic and has been measured down to 90°K. Its magnetic moment at 300°K is 5.90 BM [195].

A second crystallographic form of manganese dioxide is found in the rare mineral ramsdellite. It has a similar framework structure to β-MnO_2 but contains double octahedral chains. Each MnO_6 octahedron shares two edges with those of the other chain and neighbouring units share corners only[200]. Ramsdellite has an orthorhombic unit cell ($a = 4.53$, $b = 9.27$, $c = 2.86$ Å). The average Mn–O distance in each octahedron is 1.89 Å.

In addition to β-MnO_2 and ramsdellite, a number of other forms of manganese dioxide have been described. They have been designated as α-MnO_2, γ-MnO_2, δ-MnO_2, η-MnO_2 and ε-MnO_2[201–204], and have been mainly characterized by their X-ray powder patterns.

α-MnO_2 refers to a group of manganese dioxides which always contain a foreign ion such as K^+ or Ba^{2+}. The α-forms are usually prepared by the reduction of potassium permanganate with reagents such as hydrogen peroxide or hydrochloric acid and they can only

---

[197] A. K. Covington, T. Cressey, B. G. Lever and H. R. Thirsk, *Trans. Faraday Soc.* **58** (1962) 1975.
[198] D. B. Rogers, R. D. Shannon, A. W. Sleight and J. L. Gillson, *Inorg. Chem.* **8** (1969) 841.
[199] J. Ambrose, A. K. Covington and H. R. Thirsk, *Trans. Faraday Soc.* **65** (1969) 1897.
[200] A. M. Byström, *Acta Chem. Scand.* **3** (1949) 163.
[201] O. Glemser, G. Gattow and H. Meisiek, *Z. anorg. allgem. Chem.* **309** (1961) 1.
[202] G. Gattow and O. Glemser, *Z. anorg. allgem. Chem.* **309** (1961) 20.
[203] G. Gattow and O. Glemser, *Z. anorg. allgem. Chem.* **309** (1961) 121.
[204] K. H. Maxwell and H. R. Thirsk, *J. Chem. Soc.* (1955) 4054.

be isolated in the presence of a large cation[201,204]. The minerals hollandite, cryptomelane and coronadite, together with α-MnO_2, form an isostructural series of the general formula $A_{2-y}B_{8-z}X_{16}$, where A is a large ion such as Ba^{2+}, Pb^{2+} or K^+, B is an ion such as Mn^{4+}, Fe^{2+} or Mn^{2+} and X is O^{2-} or OH^-. In the cases investigated y varies from 0.8 to 1.3 and z varies from 0.1 to 0.5 [205,206]. In these structures some of the Mn^{4+} ions in a MnO_2 framework are replaced by Mn^{2+} ions, and since the framework then develops a negative charge, positive ions such as Ba^{2+} or K^+ must be present in the interstices. In an α-form isolated from manganese sulphate and ammonium persulphate, NH_4^+ ions are probably present in the structure[207]. The structure of psilomelane, $(Ba, H_2O)_2Mn_5O_{10}$, which has a similar composition to hollandite, $Ba_{2-y}Mn_8O_{16}$ ($y \approx 1$), except that the former contains water, has also been studied[208]. The structure consists of treble strings of MnO_6 octahedra joined by double strings to form a series of tunnels which contain the Ba^{2+} ions and water molecules. On heating[205] to 550°C, psilomelane is converted to hollandite.

α-MnO_2 shows cation exchange like the zeolites and Ag^+ ions enter the structure more readily than the larger Pb^{2+} or Ba^{2+} ions[205].

δ-MnO_2 refers to a group of manganese dioxides which are usually prepared either by the oxidation of the manganese(II) ion at low temperatures[202,204] or by the electrolytic deposition of MnO_2 at the anode[209,210]. γ-MnO_2 is usually poorly crystalline and the phases of increasing crystallinity γ, γ′, γ″ have been described[202]. By treating Mn_3O_4 with hot dilute nitric acid a crystalline sample of γ-MnO_2 has been obtained[211]. Electron and X-ray diffraction data[211] show that the product consists of a ramsdellite matrix with statistically distributed pyrolusite microdomains as had been previously suggested[212]. γ-MnO_2 is transformed by heating in air into Mn_3O_4 according to the following sequence[202]:

$$\gamma\text{-}MnO_2 \rightarrow \beta'\text{-}MnO_2 \rightarrow \beta\text{-}MnO_2 \rightarrow \alpha\text{-}Mn_2O_3 \rightarrow Mn_3O_4$$

At 120° γ-MnO_2 looses water[202].

δ-MnO_2 refers to a group of manganese dioxides which are again poorly crystalline and δ, δ′ and δ″ phases have been described[201]. They have been prepared by the alkaline oxidation of $Mn(OH)_2$ or by the reduction of permanganates[201,204]. On heating in air, δ-MnO_2 is converted to α-Mn_2O_3 by the following sequence[201]:

$$\delta\text{-}MnO_2 \rightarrow \gamma''\text{-}MnO_2 \rightarrow \beta'\text{-}MnO_2 \rightarrow \beta\text{-}MnO_2 \rightarrow \alpha\text{-}Mn_2O_3$$

However, δ-species which contain foreign ions are converted into α-MnO_2 on annealing [201,204].

In addition to the phases mentioned above, η-phases (η, η′, η″) and ε-phases (ε_1 and ε_2) have been described[202,203], and the form ρ-MnO_2 [213] also belongs to the η group[202]. However, it has been suggested that there is no need to differentiate between η- and γ-phases since they have the same lattice and differ only by crystallite size and concentration of

---

[205] A. Byström and A. M. Byström, *Acta Cryst.* **3** (1950) 146; A. Byström and A. M. Byström, *Acta Cryst.* **4** (1951) 469.

[206] B. Mukherjee, *Acta Cryst.* **13** (1960) 164.

[207] G. Butler and H. R. Thirsk, *Acta Cryst.* **5** (1952) 288.

[208] A. D. Wadsley, *Acta Cryst.* **6** (1953) 433.

[209] T. W. Clapper, *Encyclopaedia of Electrochemistry* (edited by C. A. Hampel), Reinhold, New York (1964), p. 789.

[210] W. F. Cole, A. D. Wadsley and A. Walkley, *Trans. Electrochem. Soc.* **92** (1947) 133.

[211] R. Giovanoli, R. Maurer and W. Feitknecht, *Helv. Chim. Acta* **50** (1967) 1072.

[212] P. M. De Wolff, *Acta Cryst.* **12** (1959) 341.

[213] H. Kedesdy, G. Katz and S. B. Levin, *Acta Cryst.* **10** (1957) 780.

microdomains[211]. The action of heat on the η-group cause similar transformations to those found in the γ-group[202]:

$$\eta\text{-}MnO_2 \rightarrow \beta'\text{-}MnO_2 \rightarrow \beta\text{-}MnO_2 \rightarrow \alpha\text{-}Mn_2O_3 \rightarrow Mn_3O_4$$

However, the hydrothermal annealing of δ-, γ- and η-phases which contain foreign ions give η''-MnO_2 [202].

The ε_1 and ε_2 forms are not interconvertible but both are transformed to α-Mn_2O_3 on heating[203].

$$(\varepsilon_1 \text{ or } \varepsilon_2)\text{-}MnO_2 \rightarrow \beta'\text{-}MnO_2 \rightarrow \beta\text{-}MnO_2 \rightarrow \alpha\text{-}Mn_2O_3$$

Manganese dioxide is widely used as a depolarizer in Leclanché type dry cells[214]. Only γ-forms of manganese are suitable for use in the battery, and these either come from ores, e.g. ramsdellite, or are produced chemically or electrolytically[209]. The electrochemical system usually present in a battery is Zn/NH_4Cl, $ZnCl_2/MnO_2$, C, and although the reactions occurring at the cathode are complex and depend on the pH and composition of the electrolyte[214–216], the most common reaction is thought to be

$$MnO_2 + H^+ + e = MnOOH$$

In view of the importance of manganese dioxide in these systems the electrode potentials and related properties of various forms of manganese dioxide have been widely studied[199, 217]. The electrode potentials of variously prepared and treated samples of β-MnO_2 have been studied in detail, and values from 1.195 to 1.244 V have been found[199]. It appears that the lowest standard potentials are shown by the most highly crystalline samples and those being the most stoichiometric[199]. If the samples are heated in oxygen the stoichiometry increases and so does the standard potential. β-MnO_2 removes H^+ ions from hydrochloric acid–potassium chloride solutions with the formation of Mn^{2+} ions in solution. It is concluded that the release of Mn^{2+} ion cannot be entirely explained in terms of ion exchange, and a diffusion process has been invoked in which lower valent manganese ions diffuse from the interior of the manganese dioxide particles to the surface where they react with acid. When the ion-exchange capacities are high the standard potentials of the samples are also high[199].

Recently organic cathode materials, e.g. *meta*-dinitrobenzene, have been used in batteries in place of MnO_2 [218].

The stability of manganese dioxide is due primarily to its insolubility. It is, however, readily attacked by reducing agents in acid solution, for example oxidizing concentrated hydrochloric acid to chlorine. In hot concentrated alkali it dissolves to give a purple solution which contains an equimolar mixture of trivalent manganese, probably as $Mn(OH)_6^{3-}$ and manganate(V), MnO_4^{3-} [167]. Manganese dioxide is also one of the most active catalysts for the oxidation of carbon monoxide near room temperature[219].

Manganese dioxide (pyrolusite, glass-makers' soap) has long been used to decolorize commercial glass. When the manganese dioxide is added to the molten glass the dioxide

---

[214] W. S. Herbert, *Encyclopaedia of Electrochemistry* (edited by C. A. Hampel), Reinhold, New York (1964), p. 70.

[215] P. Benson, W. B. Price and F. L. Tye, *Electrochem. Technology* 5 (1967) 517.

[216] A. Kozawa and R. A. Powers, *Electrochem. Technology* 5 (1967) 535.

[217] A. K. Covington, P. K. Talukdar and H. R. Thirsk, *Electrochem. Technology* 5 (1967) 523.

[218] J. J. Murphy, *Electrochem. Technology* 5 (1967) 498.

[219] M. Katz, *Advances in Catalysis* (edited by W. G. Frankenberg, V. I. Komarewsky and E. K. Rideal), Academic Press, Vol. V (1953), p. 177.

decomposes to form a small amount of Mn^{3+} ions. These red–brown Mn^{3+} ions can then simply mask the blue–green colour from iron (which is unavoidably present as Fe_2O_3) since complementary colours are now present. The result is to produce a glass which now appears colourless (grey) to the eye. Maintaining the correct concentration of Mn^{3+} ion in the glass melt is difficult since it depends on a number of variables such as furnace atmosphere, batch material changes and degassing agents. In present-day commercial continuous processes it is very difficult to maintain the conditions necessary for the formation of the correct amount of Mn^{3+} ion, and selenium along with cobalt are now used in place of manganese in the decolouring process[220]. Manganese dioxide is used to colour glasses and, depending on the amount used, it can impart pink through purple to black colorations[203,221].

Other uses of manganese dioxide include its use as an oxidizing agent in organic chemistry (see later) and as an oxidizing agent in safety matches, fireworks and flares. It is also an effective adsorbent for hydrogen sulphide and is also used to colour ceramics[221].

Mn_2O_7

Manganese(VII) oxide is obtained as an oil with a green metallic lustre in reflected light by the action of concentrated sulphuric acid on very pure potassium permanganate[13]. The compound is extremely explosive and great care must be observed in the preparation and handling of this compound. Some physical properties of the compound are given in Table 12. The compound dissociates at about 55°C and detonates at 95°C. In a vacuum rapid and explosive decomposition occurs above 10°C. During explosive decomposition α-Mn_2O_3 results, but when dissociation is slow γ-MnO_2 is formed. Mn_2O_7 is hygroscopic and in moist air it decomposes to MnO_2 and a mixture of ozone and oxygen. The compound is stable below -10°C in anhydrous conditions. It reacts explosively with most organic compounds and attacks carbon tetrachloride even below room temperature[13].

COMPLEX MANGANESE OXIDES

There are many complex manganese oxides of general formula $A_xMn_yO_z$ containing another atom A in addition to manganese and oxygen. The oxidation state of the manganese in these mixed metals oxides is either two, three or four, and the manganese ion is usually either tetrahedrally or octahedrally coordinated by oxide anions. The compounds are usually prepared by heating together the appropriate metal oxides, carbonates, oxalates, etc., either in the presence or absence of oxygen, e.g.

$$x/2\,Li_2O_2+(1-x)MnO \xrightarrow{\text{in vacuo}} Li_xMn_{1-x}O$$

$$Al_2O_3+MnO \xrightarrow[\text{of air}]{\text{in absence}} MnAl_2O_4$$

$$8MgO+MnCO_3 \xrightarrow{O_2} Mg_6Mn^{IV}O_8+2MgO$$

$$CaO+MnO_2 \xrightarrow{O_2} CaMnO_3$$

$$2CaCO_3+Mn_2O_3 \xrightarrow{O_2} 2CaMnO_3$$

---

[220] D. Dingledy, *J. Chem. Education* **42** (1965) 160.

[221] J. O. Hay, in *Kirk–Othmer Encyclopaedia of Chemical Technology*, 2nd edn., Interscience, Vol. 13 (1967), p. 1.

From the reaction of calcium oxide with manganese dioxide in various ratios the complexes $CaMnO_3$, Ca_2MnO_4, $Ca_3Mn_2O_7$ and $Ca_4Mn_3O_{10}$ have been isolated[222].

In certain complexes the manganese ions are present in two different oxidation states[180]. Thus in common with some other first-row transition metals, mixed valence manganese oxide systems based on perovskite lattices may be obtained with formulae intermediate between $M^{III}Mn^{III}O_3$ and $M^{II}Mn^{IV}O_3$, where M^{III} is commonly lanthanum and M^{II} is one of the alkaline earths. The magnetic and electrical properties of complex manganese oxides have been widely studied and further information can be found in references 16, 179, 180, 181 and 193.

PEROXY COMPOUNDS OF MANGANESE

Few peroxy compounds of manganese appear to be known[223]. The compounds

$$K_2H_2[Mn(O)(O_2)_3],\ K_3H[Mn(O)(O_2)_3],\ \text{and}\ K_2H_2[Mn(O_2)_4]$$

have been claimed to result from the action of hydrogen peroxide on a solution of potassium permanganate in 30% hydrogen peroxide at temperatures below 0°C[223]. Little is known concerning the structures of these compounds.

HYDROXIDES AND OXYHYDROXIDES OF MANGANESE

Manganese(II) hydroxide is the only stoichiometric hydroxide of manganese, and although higher valence hydroxides are mentioned in the literature there is no evidence for $Mn(OH)_3$ and $Mn(OH)_4$ [168].

Manganese(II) Hydroxide

Manganese(II) hydroxide, $Mn(OH)_2$, is precipitated from solutions containing the Mn^{2+} ion by alkali metal hydroxides as a gelatinous white precipitate which rapidly darkens in air because of air oxidation. Hence the pure compound must be prepared in the absence of oxygen[13, 168]. When free of alkaline hydroxides and amorphous components, the dry product may be kept in an air-filled desiccator for weeks. The crystalline material occurs naturally as the mineral pyrochroite.

A single crystal X-ray study[224] of $Mn(OH)_2$ shows that $Mn(OH)_2$ has the CdI_2 layer structure[16] and is isostructural with $Ca(OH)_2$. Every manganese is surrounded by six hydroxide groups, and the Mn–O distance is 2.207 Å. There is some geochemical evidence for the possible existence of an orthorhombic modification of pyrochroite, and there have been claims for the synthesis of an orthorhombic modification[168].

The thermodynamic data[95] for $Mn(OH)_2$ is as follows: $\Delta H_f^\circ = -167$ kcal mole^{-1}, $\Delta G_f^\circ = -148$ kcal mole^{-1} and $S^\circ \approx 23$ cal mole^{-1} deg^{-1}.

$Mn(OH)_2$ is only slightly amphoteric[225].

$$Mn(OH)_2 + OH^- = Mn(OH)_3^-; \quad K \approx 10^{-5}$$

---

[222] J. B. MacChesney, H. J. Williams, J. F. Potter and R. C. Sherwood, *Phys. Rev.* **164** (1967) 779.

[223] J. A. Connor and E. A. V. Ebsworth, *Advances in Inorganic and Radiochemistry* (edited by H. J. Emeléus and A. G. Sharpe), Vol. 6 (1964), p. 279.

[224] A. N. Christensen, *Acta Chem. Scand.* **19** (1965) 1765.

[225] L. G. Sillen and A. E. Martell, *Stability Constants of Metal-ion Complexes*, Spec. Publ. Chem. Soc. (London), 2nd edn., No. 17 (1964).

The complex hydroxides $Na_2Mn(OH)_4$ and $AMn(OH)_4$ (A = Ba or Sr) are formed in alkaline solution[226], and the former has been prepared[227] by heating stoichiometric mixtures of sodium hydroxide and $Mn(OH)_2$.

The Weiss constant of $Mn(OH)_2$ is 10°, and the unusual degree of magnetic dilution in this compound is related to the large distance between nearest manganese neighbours in the structure[168, 228].

Both foreign and various manganese ions can be incorporated within the layer structure of manganese(II) hydroxide[229–231]. The oxidation of $Mn(OH)_2$ has been studied[19, 230].

Manganese(III) Oxide Hydroxide

There are probably at least three modifications of the substance MnOOH which usually results from the air oxidation of the manganese(II) ion in basic solution. However, the oxidation products of divalent manganese in basic solution depend upon a number of factors such as concentration of the solution, the oxidant and the temperature as well as the period of oxidation[168, 230]. The preparation of the γ-form γ-MnOOH, which corresponds to the natural substance manganite, involves an almost identical method to that used for γ-Mn_2O_3. The only difference is that the precipitate obtained by adding ammonium hydroxide to a manganese(II) sulphate solution in the presence of hydrogen peroxide was dried at 50°C [13, 168]. The product is black. The structure of manganite, γ-MnOOH, has been studied by neutron and X-ray diffraction. It has a monoclinic, pseudo-orthorhombic cell, and its structure is a super-structure based upon the marcasite FeS_2 type [232, 233].

In addition to manganite, other forms of MnOOH appear to exist, but the degree of hydration varies in different preparations. The structure of the mineral groutite, which is designated α-MnOOH, is almost the same as that of diaspore (α-AlOOH). It has an orthorhombic unit cell but accurate bond lengths are not known. Hence it is not possible to comment upon possible distortions of the octahedron due to the high spin d^4 Mn^{3+} ion[234].

The magnetic structure of manganite has been investigated[235] at 4.2°K and the infrared spectra of natural and synthetically prepared manganite (γ-MnOOH and γ-MnOOD) have been studied over a temperature range[236].

Although there is no evidence for $Mn(OH)_3$, complex hydroxides of manganese(III), e.g. $Na_3Mn(OH)_6$, are known[237].

MANGANESE HYDROXIDE HALIDES

The compounds MnOHCl and $Mn_2(OH)_3X$ (or $3Mn(OH)_2 \cdot MnX_2$, X = Cl, Br or I) are known[238, 239]. The compound MnOHCl has a layer lattice[238]. α-$Mn_2(OH)_3Cl$ is hexagonal,

---

[226] R. Scholder and A. Kolb, *Z. anorg. allgem. Chem.* **264** (1951) 209.

[227] R. Scholder and F. Schwochow, *Angew. Chem.*, Int. Edn., **5** (1966) 1047.

[228] P. W. Selwood, M. Ellis and C. F. Davis, *J. Am. Chem. Soc.* **72** (1950) 3549.

[229] E. Ya. Rode, *Zh. Neorg. Khim.* **1** (1956) 1430.

[230] W. Feitknecht and W. Marti, *Helv. Chim. Acta* **28** (1945) 129, 149.

[231] W. Buser and P. Graf, *Helv. Chim. Acta* **38** (1955) 810.

[232] H. Dachs, *Z. Krist.* **118** (1963) 303.

[233] M. J. Buerger, *Z. Krist.* **95** (1936) 163.

[234] R. L. Collin and W. N. Lipscomb, *Acta Cryst.* **2** (1949) 104.

[235] H. Dachs, *J. de Physique* **25** (1964) 563.

[236] E. Schwarzmann and H. Marsmann, *Z. Naturforsch.* **20b** (1965) 1124.

[237] M. Géloso and J. Faucherre, *Nouveau Traité de Chemie Minérale* (edited by P. Pascal), Masson et Cie, Vol. 15 (1960), p. 1008.

[238] H. R. Oswald and W. Feitknecht, *Helv. Chim. Acta* **44** (1961) 847.

[239] H. R. Oswald and W. Feitknecht, *Helv. Chim. Acta* **47** (1964) 272.

β-$Mn_2(OH)_3Cl$ is orthorhombic, $Mn_2(OH)_3Br$ is orthorhombic and $Mn_2(OH)_3I$ is monoclinic[239].

MANGANESE OXYANIONS

A number of salts of manganate(V), MnO_4^{3-}, manganate(VI), MnO_4^{2-}, and manganate (VII), MnO_4^-, are known which all contain tetrahedrally coordinated manganese. The so-called manganites, X_2MnO_3, where X is usually either an alkali metal or X_2 an alkaline earth cation, are only known as solid products of alkali fusion of manganese dioxide (see page 805). These compounds invariably contain octahedrally coordinated manganese, and discrete MnO_3^{2-} anions are not present. However, there is evidence for the transient existence of (MnO_3) anions in several oxidations[167, 240].

Some oxidation potentials of the manganate ions are given in Table 4.

Manganates(V)

Although there is evidence for manganates(V) (hypomanganates), MnO_4^{3-}, in the early literature, the first pure manganate(V) was not isolated until 1946[241, 242]. This compound was first formulated as $Na_3MnO_4 \cdot 10H_2O$ but later work showed that the stoichiometry was $Na_3MnO_4 \cdot 0.25NaOH \cdot 12H_2O$[243]. The compound is best prepared by treating alkaline $KMnO_4$ with sodium sulphite[13]. The compound, sodium manganate(V), is stable at 0°C in the absence of water and carbon dioxide. The salt can be dehydrated in vacuum[243]. A solution of the salt in potassium hydroxide, which is less than 8M, rapidly disproportionates into manganese(IV) and manganese(VI)

$$2Na_3MnO_4+2H_2O \rightarrow Na_2MnO_4+MnO_2+4NaOH$$

The disproportionation reaction probably involves[240] the ion $(HMnO_4)^{2-}$.

Other salts of the manganate(V) anion are also known[243, 244, 245], e.g. Li_3MnO_4, K_3MnO_4, $Ba_3(MnO_4)_2$ and $Ba_5(MnO_4)_3OH$, and recently a chlorapatite of manganese(V), $Ba_5(MnO_4)_3Cl$, has been prepared[242]. The salt, K_3MnO_4, is stable to at least 800°C[246].

The formulation of manganese(V) compounds must be well supported by experimental evidence. Magnetic and/or spectroscopic evidence is necessary since analytical data alone does not necessarily differentiate between manganese(V) and equimolar proportions of manganese(IV) and manganese (VI).

X-ray powder data is available for some salts[242, 245]. Magnetic data on the manganates(V) is available[195] and the electronic structure and spectra of the anion have recently been reviewed[167, 247]. The infrared spectra of some manganates(V) have been studied[248].

The exchange reaction $MnO_4^- + MnO_4^{3-} \rightarrow 2MnO_4^{2-}$ is extremely rapid[167].

The manganate(V) ion is formed as a reactive intermediate in the oxidation of certain organic compounds by $KMnO_4$ or K_2MnO_4[167, 240].

---

[240] W. A. Waters, *Quart. Rev.* **12** (1958) 277.

[241] H. Lux, *Z. Naturforsch.* **1** (1946) 281.

[242] L. H. Brixner and J. F. Weiher, *Inorg. Chem.* **7** (1968) 1474.

[243] R. Scholder, D. Fischer and H. Waterstradt, *Z. anorg. allgem. Chem.* **277** (1954) 234.

[244] R. Scholder, *Angew. Chem.* **66** (1954) 461.

[245] W. Klemm, *Angew. Chem.* **66** (1954) 468.

[246] H. Peters, K. H. Radeke and L. Till, *Z. anorg. allgem. Chem.* **346** (1966) 1.

[247] G. De Michelis, L. Oleari, L. Di Sipio and E. Tondello, *Coord. Chem. Revs.* **2** (1967) 53.

[248] D. M. Adams, *Metal-Ligand and Related Vibrations*, Arnold (1967).

Manganates(VI)

Potassium manganate(VI) has been prepared either by fusion of potassium hydroxide with manganese(IV) oxide and potassium nitrate or by the decomposition of potassium permanganate [manganate(VII)] in strong potassium hydroxide[249]. However, unless certain precautions are taken the sample is very easily contaminated with manganese dioxide[249]. A very pure sample of K_2MnO_4 can be prepared by adding a mixture of $KMnO_4$ and KOH to water in the absence of carbon dioxide.

$$2KMnO_4+2KOH \rightarrow 2K_2MnO_4+0.5O_2+H_2O$$

Since carbonic acid is sufficiently strong enough to cause immediate disproportionation of the MnO_4^{2-} ion, all water and solvents used in the preparation must be boiled to remove dissolved carbon dioxide. Pure $BaMnO_4$ may be precipitated quantitatively by adding a solution of permanganate to a solution containing iodide and excess barium hydroxide[249, 250]. The sodium salt exists in several hydrated forms[19].

The solid-state preparation of K_2MnO_4 which involves treating manganese dioxide with $KClO_3$ or KNO_3 in the presence of potassium hydroxide becomes explosive at very high pressures[251].

The most important manganate(VI) is the potassium salt, K_2MnO_4. It forms dark green crystals which decompose at 640–680°C [246]. Samples usually resemble $KMnO_4$ since by reflected light they appear violet–brown and also the compound very readily forms a surface film of permanganate[249]. K_2MnO_4 disproportionates slowly in alkali and rapidly in acids:

$$3MnO_4^{2-}+2H_2O \rightarrow 2MnO_4^-+MnO_2+4OH^-$$

The disproportionation reactions of MnO_4^{2-} and MnO_4^{3-} probably involve the ions $HMnO_4^-$ and $HMnO_4^{2-}$. These ions almost certainly undergo displacement reactions involving hydroxyl since it is known that alkaline MnO_4^- slowly exchanges oxygen with $H_2{}^{18}O$ [166, 246]. However, solutions are stable in the presence of excess potassium hydroxide, and its solubility in 2 M potassium hydroxide at 20°C is 224.7 $g\,l^{-1}$ [13]. Although $BaMnO_4$ is insoluble in water, on contact with water or acids it also disproportionates to MnO_2 and $Ba(MnO_4)_2$ [249].

A recent single crystal X-ray structure determination of K_2MnO_4 shows that it has an orthorhombic unit cell[252]. The average Mn–O bond distance is 1.659 Å and the manganese is tetrahedrally coordinated. The OMnO angle is 109.5°. It is isomorphous with K_2SO_4 and K_2CrO_4. The heats of formation of K_2MnO_4 and Na_2MnO_4 are about -283 and -274 kcal $mole^{-1}$ respectively[253].

The electronic and e.s.r. spectra of K_2MnO_4 have been reviewed[167, 247]. The main conclusions are that (a) the unpaired electron in the unperturbed tetrahedral manganate(VI) ion is in a doubly degenerate orbital, (b) the unpaired electron is concentrated mainly on the manganese, and (c) the lowest excited orbital of t_2 symmetry in the unperturbed ion is spread over the whole ion[167]. The magnetic moment corresponds closely to that for one

---

[249] R. S. Nyholm and P. R. Woolliams, *Inorganic Synthesis* (edited by W. L. Jolly), McGraw-Hill, Vol. XI (1968), p. 56.

[250] F. Jellinek, *J. Inorg. Nucl. Chem.* **13** (1960) 329.

[251] E. Molinari and J. L. Margrave, *Inorg. Chem.* **3** (1964) 898.

[252] G. J. Palenik, *Inorg. Chem.* **6** (1967) 507.

[253] R. A. W. Hill and J. F. Williamson, *J. Chem. Soc.* (1957) 2417.

unpaired electron. At room temperature it is 1.75 BM[249], and at 90°K it is 1.69 BM[195], and the susceptibility follows the Curie law[249]. The room temperature magnetic moment of $BaMnO_4$ is 1.80 BM [195].

The kinetics of the fast reaction between ruthenate(VII), RuO_4^-, and manganate(VI), MnO_4^{2-}, have been studied[254]. The reaction is presumed to proceed via an outer sphere mechanism. The rapid exchange between MnO_4^{2-} and MnO_4^- has been studied in detail by a variety of techniques[255]. Cationic effects on the rate of reaction have been demonstrated: $Cs^+ > K^+ > Na^+ \sim Li$. These cationic effects are consistent with the formation of outer sphere bridged activated complexes which may possibly be formulated as $[O_3MnOCsOMnO_3]^{2-}$.

Infrared data on some manganates(VI) have been reviewed[248].

Manganate(VII)

Salts of the manganate(VII) or permanganate MnO_4^- ion are prepared by oxidizing manganese(II) salts or manganese dioxide in the presence of alkali in a variety of ways. Low concentrations of alkali tends to favour manganate(VII) while high concentrations of alkali favour manganese(VI). A convenient preparation of potassium permanganate involves the electrolytic oxidation of K_2MnO_4 at a smooth platinum anode[51]. On a large scale[221] the starting material is pyrolusite ore containing at least 60% MnO_2 which is first converted to potassium manganate(VI) in the presence of potassium hydroxide. The second stage is then accomplished by electrolytic oxidation

$$K_2MnO_4 + H_2O \rightarrow KMnO_4 + KOH + \tfrac{1}{2}H_2$$

An older method involves treating the solution with carbon dioxide which neutralizes the alkali so that a disproportionation reaction occurs:

$$3K_2MnO_4 + 2CO_2 \rightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3$$

In addition to the potassium salt, salts of the other alkali metals[221], the alkaline earth[13, 221], the ammonium ion [221] and silver(I)[13] ion are among other salts which are known. Aluminium manganate(VII), $Al(MnO_4)_3$, is an important compound since it can be used commercially for the synthesis of a number of other metal permanganates via metathesis[221]. Thus, for example, $Al(MnO_4)_3$ can be reacted with the oxides, hydroxide or carbonates of the alkali metals, calcium, barium, zinc and the ammonium ion. Stoichiometric quantities of reactants must be used to prevent contamination of the permanganate solution. After the reaction, the aluminium hydroxide which is formed is filtered off and the solution can be concentrated to give crystals of the required permanganate. Since $Al(MnO_4)_3$ is unstable above 80°C, the reaction is usually conducted below this temperature. The aluminium permanganate can be readily prepared from potassium permanganate[221]:

$$6KMnO_4 + 4Al_2(SO_4)_3 \cdot 18H_2O + 6H_2O \rightarrow 2Al(MnO_4)_3 + 6KAl(SO_4)_2 \cdot 12H_2O$$

Potassium permanganate forms glittering dark purple crystals which often appear violet because of a slight surface reduction. It is soluble in water to give a dark purple solution (solubility 6.34 g per 100 g of water at 20°C[221]). It is also soluble to some extent in methyl alcohol, glacial acetic acid, acetone and pyridine. The initial decomposition products on

---

[254] E. V. Luoma and C. H. Brubaker, *Inorg. Chem.* 5 (1966) 1637.

[255] A. G. Sykes, *Advances in Inorganic and Radiochemistry* (edited by H. J. Emeléus and A. G. Sharpe), Vol. 10 (1967), p. 153.

heating $KMnO_4$ are K_2MnO_4, K_3MnO_4 and MnO_2 [246]. Although potassium permanganate is widely used in analysis, it cannot be used as a primary standard[256]. It is difficult to obtain completely free of manganese dioxide and, moreover, both distilled and deionized water are likely to contain organic matter which will reduce the MnO_4^- ion to manganese dioxide. The presence of the latter then catalyses the auto-decomposition of the permanganate solution on standing:

$$4MnO_4^- + 2H_2O \rightarrow 4MnO_2 + 3O_2 + 4OH^-$$

Hence a standard solution of permanganate cannot be prepared by dissolving a weighed amount of the purified salt in water. It is usual to first boil a solution of permanganate, filter off any manganese dioxide formed and then standardize the resulting solution for accurate work. Since the decomposition to manganese dioxide is catalysed by light, standard solutions must be stored in dark bottles.

The most important reactions of the permanganate ion are those in which it functions as an oxidizing agent. The course of the reaction is governed by the pH of the solution. In basic solution the following reaction occurs[95]:

$$MnO_4^- + 2H_2O + 3e = MnO_2(s) + 4OH^-$$

However, in strong base and with excess MnO_4^-, manganate(VI) is produced[95]:

$$MnO_4^- + e = MnO_4^{2-}$$

In acid solution permanganate is reduced to Mn^{2+} by an excess of the reducing agent[95]:

$$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$$

However, in neutral or weakly acid solutions Mn^{2+} is oxidized by excess permanganate to manganese dioxide:

$$2MnO_4 + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+$$

Since the redox potentials for the systems MnO_4^-/MnO_4^{2-} and Mn^{3+}/Mn^{2+} are $+0.6$ V and $+0.51$ V respectively[95], the oxidation of Mn^{2+} can only proceed significantly if (a) the acidity is low enough for the subsequent disproportionation of Mn^{3+} to Mn^{2+} and Mn^{4+} to occur with the removal of Mn^{4+} as hydrated manganese dioxide, or (b) if a complexing agent has been added to lower the concentration of Mn^{3+} ions[240]. Thus if pyrophosphate is added, Mn^{2+} ions can be quantitatively estimated with permanganate[21].

$$4Mn^{2+} + MnO_4^- + 8H^+ + 15(H_2P_2O_7)^{2-} \rightarrow 5[Mn(H_2P_2O_7)_3]^{3-} + 4H_2O$$

The rapid reduction of MnO_4^- to Mn^{3+} or Mn^{2+} in acid solution must involve a mechanism that does not involve any significant amount of Mn^{4+} since this would be precipitated as hydrated manganese dioxide. The oxidation of organic compounds by MnO_4^- is discussed later.

The addition of potassium permanganate to concentrated sulphuric acid gives a clear, green solution. It has been claimed that this solution contains the MnO_3^+ ion, but it seems more likely that the species present is, in fact, O_3MnOSO_3H rather than a simple oxycation[167]. If either a little water or a large amount of $KMnO_4$ is added to the green solution, the unstable and explosive heptoxide Mn_2O_7 precipitates out as an oil. In the early literature it was claimed that a volatile trioxide MnO_3 could be obtained by heating a solution of $KMnO_4$ in H_2SO_4. However, this was later refuted[19], and at the present time MnO_3 is an unknown compound.

[256] A. I. Vogel, *Quantitative Inorganic Analysis*, 3rd edn., Longmans (1961).

A recent X-ray structure determination of $KMnO_4$ shows the manganese is at the centre of a regular tetrahedron and that the average Mn–O bond distance is 1.629 Å [257]. The unit cell is orthorhombic. X-ray data is also available for other salts, e.g. $LiMnO_4 \cdot 3H_2O$ is reported to be hexagonal[258] and $Ba(MnO_4)_2$ is reported to be orthorhombic[259]. It is interesting to note that an old structure determination[260] of $AgMnO_4$ shows that one of the Mn–O bond distances is longer than the other three and hence some cationic–anionic interaction may be present in this salt. In this context it is also noteworthy that silver ions have a marked effect on the spectrum of permanganate[167].

The standard heat of formation of $KMnO_4$ is -200.6 kcal mole^{-1}, ΔG_f° is -176.8 and S° is 41.3 cal mole^{-1} deg^{-1} [95].

Heptavalent manganese in the form of the permanganate ion exhibits a positive magnetic susceptibility of about 70×10^{-6} c.g.s. mole^{-1} which is temperature independent. This small susceptibility arises from the second-order Zeeman effect between the higher lying molecular orbital levels of the ion and the ground level[195].

The electronic[167, 247] and infrared spectra[248] of the permanganate ion have been reviewed.

Permanganic Acid

Crystalline permanganic acid, $HMnO_4$, may be prepared by vacuum sublimation of frozen, aqueous $HMnO_4$ prepared by the addition of sulphuric acid to aqueous $Ba(MnO_4)_2$ below 1°C. From this reaction the hydrate $HMnO_4 \cdot 2H_2O$ may also be isolated[261]. $HMnO_4$ is a violent oxidant, and most common organic materials, with the exception of CCl_4, $CHCl_3$ and CH_2Cl_2, explode and burst into flame on contact. The acid is hygroscopic, very soluble in water, slightly soluble in perfluorodecalin and CCl_3CF_3 and insoluble in CCl_4 or $CHCl_3$. Above 3°C, $HMnO_4$ often decomposes violently. The reactions of the dihydrate are similar but it is less violent. In many ways $HMnO_4$ resembles $HClO_4$ [261].

USE OF MANGANESE COMPOUNDS AS OXIDANTS IN ORGANIC CHEMISTRY

A number of manganese compounds, e.g. potassium permanganate, manganese dioxide and manganese(III) pyrophosphate, have acted as useful oxidizing agents in organic chemistry.

Potassium permanganate is probably one of the most powerful oxidizing agents available in this field and will effect the oxidation of a large range of organic compounds, e.g. certain hydrocarbons, olefins, alcohols, aldehydes and phenols[167, 240, 262, 263, 264]. The other oxo anions, manganate(VI) and manganate(V), will also act as oxidizing agents but, as would be expected, their oxidizing power increases in the order $MnO_4^{3-} < MnO_4^{2-} < MnO_4^-$ [240]. In alkaline solution the reduction product of potassium permanganate is α-MnO_2 [265].

---

[257] G. J. Palenik, *Inorg. Chem.* **6** (1967) 503.
[258] J. A. A. Ketelaar, *Z. Krist.* **92** (1935) 155.
[259] A. Hardy, C. Piekarski and P. Hagen-Muller, *Compt. rend.* **249** (1959) 2579.
[260] K. Sasvari, *Z. Krist.* **99** (1938) 9.
[261] N. A. Frigerio, *J. Am. Chem. Soc.* **91** (1969) 6200.
[262] J. W. Ladbury and C. F. Cullis, *Chem. Revs.* **58** (1958) 403.
[263] W. A. Waters, *Mechanisms of Oxidation of Organic Compounds*, Methuen, London (1964).
[264] R. Stewart, *Oxidation Mechanisms, Applications to Organic Chemistry*, Benjamin (1964).
[265] G. S. Bell and R. Huber, *Electrochim. Acta* **10** (1965) 509.

Manganese dioxide is a very effective reagent for the oxidation of unsaturated alcohols to the corresponding carbonyl compounds and other compounds[266, 267] but, in contrast to the reactions with $KMnO_4$, oxidations with MnO_2 are heterogeneous in nature.

The manganese(III) ion Mn^{3+} is only stable in very acidic solution (*ca* 4.5 M H_2SO_4). In less acidic solutions it disproportionates to Mn^{2+} and MnO_2. However, the trivalent ion can be stabilized in neutral solution by pyrophosphate to give the complex ion $Mn(H_2P_2O_7)_3^{3-}$ which can then be used as an oxidizing agent. The reagent[263, 264] does not attack ordinary alcohols and olefins but will oxidize aldehydes and ketones which are able to enolize. The oxidation of α-glycols is also possible and this reaction has been extensively studied.

MANGANESE SULPHIDES, SELENIDES AND TELLURIDES

Manganese sulphides have recently been reviewed[268], and further structural data on manganese sulphides, selenides and tellurides is given in ref. 269. All the compounds have semiconducting properties[269].

Manganese Sulphides

The monosulphide MnS, the disulphide $Mn^{II}S_2$, and possibly the trisulphide MnS_3, exist. In general the structures and phase relations of the Mn–S system are similar to the zinc and cadmium sulphides at elevated pressures, and this is probably a consequence of the spherical symmetry of the high spin d^5 Mn^{2+} ion which is present in MnS and MnS_2.

Manganese(II) sulphide, MnS, exists in three forms[268]. The stable green form (alabandite), designated α-MnS, has a rocksalt structure with octahedrally coordinated Mn^{2+} and S^{2-} ions. The red forms, designated β-MnS and γ-MnS, have the cubic zincblend and the hexagonal wurtzite structures respectively in which the M^{2+} and S^{2-} ions are tetrahedrally coordinated. The red forms are metastable, and on heating to 200°C they are converted to the stable green form[268]. All three forms can be prepared by precipitation with H_2S gas from aqueous manganese(II) solutions[13, 270], but only α-MnS can be obtained by direct reaction between the elements[270]. The melting point of MnS is 1600 ± 10°C[3]. The values of ΔH_f°, ΔG_f°, and S° are -49.5 kcal mole^{-1}, -50.5 kcal mole^{-1} and 18.7 cal mole^{-1} deg^{-1} respectively[95].

Manganese(II) disulphide occurs naturally as the mineral hanerite and can also be synthesized[13, 271]. It has a pyrite type structure and is composed of Mn^{2+} and S_2^{2-} ions. Every Mn^{2+} ion is octahedrally coordinated. MnS_2 is decomposed to MnS and sulphur on heating.

The electronic spectra of the three forms of MnS have been studied in detail as have the electronic spectra of Mn^{2+} in ZnS and e.s.r. spectra of Mn^{2+} in diamagnetic sulphide. All these studies suggest that there is considerable mixing of the manganese $3d$ orbitals with sulphide orbitals. MnS and MnS_2 are both semiconductors. The magnetic properties of

---

[266] R. M. Evans, *Quart. Rev.* **13** (1959) 61.

[267] S. P. Korshunov and L. I. Vereshchagin, *Uspekhi Khim.* **35** (1966) 2255.

[268] F. Jellinek, *Inorganic Sulphur Chemistry* (edited by G. Nickless), Elsevier (1968), p. 669.

[269] F. Hulliger, *Structure and Bonding* **4** (1968) 83.

[270] S. Furuseth and A. Kjekshus, *Acta Chem. Scand.* **19** (1965) 1405.

[271] W. Biltz and F. Weichmann, *Z. anorg. allgem. Chem.* **228** (1936) 268.

MnS_2 and of the three forms of MnS have been studied in detail. They become antiferromagnetic at low temperatures and the crystallographic symmetry is lowered below the Néel point[268, 269].

Mass spectrometric studies on stoichiometric MnS and a mixture of MnS and graphite show that the former vaporizes congruently to give Mn(g) and $\frac{1}{2}S_2$(g) and that the latter reacts to give Mn(g) and CS(g). Small quantities of MnS^+, MnS_2^+ and MnS_3^+ are also observed[272]. From these measurements a value of 67 ± 6 kcal $mole^{-1}$ has been determined for the heat of formation of MnS gas. The dissociation of MnS gas is 71 ± 4 kcal $mole^{-1}$.

A revised MnS–MnO phase diagram has been presented. The eutectic temperature is 1232 ± 5°C and the eutectic composition is 64 wt. % of MnS [273].

The reaction of oxygen with heated α-MnS gives an oxysulphide, MnOS [274], and α-MnS appears to oxidize to MnOS while its X-ray powder pattern is being recorded in air. Although Mn_2O_7 reacts with sulphur to give an impure sample of MnS_2 [275], manganese dioxide does not react with sulphur up to temperatures of 400°C [275].

The reactions of halogens with MnS give the compounds $MnSCl_2$, MnSBr, and MnSI. These materials appear to be distinct compounds of manganese(IV) and manganese(III), but no magnetic data appears to be available[274].

Some hydrous manganese(II) sulphides have been described[1]. A polysulphide, MnS_3, together with MnS_2, is said to result from the system $MnSO_4$–Na_2S_n–H_2O_2 ($n = 2$ or 3), but its existence needs confirmation[268, 276]. A number of ternary manganese sulphide systems are known[268, 269], and a few examples are given here. The complexes $A_2Mn_3S_4$ (A = K, Rb or Cs) contain tetrahedrally coordinated Mn^{2+} and exhibit antiferromagnetism. In NbS_2 and TaS_2 up to two-thirds of the octahedral sites can be occupied by Mn^{2+}, and the compound $MnNb_3S_6$ becomes ferromagnetic at low temperatures. The complex $MnAl_2S_4$ has a rhombohedral layer structure, and in $MnIn_2S_4$ the cations are statistically distributed. $MnSc_2S_4$ and $MnLu_2S_4$ have normal spinel structures.

Manganese Selenides

The monoselenide MnSe and the diselenide $MnSe_2$ are known. Manganese(II) selenide appears to exist in three forms[277]. α-MnSe, which has a NaCl structure, is obtained by the ageing of a MnSe precipitate formed by treating a manganese(II) sulphate, chloride or acetate solution with $(NH_4)_2Se$ in the presence of ammonium acetate. β-MnSe, which has a zincblend (sphalerite) structure, is obtained by exposing a manganese(II) acetate solution for several hours to an atmosphere of H_2Se. γ-MnSe, which has a wurtzite type structure, is obtained by the action of H_2Se and ammonia on a boiling solution of $MnCl_2$ or $MnSO_4$. The β- and γ-forms are metastable and readily revert to the stable α-form. However, it is reported that at low temperatures α-MnSe transforms to β-MnSe [278]. α-MnS is readily obtained by heating stoichiometric amounts of the powdered constituents[279]. Manganese diselenide can be synthesized by heating stoichiometric amounts of the constituents in sealed

---

[272] H. Wiedemeier and P. W. Gilles, *J. Chem. Phys.* **42** (1965) 2765.
[273] H. C. Chao, Y. E. Smith and L. H. Van Vlack, *Trans. AIME* **227** (1963) 796.
[274] S. S. Batsanav and L. I. Gorogotskaya, *Zh. Neorg. Khim.* **4** (1959) 62.
[275] G. W. Watt and U. Kask, *J. Inorg. Nucl. Chem.* **27** (1965) 1925.
[276] E. M. Nanobashvili and S. G. Kurashvili, *Chem. Abs.* **55** (1961) 7124h.
[277] A. Baroni, *Z. Krist.* **99** (1938) 336.
[278] N. N. Sirota and G. I. Makovetokii, *Chem. Abs.* **66** (1967) 32670x.
[279] W. D. Johnston and R. R. Heikes, *J. Am. Chem. Soc.* **80** (1958) 5904.

tubes at 550°C [280]. It has a pyrite-type structure and is composed of Mn^{2+} and Se_2^{2-} ions[280]. The heat of formation of MnSe [281] is -37.7 kcal $mole^{-1}$ and $\triangle H_f^\circ$ for $MnSe_2$ has been calculated to be -96 ± 8 kcal $mole^{-1}$ [282]. The magnetic properties of MnSe and $MnSe_2$ have been studied in detail[269].

The system MnSe–MnTe has been studied over the entire composition range[283], and the magnetic properties of the system $Li_xMn_{(1-x)}Se$ have been investigated[279]. It is found that the introduction of Li into the MnSe crystal lattice induces ferromagnetism at liquid nitrogen temperatures.

Manganese(II) selenide is converted by dry chlorine to MnSeCl. The compound MnSeCl is decomposed by air, water and organic solvents, but on heating *in vacuo* to 80–90°C, chlorine is lost and the compound Mn_2Se_2Cl results. The compounds $MnSeBr_2$, Mn_2SeBr_2 and $MnSeI_2$ are also known[284]. The structures of these materials are not known.

Manganese Tellurides

The compounds MnTe and $MnTe_2$ are known. They can be conveniently prepared by heating stoichiometric amounts of the constituents in sealed vessels *in vacuo*[280, 285]. MnTe has the NiAs structure[287]. $MnTe_2$ has the pyrite structure and is composed of Mn^{2+} and Te_2^{2-} ions[280,286]. There is no crystallographic transition in MnTe at 130° [287]. The heat of formation of MnTe is -26.6 kcal $mole^{-1}$.

The magnetic properties of MnTe and $MnTe_2$ have been studied in detail[269].

The systems MnSe–MnTe [283], $Li_xMn_{1-x}Te$ and $Na_xMn_{1-x}Te$ have been investigated[288].

MANGANESE NITRIDES, PHOSPHIDES, ARSENIDES AND ANTIMONIDES

Nitrides

Manganese nitrides have recently been reviewed[181, 289]. Although the manganese–nitrogen phase diagram has been studied extensively, the results are not conclusive[289]. Structural data and some thermodynamic properties of manganese nitrides are given in Table 13.

Manganese nitrides have been prepared by a number of methods but the most important method is probably that of the direct action of nitrogen on manganese since high purity manganese is readily available. The phase obtained will, of course, be the one that is in equilibrium at the given temperature and pressure of the nitrogen being used. Thus at 750°C and 1 atm of nitrogen, a product with about 22 atom % nitrogen results while at 740°C and 200 atm the product contains 32 atom % nitrogen. If the metal is heated in a nitrogen atmosphere it begins to glow at 1210–1220° and then burns with a flame and absorbs nitrogen even more readily than magnesium[19]. Another good method of obtaining manganese nitrides is to treat manganese amalgam with ammonia. As the temperature increases the amalgam

---

[280] N. Elliot, *J. Am. Chem. Soc.* **59** (1937) 1958.

[281] M. P. Morozova and T. A. Stolyarova, *Chem. Abs.* **62** (1965) 2297e.

[282] J. J. Murray and R. D. Heyding, *Can. J. Chem.* **45** (1967) 2675.

[283] A J. Panson and W. D. Johnston, *J. Inorg. Nucl. Chem.* **26** (1964) 701.

[284] S. S. Batsanov and L. I. Gorogotskaya, *Chem. Abs.* **53** (1959) 19655c.

[285] W. D. Johnston and D. E. Sestrich, *J. Inorg. Nucl. Chem.* **19** (1961) 229.

[286] S. Furberg, *Acta Chem. Scand.* **7** (1953) 693.

[287] N. Kunitonsi, Y. Hamaguchi and S. Anzai, *J. Phys. Soc. Japan* **18** (1963) 744.

[288] A. J. Panson and W. D. Johnston, *J. Inorg. Nucl. Chem.* **26** (1964) 705.

[289] R. Juza, *Advances in Inorganic and Radiochemistry* (edited by H. J. Emeléus and A. G. Sharpe), Academic Press, Vol. 9 (1966), p. 81.

TABLE 13. SOME PROPERTIES OF MANGANESE NITRIDES[a]

Phase	Composition	ΔH_{298} (kcal mole^{-1})	Structure type	Lattice constants (Å)	
				a	*c*
MnN	$MnN_{1.04}$		Cubic[b]	4.435	—
Mn_6N_5	$Mn_6N_{5.25}$ to Mn_6N_5		Tetragonal face-centred	4.2218 4.2145	4.1136 4.1486
Mn_3N_2	$Mn_3N_{2.08}$ to $Mn_3N_{1.85}$		Body-centred tetragonal	4.2074 4.2044	4.0410 4.0464
Mn_2N	$Mn_2N_{1.06}$ to $Mn_2N_{0.79}$	c	Hexagonal	2.8179 2.7757	4.5346 4.5284
Mn_4N	Mn_4N to $Mn_4N_{0.435}$	-30.3	Cubic-face-centred	3.863 3.763	— —
Mn_xN	$Mn_{9.2}N$ to $Mn_{25.3}$		Tetragonal face-centred	3.764 3.765	3.729 3.610

[a] Ref. 289.
[b] Lattice constant probably in error.
[c] ΔH_{298} $Mn_{2.5}N$ is -30.3 kcal mole^{-1}.

decomposes to give very finely divided manganese which is readily nitrided by the ammonia. Using this method, highly nitrided products may be obtained at relatively low temperatures[289].

The manganese nitrides are all slowly decomposed by water and dissolve in dilute non-oxidizing acids with the formation of ammonium salts. X-ray determination of the atomic factor for nitrogen in Mn_4N shows that the nitrogen is present as either N^0 or N^{1-} but not N^{3+}, i.e. the nitrogen is not an electron donor[289]. The phases $MnN_{0.41}$, $MnN_{0.48}$ and $MnN_{0.65}$ are paramagnetic but Mn_4N exhibits ferrimagnetism[289].

Many ternary manganese nitride systems are known such as Ta_3MnN_4, Mn_3MeN (where Me = Cu, Ag, Zn, Ga or In) and Li_7MnN_4. Also nitrogen may be replaced by carbon in Mn_4N up to the composition $Mn_4N_{0.2}C_{0.8}$.

Manganese nitrides are used as nitrogen-containing intermediate alloys in steel making.

Phosphides, Arsenides and Antimonides

Mn_3P, Mn_2P, MnP, MnP_3, Mn_3As, Mn_2As, Mn_3As_2, MnAs, Mn_2Sb, Mn_3Sb_2 and MnSb have been identified, and the structural, magnetic and semi-conducting properties of these compounds may be found in references 14, 269 and 293. Since interstitial structures are generally not possible for the larger P and As atoms, there is generally little similarity between the nitrides and these compounds. The phosphides are not readily hydrolysed by water but on prolonged action, phosphine and hydroxide results[221].

MANGANESE CARBIDES AND SILICIDES

Manganese Carbides

The carbides of manganese have recently been reviewed[290]. There are many contradictory results reported but the carbides which appear to exist are: $Mn_{23}C_6$ (cubic, m.p. 1010°C);

---

[290] W. A. Frad, *Advances in Inorganic and Radiochemistry* (edited by H. J. Emeléus and A. G. Sharpe), Vol. 11 (1968), p. 153.

Mn_3C (orthorhombic, m.p. 1520°C); Mn_7C_3 (monoclinic); Mn_2C_7 (orthorhombic pseudohexagonal, m.p. 1340°C); and $Mn_{15}C_4$, which has hexagonal symmetry and corresponds to the phase which was originally reported to be Mn_7C_2. The early studies on the manganese carbides were carried out using material which had been obtained by acid or electrolytic isolation from cast-irons and steel. However, most of the more recent work has used distilled manganese and graphite or sugar charcoal. In general the work is complicated by the volatility of manganese, its affinity for oxygen and nitrogen and its reactivity towards refractories. Mn_3C is hydrolysed by water to give a complex mixture of gaseous products. The main products are 75% H_2, 12–15% CH_4 and 6–8% C_2H_6. The solid phase is $Mn(OH)_2$ [291]. Acid hydrolysis promotes formation of free carbon, hydrogen and liquid hydrocarbons.

The report that a manganese acetylide can be prepared by the action of calcium carbide on manganese(III) salts has not been substantiated. Similarly, the action of acetylene gas on manganese(II) salts does not precipitate a manganese acetylide[292].

In isolated form the carbides of manganese have practically no use. However, they are important in steel and other ferrous alloys either as compounds of manganese and carbon or as constituents of more complex metallic alloys.

A number of ternary systems have been studied. These include the Fe–Mn–C system and the phases Mn_3M_3C (M = Nb, Ta, Mo and W).

Manganese Silicides

There have been many investigations on the manganese silicon system[181, 292], and structural data on the known phases are given in Table 14. A number of ternary systems, e.g. Mn_3Si/Fe_3Si and Mn_5Si_3/Fe_5Si_3, have been studied. Valuable heat-resisting properties have been claimed for manganese silicides[181].

TABLE 14. SOME PROPERTIES OF MANGANESE SILICIDES

	M.p. (°C) [a]	Structure type[b]	Lattice constants (Å)
Mn_3Si	—	Body-centred cubic	$a=5.714$
Mn_5Si_3	1280	Tetragonal	$a=6.912$; $c=4.812$
MnSi	1275	FeSi type	$a=4.557$
$MnSi_{1.7}$	—	Tetragonal	$a=5.49$; $c=112.42$

[a] H. J. Goldschmidt, *Interstitial Alloys*, Butterworths (1967).

[b] B. Aronsson, T. Lundström and S. Rundqvist, *Borides, Silicides and Phosphides*, Methuen (1965).

MANGANESE BORIDES

Five manganese borides have been identified: Mn_4B (orthorhombic, a = 14.53, b = 7.292, c = 4.209 Å); Mn_2B (tetragonal, a = 5.148, c = 4.208 Å); MnB (orthorhombic,

---

[291] W. R. Myers and W. P. Fishel, *J. Am. Chem. Soc.* **67** (1945) 1962.

[292] N. N. Greenwood and G. E. Toogood, *Inorg. Chem.* **3** (1964) 1336.

$a = 5.560$, $b = 2.977$, $c = 4.145$ Å); Mn_3B_4 (orthorhombic, $a = 3.032$, $b = 12.86$, $c = 2.960$ Å); MnB_2 (tetragonal, $a = 3.009$, $c = 3.039$ Å). Further data can be found in references 181 and 293.

MANGANESE AZIDES

Manganese(II) azide, $Mn(N_3)_2$, can be prepared by the action of an alkylammonium azide on a solution of manganese(II) in a non-aqueous solvent. Evaporation of an aqueous solution of $Mn(N_3)_2$ gives an insoluble basic salt[294, 295]. The standard heat of formation of $Mn(N_3)_2$ has been given as 94 kcal mole^{-1}, but this figure requires confirmation[296, 297]. Solutions of the compound in methyl cyanide, trimethylphosphate and propanediol 1,2-carbonate have been investigated, and on the basis of spectrophotometric, potentiometric and conductometric investigations, it appears that $Mn(N_3)_2$ exists in all three solvents, $Mn(N_3)_4^{2-}$ exists in methyl cyanide and propanediol 1,2-carbonate and $[Mn(N_3)_x(Me_3PO_4)_{6-x}]^{+2-x}$ exists in trimethyl phosphate[294].

The complex azide $(Et_4N)_2Mn(N_3)_4$ has been obtained by the action of silver azide on $(Et_4N)_2MnBr_4$, and the infrared spectrum of the complex has been measured[298].

A hydroxy manganese azide, $Mn(OH)N_3$, has been obtained, and it is said to crystallize in a C19 structure[299].

The kinetics and stoichiometry of the reaction between Mn^{3+} and hydrazoic acid in perchloric acid solution have been investigated by two groups of workers[300, 301]. The products of reaction are nitrogen and the manganese(II) ion. At low concentrations of hydrazoic acid the formation of the radical H_6N_2 has been postulated as an intermediate, but at higher concentrations the kinetic dependancies become more complex and a different mechanism has been postulated.

Mixtures of Mn^{3+} and hydrazoic acid in perchlorate media in the absence of air initiate the polymerization of acrylonitrile[301].

MANGANESE FULMINATES, CYANATES, THIOCYANATES AND SELENOCYANATES

Fulminates

Fulminate complexes of manganese(II) have been described. The complexes which have been isolated are of the type $L_2Mn(CNO)_2$, where L = NH_3 [302, 303] and L_2 [304] = dipyridyl or ortho-phenothroline. The complexes are high spin, as would be expected, and are interesting in that they contain manganese–carbon bonds. Their electronic and infrared spectra have been examined[304].

[293] B. Aronsson, T. Lundström and S. Rundqvist, *Borides, Silicides and Phosphides*, Methuen (1965).

[294] V. Gutmann and W. K. Lux, *J. Inorg. Nucl. Chem.* **29** (1967) 2391.

[295] L. F. Audrieth, *Chem. Revs.* **15** (1934) 169.

[296] P. Gray, *Quart. Revs.* **17** (1963) 441.

[297] B. L. Evans, P. Gray and A. D. Yoffe, *Chem. Revs.* **59** (1959) 515.

[298] W. Beck, W. P. Fehlhammer, P. Pöllmann, E. Schuierer and K. Feldl, *Chem. Ber.* **100** (1967) 2335.

[299] W. Feitknecht and H. Zschaler, *Chem. Abs.* **54** (1960) 10620g.

[300] G. Davies, *Coord. Chem. Rev.* **4** (1969) 199.

[301] C. F. Wells and D. Mays, *J. Chem. Soc.* A (1968) 1622.

[302] L. Wöhler and A. Weber, *Chem. Ber.* **62B** (1929) 2742.

[303] L. Wöhler, A. Weber and A. Berthman, US Dep. Comm., AD 633399 (1966).

[304] W. Beck and E. Schuierer, *Chem. Ber.* **95** (1962) 3048.

Cyanates

The cyanate ligand NCO^-, which is, of course, isomeric with the fulminate ion, also coordinates to manganese(II). The complex $(Et_4N)_2Mn(NCO)_4$ is obtained[305] by the action of silver cyanate on $(Et_4N)_2MnBr_4$. The magnetic and electronic properties of the complex have been examined and the manganese(II) ion is tetrahedrally coordinated[305]. On the basis of infrared studies[306, 307] the NCO^- ligand appears to be coordinated via the nitrogen atom.

Thiocyanates

In contrast to isocyanate complexes of manganese there are a number of manganese thiocyanate complexes known.

The manganese(I) thiocyanate complex $MnSCN(CO)_5$ can be prepared by the action of sodium pentacarbonylmanganate (-1) on thiocyanogen chloride[308]. Infrared studies reveal that in the solid state the compound is S-bonded. However, in acetonitrile solutions the complex isomerizes exclusively to the N-bonded form, $MnNCS(CO)_5$, and in other solvents such as dichloromethane, 1,2-dichloroethane, chloroform and ethylacetate an equilibrium exists between the two linkage isomers[308]. A series of thiocyanatocarbonyl complexes of manganese(I) have been prepared either by the reaction of $MnSCN(CO)_5$ with a series of neutral ligands L (L = amine, phosphine, arsine or stibine) or by metathesis of the chloro or bromo analogues with potassium thiocyanate. Infrared studies suggest that the tetracarbonyls $MnSCN(CO)_4L$ are S-bonded in the solid phase and in chloroform solutions. The *cis*- and *trans*-tricarbonyl complexes $MnNCS(CO)_3L_2$, however, are usually N-bonded except for the compounds *cis*-$MnSCN(CO)_3(AsPh_3)_2$ and *cis*-$MnSCN(CO)_3(SbPh_3)_2$, which are S-bonded. The formation of either N- or S-bonded manganese(I) thiocyanate complexes has been discussed in terms of metal–carbonyl π-bonding and steric effects[309].

There are a number of manganese(II) thiocyanate complexes known which all contain N-bonded thiocyanate.

Anhydrous manganese(II) thiocyanate can be prepared by dehydration of the alcohol adducts $Mn(NCS)_2(ROH)_2$ (R = Me or Et) *in vacuo*[310]. The spectral and magnetic properties of $Mn(NCS)_2$ have been examined, and it is suggested that the structure involves a tetragonal N_2S_4 coordination sphere with triple bridging thiocyanate ions[310]. Spectroscopic studies[311] on salts of the ions $Mn(NCS)_6^{4-}$ and $Mn(NCS)_4^{2-}$ are consistent with an octahedral and tetrahedral coordination respectively about the manganese. Solutions of the compound quinolinium hexaisothiocyanatomanganese(II), $(C_9H_8N)_4Mn(NCS)_6$, in organic solvents such as nitromethane, however, appear to contain tetrahedral $Mn(NCS)_4^{2-}$ ions, and the compound $HgMn(NCS)_4$ also appears to contain tetrahedral manganese[311]. The coordination polyhedron of the manganese(II) ion in the complex $Mn(NCS)_2(thiourea)_2$ approximates to D_{4h} symmetry with infinite chains of bridging sulphur atoms from the thiourea in the plane and N-bonded thiocyanate groups in the axial positions[312, 313]. Octahedrally

---

[305] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.* (1964) 2790.
[306] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.* (1965) 262.
[307] A. Sabatini and I. Bertini, *Inorg. Chem.* **4** (1965) 959.
[308] M. F. Farona and A. Wojcicki, *Inorg. Chem.* **4** (1965) 857.
[309] M. F. Farona and A. Wojcicki, *Inorg. Chem.* **4** (1965) 1402.
[310] C. D. Flint and M. Goodgame, *J, Chem. Soc.* A (1970) 442.
[311] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.* (1965) 268.
[312] M. Nardelli, G. F. Gosparri, G. G. Battistini and P. Dominio, *Acta Cryst.* **20** (1966) 349.
[313] C. D. Flint and M. Goodgame, *Inorg. Chem.* **8** (1969) 1833.

coordinated manganese is also present in the complexes *trans*-$Mn(NCS)_4(py)_2$ and polymeric $Mn(NCS)_2(py)_2$ [314, 315]. Crystallographic data on the complex $Mn(NCS)_2(N_2H_4)_2$ suggests that the N_2H_4 molecules are bonded to two manganese atoms to form double bridged complexes[316]. Clathrate complexes are formed between xylenes and $Mn(NCS)_2$(4-ethylpyridine)$_4$ [317].

The hydrates $Mn(NCS)_2 \cdot nH_2O$ ($n = 4$, 3 and 2) have been reported[318].

The reactions of a variety of manganese compounds with molten KNCS have been examined but no thiocyanate complexes were detected[319].

The Raman spectra of some manganese(II) thiocyanate complexes have been investigated[320].

Selenocyanates

Like thiocyanate complexes of manganese(II), all the selenocyanate complexes of manganese(II) which have been studied are N-bonded. The electronic spectra and magnetic properties of salts of the octahedral $Mn(NCSe)_6^{2-}$ and tetrahedral $Mn(NCSe)_4^{2-}$ ions have been examined together with their infrared spectra[321]. The adducts $Mn(NCSe)_2L_4$ (L = pyridine[322] or dimethyformamide[323]) have *trans*-octahedral structures and the lattice constants and space group of the latter adduct have been determined.

MANGANESE BORATES

A summary of the earlier work on the manganese borates, some of which occur naturally, can be found in ref. 324.

The thermodynamic properties of the $MnO–B_2O_3$ system have been investigated[325].

MANGANESE CARBONATE

Manganese(II) carbonate, $MnCO_3$, occurs naturally as the mineral rhodochrosite[3]. The pure salt can be prepared by addition of carbonate to a solution of manganese(II) nitrate. The precipitate is washed in the absence of oxygen and dried in a vacuum desiccator[168]. The hydrous compound can also be dehydrated by heating to 100–200°C[326]. Fine crystals of the compound have also been obtained[327]. The stability of manganese(II) carbonate is largely due to its insolubility (the solubility product is 8.8×10^{-11} at 25°C) and

---

[314] R. J. H. Clark and C. S. Williams, *Spectrochim. Acta* **22** (1966) 1081.

[315] C. W. Frank and L. B. Rogers, *Inorg. Chem.* **5** (1966) 615.

[316] A. Ferrari, A. Braibanti and A. Lanfredi, *Gazz. chim. ital.* **91** (1961) 69.

[317] G. Gawalek and H. G. Koennecke, *Chem. Abs.* **61** (1964) 5177h.

[318] M. Géloso and J. Faucherre, *Nouveau Traité de Chimie Minérale* (edited by P. Pascal), Masson et Cie, Vol. 15 (1960), p. 940.

[319] D. H. Kerridge and M. Mosley, *J. Chem. Soc.* A (1967) 352.

[320] A Tramer, *J Chim. Phys.* **59** (1962) 232, 241.

[321] D. Forster and D. M. L. Goodgame, *Inorg. Chem.* **4** (1965) 1712.

[322] Yu. Ya. Kharitonov and V. V. Skopenko *Zh. Neorg. Khim.* **10** (1965) 1803.

[323] V. V. Skopenko and G. V. Tsintsadze, *Zh. Neorg. Khim.* **9** (1964) 2675.

[324] M. Géloso and J. Faucherre, *Nouveau Traité de Chimie Minérale* (edited by P. Pascal), Masson et Cie, Vol. 16 (1960), p. 946.

[325] B. M. Lepinskikh and O. A. Esin, *Zh. Neorg. Khim.* **6** (1961) 1223.

[326] E. Schulek and E. Pungor, *Chem. Abs.* **56** (1962) 2890c.

[327] N. Yu. Ikornikova, *Kristallografiya* **6** (1961) 745.

the solid is only slightly hydrolysed even in boiling water. The pure salt is pink and slowly darkens in air due to air oxidation[19, 328]. The carbonate decomposes on heating to give oxides of manganese, the oxidation states of these oxides depending on whether the decomposition is performed in the absence or presence of oxygen.

Manganese(II) carbonate has a rhombohedral calcite structure[331].

For crystalline $MnCO_3$, $\triangle H_f^\circ$ is -214 kcal mole^{-1}, $\triangle G_f^\circ$ is -196 kcal mole^{-1} and S° is 20.5 cal mole^{-1} deg^{-1}. The corresponding values for precipitated $MnCO_3$ are -211, -194 and 27.0 respectively[95].

$MnCO_3$ is antiferromagnetic[195] and the compound has been the subject of a Raman study[332].

MANGANESE SALTS OF SIMPLE CARBOXYLIC ACIDS

Many manganese salts of both monobasic and dibasic carboxylic acids are known and compounds of manganese(I), (II), (III) and (IV) exist. In this section only derivatives of simple acids will be discussed. Important salts of more complex acids, e.g. ethylenediamine-tetra-acetic acid, will be discussed under complexes of manganese.

The stability constants of a wide variety of organic acids with manganese(II) and manganese(III) have been determined[225].

Monocarboxylic acids

Manganese(I) Compounds

Some manganese(I) carboxylate compounds have been stabilized in carbonyl compounds of the type $Mn(OCOR)(CO)_5$, where R = CF_3, C_2F_5 and C_3F_7. The compounds have been prepared either by the action of trifluoroacetic acid[333] on $Mn(\sigma\text{-}C_3H_5)(CO)_5$ or by metathesis between the appropriate silver salt and $MnCl(CO)_5$[334]. Their infrared and ^{19}F n.m.r. spectra have been reported[334].

Dithiobenzoic acid reacts with $MnBr(CO)_5$ to give a monomeric complex, $Mn(SSCC_6H_5)(CO)_4$, which contains a bidentate dithiobenzoate group[335]. This complex is interesting since when refluxed in methanol for 3 days it gives an 83% yield of $Mn_2(CO)_{10}$. In view of this high yield it seems likely that the methanol acts as a source of carbon monoxide in this reaction[335].

Manganese(II) Compounds

Manganese(II) formate dihydrate, $Mn(OCOH)_2 \cdot 2H_2O$, is readily obtained by the action of formic acid on $MnCO_3$[336]. The compound forms red crystals which are monoclinic. In the unit cell there are four Mn^{+2} ions present which are divided equally between two kinds

---

[328] A. J. Hegedus and K. Martin, *Mikrochim. Acta* (1966) 833.

[329] D. Dollimore and K. H. Tonge, *5th Intern. Symp. Reactivity Solids*, Munich (1964), p. 497.

[330] K. Ito and T. Takahashi, *Chem. Abs.* **57** (1962) 4268f.

[331] D. L. Graf, *Am. Minerologist* **46** (1961) 1283.

[332] J. Louisfert, *Compt. rend.* **233** (1951) 381.

[333] M. L. H. Green, A. G. Massey, J. T. Moelwyn-Hughes and P. L. I. Nagy, *J. Organomet. Chem.* **8** (1967) 511.

[334] R. B. King and R. N. Kapoor, *J. Organomet. Chem.* **15** (1968) 457.

[335] I. A. Cohen and F. Basolo, *Inorg. Chem.* **3** (1964) 1641.

[336] M. Géloso and J. Faucherre, *Nouveau Traité de Chimie Minérale* (edited by P. Pascal), Masson et Cie, Vol. 15 (1960), p. 693.

of inequivalent sites[337]. The Mn^{+2} ions on A sites are surrounded octahedrally by six oxygen atoms belonging to formate groups. The Mn^{2+} ions on B sites are also surrounded by an octahedron formed by four water molecules and two oxygen atoms which belong to formate groups. The magnetic properties of single crystals of $Mn(OCOH)_2 \cdot 2H_2O$ have been studied and interpreted in the light of this structure[338] and susceptibility measurements have also been recorded below 1°K[338, 339].

A meaningful value of the activation energy for the dehydration of $Mn(OCOH)_2 \cdot 2H_2O$ has been obtained by differential enthalpic analysis[340].

Manganese(II) acetate, $Mn(OCOCH_3)_2 \cdot 4H_2O$, is readily obtained by treating $MnCO_3$ with acetic acid. The compound forms red crystals and is soluble in water, methanol and ethanol[336].

$Mn(OCOCH_3)_2 \cdot 4H_2O$ is monoclinic but no detailed structural work appears to be available[341, 342]. It is possible that two types of Mn^{2+} ion are present in the unit cell, as is observed in the formate compound, and this idea has been used to explain the weak ferromagnetic interaction present in the compound[343].

Complex derivatives of manganese(II) acetate are known. Crystals of the hydrazine complex $Mn(OCOCH_3)_2(N_2H_4)_2$ are triclinic and twinned and contain bridging N_2H_4 groups as is observed in the complex $ZnCl_2(N_2H_4)_2$ [343]. It is also possible that the complex[342] $Mn(OCOCH_3)_2 \cdot (C_6H_5NHNH_2)_2$ may have a similar structure. Some curious polynuclear complexes, $Mn_2(OCOCH_3)_2(\text{picrate})_2$ and $Mn_3(OCOCH_3)_4$(*p*-nitrophenolate)$_2 \cdot CH_3CO_2H \cdot 9H_2O$, have been described in the earlier literature but their structures are unknown[344].

Anhydrous $Mn(OCOCF_3)_2$ has been prepared by the action of silver trifluoroacetate on a mixture of manganese(II) chloride and manganese powder in nitromethane or diethylether. The compound is pink and presumably contains octahedral manganese(II). It is slightly soluble in benzene. Its infrared spectrum has been recorded and thermal decomposition of the compound gives MnF_2 and a variety of fluorocarbons in addition to CO and CO_2 [345]. $Mn(OCOCCl_3)_2$ has been prepared by an analogous method to the trifluoroacetate[346]. The adducts $Mn(OCOCX_3)_2L_4$ (X = F or Cl; L = pyridine or γ-picoline), $Mn(OCOCX_3)_2L_2$ and $Mn(OCOCX_3)_2L$ (L = pyridine *N*-oxide or γ-picoline *N*-oxide) have also been isolated and characterized by infrared and electronic spectra and magnetic measurements. All these compounds appear to contain octahedral manganese(II) [346].

Manganese metal is rapidly dissolved by peroxytrifluoroacetic acid which is obtained by mixing trifluoroacetic acid with hydrogen peroxide, but the nature of the manganese solution obtained appears to be unknown[347].

---

[337] K. Osaki, Y. Nakai, and T. Watanabe, *J. Phys. Soc. Japan* **19** (1964) 717.

[338] N. Uryû, *J. Chem. Phys.* **42** (1965) 234.

[339] K. Yamgata and H. Abe, *J. Phys. Soc. Japan* **20** (1965) 906.

[340] J. M. Thomas and T. A. Clarke, *J. Chem. Soc.* A (1968) 457.

[341] R. B. Flippen and S. A. Friedberg, *J. Chem. Phys.* **121** (1961) 1591.

[342] C. Oldham, *Progress in Inorganic Chemistry* (edited by F. A. Cotton), Interscience, Vol. 10 (1968), p. 223.

[343] A. Ferrari, A. Braibanti, G. Bigliardi and A. M. Lanfredi, *Gazz. chim. ital.* **93** (1963) 937.

[344] R. Weinland and H. Schlaich, *Z. anorg. allgem. Chem.* **150** (1925) 35.

[345] M. J. Baillie, D. H. Brown, K. C. Moss and D. W. A. Sharp, *J. Chem. Soc.* A (1968) 3110.

[346] S. Amasa, D. H. Brown and D. W. A. Sharp, *J. Chem. Soc.* A (1969) 2892.

[347] A. F. Scott and J. G. Shell, *J. Am. Chem. Soc.* **81** (1959) 2278.

Manganese(III) Compounds

A manganese(III) formate compound was prepared some years ago by the action of formic acid on manganese dioxide and was formulated as $[Mn_3(OCOH)_6][OCOH]_3 \cdot 2H_2O$. The compound is decomposed by water and ethanol but is soluble in acetic acid[336].

Hydrated manganese(III) acetate, $Mn(OCOCH_3)_3 \cdot 2H_2O$, is readily prepared by the oxidation of manganese(II) acetate with $KMnO_4$ in glacial acetic acid[13]. The compound. forms cinnamon-brown crystals and is immediately decomposed by cold water. The anhydrous salt $Mn(OCOCH_3)_3$ has been obtained by the action of acetic anhydride on hydrated manganese(II) nitrate and in this unusual reaction the nitric acid produced acts as the oxidant[13].

$$2Mn(NO_3)_2 \cdot 6H_2O + 15(CH_3CO)_2O = 2Mn(OCOCH_3)_3 + 4NO_2 + \tfrac{1}{2}O_2 + 24CH_3CO_2H$$

It precipitates out as a brown crystalline powder[13]. These manganese(III) acetates are useful starting materials for the preparation of other manganese(III) compounds.

The magnetic properties of $Mn(OCOCH_3)_3 \cdot 2H_2O$ have been studied between 14° and 293°K and the Curie–Weiss law is obeyed, the value of θ being 28°. At 293°K the magnetic moment is 4.94 BM. A small amount of magnetic exchange may be occurring in the compound and there may be a Mn–Mn interaction[342].

The structures of these manganese(III) acetates do not appear to be known.

The oxidation of aromatic hydrocarbons by manganese(III) acetate has been investigated in some detail[348]. The oxidation proceeds by two competing mechanisms: (i) a free radical mechanism involving the carboxymethyl radical, CH_2CO_2H, and (ii) an electron transfer mechanism. The oxidation of aromatic ethers and amines and other aromatic compounds having low ionization potentials has also been studied (see ref. 348). Reactions of $Mn(OCOCH_3)_3$ with olefins gives γ-lactones[349].

Dicarboxylic Acids

Oxalate complexes of manganese have been widely studied. The simple salts of manganese(II), i.e. MnC_2O_4, $MnC_2O_4 \cdot 2H_2O$ and $MnC_2O_4 \cdot 3H_2O$, are known[336] and they probably contain octahedral manganese(II)[350]. Salts such as $K_2Mn(C_2O_4)_2 \cdot 2H_2O$ also exist[336] and it seems likely that octahedral manganese(II) is again present. The magnetic moments of MnC_2O_4 and $K_2Mn(C_2O_4)_2 \cdot 2H_2O$ have been measured[351].

The manganese(III) complex $K_3Mn(C_2O_4)_3 \cdot 3H_2O$ can be readily prepared by addition of $KMnO_4$ to a hot solution of oxalic acid followed by addition of potassium carbonate[13, 352]. The very pure salt can be stored for long periods at 20°C in the absence of air and light. At −6°C it is stable for an almost unlimited time. $K_3Mn(C_2O_4)_3 \cdot 3H_2O$ is readily soluble in water and concentrated solutions are deep reddish brown. However, on dilution or acidification solutions become yellowish brown due to hydrolysis[13, 352]:

$$[Mn(C_2O_4)_3]^{3-} + 2H_2O = [Mn(C_2O_4)_2(H_2O)_2]^{1-} + C_2O_4^{2-}$$

---

[348] E. I. Heiba, R. M. Dessau and W. J. Koehl, Jr., *J. Am. Chem. Soc.* **91** (1969) 138.

[349] J. B. Bush, Jr. and H. Finkbeiner, *J. Am. Chem. Soc.* **90** (1968) 5903; E. I. Heiba, R. M. Dessau and W. J. Koehl, Jr., *J. Am. Chem. Soc.* **90** (1968) 5905.

[350] C. K. Jørgensen, *Inorganic Complexes*, Academic Press (1963).

[351] N. Goldenberg, *Trans. Faraday Soc.* **36** (1940) 847.

[352] G. H. Cartledge and W. P. Ericks, *J. Am. Chem. Soc.* **58** (1936) 2061, 2065, 2069.

This reaction may be easily reversed by addition of excess oxalate[352]. The rate of hydrolysis of $[Mn(C_2O_4)_3]^{3-}$ has been measured[353].

The $[Mn(C_2O_4)_3]^{3-}$ ion is photochemically unstable and the electronic spectrum of the ion has been examined[300]. The photochemical and thermal dissociation of $K_3Mn(C_2O_4)_3 \cdot 3H_2O$ have been studied in both aqueous solutions and in the solid states[354]. The stoichiometry of the photochemical and thermal dissociation reaction[354] is

$$2K_3[Mn(C_2O_4)_3] \cdot 3H_2O(s) \xrightarrow[85°C]{h\nu \text{ or}} 2K_2[Mn(C_2O_4)_2](s) + K_2C_2O_4(s) + 2CO_2(g) + 6H_2O(g)$$

The mechanism of oxidation of oxalate by permanganate has been studied in some detail[262].

A manganese(IV) oxalate complex may also be obtained from the reaction of potassium permanganate and oxalic acid[13, 352]. This compound has been formulated as $K_2[Mn(C_2O_4)_2(OH)_2] \cdot 2H_2O$. However, the magnetic moment of this compound is reported to be 2.79 BM at 303°K, and since this low value is probably a consequence of magnetic exchange it has been suggested[195] that the true formula may involve a compound with Mn–O–Mn linkages in place of the hydroxyl groups. The effect of reformulating the complex in this way would have little effect on the analytical data.

As prepared, the salt consists of green and orange rods and is rapidly decomposed at room temperature particularly when exposed to light. However, it is stable for a few weeks at −6°C if light is excluded. Solutions of the salt are green but rapidly turn brown and become cloudy. They are more stable in the presence of oxalic acid.

Although malonate complexes of manganese(III) are less stable than oxalate complexes, the malonate complexes of maganese(III) are easier to prepare since the acid is not oxidized so readily. Salts of the type $[Mn(malonate)_3]^{3-}$ and $[Mn(malonate)_2(H_2O]^{1-}$ are known[19, 355]. The electronic spectra of these complexes have been examined and interpreted[116, 356].

Diketocyclobutenediol, squaric acid, which structurally resembles oxalic acid, forms less stable complexes with manganese(II) than oxalic acid[357].

The manganese salts of squaric acid and croconic acid (Fig. 1), $MnC_4O_4 \cdot 2H_2O$ [358] and $MnC_5O_5 \cdot 3H_2O$ [359], respectively, have been prepared and their magnetic moments have been

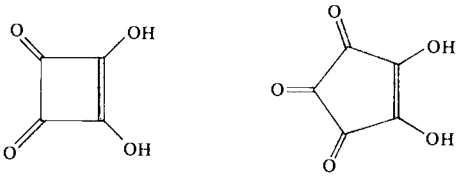

Squaric acid Croconic acid

FIG. 1.

---

[353] D. R. Stranks, *Modern Coordination Chemistry* (edited by J. Lewis and R. G. Wilkins), Interscience (1960).

[354] E. L. Simmons and W. W. Wendlandt, *J. Inorg. Nucl. Chem.* **27** (1965) 2325.

[355] T. N. Srivastava, *Z. anorg. allgem. Chem.* **288** (1956) 288.

[356] R. Dingle, *Acta Chem. Scand.* **20** (1966) 33.

[357] P. H. Tedesco and H. F. Walton, *Inorg. Chem.* **8** (1969) 932.

[358] R. West and H. Y. Niu, *J. Am. Chem. Soc.* **85** (1963) 2589.

[359] R. West and H. Y. Niu, *J. Am. Chem. Soc.* **85** (1963) 2586.

measured. The compound $MnC_5O_5 \cdot 3H_2O$ has a polymeric structure and contains octahedral manganese(II) [360].

Manganese(II) ions like other divalent metal ions catalyse the decarboxylation of β-keto acids and the catalysis is enhanced by the presence of aromatic amine ligands[361].

MANGANESE NITRITES AND NITRATES

Manganese Nitrites

Simple nitrites of manganese(II) are described in the older literature[336] but there is no recent work on these compounds[3]. In aqueous solution, manganese(II) nitrite is reported to decompose to NO, NO_2, N_2, MnO_2, Mn_2O_3 and $Mn(NO_3)_2$ [362]. Alcoholic solutions of manganese(II) nitrite can be prepared metathetically from hydrated manganese(II) bromide and excess silver nitrite[363, 364].

Salts of the complex anion $Mn(NO_2)_4^{2-}$ and the complex $Cs_3Mn(NO_2)_5$ have been prepared[363, 364] but the detailed crystal structures of these complexes are not known. On the basis of spectroscopic studies it has been suggested that the anion $Mn(NO_2)_4^{2-}$ contains bidentate nitrite ions and that the manganese is 8-coordinate[364]. Similar investigations on the compound $Cs_3Mn(NO_2)_5$ suggest that both N- and O-bonded nitrite groups are probably present in this complex[363].

It is reported that both nitro- and nitrito-pentacarbonylmanganese(I) compounds, $MnNO_2(CO)_5$, are formed as byproducts of the action of dinitrogen tetroxide on dimanganese decarbonyl[365].

Manganese(I) Nitrates

A manganese(I) nitrate complex has been stabilized in the carbonyl compound $MnONO_2(CO)_5$ [365]. The compound is obtained by the action of dinitrogen tetroxide on dimanganese decarbonyl in light petroleum at 0°C. Attempts to obtain $MnONO_2(CO)_5$ by the action of either silver or lead nitrates on $MnCl(CO)_5$ were not successful. The compound is stable at room temperature for several weeks, but on heating it disproportionates:

$$4MnONO_2(CO)_5 = Mn_2(CO)_{10} + 2Mn(NO_3)_2 + 10CO$$

$MnONO_2(CO)_5$ is readily soluble in ethanol, acetone, chloroform, and sparingly soluble in benzene, water, ether and carbon tetrachloride. In solution it is a non-electrolyte but the conductivities of solutions increase with time. This is probably due to the equilibrium reaction

$$MnONO_2(CO)_5 + \text{solvent} \rightleftharpoons Mn(CO)_5\text{solvent}^+NO_3^-$$

being initially set up followed by decomposition of the ionic carbonyl species to more stable electrolytes.

On the basis of infrared studies it appears that $MnONO_2(CO)_5$ contains a unidentate, oxygen bound, nitrate group[365].

---

[360] M. D. Glick and L. F. Dahl, *Inorg. Chem.* **5** (1966) 289.
[361] J. V. Rund and K. G. Claus, *Inorg. Chem.* **7** (1968) 860.
[362] C. Montemartini and E. Vernazzo, *Industria chim.* **7** (1932) 577.
[363] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.* **6** (1967) 813.
[364] D. M. L. Goodgame and M. A. Hitchman, *J. Chem. Soc.* A (1967) 612.
[365] C. C. Addison, M. Kilner and A. Wojcicki, *J. Chem. Soc.* (1961) 4839.

Nitrato-pentacarbonylmanganese(I) reacts with pyridine and dipyridyl to yield the disubstituted compounds $MnONO_2(CO)_3py_2$ and $Mn(ONO_2)(CO)_3dipy$. Further substitution with pyridine and triphenylphosphine give the ionic complexes $Mn(CO)_3(dipy)(py)^+NO_3^-$ and $Mn(CO)_3(dipy)(PPh_3)^+NO_3^-$ [366]. The latter complex is interesting since on heating *in vacuo* at 130° triphenylphosphine is lost and the covalent nitrate complex $MnONO_2(CO)_3dipy$ is reformed. $Mn(CO)_3(dipy)(PPh_3)_3^+NO_3^-$ reacts with excess triphenylphosphine to give the *cis*-dicarbonyl complex $Mn(CO)_2(dipy)(PPh_3)_2^+NO_3^-$. This complex appears to exist in two forms. These may be isomers in which the PPh_3 groups are either in *cis*- or *trans*-positions in the octahedron.

Manganese(II) Nitrates

Anhydrous manganese(II) nitrate is most simply prepared by dehydration of the solid hydrate in a vacuum desiccator at room temperature over phosphoric pentoxide[19]. It has also been prepared by the action of either dinitrogen pentoxide or chlorine nitrate on anhydrous $MnCl_2$ [367]. In both these reactions a solvate $Mn(NO_3)_2 \cdot N_2O_4$ is obtained, but on heating in vacuum to 90°C the dinitrogen tetroxide can be removed to give the unsolvated compound. $Mn(NO_3)_2 \cdot 2N_2O_4$ may also be obtained either by the action of dinitrogen tetroxide on $Mn_2(CO)_{10}$ or by the action of dinitrogen tetroxide–ethyl acetate mixtures on manganese metal[368]. Thermal decomposition of hydrated manganese(II) nitrate *in vacuo* also yields the anhydrous salt[369]. Anhydrous $Mn(NO_3)_2$ is a colourless compound. It is hygroscopic and is soluble in water, dioxan, tetrahydrofuran and acetonitrile[367]. On heating it decomposes to manganese dioxide and nitrogen dioxide[368].

The infrared spectrum of $Mn(NO_3)_2$ indicates the presence of covalent manganese nitrate bonds[367, 368, 370]. $Mn(NO_3)_2$ has an orthorhombic unit cell like that of copper but with slightly larger lattice parameters[369]. It has a magnetic moment of 5.48 BM [367].

The standard heat of formation of $Mn(NO_3)_2$ is -167 kcal mole^{-1} [95].

Manganese(II) nitrate forms hydrates with six, four, two and one molecules of water[19, 336]. The existence of a trihydrate has not been confirmed. The hexahydrate melts at 25.8°C and the phase diagrams of the manganese(II) nitrate–water and manganese(II) nitrate–nitric acid–water systems have been studied in detail[19, 336]. In this latter ternary system the hexahydrate, tetrahydrate, dihydrate, sesquihydrate, monohydrate and hemihydrate exist. Hydrated manganese(II) nitrate is readily obtained by treating the metal or an appropriate salt with nitric acid. $Mn(NO_3)_2 \cdot 2H_2O$ is even formed from anhydrous $MnCl_2$ and anhydrous nitric acid[368]. The hexahydrate is polymorphic[371].

The standard heat of formation of crystalline and liquid $Mn(NO_3)_2 \cdot 6H_2O$ is -566.9 and -557.3 kcal mole^{-1} respectively[95].

The complex tetranitrato-manganate(II) anion is known in the complex $(Ph_3AsMe)_2Mn(NO_3)_4$ and the magnetic moment and electronic and infrared spectrum of the complex have been recorded[372]. An X-ray study on the complex shows that the complex anion contains bidentate nitrate groups[373]. The 8-coordination of the polyhedron is of

---

[366] C. C. Addison and M. Kilner, *J. Chem. Soc.* A (1966) 1249.

[367] K. Dehnicke and J. Strähle, *Chem. Ber.* **97** (1964) 1502.

[368] C. C. Addison and N. Logan, *Advances in Inorganic and Radiochemistry* (edited by H. J. Emeléus and A. G. Sharpe), Vol. 6 (1964), p. 71.

[369] D. Weigel, B. Imelik and M. Prettre, *Bull. Soc. chim. France* (1964) 2600.

[370] J. R. Ferraro and A. Walker, *J. Chem. Phys.* **42** (1965) 1273.

[371] P. Pouillen, *Compt. rend.* **250** (1960) 3318.

[372] D. K. Straub, R. S. Drago and J. T. Donoghue, *Inorg. Chem.* **1** (1962) 848.

approximate D_{2d} (dodecahedral) symmetry. The variation in Mn–O bond lengths have been correlated with the metal atom radius and the *d*-electron configuration.

A number of adducts of the type $L_2Mn(NO_3)_2$, where L is either an oxygen or nitrogen donor ligand, are known, but it is not completely clear whether these compounds contain unidentate or bidentate nitrate. Pyridine N-oxide reacts with hydrated manganese(II) nitrate to give the complexes $[Mn(C_5H_5NO)_6](NO_3)_2$ and $(C_5H_5NO)_2Mn(NO_3)_2$. On the basis of magnetic and spectral studies it is suggested that the former contains ionic nitrate while the latter complex contains bidentate nitrate[374]. The complex dipy$Mn(NO_3)_2$ has been obtained from the action of 2,2′-dipyridyl on $Mn(NO_3)_2 \cdot 6H_2O$ and also from the action of dipy on $MnONO_2(CO)_5$ [366]. Dipy$Mn(NO_3)_2$ exists in two forms, and it is suggested that these contain octahedral manganese(II) with either *cis*- or *trans*-unidentate nitrate groups. The electronic spectrum of $(Ph_3PO)_2Mn(NO_3)_2$ suggests that a tetrahedral geometry is probably not present in this compound.

The infrared spectrum[375] of $py_2Mn(NO_3)_2 \cdot 2H_2O$ and differential thermal analysis[376] of $py_2Mn(NO_3)_2$ have been reported.

$Mn(NO_3)_2 \cdot 2N_2H_4$ forms hexagonal crystals, and although it burns at 150°C it is apparently not sensitive to shock[336].

Manganese(II) nitrate forms an unstable complex with hexamethylenetetramine, $Mn(NO_3)_2 \cdot 2C_6H_{12}N_4$, and a number of double nitrates and basic nitrates of manganese have been reported[1, 336]. Their structures are not known.

Manganese(III) Nitrates

Attempts to obtain manganese(III) nitrate compounds have not been successful[1, 336].

MANGANESE SALTS OF PHOSPHORUS OXYACIDS

In this section hypophosphites, phosphites, orthophosphates and pyrophosphates of manganese are reviewed. Data on metaphosphates and manganese salts of arsenic oxyacids can be found in ref. 336.

Hypophosphites

Manganese(II) Hypophosphites

Manganese(II) hypophosphite, $Mn(H_2PO_2)_2 \cdot H_2O$, can be prepared by treating manganese(II) oxalate with calcium hypophosphite or manganese(II) sulphate with barium hypophosphite[336]. Its infrared spectrum has been studied[377].

Phosphites

Manganese(II) Phosphites

The manganese(II) phosphite compound $MnHPO_3 \cdot H_2O$ is reported to be formed on addition of phosphorous acid to $MnCO_3$. The compound is not very soluble in water. It decomposes when heated but there is disagreement concerning the products of decomposition[336].

---

[373] J. Drummond and J. S. Wood, *J. Chem. Soc.* A (1970) 226.
[374] R. L. Carlin and M. J. Baker, *J. Chem. Soc.* A (1964) 5008.
[375] C. W. Frank and L. B. Rogers, *Inorg. Chem.* **5** (1966) 615.
[376] P. B. Bowman and L. B. Rogers, *J. Inorg. Nucl. Chem.* **28** (1966) 2215.
[377] L. S. Mayants and E. I. Matrosov, *Chem. Abs.* **63** (1965) 10855f.

Orthophosphates

Manganese(II) Orthophosphates

There are many orthophosphates of manganese[1, 336]. Some of these occur naturally, and crystallographic data on these minerals is summarized in Table 15. Manganese forms orthophosphates of the wagnerite type $Mn_4(PO_4)_2Y_2$ and apatite type $Mn_{10}(PO_4)_6Y_2$ ($Y = F$, Cl, Br, I, OH) [378].

TABLE 15. SOME NATURALLY OCCURRING MANGANESE PHOSPHATE MINERALS [a]

Compound	Name	Lattice type
$(Mn, Ca)_3(PO_4)_2 \cdot 2H_2O$	Fairfieldite	
$Mn_4(PO_4)_2Y_2$ [b]	Wagnerites	Monoclinic
$Mn_{10}(PO_4)_6Y_2$ [b]	Apatites	Hexagonal
$Mn_2(OH)PO_4$	Triploidite	Monoclinic
$Mn_5H_2(PO_4)_4 \cdot 4H_2O$	Hureaulite	Monoclinic
$NaMnPO_4$	Natrophilite	Orthorhombic
$Na_6Mn_{14}H_2(PO_4)_{12} \cdot H_2O$	Dickinsonite	Monoclinic
$(Na, Al, Ca, Fe)_6Mn_4(OH)_4 \cdot (PO_4)_5$	Griphite	Cubic
$Mn_8^{III}(Mn^{II}, Mg)_5(OH)_{10}(PO_4)_8 \cdot 15H_2O$	Bermanite	Orthorhombic

[a] Ref. 336.
[b] $Y = F$, Cl. Compounds with $Y = Br$, I, OH can also be synthesized[378].

Manganese(II) orthophosphate heptahydrate, $Mn_3(PO_4)_2 \cdot 7H_2O$, is formed as a white precipitate when a solution of a manganese(II) salt is treated with disodium orthophosphate[1, 336]. The compound is not very soluble in water and is decomposed by alkali. The heptahydrate is partially dehydrated over concentrated sulphuric acid to give another hydrate which is reported to be $Mn_3(PO_4)_2 \cdot 3.5H_2O$ [1]. This latter compound can be further dehydrated at 100°C to give the trihydrate $Mn_3(PO_4)_2 \cdot 3H_2O$, which occurs naturally as the mineral reddingite[1, 236]. The trihydrate is also formed by heating $MnHPO_4$ with water at 100° to 140°C or by boiling manganese(II) carbonate with orthophosphoric acid. $Mn_3(PO_4)_2 \cdot 5H_2O$ and $Mn_3(PO_4)_3 \cdot H_2O$ have also been reported. The former is obtained from the action of water on NH_4MnPO_4 and the latter by heating the trihydrate with water in a sealed tube at 250°C [1, 336]. The anhydrous salt $Mn_3(PO_4)_2$ is said to be formed by heating a hydrated salt to redness[1, 336].

Numerous iron–manganese(II) orthophosphate hydrates are known. These compounds contain octahedral manganese(II) and their structures have been classified[379].

Manganese(II) hydrogen phosphate trihydrate, $MnHPO_4 \cdot 3H_2O$, has been prepared in a number of ways[1, 336, 380, 381]. The compound exists in two forms[381]. The grey form is obtained from phosphoric acid and manganese(II) carbonate and also by hydrolysis of $Mn(H_2PO_4)_2 \cdot 2H_2O$. The pink form, which is metastable, is obtained by treating manganese(II) phosphate with phosphoric acid when the effective concentration of P_2O_5 is 0.6–28 %. The grey form dissolves only in hot concentrated hydrochloric acid while the pink

---

[378] R. Klement and H. Haselbeck, *Z. anorg. allgem. Chem.* **336** (1965) 113.
[379] P. B. Moore, *Am. Mineralogist* **50** (1965) 2052.
[380] R. Klement and H. Haselbeck, *Z. anorg. allgem. Chem.* **334** (1964) 27.
[381] M. V. Goloshchapov, B. A. Martynenko and T. N. Filatova, *Zh. Neorg. Khim.* **11** (1966) 935.

form is readily soluble in all dilute strong acids. The pink form dissolves with decomposition according to the equation

$$3MnHPO_4 = Mn_3(PO_4)_2 + H_3PO_4$$

and the decomposition is accelerated by small concentrations of nitric and sulphuric acids. A similar decomposition does not occur with the grey modification, and its solubility has been determined.

The action of $(NH_4)_2HPO_4$ on $Mn_3(PO_4)_2$ gives two phases of stoichiometry, $MnHPO_4 \cdot 1.5H_2O$ and $2MnHPO_4 \cdot (NH_4)_2 \cdot HPO_4 \cdot 2H_2O$, depending on the concentration of the solutions[382].

Manganese(II) dihydrogen phosphate dihydrate, $Mn(H_2PO_4)_2 \cdot 2H_2O$, is obtained by dissolving $Mn_3(PO_4)_2$ in phosphoric acid. The compound is deliquescent, and in moist air a manganese(II) hydrogen phosphate is formed[1, 336]. Solutions of the compound are acidic and the following salts may be prepared: $K_3H[Mn(PO_4)_2] \cdot 5H_2O$ and $Na_2H_2[Mn(PO_4)_2] \cdot 4H_2O$ [336].

Thermal decomposition of $Mn(H_2PO_4)_2 \cdot 2H_2O$ or the action of phosphoric acid on MnO or $MnCO_3$ at 400–500°C gives the tetrametaphosphate $Mn_2P_4O_{12}$ [383].

Hydrogen phosphates and dihydrogen phosphates exist in the $MnO–P_2O_5–H_2O$ system which has been studied by a number of workers[381]. The solid phases formed in this system depend markedly on the methods of preparation, and two 25°C isotherms can be obtained. The isotherm obtained from solutions of $MnCO_3$ and phosphoric acid has branches corresponding to $MnHPO_4 \cdot 3H_2O$ and $Mn(H_2PO_4)_2 \cdot 2H_2O$. The other isotherm is obtained when phosphoric acid and freshly prepared $Mn_3(PO_4)_2$ are mixed. This isotherm shows three sections corresponding to $Mn_3(PO_4)_2 \cdot 3H_2O$, $MnHPO_4 \cdot 3H_2O$ and $Mn(H_2PO_4)_2 \cdot 2H_2O$.

Manganese dihydrogen phosphate is used in phosphatizing iron and steel surfaces[221].

A number of double phosphates of manganese(II) exist of general formula $AMnPO_4$ (where A = Li, Na, K, NH_4, and 2A = Ca) [1,336]. Some of these occur naturally, and the ammonium salt $NH_4MnPO_4 \cdot H_2O$, which is precipitated in slightly alkaline solution, is used to estimate manganese gravimetrically. The precipitate is usually ignited to the pyrophosphate $Mn_2P_2O_7$ [21]. The thermal decomposition of NH_4MnPO_4 proceeds through the intermediate formation of maganese hydrogen phosphate, $MnHPO_4$ [336, 384].

Manganese(III) Phosphates

Manganese(III) orthophosphate, $MnPO_4.H_2O$, can be obtained by a number of methods[1, 336]. These include the reaction of manganese(III) acetate with phosphoric acid, the addition of a solution of manganese(II) nitrate in nitric acid to a hot solution of phosphoric acid and the reaction of manganese dioxide with phosphoric acid. In general, olive-green manganese(III) phosphate is precipitated from the purple solutions manganese(III) forms with strong aqueous phosphoric acid. $MnPO_4 \cdot H_2O$ is very stable. It slowly looses water at 300–400°C, and at red heat it looses oxygen to give manganese(II) pyrophosphate, $Mn_2P_2O_7$.

$MnPO_4 \cdot H_2O$ is insoluble in water. It is not attacked by dilute nitric or sulphuric acids, but it reacts with concentrated hydrochloric acid when heated to give chlorine gas. In concentrated sulphuric acid, $MnPO_4 \cdot H_2O$ gives a violet solution[1, 336].

---

[382] M. V. Goloshchapov, *Chem. Abs.* **64** (1966) 13458f.

[383] E. Thilo and I. Grunze, *Z. anorg. allgem. Chem.* **290** (1957) 209.

[384] J. J. Etienne, A. de Sallier Dupin and A. Boullé, *Compt. rend.* **256** (1963) 172.

$MnPO_4$ is isostructural[385] with $FePO_4$, and at 450° and 55,000 bars pressure a new form is produced[386].

$MnPO_4 \cdot H_2O$ follows a Curie–Weiss law between 93° and 350°K. The value of θ is 53° and μ_{eff} is 4.5 BM at 290°K. There is a certain amount of magnetic interaction present[195].

The violet solution obtained by dissolving $Mn(OCOCH_3)_3$ in concentrated phosphoric acid contains an acid phosphate complex of manganese(III). Transport experiments show that all the manganese is in the anion and it may be assumed, from the composition of its salts, that its formula may be written as $H_3[Mn(PO_4)_2] \cdot 3H_2O$ [19]. Only one of its hydrogens may be replaced by a cation to give salts of composition $MH_2[Mn(PO_4)_2] \cdot 3H_2O$ ($M = NH_4^+$ or Na^+) [1, 19, 336], and in view of this it seems likely that their structures are $M[Mn(HPO_4)_2(H_2O)_2] \cdot H_2O$ [19]. On dilution the complex breaks down and $MnPO_4 \cdot H_2O$ is precipitated[19]. The complexes $M[Mn(HPO_4)_2(H_2O)_2] \cdot H_2O$ probably have similar structures[19] to the corresponding diaquo-oxalato and diaquo-malonato manganese(III) complexes already mentioned.

Manganese(IV) Phosphates

It is possible that phosphate complexes of manganese(IV) have some existence in solutions of manganese dioxide or potassium permanganate in concentrated phosphoric acid [1, 336]. However, the complexes are presumably not very stable since attempts to isolate them result in the deposition of manganese(III) phosphate[1, 336].

Pyrophosphates

Manganese(II) Pyrophosphates

Manganese(II) pyrophosphate, $Mn_2P_2O_7$, is readily formed by igniting a precipitate of NH_4MnPO_4. A trihydrate, $Mn_2P_2O_7 \cdot 3H_2O$, is said to be formed if normal sodium pyrophosphate is added to a solution of manganese(II) sulphate. An enneahydrate has also been claimed, $Mn_2P_2O_2 \cdot 9H_2O$, and if this is dried at 120°C a monohydrate, $Mn_2P_2O_7 \cdot H_2O$, is formed[1, 336]. The anhydrous salt is pale pink and it is isomorphous with $Sc_2Si_2O_7$ and β-$Mg_2P_2O_7$. The compound is monoclinic and a complete structure determination shows that it contains discrete $P_2O_7^{4-}$ anions[385].

A manganese(II) dihydrogen pyrophosphate, $MnH_2P_2O_7 \cdot 4H_2O$, is formed when a solution of $Mn_2P_2O_7 \cdot 3H_2O$ is boiled with oxalic acid[1, 336].

A number of complex manganese(II) pyrophosphates are known[1, 336, 387].

Manganese(III) Pyrophosphates

Hydrated manganese(III) pyrophosphates, $Mn_4(P_2O_7)_3 \cdot H_2O$, have been prepared by a number of methods which generally involve heating MnO_2, Mn_3O_4 or $KMnO_4$ with phosphoric acid at high temperatures[1, 336]. The compounds are violet and their absorption spectra have been studied[388].

Manganese(III) forms stable complexes with pyrophosphate. The violet complex ion of manganese(III) in pyrophosphoric acid has the stoichiometry $[Mn(H_2P_2O_7)_3]^{3-}$, and this

---

[385] R. W. G. Wyckoff, *Crystal Structures*, 2nd edn., Interscience, Vol. 3 (1965).
[386] F. Dachille and R. Roy, *Z. Krist.* **111** (1959) 451.
[387] J. I. Watters and I. M. Kolthoff, *J. Am. Chem. Soc.* **70** (1948) 2455.
[388] C. Furlani and A. Ciana, *Ann. Chim.* **48** (1958) 286.

complex has been widely used for analytical purposes[300]. Thus, for example, in neutral pyrophosphate solution, manganese(II) is readily oxidized to manganese(III) by permanganate which in turn is reduced to manganese(III) [21]:

$$4Mn^{2+} + MnO_4^- + 8H^+ + 15H_2P_2O_7^{2-} = 5[Mn(H_2P_2O_7)_3]^{3-} + 4H_2O$$

The p*K* of the reaction

$$Mn(H_2P_2O_7)_3^{3-} \rightleftharpoons Mn(HP_2O_7)_2^{3-} + H_4P_2O_7$$

has been found to be 4.25 at 25°C [300].

The oxidation potential for the reaction

$$Mn^{II}(H_2P_2O_7)_2^{2-} + H_4P_2O_7 \rightleftharpoons Mn^{III}(H_2P_2O_7)_3^{3-} + 2H^+ + e^-$$

is about 1.15 V [387], and the oxidation of many organic compounds by manganese(III) pyrophosphates has been studied[263]. The oxidation of various iron(II) (*o*)-phenanthroline complexes with manganese(III) pyrophosphate complexes have also been investigated[300].

Manganese violet, a finely powdered pigment, has the formula $NH_4MnP_2O_7$, and it has been shown[389] that the compound contains the pyrophosphate group. Other possibilities, such as an equimolar mixture of ortho- and tri-polyphosphates, have been ruled out on the basis of spectroscopic and magnetic evidence. Depending on the conditions, thermal decomposition of $NH_4MnP_2O_7$ can give either manganese(II) trimetaphosphate or a mixture of manganese(II) tri- and tetra-metaphosphates[388].

$NH_4MnP_2O_7$ has a magnetic moment of 4.88 BM at 300°K and a θ value of 10° in the temperature range 93–473°K [195].

Many other examples of manganese(III) pyrophosphate complexes are known such as $NaMnP_2O_7 \cdot 5H_2O$, $KMnP_2O_7 \cdot 3H_2O$ and $NH_4MnP_2O_7 \cdot 3H_2O$ [1, 366, 388].

MANGANESE SULPHITES AND SULPHATES

In this section only sulphites and sulphates are reviewed. Data on thiosulphates, dithionates, etc., and salts of oxy-acids of selenium and tellurium can be found in ref. 336.

Sulphites

Manganese(II) Sulphites

The trihydrate $MnSO_3 \cdot 3H_2O$ is precipitated when sulphur dioxide is passed through a hot slurry of manganese(II) carbonate. It can also be obtained by the action of sodium sulphite on manganese(II) sulphate in the presence of acetic acid[336]. It forms pale red crystals which are not very soluble in water. It does, however, dissolve in a solution of sulphur dioxide. The compound is easily decomposed by acids and it is reported to be oxidized in moist air[336].

The hydrates $MnSO_3 \cdot H_2O$ and $MnSO_3 \cdot 2H_2O$ have also been reported, but easily add water to form the more stable trihydrate[336].

Thermal decomposition of manganese(II) sulphite at temperatures up to 300°C produces SO_2, MnS and $MnSO_4$. At higher temperatures (420°C) large amounts of Mn_2O_3 are formed[390].

---

[389] J. D. Lee and L. S. Browne, *J. Chem. Soc.* A (1968) 559.

[390] M. Cola and S. Tarantino, *Gazz. chim. ital.* **92** (1962) 201.

The action of sulphur dioxide on manganese dioxide produces manganese dithionate, and it was by this reaction that Gay-Lussac first discovered dithionic acid in 1819[19]. Some manganese(II) sulphate is also formed in this reaction, and it seems likely that two reactions are taking place[19]. First there is a reaction of MnO_2 with SO_2 to form $MnSO_4$, and in the second the MnO_2 is reduced to Mn_2O_3 which reacts to form $Mn_2(SO_3)_3$ which then reacts further to give $MnSO_3$ and MnS_2O_6.

A number of double sulphites, $(NH_4)_2Mn(SO_3)_2$, $Na_2Mn(SO_3)_2 \cdot H_2O$ and $K_2Mn(SO_3)_2$, are known[336]. An infrared study on the compound $(NH_4)_2Mn(SO_3)_2$ shows that the sulphur-oxygen stretching and bending frequencies are very similar to those observed in sodium sulphite itself, and it therefore seems likely that $(NH_4)_2Mn(SO_3)_2$ is not a complex but is simply a double salt[391].

Sulphates

Manganese(II) Sulphates

Manganese(II) sulphate, $MnSO_4$, is one of the most stable manganese(II) compounds known. It can be obtained by treating any compound of manganese with sulphuric acid and is readily formed by treating manganese(II) oxide or carbonate with sulphuric acid[1]. Commercially it is obtained by the action of sulphuric acid and a reducing agent on manganese dioxide[221]:

$$2MnO_2 + C(\text{coal}) + 2H_2SO_4 = 2MnSO_4 \cdot H_2O + CO_2$$

It is also obtained as a byproduct in the manufacture of hydroquinone since in one of the steps manganese dioxide is usually used as the oxidizing agent to convert aniline to quinone[221]:

$$2C_6H_5NH_2 + 4MnO_2 + 5H_2SO_4 \rightarrow 2(O = C_6H_4 = O) + 4MnSO_4 + (NH_4)_2SO_4 + 4H_2O$$

Other processes include the action of sulphur dioxide on a slurry of manganese dioxide in sulphuric acid followed by decomposition by steam of the resulting manganese(II) dithionate, MnS_2O_6, to $MnSO_4$, and the roasting of a mixture of pyrolusite ore, ferrous sulphate and coal followed by leaching and crystallization.

Manganese(II) sulphate can crystallize with 7, 5, 4, 2, 1 and 0 molecules of H_2O, and phase diagrams for the $MnSO_4$–H_2O systems are known[336]. Thermal transitions and dehydrations of the hydrates have also been studied[392].

The heptahydrate $MnSO_4 \cdot 7H_2O$, which occurs naturally as the mineral mallardite, can be obtained by crystallizing a solution containing 70 parts of $MnSO_4$ to 100 parts of water between $-10°$ to $+9°C$ [336]. The crystals are monoclinic, but a metastable orthorhombic form can be obtained if the crystallizing solution is seeded with a crystal of $MgSO_4 \cdot 7H_2O$. Mixed crystals of $MnSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 7H_2O$ also have an orthorhombic unit cell[336]. The heat of formation of $MnSO_4 \cdot 7H_2O$ is -750 kcal mole^{-1} [336].

The pentahydrate, $MnSO_4 \cdot 5H_2O$, can be obtained by crystallizing an aqueous saturated solution of manganese(II) sulphate between 9–24°C [336]. The crystals are triclinic and are isomorphous with $CuSO_4 \cdot 5H_2O$, and this suggests that the coordination around the manganese(II) could contain four water molecules in a plane as is observed in $CuSO_4 \cdot 5H_2O$. Magnetic data on $MnSO_4 \cdot 5H_2O$ is available[336].

[391] G. Newman and D. B. Powell, *Spectrochim. Acta* **19** (1963) 213.

[392] H. Chihara and S. Seki, *Bull. Chem. Soc. Japan* **26** (1953) 88.

The tetrahydrate, $MnSO_4 \cdot 4H_2O$, is obtained by crystallizing a concentrated solution of manganese(II) sulphate after the addition of ethanol at 95°C [336]. Below 27.5°C it has no existence[393]. It has been claimed that the tetrahydrate crystallizes in orthorhombic and monoclinic forms, but it seems likely, although not certain, that there is only a monoclinic variety[336]. $MnSO_4 \cdot 4H_2O$ effloresces in air and looses water rapidly at 60°C to give the monohydrate $MnSO_4 \cdot H_2O$. The standard heat of formation[336] of $MnSO_4 \cdot H_2O$ is -539.3 kcal $mole^{-1}$ and magnetic data has been reported[336].

The dihydrate $MnSO_4 \cdot 2H_2O$ is not very stable. One of the best methods of preparation is probably to shake a saturated solution of the heptahydrate for 150 hr at 36°C. Little data appears to be available for this compound.

The monohydrate $MnSO_4 \cdot H_2O$, which occurs naturally as the mineral szmikite[1], can be obtained by dehydrating the heptahydrate above 100°C. $MnSO_4 \cdot H_2O$ is monoclinic and has the same structure as kieserite, $MgSO_4 \cdot H_2O$. The infrared and ^1H n.m.r. spectra of $MnSO_4 \cdot H_2O$ have also been recorded, and this, together with the structural data, indicate that the suggested structures, MnH_2SO_5 or $Mn(OH)SO_4H$, are wrong[394]. The values of $\triangle H_f^\circ$ and $\triangle G_f^\circ$ for $MnSO \cdot H_2O_4$ are -392.2 and -289.9 kcal $mole^{-1}$ respectively[95]. Magnetic data is available[336].

Anhydrous manganese(II) sulphate, $MnSO_4$, can readily be obtained by heating a hydrated salt above 200°C. The sulphate is remarkably stable and can be heated at a red heat without decomposition. At these temperatures, iron(II), cobalt(II) and nickel(II) sulphates are decomposed[16]. $MnSO_4$ has an orthorhombic unit cell. The sulphur atoms are at the centre of slightly distorted tetrahedra, and the manganese(II) ions are at the centre of a tetragonally distorted octahedra with four Mn–O bond lengths of 2.25 Å and two Mn–O bond lengths of 2.11 Å [395]. At high temperatures and pressures other phases of $MnSO_4$ are formed[396, 397].

The magnetic structure of $MnSO_4$ has been determined from a powder neutron diffraction study. It consists of a cycloidal spiral arrangement related to the simple $CrVO_4$ type of magnetic structure[398]. In the temperature range 77–600°K, μ_{eff} is 5.7 BM [195]. The values of $\triangle H_f^\circ$, $\triangle G_f^\circ$ and S° are -254.9 kcal $mole^{-1}$, -229.1 kcal $mole^{-1}$ and 26.8 cal deg^{-1} $mole^{-1}$ respectively[95].

Manganese(II) sulphate forms a number of adducts[1, 336] with ammonia of the type $MnSO_4 \cdot nNH_3$, where $n = 1, 2, 3, 4, 5$ and 6. The differential thermal analysis of $MnSO_4 \cdot 4NH_3$ shows two peaks corresponding to the formation of the mono-adduct and anhydrous salt[399].

Manganese(II) sulphate forms adducts with hydrazine[1], urea[400] and other bases[1]. Both basic, $2MnSO_4 \cdot Mn(OH)_2$, and acidic, $MnSO_4 \cdot H_2SO_4$, $MnSO_4 \cdot 3H_2SO_4$ and $MnSO_4 \cdot H_2SO_4 \cdot H_2O$, salts have been reported[336].

Manganese(II) sulphate forms a number of double sulphates with the sulphates of sodium, potassium, rubidium, caesium, ammonium, thallium(I), aluminium(III), iron(III),

---

[393] J. Myl and D. Koubova, *Chem. Abs.* **64** (1966) 4571f.

[394] H. R. Oswald, *Helv. Chim. Acta* **48** (1965) 590, 600.

[395] D. E. Cox, B. C. Frazer and G Will, *Acta Cryst.* **19** (1965) 854.

[396] C. W. F. T. Pistorius, *Z. Krist.* **116** (1961) 222.

[397] T. R. Ingraham and P. Marier, *Can. Met. Quart.* **4** (1965) 169.

[398] P. J. Brown, D. E. Cox, B. C. Frazer, G. Shirane and G. Will, *Phys. Rev.* **140** (1965) A2139.

[399] W. W. Wendlandt and J. P. Smith, *Nature* **201** (1964) 73.

[400] I. G. Druzhinin and N. Duishenalieva, *Chem. Abs.* **65** (1966) 6425c; **59** (1963) 1264f.

and chromium(III) [1,336]. X-ray structural data is available for some of these compounds, e.g. $K_2Mn(SO_4)_2 \cdot 4H_2O$ [401] and $M_2Mn_2(SO_4)_3$, where M = K, NH_4, Rb or Tl [402,403].

The acid sulphate $MnSO_4 \cdot 2K_2SO_4 \cdot H_2SO_4 \cdot H_2O$ forms orthorhombic crystals, and the ultraviolet absorption spectrum has been studied[404].

Manganese(III) Sulphates

Manganese(III) sulphate, $Mn_2(SO_4)_3$, is prepared by the reaction of concentrated sulphuric acid (density 1.84) with potassium permanganate under carefully controlled conditions[13]. Since Mn_2O_7 is formed in this reaction, care must be taken in its preparation. $Mn_2(SO_4)_3$ crystallizes as dark green needles, which are extremely hygroscopic, and begin to decompose at 300°C. It is soluble in concentrated sulphuric acid without reaction, but in 70% sulphuric acid a brown salt crystallizes out of composition $Mn_2(SO_4)_3 \cdot H_2SO_4 \cdot 6H_2O$ [13]. If the concentration of the sulphuric acid is less than 52%, hydrolysis occurs[13]. The equilibrium constant K_s for the reaction

$$2Mn^{3+} + 2H_2O = MnO_2 + Mn^{2+} + 4H^+$$

has been determined. In the acid range 2.40–7.44 M H_2SO_4 and with a concentration of Mn^{2+} equal to 0.138–0.364 M at 15°C, $K_s = 1.8 \times 10^6\ M^3$. The equilibrium is slow from left to right but is fast from right to left using freshly prepared manganese dioxide[300].

The reaction

$$4Mn^{II} + Mn^{VII} = 5Mn^{III}$$

is too slow in sulphuric acid for analytical application[300]. The equilibrium constants for the reaction

$$2Mn^{III} = Mn^{IV} + Mn^{II}$$

decreases from 4.8×10^{-2} to 2.0×10^{-3} on going from 4.5 to 12 M H_2SO_4 [300].

Manganese(III) sulphate is an oxidizing agent and its action on a number of organic compounds, e.g. formaldehyde, formic acid, malonic acid and xylenes, have been investigated[405,406].

A number of alums of manganese(III) are known. One of the best known compounds is caesium manganese alum, $CsMn(SO_4)_2 \cdot 12H_2O$. It is readily prepared by mixing solutions of $Mn(OCOCH_3)_3 \cdot 2H_2O$ and Cs_2SO_4 in concentrated sulphuric acid[13]. The compound is a coral red crystalline powder which melts at 40°C in its water of hydration. However, just above room temperature it becomes a brown–black colour. On addition of water, hydrated manganese(III) oxide is precipitated[13].

The crystal spectrum of $CsMn(SO_4)_2 \cdot 12H_2O$ has been determined and analysed[57,119], and in this compound the manganese(III) ion is surrounded by a nearly regular octahedron of water molecules[57]. Its magnetic moment is 4.81 BM at 290°K [195].

The rubidium, potassium and sodium manganese alums are also known, but they become increasingly unstable and are prepared at low temperatures[19]. The rubidium alum

---

[401] W. Schneider, *Acta Cryst.* **14** (1961) 784.

[402] K. Kohler and W. Franke, *Acta Cryst.* **17** (1964) 1088.

[403] G. Gattow and J. Zemann, *Z. anorg. allgem. Chem.* **293** (1958) 233.

[404] A. Le Paillier-Malecot, *Compt. rend.* **261** (1965) 943.

[405] T. J. Kemp and W. A. Waters, *J. Chem. Soc.* (1964) 339, 1489.

[406] R. Ramaswamy, M. S. Venkatachalapathy and H. V. K. Udupa, *J. Electrochem. Soc.* **110** (1963) 202.

melts at room temperature[13]. These alums, especially the ammonium and rubidium salts, can be dehydrated easily to give anhydrous double salts $MMn(SO_4)_2$ [19]. Double salts of manganese(III) and aluminium(III) sulphates are also known[336].

Manganese(IV) Sulphates

Although there is no definite evidence of solid complexes of manganese(IV) sulphates[336], it does seem likely that manganese(IV) has some existence in concentrated sulphuric acid and that electrolytic oxidation of manganese in concentrated sulphuric acid gives manganese(IV) compounds[407].

MANGANESE HALITES, HALATES AND PERHALATES

Manganese(II) Chlorite

Manganese(II) chlorite has been prepared by passing ClO_2 into a suspension of manganese(II) carbonate containing a stoichiometric amount of hydrogen peroxide[408, 409].

Manganese(II) Chlorate

Manganese(II) chlorate has been prepared by the reaction of manganese(II) sulphate with barium chlorate. Aqueous solutions of the salt are relatively stable but the salt, $Mn(ClO_3)_2 \cdot 6H_2O$, decomposes explosively to give manganese dioxide and chlorine dioxide[336]:

$$Mn(ClO_3)_2 \cdot 6H_2O = MnO_2 + 2ClO_2 + 6H_2O$$

Manganese(II) Perchlorate

Aqueous solutions of manganese(II) perchlorate can be prepared either by the reaction of barium perchlorate with manganese(II) sulphate or from perchloric acid and manganese(II) carbonate[336]. Rose-coloured prisms of the hexahydrate $Mn(ClO_4)_2 \cdot 6H_2O$ can be crystallized from solution. $Mn(ClO_4)_2 \cdot 6H_2O$ loses two molecules of water at 115°C to give the tetrahydrate $Mn(ClO_4)_2 \cdot 4H_2O$ [336]. At 150°C manganese dioxide begins to form and at 195°C it explodes[19]. Both hydrates are deliquescent and are very soluble in water[19]. Anhydrous $Mn(ClO_4)_2$ can be prepared by the reaction of silver perchlorate with a manganese(II) halide in anhydrous ether[410].

A ^{35}Cl n.m.r. study of manganese(II) perchlorate in perchloric acid shows that there is a detectable broadening of the resonance line and this has been used as evidence for the presence of a weak inner-sphere complex between Mn^{2+} and ClO_4^- in these solutions[411].

A number of adducts of manganese(II) perchlorate of the type $MnL_4(ClO_4)_2$, where L is an oxygen or nitrogen donor ligand, are known, and in some of these complexes there is evidence of bonding between the manganese and one or both of the perchlorate groups. Thus the complex $Mn(Ph_2MeAsO)_4$–$(ClO_4)_2$ contains 5-coordinate manganese(II) in which the fifth position of the square-based pyramid arrangement is occupied by a perchlorate group[412]. There is also evidence that the complexes $MnL_4(ClO_4)_2$, where L = pyridine or γ-picoline,

---

[407] N. I. Kharabadze, *Chem. Abs.* **62** (1965) 4906f; 3664d.

[408] C. Bertoglio, *Ann. chim.* (*Rome*) **43** (1953) 564.

[409] G. R. Levi and R. Curti, *Ricerca Sci.* **23** (1953) 1798.

[410] G. Monnier, *Ann. chim.* (*Paris*) **2** (1957) 14.

[411] F. Klanberg, J. P. Hunt and H. W. Dodgen, *Inorg. Chem.* **2** (1963) 139.

[412] J. Lewis, R. S. Nyholm and G. A. Ridley, *Nature* **207** (1965) 72.

contain complexed perchlorate, but it is not clear whether both perchlorates are coordinated or whether one is ionic and one acts as a bidentate ligand[413]. It is possible in the quinoline complexes $MnQ_2(ClO_4)_2$ that both perchlorate groups are bidentate[413]. In the complex $Mn(MeCN)_4(ClO_4)_2$ it is possible that the manganese is octahedrally coordinated with two *trans*-unidentate perchlorate groups[414]. Ionic perchlorate anions only are probably present in the complexes $[Mn(NH_3)_6](ClO_4)_2$ [336], $[Mn(NH_5)_5H_2O](ClO_4)_2$ [336], $Mn(Me_3NO)_4(ClO_4)_2$ [417] and $[Mn(diacetamide)_3](ClO_4)_2$ [416].

Manganese(III) Perchlorate

The manganese(III) ion can be generated in perchlorate media by electrolytic oxidation under nitrogen[300, 417]. A spectrophotometric study indicates that both the hexa-aquo-ion and hydroxy-penta-aquo-ion are present in the solutions[417].

Manganese(II) Bromate

A solution of manganese(II) bromate, $Mn(BrO_3)_2$, can be prepared by treating manganese(II) carbonate with bromic acid. The solution is not very stable[336].

Manganese(II) Iodate

Manganese(II) iodate, $Mn(IO_3)_2$, is not very soluble in water, and it is precipitated on mixing solutions of iodic acid and manganese(II) chloride[418]. The infrared spectrum of the compound has been recorded but not interpreted, and it is not clear whether ionic iodate anions are present[419]. The standard heat and free energy of formation of $Mn(IO_3)_2$ are -161.3 and -124.9 kcal $mole^{-1}$ respectively[95].

Manganese(III) Iodates

Manganese(III) iodate, $Mn(IO_3)_3$, is reported to be formed as a grey–lilac to brown–violet powder on dissolving freshly precipitated manganese dioxide in iodic acid in the presence of manganese(II) iodate[336]. The complexes $M_2Mn(IO_3)_5$ ($M = K$, Rb, Cs or NH_4) are also said to be formed by the action of the appropriate iodate on the manganese(III) compound $Mn(OCOCH_3)_3 \cdot 2H_2O.HIO_3$ [420, 421]. Kinetic studies[421] of the disproportionation reaction of manganese(III) in various aqueous iodate systems show that the equilibrium

$$Mn(IV) + Mn(II) \rightleftharpoons 2Mn(III)$$

is rapidly established.

Manganese(IV) Iodates

Solutions of manganese(IV) iodate are best prepared by dissolving freshly prepared manganese dioxide in iodic acid followed by careful oxidation of the manganese(III) formed with periodic acid[421]. These solutions invariably contain small amounts of manganese(III). Solutions of manganese(IV) periodate are amber or brown but over a period of days in the

---

[413] D. H. Brown, R. H. Nuttall and D. W. A. Sharp, *J. Chem. Soc.* A (1966) 892.
[414] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.* (1961) 3091.
[415] R. S. Drago, J. T. Donoghue and D. W. Herlocker, *Inorg. Chem.* **4** (1965) 836.
[416] C. S. Kraihanzel and S. C. Grenda, *Inorg. Chem.* **4** (1965) 1037.
[417] C. F. Wells and G. Davies, *J. Chem. Soc.* A (1967) 1858.
[418] A. M. Hayes and D. S. Martin, Jr., *J. Am. Chem. Soc.* **73** (1951) 4853.
[419] C. Rocchiccoilo, *Compt. rend.* **250** (1960) 1232.
[420] F. Olsson, *Arkiv Kemi Mineral. Geol.* **9** (1929) 5.
[421] G. R. Waterbury and D. S. Martin, Jr., *J. Am. Chem. Soc.* **75** (1953) 4162.

presence of air they become violet due to the formation of manganese(III). The solutions are stable in sealed quartz vessels, but in glass a red precipitate of the complex $K_2Mn(IO_3)_6$ is formed. Complexes of this type have also been prepared by the action of iodic acid and alkali iodate on manganese dioxide suspended in water[420]. The complexes are always contaminated with manganese dioxide and the recorded magnetic moment of the potassium salt has been corrected for this impurity[351].

Manganese Periodates

Manganese(II) is oxidized by periodate at room temperature and this reaction

$$2Mn^{2+}+5IO_4^-+3H_2O = 2MnO_4^-+5IO_3^-+6H^+$$

is used in the colorimetric determination of manganese[21,422]. The kinetics of this reaction, which is autocatalytic, have been determined and a mechanism has been proposed[422].

Complex periodates of manganese(IV) have been prepared by reacting sodium (or potassium) hypochlorite and periodate with a solution of manganese(II) chloride[423,424]. The products have the stoichiometry $Na_7H_4Mn(IO_6)_3\cdot 17H_2O$ and $K_7H_4Mn(IO_6)_3\cdot 8H_2O$, and their redox behaviour and magnetic moments indicate that they are complexes of manganese(IV). In solution the complexes slowly decompose to permanganate and iodate, and the kinetics of the decomposition of the sodium salt have been measured[423,424,425].

The visible and ultraviolet spectra of the complexes have been studied[426]. An X-ray structure analysis of the complex $Na_7H_4Mn(IO_6)_3\cdot 17H_2O$ shows that the manganese(IV) atom is at the centre of a regular octahedron formed by three bidentate periodate octahedra[427].

The complexes originally formulated as $Na_2Mn_2I_2O_{11}$ and $K_2Mn_2I_2O_{11}$ have been shown to be the manganese(IV) periodate complexes $NaMnIO_6\cdot \frac{1}{2}H_2O$ and $KMnIO_6\cdot \frac{1}{2}H_2O$ respectively[428].

MANGANESE CARBONYL

Only one binary metal carbonyl of manganese is known, namely decarbonyldimanganese, $Mn_2(CO)_{10}$, and reviews on the compound can be found in refs. 429 and 430. Manganese carbonyl, $Mn_2(CO)_{10}$, was first prepared in 1949 by reducing manganese(II) iodide with a Grignard reagent under a pressure of carbon monoxide. Later, in 1954, a 1% yield of the compound was obtained by treating manganese(II) iodide with magnesium metal again in the presence of a pressure of carbon monoxide[429]. Since that time greatly improved methods of preparation have been devised, and metallic sodium, sodium hydride and lithium aluminium hydride have been employed as reducing agents in place of a Grignard reagent. Radical anions such as benzophenone ketyl, Ph_2CONa, or sodium naphthalenide can also be used, but the best yields (as high as 54%) have been obtained using aluminium alkyls, diethylzinc,

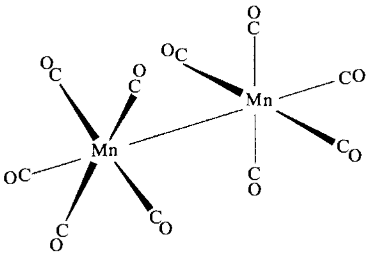
---

[422] G. R. Waterbury, A. M. Hayes and D. S. Martin, Jr., *J. Am. Chem. Soc.* **74** (1952) 15.
[423] M. W. Lister and Y. Yoshino, *Can. J. Chem.* **38** (1960) 1291.
[424] M. W. Lister, *Can. J. Chem.* **39** (1961) 2330.
[425] Y. Yoshino, T. Takeuchi and H. Kinoshita, *Chem. Abs.* **64** (1966) 10738g.
[426] R. Pappalardo and S. Losi, *Ann. chim. (Rome)* **54** (1964) 156.
[427] A. Linek, *Czech. J. Phys.* **13** (1963) 398.
[428] I. Reimer and M. W. Lister, *Can. J. Chem.* **39** (1961) 2431.
[429] K. N. Anisimor, A. A. Ioganson and N. E. Kolobova, *Uspekhi Khim.* **37** (1968) 380.

or aluminium activated by an alkyl aluminium compound[429, 430]. All these methods have the disadvantage that high-pressure equipment is necessary. However, a very easy low-pressure synthesis has been devised using the commercially available compound methylcyclopentadienyl manganese tricarbonyl (π-MeC_5H_4)$Mn(CO)_3$ [431]. In this reaction methylcyclopentadienyl manganese tricarbonyl is treated with sodium in refluxing diglyme (dimethyl ether of diethylene glycol) in an atmosphere of carbon monoxide.

Manganese carbonyl forms golden yellow crystals which melt at 154–155°C. It sublimes readily in a vacuum, the heat of sublimation being 15 kcal mole^{-1} [429]. The compound is stable in air at room temperature for several months, but when heated in air above 110°C it decomposes to give carbon monoxide and a metallic mirror of manganese. In the presence of carbon monoxide gas it is stable to 250°C. The thermal decomposition of $Mn_2(CO)_{10}$ in high vacuum at 260–500°C has been investigated but no polynuclear manganese carbonyls were detected[432]. The standard heat of formation of crystalline $Mn_2(CO)_{10}$ is -400.9 kcal mole^{-1} [95]. For the gaseous compound the value is -385.9 kcal mole^{-1} [95].

Manganese carbonyl is soluble to a certain extent in most organic solvents but it is insoluble in water. Solutions in the presence of air decompose at room temperature[429, 430]. An X-ray crystal structure determination on the compound shows that it consists of two square pyramidal $Mn(CO)_5$ units joined solely by a metal–metal bond (Fig. 2)[433].



Manganese carbonyl

FIG. 2.

The two $Mn(CO)_5$ units are in a staggered conformation presumably to relieve intramolecular repulsions. The Mn–Mn bond length in $Mn_2(CO)_{10}$ is 2.93 Å, and although this was considered to be a long bond[433] it has been argued that this is a value not significantly greater than would be expected[434]. Thus the Mn(I)–Mn(I) bond length has been calculated to be 2.76 Å, and since it appears from other organometallic molecules that on changing the oxidation state of the metal by one unit there is a change in metal radius of about 0.05 Å, the Mn(0)–Mn(0) bond length would be expected to be around 2.86 Å. Other workers are essentially in agreement with this value and have suggested a covalent manganese radius of 1.39–1.43 Å [435].

---

[430] F. Calderazzo, R. Ercoli and G. Natta, *Organic Synthesis via Metal Carbonyls* (edited by I. Wender and P. Pino), Interscience, Vol. 1 (1968).

[431] R. B. King, T. F. Korenowski and J. C. Stokes, *J. Organomet. Chem.* **11** (1968) 641.

[432] H. Lux and A. Ignatowicz, *Chem. Ber.* **101** (1968) 2995.

[433] L. F. Dahl, E. Ishishi and R. E. Rundle, *J. Chem. Phys.* **26** (1957) 1750; L. F. Dahl and R. E. Rundle, *Acta Cryst.* **16** (1963) 419.

[434] M. J. Bennett and R. Mason, *Nature* **205** (1965) 760.

[435] F. A. Cotton and D. C. Richardson, *Inorg. Chem.* **5** (1966) 1851.

The Mn–Mn bond strength of $Mn_2(CO)_{10}$ is in reasonable agreement with these ideas that the bond is normal and not exceptionally long. The bond strength was first estimated[436] to be 34 ± 13 kcal $mole^{-1}$, and recent kinetic studies on the reaction of $Mn_2(CO)_{10}$ with triphenylphosphine and iodine gives an Arrhenius activation energy of 37 ± 0.27 kcal $mole^{-1}$ for the homolytic fusion of the Mn–Mn bond[437]. Differences in the appearance potential of $Mn_2(CO)_{10}$ at a low and high temperature have given a value of 18.9 ± 1.4 kcal $mole^{-1}$ for the energy required to form two $Mn(CO)_5$ radicals. This lower value has been reconciled with the previous values on the basis that the geometry of the $Mn(CO)_5$ radicals produced thermally in the mass spectrometer will be different to those produced in the kinetic studies[437].

A second feature of the structure of $Mn_2(CO)_{10}$ concerns the fact that the four equatorial carbonyl groups in each $Mn(CO)_5$ unit are bent towards each other. It has been suggested that this angular distortion of the carbonyl groups from square pyramidal symmetry leads to an increase in the amount of p and d character in the Mn–Mn bond. This has the effect of lengthening the metal–metal bond and reducing repulsions between the non-bonding d_{xz} and d_{yz} orbitals since these orbitals will now contain more p character. These two effects will then minimize the repulsions between non-bonded carbonyl groups [434]. However, it should be noted that steric effects could also play a part in these angular distortions since as the Mn–Mn bond is long repulsions between the axial carbonyl and four equatorial carbonyl groups in each $Mn(CO)_5$ unit could become important. It is noteworthy that similar distortions are observed in all the metal–$Mn(CO)_5$ compounds, e.g. $R_3SnMn(CO)_5$ and $Ph_3PAuMn(CO)_5$, so far examined (see Table 16, p. 848).

The overall symmetry of manganese carbonyl is D_{4d} which is in agreement with the vibrational spectra of the compound[248]. The infrared spectrum is characterized by strong bonds at 2044, 2013 and 1983 cm^{-1}.

The ^{55}Mn and ^{17}O n.m.r. spectra of $Mn_2(CO)_{10}$ have been recorded[18, 438].

The mass spectrum of $Mn_2(CO)_{10}$ is given in ref. 439.

SUBSTITUTION REACTIONS OF MANGANESE CARBONYL

The carbonyl groups in $Mn_2(CO)_{10}$ can be substituted by a wide variety of ligands and reviews on Group V donors (N, P, As, Sb) and Group VI donors (S, Se, Te) are available[430, 440, 441, 442]. In general either one or two carbonyl ligands only are replaced to give compounds of the type $Mn_2(CO)_9L$ or $Mn_2(CO)_8L_2$ [440, 441]. With certain more basic nitrogen donor ligands, however, the Mn–Mn bond is cleaved to give ionic compounds, e.g. $[MnL_6][Mn(CO)_5]_2$. Presumably with the more basic nitrogen donor ligand an intermediate complex is formed which causes polarization of the Mn–Mn bond[440], e.g.

$$(CO)_5\overset{\delta-}{Mn}\text{—}\overset{\delta+}{Mn}(CO)_4L$$

---

[436] F. A. Cotton and R. R. Monchamp, *J. Chem. Soc.* (1960) 533.

[437] L. I. B. Haines, D. Hopgood and A. J. Poe, *J. Chem. Soc.* A (1968) 421.

[438] R. Bramley, B. N. Figgis and R. S. Nyholm, *Trans. Faraday Soc.* **58** (1962) 1893.

[439] B. F. G. Johnson and J. Lewis, *Acc. Chem. Res.* **1** (1968) 245.

[440] M. C. Baird, *Progress in Inorganic Chemistry* (edited by F. A. Cotton), Interscience, Vol. 9 (1968), p. 1.

[441] T. A. Manuel, *Advances in Organometallic Chemistry* (edited by F. G. A. Stone), Academic Press, New York, Vol. 3 (1965), p. 181.

[442] E. W. Abel and B. C. Crosse, *Organomet. Chem. Revs.* **2** (1967) 443.

Hence fission of the bond then becomes more likely especially in the presence of a polar solvent. Infrared evidence does in fact suggest that an intermediate salt, $[Mn(CO)_5(C_4H_9NH_2)][Mn(CO)_5]$, is formed in the course of reaction of n-$BuNH_2$ and $Mn_2(CO)_{10}$ [430].

Heterolytic fission of the Mn–Mn bond has not been observed to occur with the less basic phosphorus and arsenic ligands and generally simple substitution occurs to leave the Mn–Mn bond intact. However, with certain phosphines and arsines it appears that the Mn–Mn bond can be cleaved homolytically to give paramagnetic monomers, $Mn(CO)_4L$ [440].

The compounds $[Mn(CO)_4L]_2$ can assume either *cis*- or *trans*-configurations. Generally the compounds have D_{4d} or D_{4h} symmetry, i.e. they have *trans*-structures, but in certain cases, e.g. $[Mn(CO)_4NCR]_2$, the compounds assume *cis*-configurations. These differences have been ascribed to both electronic and steric effects [440].

Studies of carbon monoxide exchange on $Mn_2(CO)_{10}$ have suggested that unimolecular dissociation of a coordinated carbon monoxide molecule was the rate-determining step[443], but recent work has cast doubt on this simple interpretation[444].

Kinetic data on the substitution reactions of manganese carbonyl and its derivatives are reviewed in ref. 445.

Nitrogen Donor Ligands

The reactions of nitrogen bases with $Mn_2(CO)_{10}$ can give either a simple substitution product which still contains a Mn–Mn bond or can result in metal–metal bond cleavage to give a salt containing a complex Mn(I) or Mn(II) cation and the carbonylate anion $Mn(CO)_5^{1-}$ [440, 441].

The reaction of pyridine and nitriles with $Mn_2(CO)_{10}$ in an inert solvent in the presence of ultraviolet light gives the complexes $Mn_2(CO)_9py$ and $Mn_2(CO)_9(NCR)$, where R = Me, Et, Ph, and vinyl respectively. These compounds could obviously have two structures depending on whether an axial or equatorial carbonyl group is displaced. The infrared evidence, however, suggests that in each case equatorial substitution occurs[440]. The orange–red $Mn_2(CO)_9NH_3$ has been obtained by treating $Mn(CO)_5^-$ with hydroxylamine-*O*-sulphonic acid (NH_2OSO_2H) in aqueous alkali. The compound decomposes at 30°C and is less stable than $Mn_2(CO)_9py$. The reactions of α,α'-dipyridyl in an inert solvent and (*o*)-phenanthroline in pyridine with $Mn_2(CO)_{10}$ gives the dark red diamagnetic compounds $Mn_2(CO)_8(dipy)$ and $Mn_2(CO)_8[(o)\text{-phen}]$ respectively. Under irradiation with visible light, solutions of these complexes react further to give dark precipitates of the complexes $[Mn(CO)_3dipy]_2$, $[Mn(CO)_3\{(o)\text{-phen}\}]_2$, and $Mn_2(CO)_{10}$ [440].

The reactions of ammonia and the nitrogen ligands, L, where L is pyridine, γ-picoline, diethanolamine, morpholine, diethylenetriamine or piperidine with $Mn_2(CO)_{10}$, result in Mn–Mn bond cleavage [440].

$$Mn_2(CO)_{10}+3NH_3 = [Mn(CO)_3(NH_3)_3][Mn(CO)_5]+2CO$$

$$Mn_2(CO)_{10}+12L = 2[MnL_6][Mn(CO)_5]_2+10CO$$

---

[443] F. Basolo and R. G. Pearson, *Advances in Inorganic and Radiochemistry* (edited by H. J. Emeléus and A. G. Sharpe), Academic Press, Vol. 1 (1961), p. 1.

[444] L. R. Kangas, R. F. Heck, P. M. Henry, S. Breitschaft, E. M. Thorsteinson and F. Basolo, *J. Am. Chem. Soc.* **88** (1966) 2334.

[445] R. J. Angelici, *Organomet. Chem. Revs.*, Section A, **3** (1968) 173.

Phosphorus, Arsenic and Antimony Donor Ligands

The reactions of tertiary phosphorus, arsenic or antimony donor ligands usually result in either monosubstituted compounds $Mn_2(CO)_9L$, where L = PPh_3, PBu_3, $P(OPh)_3$ and $AsPh_3$, or disubstituted compounds $Mn_2(CO)_8L_2$, where L = PF_3, PCl_3, PEt_3, PBu_3, PPh_3, $P(OPh)_3$, P(cyclohexyl)$_3$, $AsPh_3$, and L_2 = $Ph_2PCH_2CH_2PPh_2$ [440]. Under vigorous conditions $AsPh_3$ reacts with $Mn_2(CO)_{10}$ to produce a dimeric arsenic-bridged compound $[MnAsPh_2(CO)_4]_2$ [441]. Reactions of diphosphines and arsines with $Mn_2(CO)_{10}$ give similar bridged compounds[429, 441]. The reaction of $Ph_2PCH_2CH_2PPh_2$ (L–L) has been reported to give the complexes $Mn(CO)_3$(L–L), Mn(CO)(L–L)$_2$, $[Mn(CO)_2(L\text{–}L)_2]^+[Mn(CO)_5]^-$ or $Mn_2(CO)_8(L\text{–}L)_2$ depending on the reaction conditions. There is some confusion in the literature as to whether the compounds $Mn_2(CO)_8L_2$ can exist as paramagnetic monomers $Mn(CO)_4L$. The initial reports of the preparation of the monomeric and paramagnetic compound $Mn(CO)_4PPh_3$ have not been substantiated, and it is now known that this compound is dimeric and diamagnetic both in solution and the solid state[440]. However, it does appear that the compounds $Mn(CO)_4L$, where L is $(p\text{-}FC_6H_4)_3P$, and $AsPh_3$ and $Mn(CO)_3L_2$, where L_2 is *o*-phenylenebisdimethylarsine or ethylene-1,2-bisdiphenylphosphine can exist as genuine paramagnetic monomers[429, 440]. It would be particularly interesting to study the e.s.r. spectra of these compounds since this would not only clearly show whether the compounds are paramagnetic but it could also give detailed knowledge of the structure and bonding in these molecules.

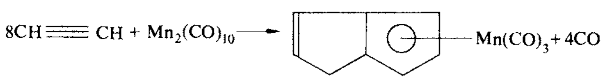
The infrared spectra of many of the compounds $Mn_2(CO)_8L_2$ have been studied and have been found to be consistent with axial substitution with either D_{4d} or D_{4h} symmetry. X-ray structural studies on the compounds $Mn_2(CO)_8(PF_3)_2$ and $Mn_2(CO)_8(PEt_3)_2$ have confirmed that axial substitution occurs in these compounds[440]. The Mn–Mn bond length in the former is 2.92 Å [440] and 2.91 Å in the latter[446].

The reaction of PF_3 with $Mn_2(CO)_{10}$ has yielded the compounds $Mn_2(CO)_9PF_3$, $Mn_2(CO)_8(PF_3)_2$ and $Mn_2(CO)_7(PF_3)_3$ [447]. These compounds are stable in air but react rapidly with alcohols yielding solvolysis products of such as $Mn_2(CO)_9P(OMe)_3$.

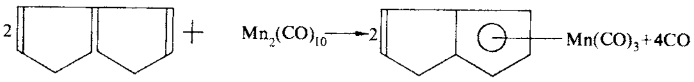
Reactions with Olefins and Acetylenes

Butadiene reacts with $Mn_2(CO)_{10}$ to give a low yield of the chelate complex $Mn_2(CO)_8C_4H_6$. The infrared spectrum of this complex suggests that it has an asymmetric structure[440].

Acetylene undergoes a very interesting reaction with $Mn_2(CO)_{10}$ to give π-dihydropentalenyl manganese tricarbonyl:



This reaction takes place at 150°C and 40–45 atm of acetylene gas and the same product can be obtained using $(\pi\text{-}CH_3C_5H_4)Mn(CO)_3$ in place of $Mn_2(CO)_{10}$ [429]. It can also be obtained directly from dihydropentalene and $Mn_2(CO)_{10}$ [429].



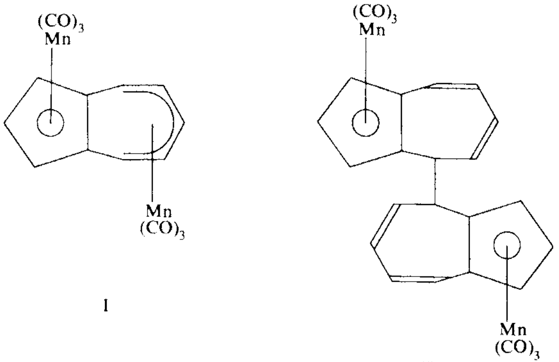
---

[446] M. J. Bennett and R. Mason, *J. Chem. Soc.* A (1968) 75.

[447] R. J. Clark, J. P. Hargaden, H. Haas and R. K. Sheline, *Inorg. Chem.* 7 (1968) 673.

Similar complexes have been obtained from the reactions of azulene and indene with $Mn_2(CO)_{10}$ [429].

The reaction of azulene with $Mn_2(CO)_{10}$ has been reported to yield the products *trans*-$C_{10}H_8Mn_2(CO)_6$ (I) and $[C_{10}H_8Mn(CO)_3]_2$ (II). The former has been the subject of an X-ray structural determination[448], and the structure of the compound is shown in Fig. 3.



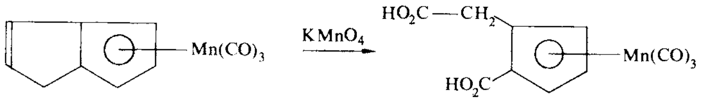
I

II

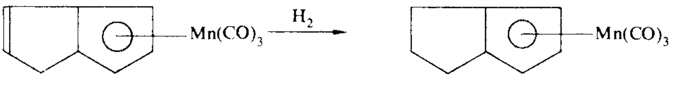
FIG. 3. Products from the reaction of azulene with manganese carbonyl.

The structure of (II) is probably as shown rather than the Mn–Mn bonded structure initally suggested[448]. The reaction of 4,6,8-trimethylazulene is also reported to yield a compound of type (II), but in view of the positions of the methyl groups it cannot have the same structure as (II) [449].

π-dihydropentalenylmanganese tricarbonyl undergoes reaction with $KMnO_4$ as follows:



Reduction of the compound using Raney nickel gives a π-tetrahydropentalenyl complex



and this complex can be prepared directly from cyclo-octatetraene and $Mn_2(CO)_{10}$ [429]:

---

[448] M. R. Churchill and P. H. Bird, *Inorg. Chem.* 7 (1968) 1793.
[449] R. Burton, L. Pratt and G. Wilkinson, *J. Chem. Soc.* (1960) 4290.

Manganese Carbonyl Halides

Manganese carbonyl reacts readily with halogens to give the manganese pentacarbonyl halides[429, 450].

$$Mn_2(CO)_{10}+X_2 = 2MnX(CO)_5; \quad X = Cl, Br \text{ or } I$$

Other methods of preparation include heating $Mn_2(CO)_{10}$ with carbon tetrachloride, chloroform and other halogenated hydrocarbons in the presence of ultraviolet light of the alkyl and acyl manganese pentacarbonyls with halogens[429]:

$$RMn(CO)_5+Br_2 = RBr+MnBr(CO)_5$$
$$RCOMn(CO)_5+I_2 = RI+MnI(CO)_5$$

$MnI(CO)_5$ was first isolated by the action of a pressure of carbon monoxide on MnI_2 [450].

The manganese pentacarbonyl halides are stable to air and water and their stability increases from the chloro to the iodo derivatives. On heating the compounds, carbon monoxide is last, and the dimeric halogen bridged compounds $[MnX(CO)_4]_2$ are formed. The reaction is carried out in an inert solvent at a temperature of about 120°C [450]. In the presence of carbon monoxide the reaction can be reversed:

$$[MnX(CO)_4]_2+2CO \rightarrow 2MnX(CO)_5$$

An X-ray structure determination on the compound $[MnBr(CO)_4]_2$ has been performed[429, 450] and has verified the proposed structure.

Anionic carbonyl halides, *cis*-$[MnX_2(CO)_4]^-$ and *trans*-$[Mn_2X_2(CO)_8]^{2-}$, have been obtained by the action of tetra-alkylammonium halides on $MnX(CO)_5$ and $Mn_2(CO)_{10}$ respectively[450]:

$$R_4NX+MnX(CO)_5 \rightarrow R_4N[MnX_2(CO)_4]+CO$$
$$2R_4NX+Mn_2(CO)_{10} \rightarrow [R_4N]_2[Mn_2X_2(CO)_8]+2CO$$

The initial studies on the exchange of carbon monoxide in the $MnX(CO)_5$ compounds which indicated that one carbonyl ligand exchanges more rapidly than the other four have been questioned. Infrared techniques have been used to follow the rate of ^{13}CO or $C^{18}O$ incorporation into $Mn(CO)_5X$ compounds and there appears to be little or no difference in the specific rate constants for exchange of carbonyl groups in either *cis*- or *trans*-positions to the halide[451]. However, the suggestion[451] that carbon monoxide may be lost from an axial position and substituted at an equatorial position is not tenable, and it has been suggested[452] that the equality of axial and equatorial carbonyl exchange is due either to pseudo rotation, which allows a rapid non-dissociative pathway for the exchange of axial and equatorial carbonyl groups, or, alternatively, to a process involving an acyl intermediate, $Mn(CO)_4(COX)$.

The rate of carbon monoxide exchange with the compounds $MnCl(CO)_3L_2$ decreases in the order $PPh_3 \gg AsPh_3 \gg SbPh_3$. Exchange is rapid when L is NH_3 and (*o*)-phen [441]. Isotopic halogen exchange on the $MnX(CO)_5$ compounds has been studied and the reactions have been found to follow first-order kinetics. The bromo compound exchanges more rapidly than the iodo compound[450].

---

[450] F. Calderazzo, *Halogen Chemistry* (edited by V. Gutmann), Academic Press, Vol. 3 (1967), p. 383.

[451] B. F. G. Johnson, J. Lewis, J. R. Miller, B. H. Robinson, P. W. Robinson and A. Wojcicki, *J. Chem. Soc.* A (1968) 522.

[452] T. L. Brown, *Inorg. Chem.* 7 (1968) 2673.

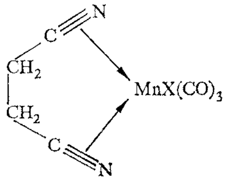
Many substitution reactions on the pentacarbonyl halides have been studied[441, 450] and kinetic studies on some of these reactions have been carried out[445]. The reaction of a ligand L [where L is PPh_3, $AsPh_3$, $SbPh_3$, C_2H_5NC, PCl_2Ph, $P(OBu)_3$, $P(OPh)_3$ and $P(OCH_2)_3CCH_3$)] with $MnX(CO)_5$ to give $MnX(CO)_4L$ takes place by an S_N1 mechanism with the rate of substitution decreasing in the order Cl > Br > I [441]. More basic ligands such as py, $PhNH_2$, p-$CH_3C_6H_4NH_2$ and PBu_3 react with $MnX(CO)_5$ to give the disubstituted compounds $MnX(CO)_3L_2$ directly[441]. Kinetic studies on the reaction of L′ with $MnX(CO)_4L$ to give $MnX(CO)_3LL'$ again follows a dissociative mechanism, and the rate of reaction decreases as the coordinated ligand L changes in the order

$$PPh_3 > AsPh_3 > PBu_3 \approx PClPh_2 > P(OPh)_3 \approx SbPh_3 > PCl_2Ph > P(OBu)_3 > P(OCH_2)_3CCH_3$$ [441]

The products $MnX(CO)_3LL'$ have a *cis*-configuration. However, compounds of the type $MnX(CO)_3LL'$ can also have a *trans*-geometry. Thus when L is PPh_3 only the *trans*-isomer can be isolated and both isomers have been isolated when L is $P(OPh)_3$ and prepared *in situ* for $P(OBu)_3$, PBu_3 and PCl_2Ph [441].

Reactions of $MnX(CO)_5$ and $[MnX(CO)_4]_2$ with a variety of N, O, S, and other donor atoms have also been described, and in certain cases ionic complexes $[Mn(CO)_4L_2]^+X^-$ have been prepared[441]. Substituted derivatives have also been obtained by chlorination of such compounds as $MnH(CO)_4PPh_3$ and $Mn_2(CO)_8\{(o)\text{-phen}\}$. Irradiation of the latter in chlorinated solvents gives a mixture of $MnCl(CO)_3\{(o)\text{-phen}\}$ and $MnCl(CO)_5$.

The halides $MnX(CO)_5$ react with succinonitrile to give the complexes in which it is believed that the triple bond of the nitrile groups coordinate to the manganese[453].



The primary amines RNH_2, where R is Me, Et or *i*-Pr, undergo an interesting reaction with $MnBr(CO)_5$ to give acyl type compounds:

$$MnBr(CO)_5 + 3RNH_2 \rightarrow cis\text{-}Mn(CONHR)(CO)_4NH_2R + RNH_3^+Br^-$$

These acyl-type derivatives which were originally formulated as 7-coordinate compounds, $Mn(NHR)(CO)_5NH_2R$, react with gaseous HCl to give the ions $[Mn(CO)_5(NH_2R)]^+$ which themselves react with RNH_2 to regenerate *cis*-$Mn(CONHR)(CO)_4(NH_2R)$ [454].

$$cis\text{-}Mn(CONHR)(CO)_4(NH_2R) + 2HCl \rightarrow [Mn(CO)_5(NH_2R)]^+Cl^- + RNH_3^+Cl^-$$

The reactions of $MnBr(CO)_5$ with alkyl-aryl-thio-derivatives of tin, R_3SnSR or $R_2Sn(SR)_2$, give rise to tetrameric compounds, $[Mn(CO)_3SR]_4$, where R is Me or Et. These compounds, which were originally formulated as trimers, have been shown to be tetramers by mass spectroscopy. However, osmometric molecular weight measurements cast some doubt

---

[453] M. F. Farona and N. J. Bremer, *J. Am. Chem. Soc.* **88** (1966) 3735.
[454] R. J. Angelici and D. L. Denton, *Inorg. Chem. Acta* **2** (1968) 3.

on the integrity of these units in solution. The tetrameric compounds have also been obtained from $Mn_2(CO)_{10}$ and methyl or ethyl thiocyanates[442, 455].

From the reactions of alkyl- and aryl-selenotin compounds with $MnX(CO)_5$ ($X = Cl$ or Br), the dimeric compounds $[Mn(CO)_4SeR]_2$ can be isolated which on heating produce the tricarbonyls $[Mn(CO)_3SeR]_n$. Dimeric compounds, $[Mn(CO)_3(PPh_3)ZR]_2$ (where Z is S or Se), are also formed from $MnCl(CO)_3(PPh_3)_2$[456]. A monomeric mono-thiol compound, $Mn(SC_6F_5)(CO)_5$, has been obtained from $MnH(CO)_5$ and C_5F_5SH[442].

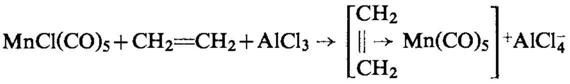
Mono-olefin complexes of manganese(I) of the type $MnX(CO)_3(L\text{–}L')$ and $Mn(CO)_4(L\text{–}L')^+$ have been obtained from the bidentate olefin phosphine ligands (L–L′) where L–L′ is $CH_3CH{=}CHC_6H_4o\text{-}PPh_2$, $CH_2{=}CHCH_2C_6H_4o\text{-}PPh_2$ or $CH_2{=}CHC_6H_4o\text{-}PPh_2$[457].

Manganese Carbonyl Cations

The hexacarbonylmanganese(I) cation $Mn(CO)_6^+$ may be prepared by treating $MnCl(CO)_5$ with aluminium trichloride under a pressure of carbon monoxide[429]:

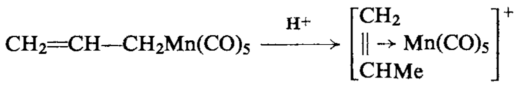
$$MnCl(CO)_5 + AlCl_3 + CO \rightarrow [Mn(CO)_6]^+AlCl_4^-$$

Ethylene may be used in place of carbon monoxide to give a substituted derivative

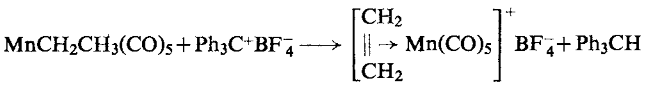


$$MnCl(CO)_5 + CH_2{=}CH_2 + AlCl_3 \rightarrow \left[\begin{matrix} CH_2 & \\ \| \rightarrow & Mn(CO)_5 \\ CH_2 & \end{matrix}\right]^+ AlCl_4^-$$

This type of carbonyl cation can also be prepared by protonation of σ-allylmanganese pentacarbonyl with perchloric acid[429] and by hydride abstraction from $MnEt(CO)_5$[458]:



$$CH_2{=}CH\text{—}CH_2Mn(CO)_5 \xrightarrow{H^+} \left[\begin{matrix} CH_2 & \\ \| \rightarrow & Mn(CO)_5 \\ CHMe & \end{matrix}\right]^+$$



$$MnCH_2CH_3(CO)_5 + Ph_3C^+BF_4^- \longrightarrow \left[\begin{matrix} CH_2 & \\ \| \rightarrow & Mn(CO)_5 \\ CH_2 & \end{matrix}\right]^+ BF_4^- + Ph_3CH$$

The reaction of ammonia with manganese carbonyl[440] and the maganese pentacarbonyl halides[429] also results in cationic manganese carbonyl species:

$$Mn_2(CO)_{10} + 3NH_3 \rightarrow [Mn(CO)_3(NH_3)_3]^+Mn(CO)_5^- + 2CO$$
$$MnX(CO)_5 + 3NH_3 \rightarrow [Mn(CO)_3(NH_3)_3]^+X^- + 2CO$$
$$MnBr(CO)_5 + 2NH_3 \rightarrow [Mn(CO)_4(NH_3)_2]^+Br^- + CO$$

Substituted carbonyl cations have been prepared by reaction of the complexes $MnCl(CO)_4L$ or $MnCl(CO)_3L_2$ with $AlCl_3$ (or other halide acceptors) and carbon monoxide at high pressure and temperature[441]. These substituted cations are easier to prepare than $[Mn(CO)_6]^+$. The reaction of $MnCl(CO)_3(PPh_3)_2$ in benzene with PPh_3 and $AlCl_3$ gives only $[Mn(CO)_4(PPh_3)_2]^+AlCl_4^-$. The cations $[Mn(CO)_4L_2]^+$, where L is PPh_3, $P(OPh)_3$ and

---

[455] B. F. G. Johnson, P. J. Pollick, I. G. Williams and A. Wojcicki, *Inorg. Chem.* 7 (1968) 831.
[456] E. W. Abel, A. M. Atkins, B. C. Crosse and G. V. Hutson, *J. Chem. Soc.* A (1968) 687.
[457] L. V. Interrante and G. V. Nelson, *Inorg. Chem.* 7 (1968) 2059.
[458] M. L. H. Green and P. L. I. Nagy, *J. Organomet. Chem.* **1** (1963) 58.

$TePh_2$, can be prepared by bubbling carbon monoxide through a benzene solution of the compounds $MnCl(CO)_3L_2$ in the presence of $AlCl_3$ [441]. The disubstituted cation $[Mn(CO)_4(PPh_3)_2]^+$ reacts with alkoxides to give the alkoxy carbonyl compounds $Mn(COOR)(CO)_3(PPh_3)_2$ which still contain *trans*-phosphine groups. These derivatives react with acids to regenerate the cation[441]:

$$Mn(COOR)(CO)_3(PPh_3)_2 + HX \rightarrow [Mn(CO)_4(PPh_3)_2]^+X^- + ROH$$

This type of reaction may also be used to generate $[Mn(CO)_6]^+BF_4^-$ which is easily prepared by treating $Mn(CO \cdot OEt)(CO)_5$ with BF_3 [459]. The oxidation of $[Mn(CO)_2(diphos)_2]^+Cl^-$ with a variety of oxidizing agents yields the interesting paramagnetic ion, *trans*-$[Mn(CO)_2(diphos)_2]^{2+}$, where diphos is $Ph_2PCH_2CH_2PPh_2$ [460].

Manganese Carbonylate Anions

Sodium pentacarbonylmanganate(-1), $Na^+Mn(CO)_5^-$, is best prepared by treating $Mn_2(CO)_{10}$ with sodium-amalgam in tetrahydrofuran solution[461,462]. The corresponding lithium salt $LiMn(CO)_5$ can be obtained if lithium is used in place of sodium amalgam[462]. The anion, $Mn(CO)_5^-$, can also be generated by the reaction of certain amines[462] with $Mn_2(CO)_{10}$ as previously mentioned. The reaction of alcoholic potassium hydroxide ion with $Mn_2(CO)_{10}$ also generates a solution whose reactions are consistent with the formation of $Mn(CO)_5^-$, and the following equation is suggested:

$$13Mn_2(CO)_{10} + 40OH^- \rightarrow 2Mn^{2+} + 24Mn(CO)_5^- + 10CO_3^{2-} + 20H_2O$$

However, the actual reaction must be more complicated than this since acidification of the green solution obtained by treating $Mn_2(CO)_{10}$ with aqueous potassium hydroxide gives a polynuclear hydride $H_3Mn_3(CO)_{12}$ [463]. Attempts to isolate anionic complexes from this green solution have so far failed. It has been claimed that the reaction of $Mn_2(CO)_{10}$ with sodium borohydride in tetrahydrofuran gives the binuclear ion, $Na_2Mn_2(CO)_9$ which on acidification gives the red volatile hydride $H_2Mn_2(CO)_9$ [462]. However, subsequent work[463] has shown that from this reaction $H_3Mn_3(CO)_{12}$ is obtained and hence the anion $Mn_2(CO)_9^{2-}$ requires confirmation.

Solutions of $Mn(CO)_5^-$ are air sensitive, and $NaMn(CO)_5$ has been isolated from a tetrahydrofuran solution as an almost colourless powder[462]. A potential of -0.68 V has been determined for the reaction[462]

$$Mn(CO)_5^- \rightarrow 1/2Mn_2(CO)_{10} + e^-$$

Although phosphine-substituted derivatives cannot be prepared by reactions with $Mn(CO)_5^-$, the anions $[Mn(CO)_4(PR_3)]^-$ can be generated from $Mn_2(CO)_8(PR_3)_2$ and sodium-amalgam in tetrahydrofuran, and, with the appropriate amalgam, lithium or magnesium salts of $[Mn(CO)_4(PPh_3)]^-$ can be obtained[441]. Empirical observations suggest that $[Mn(CO)_4PPh_3]^-$ is more basic that $[Mn(CO)_5]^-$ [464].

[459] N. A. Beach and H. B. Gray, *J. Am. Chem. Soc.* **90** (1968) 5713.

[460] M. R. Snow and M. H. B. Stiddard, *J. Chem. Soc.* A (1966) 777.

[461] R. B. King and F. G. A. Stone, *Inorganic Synthesis* (edited by J. Kleinberg), McGraw-Hill, Vol. 7 (1963), p. 198.

[462] R. B. King, *Advances in Organometallic Chemistry* (edited by F. G. A. Stone and R. West), Academic Press, Vol. 2 (1964), p. 157.

[463] B. F. G. Johnson, R. D. Johnston, J. Lewis and B. H. Robinson, *J. Organomet. Chem.* **10** (1967) 105.

[464] M. I. Bruce and F. G. A. Stone, *Angew. Chem.*, Int. Edn., **7** (1968) 747.

Disubstituted anions $[Mn(CO)_3(PR_3)_2]^-$ have been obtained by reduction of the halides $MnCl(CO)_3(PR_3)_2$ with sodium amalgam[441].

Acidification of the carbonylate anions generates the appropriate hydride compound, and the carbonylate anions are extremely useful intermediates for the synthesis of a wide variety of compounds. Further details can be found in refs. 440, 441, 462 and 464.

Manganese–Metal Bonded Compounds

Many compounds are known in which the $Mn(CO)_5$ unit is bonded to another metal[440]. These compounds have generally been prepared by treating sodium pentacarbonyl-manganate (−1), with halide derivatives of a number of metals:

$$L_mMX_n + nNaMn(CO)_5 \rightarrow L_mM[Mn(CO)_5]_n + nNaX$$

Using this type of reaction derivatives of B, Si, Ge, Sn, Pb, Mo, Fe, Co, Cu, Ag, Au, Zn, Cd and Hg have been isolated[440]. Metal manganese bonded compounds have also been prepared by insertion reactions of $Mn_2(CO)_{10}$ [465, 466], e.g.

$$\begin{aligned} Mn_2(CO)_{10} + SnCl_2 &\rightarrow Cl_2Sn[Mn(CO)_5]_2 \\ Mn_2(CO)_{10} + InBr &\rightarrow BrIn[Mn(CO)_5]_2 \\ Mn_2(CO)_{10} + Zn &\rightarrow Zn[Mn(CO)_5]_2 \\ Mn_2(CO)_{10} + Cd &\rightarrow Cd[Mn(CO)_5]_2 \end{aligned}$$

and germanium compounds have also been obtained by such methods as[440]

$$\begin{aligned} GeH_4 + 2HMn(CO)_5 &\rightarrow H_2Ge[Mn(CO)_5]_2 + 2H_2 \\ Cl_3GeH + HMn(CO)_5 &\rightarrow Cl_3GeMn(CO)_5 + H_2 \\ Cl_3GeH + ClMn(CO)_5 &\rightarrow Cl_3GeMn(CO)_5 + HCl \end{aligned}$$

The cobalt compound $(CO)_4CoMn(CO)_5$ has been prepared in two ways[440]:

$$\begin{aligned} NaCo(CO)_4 + ClMn(CO)_5 &\rightarrow NaCl + (CO)_4CoMn(CO)_5 \\ [Co(CO)_4]^- + [Mn(CO)_6]^+ &\rightarrow CO + (CO)_4CoMn(CO)_5 \end{aligned}$$

and the latter type of reaction has also been used to prepare $(CO)_5ReMn(CO)_5$ [440]. These reactions illustrate that carbonylate anions can behave as nucleophiles towards carbonyl cations[440]. Other interesting reactions of this type include[441]:

$$\begin{aligned} [Mn(CO)_4(o\text{-phen})]^+ + [Co(CO)_4]^- &\rightarrow (CO)_3(o\text{-phen})MnCo(CO)_4 + CO \\ [Mn(CO)_5(PPh_3)]^+ + [Co(CO)_3(PPh_3)]^- &\rightarrow [Mn(CO)_5(PPh_3)]^+[Co(CO)_4]^- \end{aligned}$$

In the latter reaction an ionic compound is formed and a carbonyl exchange reaction occurs.

Substituted derivatives of the type $R_3SnMn(CO)_4L$ or $Hg[Mn(CO)_4L]_2$ (L = phosphine or arsine) have been prepared either by direct substitution on the mixed metal compound or by treating the appropriate halide with the substituted carbonylate anion $Mn(CO)_4L^-$ [440].

Most of the compounds are air stable crystalline solids and some, e.g. $Me_3SnMn(CO)_5$ and $Et_3PbMn(CO)_5$, can be distilled under reduced pressure[440]. The latter compound is a

---

[465] J. Hoyano, D. J. Patmore and W. A. G. Graham, *Inorg. Nucl. Chem. Letters* **4** (1968) 201.
[466] J. M. Burlitch, *Chem. Communs.* (1968) 887.

liquid at room temperature. The structures of a number of the compounds have been studied by single crystal X-ray measurements and some data is given in Table 16.

TABLE 16. BOND LENGTH FOR SOME METAL–MANGANESE BONDED COMPOUNDS

Compound	Bond length	Å
$(CO)_5Mn{-}Mo(CO)_3Cp$	Mo–Mn [a]	3.08
$(CO)_5Mn{-}W(CO)_3Cp$	W–Mn [a]	3.16
$Ph_3Ge{-}Mn(CO)_5$	Ge–Mn [a]	2.60
$Me_3Sn{-}Mn(CO)_5$	Sn–Mn [a]	2.674
$Ph_3Sn{-}Mn(CO)_5$	Sn–Mn [b]	2.674
trans-$Ph_3Sn{-}Mn(CO)_4(PPh_3)$	Sn–Mn [b]	2.627
$Ph_2Sn{-}[Mn(CO)_5]_2$	Sn–Mn [b]	2.70
$Ph_2Sn[Mn(CO)_5][Co(CO)_4]$	Sn–Mn [a]	2.73
$(CO)_5Mn{-}Re(CO)_5$	Re–Mn [a]	2.96
$HMnRe_2(CO)_{14}$	Re–Mn [a]	2.960

[a] M. I. Bruce, *Organometallic Chem. Rev.*, Section B, **5** (1969) 351.
[b] J. F. Young, *Advances in Inorganic and Radiochemistry* (edited by H. J. Emeléus and A. G. Sharpe), Academic Press, Vol. 11 (1968), p. 92.

Substitution reactions of these metal–manganese bonded compounds, $M{-}Mn(CO)_5$, give rise to either *cis*- or *trans*-isomers, $M{-}Mn(CO)_4L$. Thus the compound $Ph_3SnMn(CO)_4PPh_3$ has a *trans*-configuration while substitution in compounds of the type $LAuMn(CO)_5$ give *cis*-isomers. These differences have been described in terms of both electronic and steric effects[440].

The physical properties of the tin compounds have been widely studied and data on their infrared and Mossbauer spectra is available[440, 467]. These compounds also undergo some interesting reactions. Thus treatment of the compound $Ph_3SnMn(CO)_5$ with chlorine and bromine results in cleavage of the phenyl–tin bonds in preference to the Sn–Mn bond:

$$Ph_3SnMn(CO)_5 + 3X_2 \rightarrow X_3SnMn(CO)_5 + 3PhX$$

With anhydrous hydrogen chloride partial cleavage of the tin–phenyl bonds occurs:

$$Ph_3SnMn(CO)_5 + 2HCl \rightarrow PhCl_2SnMn(CO)_5 + 2PhH$$

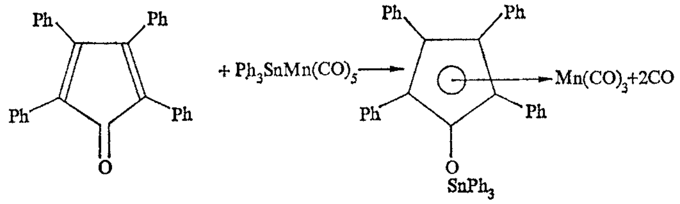
However, treatment of $Me_3SnMn(CO)_5$ with Br_2 in CCl_4 at 0°C results in cleavage of the Sn–Mn bond to give $MnBr(CO)_5$ and Me_3SnBr [467]. Redistribution reactions are also possible[440]:

$$2Ph_3SnMn(CO)_5 + Cl_3SnMn(CO)_5 \rightarrow 3Ph_2ClSnMn(CO)_5$$

and with certain reagents some interesting metal–metal bond cleavage reactions result. Thus X-ray analysis of the product obtained from tetracyclone and $Ph_3SnMn(CO)_5$ shows that Sn–Mn bond cleavage occurs[468]:

---

[467] J. Alexander and A. Wojcicki, *Organomet. Chem. Revs.*, Section B, **5** (1968) 618.
[468] R. F. Bryan and H. P. Weber, *J. Chem. Soc.* A (1967) 843.



Trialkyl and triaryl phosphites also cleave the Si–Mn bond in $Ph_3SiMn(CO)_5$ although with the corresponding tin and germanium compounds only carbonyl substitution reactions occur[469].

The reaction of tetrafluoroethylene with $Me_3M–Mn(CO)_5$, M = Ge[470] or Sn[471] gives the insertion product $Me_3MCF_2CF_2Mn(CO)_5$. However, with other fluoro-olefins no insertion products are obtained but some interesting fluoro-carbon compounds are formed. Thus $CF_2{=}CFCl$ and $Me_3SnMn(CO)_5$ react to give a number of products which include $CF_2{=}CFCOMn(CO)_5$ and $[Mn(CF{=}CF_2)(CO)_4]_2$. The latter compound is postulated to contain a bridging vinyl ligand.

Sulphur dioxide also cleaves the Sn–Mn bond of $Me_3SnMn(CO)_5$ and $Ph_3SnMn(CO)_5$ to give the adducts $[Me_3SnMn(CO)_5]_2 \cdot 3SO_2$, $[Me_3SnMn(CO)_5]_2 \cdot 5SO_2$ and $[Ph_3SnMn(CO)_5]_2 \cdot 5SO_2$, but the structures of these compounds are not known[467].

$Hg[Mn(CO)_5]_2$ has been prepared by the reaction of aqueous alkaline solutions of $NaMn(CO)_5$ with $Hg(CN)_2$, $HgSO_4$ or RHgOH [440]. In the latter reaction the intermediate $RHgMn(CO)_5$ is probably formed which then disproportionates as follows:

$$2RHgMn(CO)_5 \rightarrow R_2Hg + Hg[Mn(CO)_5]_2$$

However, it is interesting to note that when R is a halogen the above reaction lies well to the left-hand side, i.e.

$$Hg[Mn(CO)_5]_2 + HgX_2 \rightarrow 2XHgMn(CO)_5$$

The mercury compound $Hg[Mn(CO)_5]_2$ is stable to air, water and hot concentrated non-oxidizing mineral acids. However, the Hg–Mn bond is cleaved by iodine and H_2S [440].

Further information on these metal–manganese bonded compounds can be found in refs. 440 and 472.

Manganese Carbonyl Hydrides

Manganese pentacarbonyl hydride, $MnH(CO)_5$, is best prepared by acidification of $NaMn(CO)_5$ with phosphoric acid[461]. $MnH(CO)_5$ is a malodorous, light and air-sensitive colourless liquid, m.p. −24.6°C [462, 473]. The compound is a weak acid ($K = 0.8 \times 10^{-7}$). It is stable to about 100°C and its volatility is similar to the isoelectronic $Fe(CO)_5$ [462]. $MnH(CO)_5$ has also been prepared by the reaction of $Mn_2(CO)_{10}$ with a mixture of hydrogen and carbon monoxide at 250 atm and 200°C and the reduction of $Mn_2(CO)_{10}$ with magnesium in an aqueous methanolic suspension[462].

---

[469] E. P. Ross and G. R. Dobson, *Chem. Communs.* (1969) 1229.

[470] H. C. Clark, J. D. Cotton and J. H. Tsai, *Inorg. Chem.* 5 (1966) 1582.

[471] H. C. Clark and J. H. Tsai, *Inorg. Chem.* 5 (1966) 1407.

[472] N. S. Vyazankin, G. A. Razuvaev and O. A. Kruglaya, *Organomet. Chem. Rev.*, Section A, 3 (1968) 323.

[473] M. L. H. Green, *Organometallic Compounds* (by G. E. Coates, M. L. H. Green and K. Wade), 3rd edn., Methuen, Vol. 2 (1968).

X-ray structural data on $MnH(CO)_5$ shows that the carbonyl groups occupy five of the six corners of a nearly regular octahedron, the manganese atom lying slightly above the basal plane along the fourfold axis toward the axial carbonyl group. The structure of $HMn(CO)_5$ is, in fact, very similar to that of $Mn_2(CO)_{10}$ and in the crystal the hydrogen atoms lie between two manganese atoms and there may be intermolecular contact[474]. Gas phase electron diffraction data gives a Mn–H bond length of 1.42 Å which is in excellent agreement with the value of 1.44 Å determined from n.m.r. data[475].

The infrared spectrum and vibrational assignments of $MnH(CO)_5$ have now been determined in the light of the X-ray structure[476].

$MnH(CO)_5$ is a strong reducing agent and reacts with both iodine and oxygen to yield $Mn_2(CO)_{10}$ [462]. A variety of fluoro-olefins react with $MnH(CO)_5$ to give fluoro-organomanganese compounds (see later)[477].

Exchange studies with labelled carbon monoxide reveal that all five carbonyl groups in $MnH(CO)_5$ exchange at the same rate[478], and it has been suggested[452] that this reflects a rapid non-dissociative exchange of axial and equatorial carbonyl groups.

The reaction of $MnH(CO)_5$ with triphenylphosphine gives $MnH(CO)_4(PPh_3)$, and this latter compound reacts with certain phosphines and phosphites to give the disubstituted compounds $MnH(CO)_3L_2$ [479]. Substituted derivatives of this type have also been obtained by acidification of the appropriate carbonylate anion, and these hydrides are much less acidic than the parent $MnH(CO)_5$ [441, 480].

$MnH(CO)_5$ reacts with PF_3 under the influence of ultraviolet light to yield all the substituted products $MnH(PF_3)_x(CO)_{5-x}$, and since no geometric isomers can be isolated[480a] it seems possible that a non-dissociative exchange of ligands is occurring in these compounds[452]. However, geometric isomers can be isolated from the substitution products obtained from $MnR_f(CO)_5$ (R_f = CF_3, CF_3CO and HCF_2CF_2) and PF_3 [480a].

Acidification of the green solution obtained by treating $Mn_2(CO)_{10}$ with aqueous potassium hydroxide gives the red, volatile hydride, $H_3Mn_3(CO)_{12}$ [463]. This compound has also been obtained from the action of sodium borohydride on $Mn_2(CO)_{10}$ followed by acidification[463], and by the action of $NaBH_4$ on $MnMe(CO)_5$ [481]. Previous workers have reported that the hydride $H_2Mn_2(CO)_9$ may be prepared from $NaBH_4$ and $Mn_2(CO)_{10}$ [462], but this hydride requires further confirmation. The formula of $H_3Mn_3(CO)_{12}$ has been verified by mass spectroscopy[463]. It reacts with triphenyl-phosphine-arsine and stibine to yield the dimers $[Mn(CO)_4MPh_3]_2$ [463]. A green hydride which is possibly tetra-nuclear is also sometimes isolated on acidification of the $Mn_2(CO)_{10}$–potassium hydroxide reaction mixture[463].

The mixed manganese–rhenium hydrides, $HMnRe_2(CO)_{14}$ and $HMn_2Re(CO)_{14}$, have also been isolated[482]. The crystal structure of $HMnRe_2(CO)_{14}$ involves an L-shaped

---

[474] S. J. La Placa, W. C. Hamilton and J. A. Ibers, *Inorg. Chem.* **3** (1964) 1491.

[475] A. G. Robiette, G. M. Sheldrick and R. N. F. Simpson, *Chem. Communs.* (1968) 506.

[476] W. F. Edgell, J. W. Fisher, G. Asato and W. M. Risen, Jr., *Inorg. Chem.* **8** (1969) 1103.

[477] P. M. Treichel and F. G. A. Stone, *Advances in Organometallic Chemistry* (edited by F. G. A. Stone and R. West), Academic Press, Vol. 1 (1964), p. 143.

[478] P. S. Braterman, R. W. Harrill and H. D. Kaesz, *J. Am. Chem. Soc.* **89** (1967) 2851.

[479] B. L. Booth and R. N. Haszeldine, *J. Chem. Soc.* A (1966) 157.

[480] M. L. H. Green and D. J. Jones, *Advances in Inorganic and Radiochemistry* (edited by A. G. Sharpe), Academic Press, Vol. 7 (1965), p. 115.

[480a] W. J. Miles and R. J. Clark, *Inorg. Chem.* **7** (1968) 1801.

[481] R. Aumann and E. O. Fischer, *J. Organomet. Chem.* **8** (1967) 1.

[482] J. M. Smith, K. Mehner and H. D. Kaesz, *J. Am. Chem. Soc.* **89** (1967) 1759; W. Fellmann and H. D. Kaesz, *Inorg. Nucl. Chem. Letters* **2** (1966) 63.

configuration of metal atoms and it is proposed that the hydrogen atom lies between the two rhenium atoms[483].

In addition to $H_3Mn_3(CO)_{12}$, the first metal–carbonyl polyborane, $Mn_3(CO)_{10}(BH_3)_2H$, is obtained from the reaction of $Mn_2(CO)_{10}$ with $NaBH_4$. The crystal structure of this compound[484] also reveals the presence of a Mn–H–Mn system, the boron atoms being linked to the manganese atoms by bridging hydrogen atoms. This compound, together with a possible precursor $Mn(BH_4)(CO)_5$, has also been obtained from the reaction of $MnBr(CO)_5$ with $Al(BH_4)_3$ [485].

Treatment of $NaMn(CO)_5$ with Ph_2PCl yield a hydride, $(CO)_4Mn(H)PPh_2Mn(CO)_4$ [480]. An X-ray study of the compound reveals a distorted octahedral coordination around each manganese formed by four carbonyl groups and bridging hydrogen and phosphorus atoms. However, as in other systems containing Mn–H–Mn bonds, it is not possible to differentiate between a symmetric, bent, three-centre, two-electron bond Mn–H–Mn, or a Mn–H σ-bond and Mn–Mn metal–metal bond[466].

Protonation of the compound $CpFe(CO)_2Mn(CO)_5$ yields the ion $[CpFe(CO)_2Mn(CO)_5H]^+$ [480]. Infrared studies reveal the presence of a metal–hydrogen bond, but whether the Fe–Mn bond persists in the ion or a Fe–H–Mn bond is present is not known.

A nitrosyl hydride, $MnH(NO)_2(PPh_3)_2$, has been prepared from $MnBr(NO)_2(PPh_3)_2$ and sodium borohydride[480].

ORGANOMETALLIC COMPOUNDS OF MANGANESE

A number of compounds of the type RMnX, MnR_2 and $LiMnR_3$ have been prepared from MnI_2 and organo-lithium compounds, where R is an alkyl or aryl group[487]. Attempts to prepare the compounds with Grignard reagents have not been successful[487]. $Mn(CH_3)_3$ is a bright yellow powder which readily detonates[473]. It is insoluble in ether and probably polymeric. It is soluble in excess methyl-lithium to give the stable complex $LiMn(CH_3)_3$ which decomposes at 100°C. $Mn(CH_3)_2$ also reacts with MnI_2 to give MeMnI which is a heavy oil. $Mn(C_6H_5)_2$ is a sparingly soluble green solid which can be recrystallized from tetrahydrofuran. The chemical properties and structures of these interesting compounds have not been investigated in detail. It is known, however, that $Mn(Ph)_2$ will cause the trimerization of dimethylacetylene to hexamethylbenzene. The π-complex $[Mn(C_6Me_6)_2]^+$ is also formed in this reaction[488]. The tetrahydrofuran adduct $(THF)_2MnPh_2$ reacts with acetylene at $-50°$ to $-30°C$ to give, after acid hydrolysis, biphenyl (6.5 %), all *trans*-1,6-diphenyl-1,3,5-hexatriene (4 %) and trace amounts of other hydrocarbons[467].

The methyl manganese compound reacts with diphenylacetylene to give methylation, hydrogenation and oligomerization products[489], and both $MnMe_2$ and $MnPh_2$ react with hydrogen to give methane and benzene respectively[490].

The best-known manganese–carbon σ-bonded compounds are the carbonyl derivatives $MnR(CO)_5$. Although the simplest derivative, $MnCH_3(CO)_5$, has been obtained by action

[483] M. R. Churchill and R. Bau, *Inorg. Chem.* **6** (1967) 2086.

[484] H. D. Kaesz, W. Fellmann, G. R. Wilkes and L. F. Dahl, *J. Am. Chem. Soc.* **87** (1965) 2753.

[485] P. H. Bird and M. G. H. Wallbridge, *Chem. Communs.* (1968) 687.

[486] R. J. Doedens, W. T. Robinson and J. A. Ibers, *J. Am. Chem. Soc.* **89** (1967) 4323.

[487] R. Riemschneider, H. G. Kassahn and W. Schneider, *Z. Naturforsch.* **156** (1960) 547.

[488] M. Tsutsui and H. Zeiss, *J. Am. Chem. Soc.* **83** (1961) 825.

[489] J. R. C. Light and H. H. Zeiss, *J. Organomet. Chem.* **21** (1970) 517.

[490] K. Clauss and H. Bestian, *Ann.* **654** (1962) 8.

of diazomethane on $MnH(CO)_5$ [462], i.e.

$$CH_2N_2 + MnH(CO)_5 \rightarrow MnCH_3(CO)_5 + N_2$$

the simpler alkyl derivatives are best prepared from an alkyl halide and $NaMn(CO)_5$ [462],

$$RX + NaMn(CO)_5 \rightarrow MnR(CO)_5 + NaX$$

This method cannot be used to give a general synthesis of the $MnR(CO)_5$ compounds[462]. Thus vinyl and phenyl halides are not sufficiently reactive to give an organo-manganese derivative, and since secondary and tertiary alkyl manganese bonds appear to be unstable, the reactions of the halides R_2CHX and R_3CX with $NaMn(CO)_5$ yield $Mn_2(CO)_{10}$ and hydrocarbons rather than the required product[462]. However, since almost all acyl chlorides react with $NaMn(CO)_5$, as in the equation

$$RCOCl + NaMn(CO)_5 \rightarrow NaCl + RCOMn(CO)_5$$

the acyl compounds $Mn(COR)(CO)_5$ can then be readily decarbonylated on heating,

$$RCOMn(CO)_5 \rightarrow CO + MnR(CO)_5$$

to give the required organo-manganese derivatives[462].

The methyl complex $MnMe(CO)_5$ is quite stable to air and water, but the ethyl and n-propyl compounds are much more reactive[473].

On treatment with halogens or halogen acids, the Mn–C bond is cleaved[491], e.g.

$$MnR(CO)_5 + Br_2 \rightarrow MnBr(CO)_5 + RBr$$

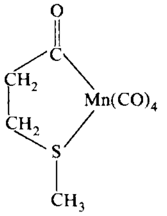
The manganese alkyl and aryl compounds $MnR(CO)_5$ undergo a carbonylation reaction with carbon monoxide[473],

$$MnR(CO)_5 + CO \rightarrow Mn(COR)(CO)_5$$

and reactions with labelled carbon monoxide show that it is a coordinated carbonyl ligand which is incorporated into the acyl group. The reactions of iodide, amines and phosphines with $MnMe(CO)_5$ also give acyl compounds[430], $Mn(COMe)(CO)_4L$, and with certain ligands a *cis*-substituted acyl compound is formed[467]. Mechanistic studies show that the carbonylation occurs by methyl migration rather than by carbon monoxide insertion and that the rate determining step is Mn–Me bond cleavage[430, 473]. It has also been shown that the rate of carbonylation decreases in the sequence

$$\text{n-Pr} \gtrsim \text{Et} > \text{Ph} > \text{Me} \gg \text{PhCH}_2 \approx \text{CF}_3 \text{ [462].}$$

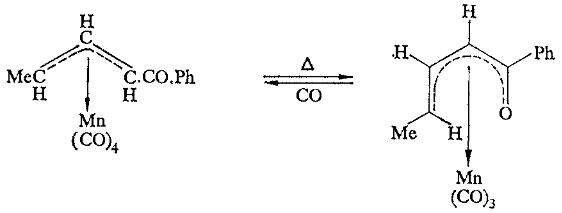
Some interesting compounds have been obtained from the reaction of $Br(CH_2)_3Br$ and $ClCH_2CH_2SCH_3$ with $NaMn(CO)_5$. The former gives $(CO)_5MnCH_2CH_2–CH_2Mn(CO)_5$ whose ^1H n.m.r. spectrum exhibits only three lines of relative intensity 1:1:1 and manganese–hydrogen interactions have been proposed[462]. The latter gives the compound[441]



---

[491] D. A. White, *Organomet. Chem. Revs.*, Section A, 3 (1968) 497.

Methyl manganese pentacarbonyl undergoes insertion reactions with C_2F_4 and C_2F_3Cl to give the products $MeCFXCF_2Mn(CO)_5$, X = F or Cl [473]. The compounds $MnR(CO)_5$, R = Me or Ph, also react with conjugated dienes, e.g. butadiene, to give π-allyl complexes, and the phenyl adduct has been shown to undergo a novel rearrangement[492]:



Sulphur dioxide reacts with the compounds $MnR(CO)_5$, where R is Me, Et, Ph or benzyl to give the S-sulphinates $Mn(SO_2R)(CO)_5$, which cannot be prepared from $MnCl(CO)_5$ and RSO_2Na or $NaMn(CO)_5$ and RSO_2Cl [467]. Interesting insertion products are also obtained from sulphur dioxide and σ-allyl manganese pentacarbonyl compounds[467]. The reaction of $Mn(CH_2C{\equiv}CH)(CO)_5$ with SO_2 gives $MnS(O)OCH{=}C{=}CH_2(CO)_5$ [467].

The manganese salt of the tricyanomethanide ion, $Mn[C(CN)_3]_2{\cdot}0.25H_2O$, is known but this compound does not contain Mn–C bonds. The compound is polymeric and the manganese(II) ion is probably octahedrally coordinated by six nitrogen atoms[493]. However, Mn–C bonds are present in $(CN)_3C{-}Mn(CO)_5$ [494].

Perfluoro Alkyl and Aryl Compounds

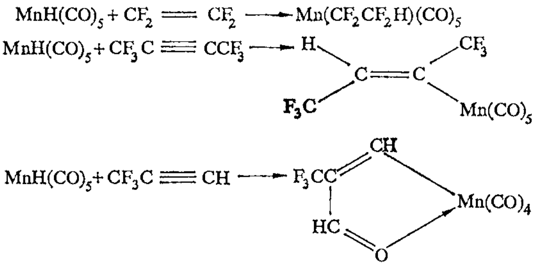
The perfluoro alkyl compounds $MnR_f(CO)_5$ cannot be prepared from the alkyl halide and $NaMn(CO)_5$ since a carbonyl halide results[462]:

$$2CF_3I + 2NaMn(CO)_5 \rightarrow IMn(CO)_5 + C_2F_6$$

However, acyl compounds can be readily formed, and these can be decarbonylated to give the perfluoroalkyl and pentafluorophenyl manganese pentacarbonyl compounds[462, 495].

$$R_fCOCl + NaMn(CO)_5 \rightarrow NaCl + Mn(COR_f)(CO)_5$$
$$Mn(COR_f)(CO)_5 \rightarrow MnR_f(CO)_5 + CO$$

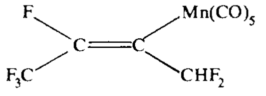
A variety of other manganese fluorocarbon compounds have been obtained from the reactions[464, 477, 495] of either $NaMn(CO)_5$ or $MnH(CO)_5$ with both fluoro-olefins and acetylenes, and these reactions have yielded some very interesting compounds, e.g.

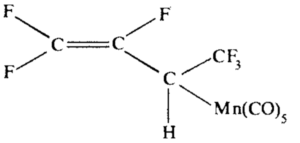


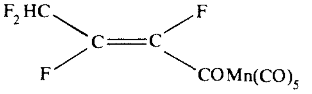
---

[492] M. Green and R. I. Hancock, *J. Chem. Soc.* A (1968) 109.
[493] J. H. Enemark and R. H. Holm, *Inorg. Chem.* 3 (1964) 1516.
[494] W. Beck, R. E. Nitzchmann and G. Neumair, *Angew. Chem.*, Int. Edn., 3 (1964) 380.
[495] M. I. Bruce and F. G. A. Stone, *Prep. Inorg. Reacts.*, Interscience, Vol., 4 (1968), p. 177.

In the latter reaction some $CH_2{=}C(CF_3)Mn(CO)_5$ is also formed and with $CF_3C{\equiv}CH$ and $MnMe(CO)_5$ a cyclic product, $O{=}C(Me)C(CF_3){=}CHMn(CO)_4$, is obtained[495]. The reaction of $CF_2{=}CF{-}CF{=}CF_2$ with $MnH(CO)_5$ gives the compounds[495]



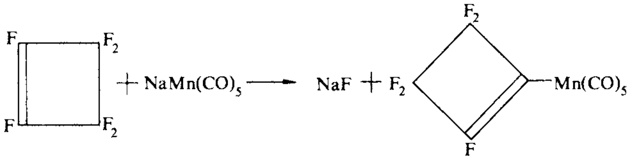


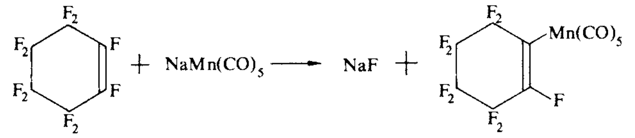


With unsymmetrical olefins a mixture of isomers can also be obtained, e.g. $MnCF_2CCl_2H(CO)_5$ and $MnCCl_2CF_2H(CO)_5$ [495].

Not all fluoro-olefins give metal complexes with $MnH(CO)_5$. Thus reduction of the fluoro-olefin to a fluoroalkane occurs with $CF_2{=}CH_2$, $CFH{=}CF_2$, and $CFH{=}CH_2$ [495].

The reaction of $NaMn(CO)_5$ with perfluorocyclobutene and perfluorocyclohexene yields alicyclic derivatives[464, 495]:





However, in contrast to these reactions $CF_2{=}CFCl$ reacts with $NaMn(CO)_5$ to give $Mn(CF_2CFClH)(CO)_5$ [464]. In general the fluorocarbon complexes are much more stable than their hydrocarbon anologues[473]. Also one of the big differences between the two classes of compounds is that the fluorocarbon derivatives do not undergo insertion reactions with carbon monoxide and other small molecules. Detailed reviews on these compounds can be found in refs. 464 and 495.

Manganese Acetylides

Addition of alkali acetylides to $Mn(SCN)_2$ in liquid ammonia gives the pink manganese(II) complexes $M_2Mn(C{\equiv}CR)_4$, where M is either Na, K or Ba, and R is H, Me or Ph [496]. An adduct $Mn(C{\equiv}CH)_4{\cdot}4NH_3$ is also known,

$$Mn(SCN)_2+2KC{\equiv}CH+4NH_3 \rightarrow Mn(C{\equiv}CH)_2{\cdot}4NH_3+2KSCN$$

---

[496] R. Nast, *Abs. Int. Conf. Coord. Chem. London, Chem. Soc. (London)*, Spec. Publ., No. 13 (1959), p. 103.

and this looses ammonia *in vacuo* at room temperature to give the black highly explosive $Mn(C{\equiv}CH)_2$ [496].

The complexes $M_2Mn(CN)_4$ are high spin and tetrahedral in contrast to the low-spin octahedral cyanide complexes $M_4Mn(CN)_6$, and this is interesting since acetylide and cyanide complexes are usually similar. It has been pointed out, however, that the complex anion $Mn(CN)_6^{4-}$ is usually obtained in aqueous solution, and in liquid ammonia a different reaction occurs,

$$Mn(SCN)_2 + 2KCN + 6NH_3 \rightarrow Mn(CN)_2 \cdot 6NH_3 + 2KSCN$$

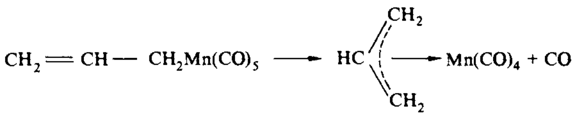
and a pink solid $Mn(CN)_2 \cdot 6NH_3$ is precipitated[496].

A dark brown highly explosive solid which may be a manganese(III) acetylide complex has been obtained by the reaction[496]

$$2K_2Mn(C{\equiv}CH)_4 + 4KC{\equiv}CH + 0.5O_2 + 2NH_3 \rightarrow 2K_3Mn(C{\equiv}CH)_6 + 2KNH_2 + H_2O$$

Allyl Complexes

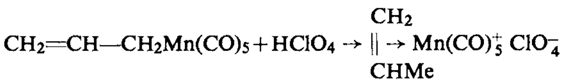
π-allylmanganese tetracarbonyl compounds Mn(π-allyl)$(CO)_4$ have been prepared in good yield either from allyl halides and $NaMn(CO)_5$ or butadienes and $MnH(CO)_5$ [497, 498]. Both of these reactions proceed through σ-allylmanganese pentacarbonyl intermediates which are distillable liquids in contrast to the π-allyl compounds which are crystalline solids. When the σ-allylmanganese pentacarbonyls are heated to 70–100°C, carbon monoxide is evolved and the π-allyl compounds are formed, e.g.



The allyl groups C_3H_5, 1-$CH_3C_3H_4$, 2-$CH_3C_3H_4$, 1-ClC_3H_4 and 1,1-$(CH_3)_2C_3H_3$ are some of the ligands which have yielded both σ- and π-allyl compounds of manganese[467,497, 498].

The reaction of butadienes with $MnMe(CO)_5$ and $MnPh(CO)_5$ also give π-allyl compounds, and the mechanistic aspects of this reaction have been studied[492].

A novel rearrangement takes place when the σ-allyl compound $CH_2{=}CH{-}CH_2Mn(CO)_5$ is treated with perchloric acid[497].



$$CH_2{=}CH{-}CH_2Mn(CO)_5 + HClO_4 \rightarrow \begin{matrix} CH_2 \\ \| \\ CHMe \end{matrix} \rightarrow Mn(CO)_5^+\ ClO_4^-$$

The reactions of sulphur dioxide with σ-allyl compounds are given in ref. 467.

A yellow liquid, π-$CH_3SCH_2Mn(CO)_4$, has been obtained from chloromethyl sulphide and $NaMn(CO)_5$. Like the π-allyl group, π-$CH_3S{=}CH_2$ appears to behave as a three-electron donor[499].

The reaction of $CF_2{=}CFCF_2Cl$ with $NaMn(CO)_5$ does not yield a σ- or π-allyl compound. Instead a σ-bonded perfluoropropenyl compound is obtained[464]:

---

[497] M. L. H. Green and P. L. I. Nagy, *Advances in Organometallic Chemistry* (edited by F. G. A. Stone and R. West), Academic Press, Vol. 2 (1964), p. 325.

[498] E. O. Fischer and H. Werner, *Metal π-Complexes*, Elsevier, Vol. 1 (1966).

[499] R. B. King and M. B. Bisnette, *Inorg. Chem.* 4 (1965) 486.

$$CF_2{=}CFCF_2Cl + NaMn(CO)_5 \rightarrow CF_3CF{=}CFMn(CO)_5 + NaCl$$

However, from the reaction of $CF_2{=}CClCF_2Cl$ with $NaMn(CO)_5$ the intermediate σ-allyl compound $CF_2{=}CClCF_2Mn(CO)_5$ can be isolated, and its isomerization to $CF_3CCl{=}CFMn(CO)_5$ has been studied[500].

Cyclopentadienyl Complexes

Bis-cyclopentadienide manganese (manganocene), $MnCp_2$, may be prepared by the action of NaCp on anhydrous $MnCl_2$ in tetrahydrofuran[473]. The compound $MnCp_2$ forms amber crystals, m.p. 172–173°C. It is soluble in ether and other common organic solvents and is readily volatile, the heat of sublimation being 17.3 kcal $mole^{-1}$ [473].

X-ray studies show that the compound has a sandwhich structure like ferrocene. Magnetic studies on dilute solutions of manganocene in $MgCp_2$ show that manganocene is paramagnetic with a magnetic moment of 5.86 ± 0.05 BM. This is consistent with the presence of the manganese(II) ion with five unpaired electrons. At low temperatures $MnCp_2$ has a rhombic structure and exhibits antiferromagnetism[473].

These properties indicate that the metal-ring bonds in manganocene are primarily ionic in nature and thus the compound is unique since all the other *d*-block metal π-C_5H_5 compounds contain covalent metal-ring bonds. Electron spin resonance studies at low temperatures are also consistent with ionic bonds in $MnCp_2$.

Electron diffraction studies on gaseous $MnCp_2$ reveal the presence of very short (2.38 Å) Mn–H distances which are attributed to a large amplitude of out-of-plane vibration[467]. In view of its structure it is not surprising that $MnCp_2$ is easily hydrolysed to $Mn(OH)_2$ and cyclopentadiene and that it reacts with CO_2 to give carboxylic acid salts in a similar fashion to the alkali metal cyclopentadienides. In ether, $MnCp_2$ reacts with $FeCl_2$ to give ferrocene.

The similarity of the infrared spectrum of manganocene and ferrocene has been used as evidence to suggest some weak covalent character in the manganese-ring bonds, but in view of the properties of the compound any covalent contribution to the bond must be very small. The conductivity of an ether solution is much lower than would possibly be expected, and hence ion-association is probably occurring[473].

Methylcyclopentadienide manganese, $Mn(\pi\text{-}MeC_5H_4)_2$, has similar properties to manganocene[501].

Manganocene reacts with carbon monoxide to give the yellow solid cyclopentadienyl manganese tricarbonyl (cymantrene), $CpMn(CO)_3$ [430]. This complex is relatively inert, but under the influence of ultraviolet light a variety of substituted derivatives, $CpMn(CO)_2L$, can be prepared. Using this technique amine, phosphine, arsine, etc., as well as olefin and acetylene complexes, have been obtained[441, 473]. Disubstituted compounds, $CpMn(CO)L_2$, are also known and kinetic data is available[441]. Photolysis of $CpMn(CO)_3$ with NaCN in methanol gives $Na^+[CpMn(CO)_2CN]^-$ and acidification of the anion with H_3PO_3 gives the isocyanic acid derivative $CpMn(CO)_2CNH$ [467].

Like chromium hexacarbonyl, $CpMn(CO)_3$ reacts with lithium alkyls to give the salts $Li[CpMn(CO)COR]$, R = Me or Ph, and treatment of the salts with diazomethane gives the carbene complexes, $CpMn(CO)_2C\{(OMe)R\}$ [502]. A rapid hydrogen–deuterium exchange of the C–CH_3 protons in the complex $MeC_5H_5Mn(CO)_2C(OMe)CH_3$ occurs in CH_3OD in the presence of catalytic amounts of CH_3ONa[467].

---

[500] H. Goldwhite, D. G. Rowsell and C. Valdez, *J. Organomet. Chem.* **12** (1968) 133.

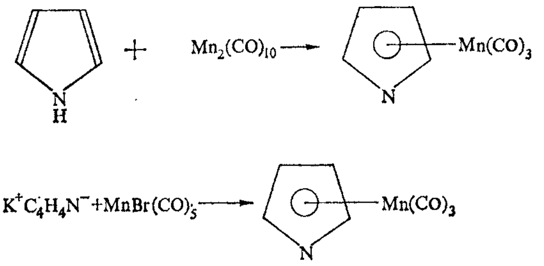
[501] L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.* **9** (1959) 86.

[502] E. O. Fischer and A. Maasböl, *Chem. Ber.* **100** (1967) 2445.

The bromination of $CpMn(CO)_3$ at room temperature gives $C_5H_5Br_5$, but no carbonyl-containing products are observed[467]. However, reaction of $CpMn(CO)_3$ with $SbCl_5$ gives an unstable red precipitate which may contain the paramagnetic ion $CpMn(CO)_3^+$ [473].

The cyclopentadienyl ring in $CpMn(CO)_3$ is susceptible to electrophilic attack and numerous organic derivatives of the compound are known. It is, however, less reactive towards Friedel–Crafts acylation than ferrocene[473].

π-Pyrrole complexes of manganese have been obtained by the reactions



Substituted derivatives are also known[503].

Arene Complexes

The pink bis-π-arene manganese(I) complex, $[Mn(C_6Me_6)_2]^+$, has been prepared by treating $MnPh_2$ with dimethylacetylene[488]. From this reaction the benzene complex $[C_6H_6MnC_6Me_6]PF_6$ has also been isolated[504]. The latter complex reacts with $LiAlH_4$ to yield the π-cyclohexadienyl complex π-C_6Me_6Mnπ-C_6H_7.

The reaction of phenylmagnesium bromide with Mn(π-$MeC_5H_4)_2$ gives the mixed complex π-MeC_5H_4Mnπ-C_6H_6 [505], and the complexes CpMnπ-C_6H_6, CpMnπ-biphenyl and CpMnπ-biphenylπ-MnCp have been synthesized[506]. Acylation of $CpMnC_6H_6$ gives the π-cycloheptatrienyl complexes [CpMnπ-$C_7H_6R]^+$ (R = Me or Ph) [506].

The reaction of benzene, toluene, mesitylene, hexamethylbenzene and naphthalene with $MnCl(CO)_5$ and aluminium trichloride gives the π-arene complex ions [Arene $Mn(CO)_3]^+$ [507]. The ion $C_6H_6Mn(CO)_3^+$ reacts with sodium borohydride to give the cyclohexadienyl complex $C_6H_7Mn(CO)_3$ and the latter complex is obtained in small yield from $Mn_2(CO)_{10}$ and cyclohexa-1,3-diene[507]. The hydride species $MnH(CO)_3$(π-1,3-C_6H_8) has also been isolated from the former reaction[430]. Lithium alkyls react with π-$C_6H_6Mn(CO)_3^+$ to give the *exo*-substituted cyclohexadienyl complexes π-$C_6H_6RMn(CO)_3$ [430].

Thiophene and substituted derivatives react with $MnCl(CO)_5$ in the presence of aluminium trichloride to give the heterocyclic complex ions (π-thiophene)$Mn(CO)_3^+$ [508].

Uses of Manganese Carbonyl and its Derivatives

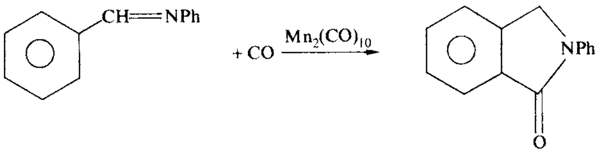
Manganese carbonyl and its derivatives can act as a source of carbon monoxide for various carbonylation reactions[429]. Thus dimethylamine is carbonylated by $Mn_2(CO)_{10}$,

$$3Mn_2(CO)_{10}+22Me_2NH \rightarrow 2[Mn(Me_2NH)_6][Mn(CO)_5]_2+10Me_2NCHO$$

---

[503] P. L. Pauson, A. R. Qazi and B. W. Rockett, *J. Organomet. Chem.* **7** (1967) 325.
[504] E. O. Fischer and M. W. Schmidt, *Chem. Ber.* **100** (1967) 3782.
[505] R. D. Closson, T. H. Coffield and V. Sandiel, *J. Am. Chem. Soc.* **79** (1957) 5826.
[506] S. Breitschaft and E. O. Fischer, *Chem. Ber.* **99** (1966) 2213.
[507] G. Winkhaus, L. Pratt and G. Wilkinson, *J. Chem. Soc.* (1961) 3807.
[508] H. Singer, *J. Organomet. Chem.* **9** (1967) 135.

The carbonylation reactions can also occur catalytically under high carbon monoxide pressure and temperature[429], e.g.



Both $Mn_2(CO)_{10}$ and $MnMe(CO)_5$ catalyse the carbonylation of primary aliphatic amines almost exclusively to 1,3-dialkylureas[509].

Manganese carbonyl can also act as an isomerization and polymerization catalyst. Thus $Mn_2(CO)_{10}$ can cause the isomerization of cyclo-octa-1,4(and 1,5)-diene into cyclo-octa-1,3-diene and $Mn_2(CO)_{10}$ and carbon tetrachloride initiate the free radical polymerization of vinyl compounds, e.g. methyl methacrylate[429]. There is, however, disagreement on the mechanism of this reaction[467].

Methylcyclopentadienylmanganese tricarbonyl has useful antiknock properties, and although it is sold primarily as an antiknock it is included in a number of antiknock mixes with tetraethyllead. Like the latter, the antiknock properties of the manganese compound are believed to result from its ability to stop chain-branching reactions which lead to knocking combustion[221].

MANGANESE BORANE AND CARBORANE COMPLEXES

A number of manganese borane and carborane complexes are known. Some of the former complexes are undoubtedly intermediates in the formation of manganese carbonyl hydrides from $Mn_2(CO)_{10}$ and sodium borohydride. The interaction of $MnBr(CO)_5$ with $Al(BH_4)_3$ yields the yellow liquid $Mn(BH_4)(CO)_5$ which decomposes rapidly at 25°C to yield $Mn_3(CO)_{10}(BH_3)_2H$ [485]. It seems likely that $Mn(BH_4)(CO)_5$ has a hydrogen bridged structure.

The chloro- and bromo-derivatives $2\text{-}ClB_5H_8$ and $2\text{-}BrB_5H_8$ react with $NaMn(CO)_5$ to generate the pentacarbonyls $2\text{-}[(CO)_5Mn]B_5H_8$ in which an essentially σ-bond between manganese and the 2-B atom is envisaged[467].

The salts $H_3BMn(CO)_5^-$ and $H_3BMn(CO)_4(PPh_3)^-$, which have been obtained from the appropriate anions and B_2H_6, are also thought to contain Mn–B σ-bonds[510].

The ligand $B_9C_2H_{11}^{2-}$, which resembles the π-bonding cyclopentadienyl ligand, forms a π-complex in its reaction with $MnBr(CO)_5$. In this reaction bromide is rapidly formed followed by a slow evolution of carbon monoxide[511]:

$$(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-} + MnBr(CO)_5 \rightarrow Br^- + [\sigma\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Mn(CO)_5^-$$
$$[\sigma\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Mn(CO)_5^- \rightarrow 2CO + [\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Mn(CO)_3^-$$

This π-bonded complex is very stable towards air oxidation and hydrolysis, and its structure is analogous to $CpMn(CO)_3$ [511].

---

[509] F. Calderazzo, *Inorg. Chem.* **4** (1965) 293.
[510] G. W. Parshall, *J. Am. Chem. Soc.* **86** (1964) 361.
[511] M. F. Hawthorne, *Acc. Chem. Res.* **1** (1968) 281.

The reaction of $MnBr(CO)_5$ with $B_7C_2H_{11}^{2-}$ gives an unidentified boron species and a compound $[B_6C_2H_8]Mn(CO)_3^-$ in which it is suggested that a tricapped trigonal prism is present[511]. A non-icosahedral complex π-$CH_3C_3B_3H_5Mn(CO)_3$ has also been described[512].

The π-complexes $Mn(B_{10}H_{10}CH)_2^{2-}$ and $(B_{10}H_{10}CH)Mn(CO)_3^{2-}$ are also known, and a sandwich complex has also been obtained from $B_{10}H_{12}CNH_3$ [513].

MANGANESE DINITROGEN COMPLEXES

The significance of manganese in a number of bacteria which fix nitrogen is not clear although it is possible that the metal is associated with the metabolism of hydrogen[514].

Nitrogen gas reacts with a mixture of $Mn(acac)_2$ and $Al(iso\text{-}Bu)_3$ to give a product which on hydrolysis gives ammonia[514], and a dinitrogen (N_2) complex of manganese is reported to be present in a 1:1 adduct formed between nitrogen gas and *N*,*N*-disalicylaldehyde-1,3-propanediiminemanganese(II) [515].

NITROSYL COMPOUNDS OF MANGANESE

Although unsubstituted manganese nitrosyl compounds are unknown, manganese nitrosyl bonds can be stabilized by cyanide, carbonyl, phosphine, organometallic, phthalocyanine, dithiolene and related ligands. It is in some of these complexes that the lowest formal oxidation states of manganese are observed, e.g. $Mn(NO)_3CO$. The nitrosyl cyanide complexes have already been discussed under cyanides. More detailed reviews on organometallic nitrosyls and on nitrosyls of manganese can be found in refs. 161 and 516.

Nitrosyl Carbonyls

Three unsubstituted nitrosyl carbonyl compounds of manganese are known: $Mn(NO)(CO)_4$, $Mn(NO)_3CO$ and $Mn_2(NO)_2(CO)_7$.

$Mn(NO)(CO)_4$, a red air-sensitive liquid, m.p. −1.5°C, is best made by the action of nitric oxide on $Mn_2(CO)_8(PPh_3)_2$. It has also been prepared by treating $MnH(CO)_5$ with *N*-methyl-*N*-nitroso-*p*-toluenesulphonamide in ether[161, 516].

The crystal structure of $Mn(NO)(CO)_4$ reveals that the compound has a trigonal bipyramidal shape with the nitrosyl group in an equatorial position[517]. Prior to this, structure determination infrared studies had suggested that the nitrosyl ligand was in an axial position[517].

$Mn(NO)_3(CO)$, a green crystalline solid, has been prepared by the reaction of nitric oxide with $MnI(CO)_5$ or $[MnI(CO)_4]_2$ at 100°C or by the action of nitric oxide on a solution of $Mn(NO)(CO)_4$ in boiling benzene. The infrared spectrum of $Mn(NO)_3CO$ suggests a distorted tetrahedral C_{3v} symmetry[161, 516].

---

[512] J. W. Howard and R. N. Grimes, *J. Am. Chem. Soc.* **91** (1969) 6499.

[513] D. E. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer and L. J. Todd, *J. Am. Chem. Soc.* **89** (1967) 3342; W. H. Knoth, *J. Am. Chem. Soc.* **89** (1967) 3342.

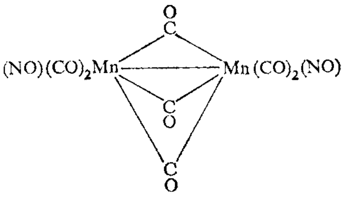
[514] R. Murray and D. C. Smith, *Coord. Chem. Revs.* **3** (1968) 429.

[515] G. L. Johnson and W. D. Beveridge, *Inorg. Nucl. Chem. Letters* **3** (1967) 323.

[516] B. F. G. Johnson and J. A. McCleverty, *Progress in Inorganic Chemistry* (edited by F. A. Cotton), Interscience, Vol. 7 (1966), p. 277.

[517] B. A. Frenz, J. H. Enemark and J. A. Ibers, *Inorg. Chem.* **8** (1969) 1288.

$Mn_2(NO)_2(CO)_7$, a purple solid, is obtained by irradiation of $Mn(NO)(CO)_4$ with ultraviolet light. The infrared spectrum suggests a structure similar to $Fe_2(CO)_9$ with bridging carbonyls and terminal nitrosyl and carbonyl ligands[161, 516]:



A number of substituted derivatives of $Mn(NO)(CO)_4$ are known of the type $Mn(NO)(CO)_3(PR_3)$ and $Mn(NO)(CO)_2(PR_3)_2$ [161, 518]. These complexes have been prepared either by the reaction of ligands with $Mn(NO)(CO)_4$ or by the action of nitric oxide on various substituted carbonyl compounds[441, 516, 518]. Substitution reactions of $Mn(NO)(CO)_4$ occur by a second-order process whereas replacement of carbon monoxide from $Mn(NO)(CO)_3L$ is largely a first-order reaction[518]. $Mn(NO)_3CO$ is very reactive, and the rate of substitution to form $Mn(NO)_3L$ derivatives depends on the nature and concentration of the reagent[518].

The crystal structures of both $MnNO(CO)_2(PPh_3)_2$ [519] and $MnNO(CO)_3(PPh_3)$ [520] reveal that the compounds have trigonal bipyramidal geometry. In the former the phosphine ligands have a *trans* configuration. In the latter the phosphine ligand is in an axial position, but it is not possible to differentiate between nitrosyl and carbonyl groups in this structure. However, infrared studies show that the nitrosyl ligand is in an equatorial position[520].

Nitrosyl Halides

Manganese nitrosyl halides of the type $MnX(NO)_2L_2$, where X is Cl, Br or I, and L is a phosphorus, arsenic or antimony donor ligands, are formed by the action of nitric oxide on the compounds $MnX(CO)_3L_2$ [516]:

$$MnX(CO)_3L_2 + 2NO \rightarrow MnX(NO)_2L_2$$

This type of compound is also formed by oxidation of $Mn(NO)(CO)_3(PPh_3)$ with iodine, bromine or cyanogen bromide to give the compounds $MnX(NO)_2(PPh_3)_2$, where X is Br, I or CN [516]. In these reactions a rearrangement of ligands occurs.

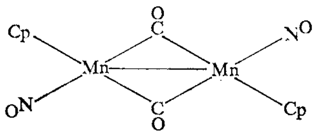
The compound $Mn(NO)Cl_3$ has been classified as a nitrosonium salt[516].

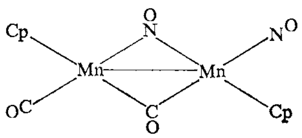
Cyclopentadienyl Nitrosyls

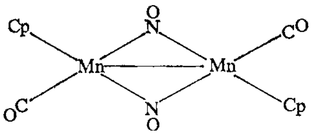
The action of nitrite and acid on $CpMn(CO)_3$ (where Cp is π-C_5H_5) gives the cationic species $CpMn(NO)(CO)_2^+$. This ion is also formed in low yield by the action of hot 3M HNO_3 on $CpMn(CO)_3$ [161, 516]. The ion reacts with sodium borohydride to give the dimer $[CpMn(NO)(CO)]_2$ [161]. Infrared data suggests that the product may have one of the following structures or possibly be an equilibrium mixture of the three forms:

---

[518] H. Wawersik and F. Basolo, *J. Am. Chem. Soc.* **89** (1967) 4626.
[519] J. H. Enemark and J. A. Ibers, *Inorg. Chem.* **6** (1967) 1575.
[520] J. H. Enemark and J. A. Ibers, *Inorg. Chem.* **7** (1968) 2339.





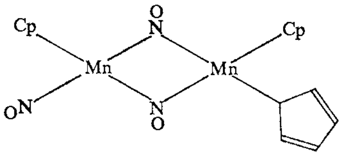


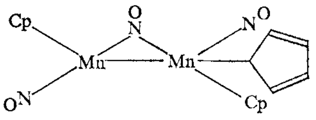
Irradiation of $[CpMn(NO)(CO)]_2$ in benzene with ultraviolet light gives a black diamagnetic compound which was formulated as $Cp_6Mn_6(NO)_8$. However, X-ray structural studies show that the formula is $Cp_3Mn_3(NO)_4$. The structure consists of a triangle of manganese atoms and a triply bridging nitrosyl group. Along each edge of the triangle there is a bridging nitrosyl ligand while a cyclopentadienyl ligand is bonded to each manganese atom[161].

Irradiation of a solution of sodium nitrite and $[CpMn(NO)(CO)_2]PF_6$ with ultraviolet light gives a black product of composition $[CpMn(NO)_2]_n$. The structure is unknown as is the value of n [161].

The action of sodium methoxide on $[CpMn(NO)(CO)_2]PF_6$ gives the alkoxycarbonyl derivative CpMn(CO·OMe)(NO)(CO) and treatment of the latter with MeMgBr gives the acetyl complex CpMn(COMe)(NO)(CO) [161].

The reaction of manganocene with nitric oxide gives $Cp_3Mn_2(NO)_3$. The n.m.r. spectrum suggests the presence of two types of cyclopentadienyl ring, and it has been suggested the compound has one of the two following structures:





$Cp_3Mn_2(NO)_3$ reacts with carbon disulphide to give the complex $[CpMn(NO)S_2]_n$. It probably has a structure similar to the Roussin red salts[161].

MANGANESE ISOCYANIDE COMPLEXES

Isocyanide complexes of manganese have recently been reviewed in detail, and complexes of manganese(0), manganese(I) and manganese(II) exist[521].

Manganese(0) Complexes

Only two isocyanide complexes of manganese(0) are known. These complexes, $Mn_2(CO)_9(CNPh)$ and $Mn_2(CO)_8(CNPh)_2$, were isolated in low yield from the reaction of either $MnCH_3(CO)_5$ or $MnPh(CO)_5$ with phenylisocyanide in tetrahydrofuran. The structures of these compounds are not known, but the infrared spectra suggest that both bridging

---

[521] L. Malatesta and F. Bonati, *Isocyanide Complexes of Metals*, Interscience (1969).

carbonyl and isocyanide ligands are absent. The compounds probably have a similar structure to $Mn_2(CO)_{10}$ and contain Mn–Mn bonds. The products derived from the methyl and phenyl groups in these reactions have not been identified[521].

Manganese(I) Complexes

Although isocyanides do not generally react with compounds of manganese(II) or manganese(III) in alcoholic solution, both alkyl and aryl isocyanides react with MnI_2 in ethanol to give manganese(I) isocyanide complexes:

$$2MnI_2 + 12RNC \rightarrow [Mn^I(CNR)_6]I + [Mn^I(CNR)_6]I_3$$

In this reaction the manganese(II) is reduced to manganese(I) and an iodide ligand is oxidized to iodine which separates out as the I_3^- anion. Thus both compounds $[Mn(CNR)_6]I$ and $[Mn(CNR)_6]I_3$ contain manganese(I) and are diamagnetic. Since in general the iodide is more soluble in ethanol than the tri-iodide the compounds are easily separated[521].

The treatment of the compounds $[Mn(CNR)_6]I$ with either an alcoholic suspension of silver oxide or with an ion-exchange resin yields the stable crystalline hydroxides $[Mn(CNR)_6]OH$. These compounds are strong bases and absorb carbon dioxide to give $[Mn(CNR)_6]HCO_3$. Chloroform solutions of the hydroxide are also able to extract Cl^-, Br^-, I^-, SCN^-, CrO_4^{2-}, MoO_4^{2-} and WO_4^{2-} from aqueous solution[521].

Either treatment of the hydroxide with acid or exchange reactions of the iodide give rise to many salts of the $[Mn(CNR)_6]^+$ ion. All these salts are stable to air both in the solid state and in solution. The salts are either colourless or pale yellow depending on whether R is an alkyl or aryl group. They are also all diamagnetic and behave as 1:1 electrolytes. Infrared data on these compounds is available[521].

Other manganese(I) isocyanide compounds have been obtained by reaction of isocyanides with either $Mn(CO)_3(\pi\text{-}C_5H_5)$ or the compounds $MnX(CO)_5$. With $Mn(CO)_3(\pi\text{-}C_5H_5)$, monosubstituted compounds $Mn(CO)_2(CNR)(\pi\text{-}C_5H_5)$ are usually formed, and the cyclohexyl isocyanide compound has also been obtained as follows:

$$Mn(CO)_2(py)(\pi\text{-}C_5H_5) + C_6H_{11}NC \rightarrow py + Mn(CO)_2(CNC_6H_{11})(\pi\text{-}C_5H_5)$$

Although direct substitution of all the carbonyl groups has not been achieved, the fully substituted compound has been obtained by the following reaction[521]:

$$[Mn(CNPh)_6]I + NaC_5H_5 \rightarrow NaI + 3PhNC + Mn(CNPh)_3(\pi\text{-}C_5H_5)$$

The course of the reaction of isocyanide with the compounds $MnX(CO)_5$ is dependent on the halide present, e.g.

$$\begin{aligned} MnCl(CO)_5 + 6PhNC &\rightarrow [Mn(CNPh)_6]Cl + 5CO \\ 2MnBr(CO)_5 + 9PhNC &\rightarrow MnBr(CO)(CNPh)_4 + MnBr(CNPh)_5 + 9CO \\ MnI(CO)_5 + 4PhNC &\rightarrow MnI(CO)(CNPh)_4 + 4CO \end{aligned}$$

Preparative and kinetic studies show that these substitution reactions are also dependent on the solvent used for the reaction[521].

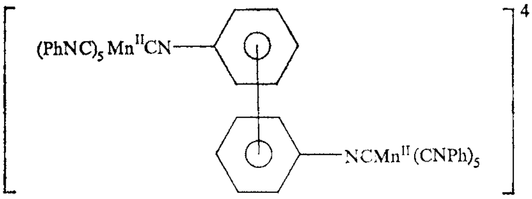
Manganese(II) Complexes

Salts of the ions $[Mn(CNR)_6]^{2+}$ have been obtained by oxidation of the corresponding manganese(I) complexes either electrolytically or with nitric acid or bromine. The complexes are stable for several months both in solution and in the solid state. They are soluble in methylene chloride, chloroform, acetone and acetic acid, but are only slightly soluble in ethanol and benzene. The alkyl isocyanide complexes are colourless, the aryl isocyanide complexes are blue–violet, and the vinyl isocyanide complex $[Mn(CNCH{=}CH_2)_6]CdBr_4$ is deep red[521].

The compounds are not attacked by strong mineral acids but are decomposed immediately by alkali. It has been suggested[521] that the equation for this decomposition is

$$13[Mn(CNR)_6]^{2+} + 14OH^- \rightarrow 12[Mn(CNR)_6]^+ + Mn(OH)_2 + 6RNCO + 6H_2O$$

The magnetic moments of the alkyl isocyanide complexes indicate that they are low-spin complexes with the presence of one unpaired electron. However, both the phenyl and vinyl isocyanide complexes have zero magnetic moments and it is suggested that these interesting complexes exist as diamagnetic dimers[522], e.g.



Paramagnetic contact shift experiments on the phenylisocyanide complex, also however, reveal that the diamagnetic dimer is in rapid equilibrium with a paramagnetic species[522].

Simple electron transfer occurs when solutions of the complexes $Mn(CNR)_6^+$ and $Mn(CNR)_6^{2+}$ are mixed (R = Et or *t*-Bu). However, on mixing solutions of manganese(I) and manganese(II) complexes (R = vinyl or Ph), the manganese(II) complexes link together and the situation whereby a manganese(II) and manganese(I) complex is joined is not observed[522].

MANGANESE PHTHALOCYANINE AND PORPHYRIN COMPLEXES

Manganese phthalocyanine and porphyrin complexes, which are structurally closely related to each other, are of interest since it is possible that similar complexes of manganese may be involved in certain biological oxidative processes, e.g. photosynthesis and the metabolism of human red blood cells[8, 523].

PHTHALOCYANINE COMPLEXES

Manganese metal reacts with either (*o*)-cyanobenzamide or phthalonitrile to give a product of unknown structure which can be sublimed to give manganese(II) phthalocyanine, (I) [524] (Fig. 4). The compound (I) also results when manganese(II) acetate is treated with phthalonitrile[524].

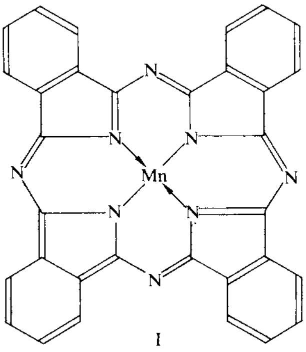
Manganese(II) phthalocyanine contains square planar coordinated manganese, and the lattice constants and space group of the complex have been determined[524]. Its density is

---

[522] D. S. Matteson and R. A. Bailey, *J. Am. Chem. Soc.* **91** (1969) 1975.

[523] J. A. Elvidge and A. B. P. Lever, *Proc. Chem. Soc.* (1969) 195.

[524] A. B. P. Lever, *Advances in Inorganic and Radiochemistry* (edited by H. J. Emeléus and A. G. Sharpe), Academic Press, Vol. 7 (1965), p. 27.



I

Manganese phthalocyanine

FIG. 4.

about 1.62 [525]. Magnetic susceptibility measurements indicate that the complex contains three unpaired electrons[524].

MnPc is demetallated in sulphuric acid and undergoes oxidation and reduction to give phthalocyanine complexes of manganese(IV), (III), (I) and (0). These different oxidation states have been largely characterized by absorption spectra and magnetic properties, and with this in mind it is noteworthy that a pyridine complex which was originally formulated as a manganese(IV) complex, MnPc(py)(O) (Pc = phthalocyanine, py = pyridine), is in fact an oxygen bridged complex of manganese(III), pyPcMn–O–MnPcpy [526].

Solutions of MnPc in methanol and ethanol undergo oxidation in the presence of air to give the octahedral manganese(III) complexes Mn(Pc)(OH)(ROH) (R = Me or Et). These latter complexes react with sodium chloride in the presence of a trace of hydrochloric acid to give the chloro-complexes Mn(Pc)(Cl)(ROH) which with pyridine give Mn(Pc)(Cl)(py) [524].

Solutions of MnPc in pyridine also undergo oxidation, but this reaction leads to a binuclear manganese–oxygen bridged complex. The product from this reaction was originally formulated as a manganese(IV) complex, Mn(Pc)(py)O [524]. However, an X-ray structure determination on this complex reveals that it is a manganese(III) complex, pyPcMn–O–MnPcpy [526], containing a linear Mn–O–Mn bridge.

Electronically the Mn–O–Mn bridge is analogous to the Ru–O–Ru bridge[527] in the diamagnetic complex $K_4[Ru_2OCl_{10}]$. Hence the diamagnetism of $(pyPcMn)_2O$ [528, 529] would be expected.

Attempts to detect the Mn–O–Mn stretching frequency, which would be expected[248] to occur around 850 cm^{-1}, have failed[529].

When the complex $(pyPcMn)_2O$ is boiled in pyridine, manganese(II) phthalocyanine is regenerated. It has been reported[524] that oxygen is also involved in this reaction, but further studies have not been able to detect this oxygen[8]. It seems likely that pyridine oxidation occurs rather than oxygen evolution[8].

The reformulation of the manganese(IV) phthalocyanine complex MnPc(Py)(O) as a manganese(III) complex $(MnPcPy)_2O$ has led to a revised scheme for the air oxidation of

---

[525] P. E. Fielding and N. C. Stephenson, *Australian J. Chem.* **18** (1965) 1691.

[526] L. H. Vogt, Jr., A. Zalkin and D. H. Templeton, *Inorg. Chem.* **6** (1967) 1725.

[527] W. P. Griffith, *The Chemistry of the Rarer Platinum Metals*, Interscience (1967), p. 134.

[528] G. Engelsma, A. Yamamoto, E. Markham and M. Calvin, *J. Phys. Chem.* **66** (1962) 2517.

[529] A. Yamamoto, L. K. Phillips and M. Calvin, *Inorg. Chem.* **7** (1968) 847.

pyridine solutions of MnPc [529]. It is considered that a dimerization of the intermediate manganese(III) complex MnPc(Py)(OH) occurs rather than an oxidation of this complex, i.e.

$$2\text{MnPc(py)}_2 \xrightleftharpoons[\substack{h\nu+\\ \text{oxidized}\\ \text{product}}]{\frac{1}{2}O_2+H_2O} 2\text{MnPc(py)(OH)} \xrightleftharpoons[+H_2O]{h\nu_2-H_2O} (\text{MnPcpy})_2\text{O}$$

It should be noted, however, that not all the observations are explained by this scheme[529].

When $(\text{MnPcpy})_2\text{O}$ is heated, pyridine is lost, and a polymeric oxymanganese(IV) complex is formed, (PcMnO) [524, 529]. A manganese(IV) phthalocyanine complex also results when manganese(II) formate is treated with 1,3-diiminoisoindoline. The structure of this complex is not known for certain but it is possibly MnPc(OH)_2 [524]. It reacts with alcoholic sodium hydroxide to give the *trans* dioxo complex $\text{Na}_2[\text{MnPcO}_2]$ whose magnetic behaviour is consistent with a manganese(IV) complex. This latter complex reacts with pyridine in the presence of air to give $(\text{MnPcpy})_2\text{O}$ [524].

MnPc reacts with sodium cyanide in ethanol to give Na[MnPc(CN)(EtOH)]. In the presence of air this reaction leads to the manganese(III) complex $\text{Na}_2[\text{MnPc(CN)}_2]$ [524]. MnPc also adds nitric oxide to give the mononitrosyl MnPcNO which in air gives an oxidation product which has tentatively been assigned the formula MnPc(NO)(OH) [530]. With pyridine, MnPcNO gives MnPc(NO)(py) [530].

Lower oxidation states of MnPc have been obtained by treating MnPc with either lithium benzophenone or lithium naphthalenide in tetrahydrofuran (THF). The reactions give LiMnPc·6THF, Li_2MnPc·6THF and Li_3MnPc·9THF [531].

A tetrasulphophthalocyanine complex of manganese(II) has been prepared. It is spin-paired in aqueous solution[532] in contrast to MnPc. Further information on manganese phthalocyanines can be found in ref. 524.

PORPHYRIN COMPLEXES

Porphyrin complexes of manganese(II), (III) and (IV) have been identified. In air the stable oxidation state of the manganese is +3 and the complexes can be oxidized to the (IV) state and reduced to the (II) state[8, 9, 528, 529]. The probable involvement of manganese in photosynthesis has led to extensive studies of both the photochemical and redox behaviour of these complexes, and a possible mechanism has been devised to account for the oxygen-evolving system in photosynthesis[9].

A number of halo(aquo)porphyrinmanganese(III) complexes (halo = F, Cl, Br, I) have been synthesized for a number of different porphyrins, and their infrared and electronic spectra have been investigated[532a].

The rates of reduction of manganese(III) tetrapyridylporphine with various reducing agents have been studied but it has not, as yet, been possible to give a detailed mechanism for the reductions[533].

[530] C. Ercolani and C. Neri, *J. Chem. Soc.* A (1967) 1715.
[531] R. Taube, *Chem. Zvesti* **19** (1965) 215.
[532] J. H. Weber and D. H. Busch, *Inorg. Chem.* **4** (1965) 469.
[532a] L. J. Boucher, *J. Am. Chem. Soc.* **92** (1970) 2725.
[533] P. Hambright and E. B. Fleischer, *Inorg. Chem.* **4** (1965) 912.

MANGANESE 1,2-DITHIOLENE COMPLEXES

Bistetraethylammonium bisdicyano-1,2-dithiolenemanganese $[Et_4N]_2[MnS_4C_4(CN)_4]$ is prepared by treating a mixture of $Et_4N \cdot Cl$ and $Na_2S_2C_2(CN)_2$ with $MnCl_2 \cdot 4H_2O$ under nitrogen[534]. This complex is difficult to purify, and meaningful conductivity and magnetic data have not been reported[534]. However, it seems likely that the manganese(II) ion is in a square planar configuration, and in view of this it is possible that bis-dithiolene manganese complexes, like the phthalocyanine complexes, could be useful model compounds for biological studies. It is known[534] that solutions of $[MnS_4C_4(CN)_4]^{2-}$ become bright red on exposure to air but the species present in solution have not be identified. However, a mononitrosyl species, $[Mn(NO)(S_4C_4(CN)_4]^{n-}$, is formed when solutions of the $Mn[S_4C_4(CN)_4]^{2-}$ are treated with nitric oxide[534].

In the presence of air and excess Mn^{2+} ions the reaction of $Na_2S_2C_2(CN)_2$ with $MnCl_2 \cdot 4H_2O$ yields the tris-dithiolene complex $[MnS_6C_6(CN)_6]^{2-}$ [534]. The bright red solutions obtained by air oxidation $[MnS_4C_4(CN)_4]^{2-}$ also yield the tris complex when treated with excess Mn^{2+} ions[534]. The magnetic properties of $[Ph_4P]_2[MnS_6C_6(CN)_6]$ are close to the spin-only value and are virtually independent of temperature and probably have orbital singlet ground states[534]. Voltammetric studies reveal that $[MnS_6C_6(CN)_6]^{2-}$ undergoes one-electron transfer reactions[534].

The action of $Na_2S_2C_2R_2$ on $MnCl(CO)_5$ gives the carbonyl complexes $[Mn(CO)_4(S_2C_2R_2)]^{-1}$ (R = CN or H) [535]. However, the reaction of toluene-3,4-dithiol with $MnBr(CO)_5$ yields the interesting paramagnetic monomer $Mn(CO)_3MeC_6H_3(SH)_2$ and diamagnetic dimer $[Mn(CO)_3S_2C_6H_3Me]_2$, and tentative structures for these complexes have been proposed[535].

Nitrosyl complexes of the type $[CpMn(NO)(S{-}S)]_n$ (where S–S represents $S_2C_2(CN)_2$, $S_2C_6Cl_4$ and $S_2C_6H_3Me$, and $n = 0$ or -1) have been described[536]. These complexes are interesting since they react with excess potassium ethoxide to give the bis-dithiolenes $[Mn(NO)(S{-}S)_2]^{2-}$ [536].

COMPLEXES OF MANGANESE

A number of the complexes of manganese, e.g. complex halides, cyanides, oxalates, thiocyanates, etc., have been reviewed in previous sections with the appropriate binary compounds. In the present section the remaining complexes of manganese(II), (III) and (IV) are discussed. Complexes of manganese(V), (VI) and (VIII) are only known in oxy-anions, and they have been reviewed in the section on oxides. Data on the electronic spectra of manganese complexes can be found in ref. 537.

Complexes of Manganese(II)

Manganese(II) forms many complexes in which the metal ion is usually octahedrally coordinated. Most of these complexes possess high spin $3d^5$ manganese(II), and hence contain no ligand field stabilization energy. This, together with the large size of Mn^{2+} as compared to the ions Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}, causes the stability constants[225] to be lower than those of the ions Fe^{2+} through to Cu^{2+}.

---

[534] M. Gerloch, J. Locke, J. A. McCleverty and E. J. Wharton, *J. Chem. Soc.* A (1968) 816.

[535] J. A. McCleverty, ***Progress in Inorganic Chemistry*** (edited by F. A. Cotton), Interscience, Vol. 10 (1968), p. 49.

[536] J. A. McCleverty, T. A. James and E. J. Wharton, ***Inorg. Chem.*** **8** (1969) 1340.

There are relatively few low spin manganese(II) complexes and they are only usually found in such complexes as $Mn(CN)_6^{4-}$ and $Mn(CNR)_6^{2+}$, etc.

In addition to the many octahedral complexes there are also a few 4-coordinate (square planar and tetrahedral), 5-coordinate, 7-coordinate and possibly 8-coordinate complexes known. In general, however, there is a lack of X-ray data to substantiate the structures of many of these complexes.

Tetrahedral manganese(II), which is found in some of the tetrahalo anions MnX_4^{2-} and also in neutral complexes such as $MnBr_2(Ph_3PO)_2$, is usually not stable in contact with water or other donor solvents. In less-polar solvents, however, the tetrahedral geometry can be preserved. The manganese(II) ion in a tetrahedral environment has a yellow–green colour which is far more intense than the pink colour of octahedral manganese(II) and the complexes usually exhibit intense yellow–green fluorescence. Use is made of this effect in fluorescent tubes where a small amount is added to the primary zinc phosphor, usually Zn_2SiO_4, wherein manganese(II) ions are substituted for some of the zirconium(II) ions in tetrahedral environments[221].

Nitrogen Donor Ligands

Manganese(II) halides react with gaseous ammonia to form the ammine complexes $[Mn(NH_3)_6]X_2$, where X = Cl, Br or I. Thermal dissociation of these complexes yields the adducts $MnX_2 \cdot nNH_3$ ($n = 4$, 2 and 1 when X = Cl, Br; and $n = 2$ when X = I) [399], and similar studies with manganese(II) sulphate give the adducts $MnSO_4 \cdot nNH_3$, where $n = 1$, 2, 4, 5 and 6[399]. The hexammine complexes $[Mn(NH_3)_6]X_2$ exhibit metal–nitrogen stretching frequencies at 307, 299 and 295 cm^{-1} for X = Cl, Br and I respectively[248]. Ammonia proton contact shift studies on the hexammine complex $[Mn(NH_3)_6][ClO_4]_2$ have been reported[538].

The action of hydrazine on $MnCl_2$ gives the adduct $MnCl_2(N_2H_4)_2$. Single crystal X-ray studies indicate that the compound contains chains of octahedral $MnCl_2(N_2H_4)_2$ units with bridging hydrazine ligands. The hydrazine ligands have a staggered conformation and the infrared spectrum of the compound has been examined[25]. Similar bromide, iodide, acetate and thiocyanate complexes are known[539]. When aqueous solutions of a manganese(II) salt and hydrazine hydrate are left in an open vessel, carbon dioxide is absorbed from the atmosphere and colourless crystals of a complex of hydrazincarboxylic acid, $Mn(NH_2NHCO_2)_2(N_2H_4)_2$, are formed[540]. This complex is isostructural with the corresponding zinc compound, and the X-ray structure of the latter reveals that the zinc is octahedrally coordinated with two *trans*-monodentate N_2H_4 ligands and two bidentate $NH_2NHCO_2^-$ ligands[540, 541].

The action of aniline and substituted anilines (e.g. (*o*)- (*m*)-, or (*p*)-toluidine) on manganese(II) halides gives the adducts MnX_2L_2 (X = Cl, Br or I; L = aniline or substituted aniline). Spectroscopic studies indicate that all these adducts are octahedral with bridging halogen atoms[25].

Many adducts of manganese(II) chloride, bromide and iodide with pyridine and substituted pyridines, e.g. quinoline and the picolines, are also known, and the spectroscopic properties and thermal decomposition of the adducts, which are generally quite similar to

[537] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier (1968).

[538] B. B. Wayland and W. L. Rice, *Inorg. Chem.* **6** (1967) 2270.

[539] A. Braibanti, F. Dallavalle, M. A. Pellinghelli and E. Leporati, *Inorg. Chem.* **7** (1968) 1430.

[540] A. Braibanti, G. Bigliardi, A. M. Manotti Lanfredi and A. Tiripicchio, *Nature* **211** (1966) 1174.

[541] A. Braibanti, G. Bigliardi and R. C. Padovani, *Gazz. chim. ital.* **95** (1965) 877.

each other, have been studied extensively[25]. The adducts $MnCl_2py_2$ and $MnCl_2py_4$ are readily obtained by the action of pyridine on $MnCl_2$ in the appropriate ratio. It has been suggested that the adduct $MnCl_2py_2$ is tetrahedral in chlorobenzene, but in the solid state it is definitely octahedral with bridging chlorine atoms[25]. $MnCl_2py_2$ decomposes thermally[25] as follows:

$$\begin{aligned} MnCl_2py_2 &\rightarrow MnCl_2py + py(g) \\ MnCl_2py &\rightarrow MnCl_2(2/3py) + 1/3py(g) \\ MnCl_2(2/3py) &\rightarrow MnCl_2 + 2/3py(g) \end{aligned}$$

Methyl cyanide and manganese(II) chloride or manganese(II) bromide react to give octahedral, halogen adducts of the type $MnX_2(MeCN)_2$, where X = Cl or Br[25]. However, manganese(II) iodide[25] gives $Mn(MeCN)_6^{2+}MnI_4^{2-}$ and acrylonitrile and propionitrile are reported to give the 1:1 adducts $MnCl_2$(nitrile) of unknown structure[542].

2,2′-dipyridyl reacts with manganese(II) salts to give the yellow tris complexes $[Mn(dipy)_3]^{2+}X_2$ [543, 544], which in water readily loose one molecule of dipyridyl to give the diaquo salt[543]. From the reaction of (*o*)-phenanthroline with $MnSO_4$ in water, a tetra (*o*)-phenanthroline complex $[Mn(o)\text{-}phen_4][ClO_4]_2\cdot 2H_2O$ may be obtained. The structure of this complex is not known, but there is infrared evidence to suggest that it contains 8-coordinate manganese. Heating the tetra complex *in vacuo* gives the tris complex $[Mn(o)\text{-}phen_3][ClO_4]_2$ [545]. The action of both these ligands on $MnCl_2$ in dimethylformamide give the adducts $MnCl_2L_2$, where L_2 = (*o*)-phen or dipy[546]. Electron spin resonance and other spectroscopic data suggest that the chloride and bromide adducts $MnX_2(o)\text{-}phen_2$ have a *cis* configuration and that the iodide has a *trans* geometry[20]. The dipyridyl complex $Mn(dipy)_3^{2+}$ is too unstable to allow measurements on its kinetics of formation and dissociation, but some data is available for the (*o*)-phenanthroline complex[547]. The infrared spectrum of the ion $Mn(dipy)_3^{2+}$ has been recorded but it is not possible to locate the position of ν(Mn–N) [548]. The reduction of $[Mn(dipy)_3]Br_2$ with Li_2(dipy) and Lidipy in tetrahydrofuran leads to the manganese(−1) and manganese(0) complexes $LiMn(dipy)_3\cdot 4THF$ and $Mn(dipy)_3$ respectively[549]. However, reduction with $LiAlH_4$ gives $Al(dipy)_3$ rather than the manganese(0) complex[550].

The 2,2′,2″ terpyridine complexes $[Mn(terpy)_2]Br_2$ and $MnCl_2$(terpy) are known[551, 552]. The latter complex contains 5-coordinated manganese[552]. Five-coordinated manganese(II) is also probably present in the adducts MnX_2L, where X = Cl or Br and L = bis(2-dimethyaminoethyl)methylamine [25, 553], and the enthalpies of formation of the 5-coordinate complexes $MnBr_2[MeN(CH_2CH_2NMe_2)_2]$ and $MnBr[N(CH_2CH_2NMe_2)_3]\cdot Br$ have been obtained[553].

---

[542] R. J. Kern, *J. Inorg. Nucl. Chem.* **25** (1963) 5.

[543] W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Revs.* **54** (1954) 959.

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

[545] A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.* **9** (1959) 211.

[546] J. A. Broomhead and F. P. Dwyer, *Australian J. Chem.* **14** (1961) 250.

[547] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle and R. G. Wilkins, *Inorg. Chem.* **4** (1965) 929.

[548] R. J. H. Clarke and C. S. Williams, *Spectrochim. Acta* **23A** (1967) 1055,

[549] S. Herzog and M. Schmidt, *Z. Chem.* **3** (1963) 392.

[550] S. Herzog and H. Praekel, *Z. Chem.* **5** (1965) 471.

[551] R. Hogg and R. G. Wilkins, *J. Chem. Soc.* (1962) 341.

[552] C. M. Harris, T. N. Lockyer and N. C. Stephenson, *Australian J. Chem.* **19** (1966) 1741.

[553] P. Paoletti and M. Ciampolini, *Inorg. Chem.* **6** (1967) 64.

The reaction of phthalimide with $MnCl_2 \cdot 4H_2O$ is reported to give manganese(II) phthalimide which reacts with aliphatic amines to give complexes of the type Mn(phthalimide)$(amine)_4$ [554].

Dimethylglyoxime reacts with Mn^{2+} to form the diaquo complex $Mn(DMG)_2(H_2O)_2$ [555].

The diethyl- and diphenylaminotroponimates of manganese(II), $Mn(Et_2ATI)_2$ and $Mn(Ph_2ATI)_2$, absorb oxygen both in solution and in the solid state[556].

Phosphorus and Arsenic Donor Ligands

The interaction of molten triphenylphosphine with manganese(II) halides is reported to give the high spin complexes $MnX_2(PPh_3)_2$, where X = Cl, Br or I, and these adducts may also be obtained using tetrahydrofuran as a solvent[557]. Later work, however, has cast doubt on the existence of the bromide, $MnBr_2(PPh_3)_2$ [558]. The structures of these complexes are not known but they may contain tetrahedral manganese(II). The corresponding triphenylarsine derivatives, $MnX_2(AsPh_3)_2$, are also high spin complexes and have been isolated from the halide and arsine in tetrahydrofuran as solvent[557]. Addition of iodine to a refluxing solution of $MnI_2(PPh_3)_2$ and triphenylphosphine in methylene chloride gives $[Mn(PPh_3)_4][I_3]_2$, and the triphenylarsine complex $[Mn(AsPh_3)_4][I_3]_2$ is reported to be formed in a similar reaction[557].

The bidentate arsine ligand *o*-phenylenebisdimethylarsine shows no tendency to coordinate to Mn^{2+} in water, methanol, ethanol or acetone as solvent. However, in dioxan the high spin complexes $MnX_2(diarsine)_2$, where X = Cl, Br or I, are formed[559].

A manganese(II) phosphide complex $K[Mn(PPh_2)_3] \cdot 2THF$ results when manganese(II) chloride or bromide is treated with $KPPh_2 \cdot 2$-dioxan in tetrahydrofuran. Recrystallization of the complex from dioxan gives $K_2[Mn(PPh_2)_4]$ and $Mn(PPh_2)_2$. The derivative $Li[Mn(PR_3)_3]$ (R = cyclohexyl) is also known[560].

Oxygen Donor Ligands

In aqueous solution the manganese(II) ion is present as the hexa-aquo species $Mn(H_2O)_6^{2+}$ [350], and ^{17}O n.m.r. and other studies reveal that there is rapid exchange between free and coordinated water[350, 561]. An infrared study of $[Mn(H_2O)_6][SiF_6]$ has been carried out and force constants have been determined[562]. The $Mn(H_2O)_6^{2+}$ ion is stable in neutral or acid solution, but in basic media $Mn(OH)_2$ is precipitated and oxidation occurs if air is present.

The manganese(II) ion forms a large number of complexes with alcohols such as methanol, ethanol, propanol and glycerol (see refs. 25 and 559), and in many cases crystalline adducts may be obtained, e.g. $MnCl_2 \cdot MeOH$, $MnCl_2 \cdot 2MeOH$, $MnCl_2 \cdot 3MeOH$ and $MnCl_2 \cdot 4MeOH$. Crystalline hexa-ethanol salts $Mn(EtOH)_6 \cdot X_2$ ($X = ClO_4^-$ and BF_4^-) have

---

[554] G. Narain and P. Shukla, *Australian J. Chem.* **20** (1967) 227.
[555] K. Burger and I. Ruff, *Talanta* **10** (1963) 329.
[556] D. R. Eaton, W. R. McClellan and J. F. Weiher, *Inorg. Chem.* **7** (1968) 2040.
[557] L. Naldini, *Chem. Abs.* **56** (1962) 13783b; *Gazz. chim. ital.* **90** (1960) 1337.
[558] D. Negoiu and C. Furlani, *Chem. Abs.* **60** (1964) 9933a.
[559] R. S. Nyholm and G. J. Sutton, *J. Chem. Soc.* (1958) 564.
[560] K. Issleib, E. Wenschuh and H. O. Freohlich, *Z. Naturforsch.* **176** (1962) 778.
[561] T. R. Stengle and C. H. Langford, *Coord. Chem. Revs.* **2** (1967) 349.
[562] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta* **20** (1964) 429.

been prepared[563] by a novel method in which ethyl orthoformate acts as a dehydrating agent.

$$Mn(H_2O)_6 \cdot X_2 + 6HC(OEt)_3 \rightarrow Mn(EtOH)_6 \cdot X_2 + 6HCO_2Et + 6EtOH$$

As would be expected, ethers coordinate less strongly and manganese(II) only forms an unstable etherate with diethy ether[350]. However, more stable complexes are formed with dioxan[559], e.g. $MnCl_2 \cdot$dioxan and $MnBr_2 \cdot 2$dioxan, which contain octahedral manganese(II) [564].

Many oxygen-bonded complexes of manganese have been prepared with various sulphoxides[25, 565, 566], diphenylselenoxide[567], dimethylformamide[568], *N*,*N*-dimethylacetamide[569], pyridine *N*-oxide[350], and dimethyl urea[570]. The complexes have usually been characterized by a variety of physical techniques. The stoichiometry of the adducts can vary and usually depends on the type of manganese compound used in the reaction. With $[Mn(H_2O)_6][ClO_4]_2$ an octahedral adduct containing the ion MnL_6^{2+} is usually formed, but with manganese(II) halides, adducts such as $MnCl_2 \cdot 3DMSO$ and $MnBr_2 \cdot 2DMSO$ are obtained (DMSO = dimethylsulphoxide). The structure of the latter complex is unknown but the former is $[Mn(DMSO)_6][MnCl_4]$ [565].

$(CH_3)_3NO$, C_5H_5NO, Ph_3PO and PH_3AsO give the tetrahedral adducts $MnBr_2L_2$ [25, 350], and the manganese(II) ion is 5-coordinate in the complex $(Ph_2MeAsO)_4Mn(ClO_4)_2$ [412].

Bis(2,4-pentanedionato) manganese(II) dihydrate, $Mn(acac)_2 \cdot 2H_2O$, is readily prepared in aqueous solution and can be dehydrated to the anhydrous compound $Mn(acac)_2$ by heating *in vacuo*[571]. The hydrate appears to be susceptible to air oxidation, but the anhydrous compound is more stable. However, some of the other β-ketoenol complexes of manganese(II), e.g. $Mn(CF_3COCHCOCF_3)_2 \cdot 2H_2O$, are not oxygen sensitive. $Mn(acac)_2$ is trimeric in hydrocarbon solvents, but its exact structure—like that of other bis(-β-diketonato) manganese(II) compounds—is not known. In the vapour state it is monomeric and probably tetrahedral. Appearance potential measurements of $Mn(acac)_2$ give a Mn–O bond energy of about 65 kcal mole^{-1} [572]. $Mn(acac)_2$ adds two molecules of a donor ligand, e.g. ammonia, pyridine, (*o*)-phenanthroline to give octahedral complexes $Mn(acac)_2 \cdot L_2$. Some of these adducts readily dissociate in solution and the bis(2-methylpyridine) adduct aquates rapidly in moist air[571]. 1:1 adducts $Mn(acac)_2 \cdot L$ also exist, but their structures are not known[571]. Addition of $MnCl_2 \cdot 4H_2O$ to acetylacetone and sodium hydroxide gives the complex $Na[Mn(acac)_3]$ [571]. Sublimation of the salt $Et_4N[Mn(dpm)_2Cl]$ (dpm = dipivaloylmethanido, $Me_3CCOCHCOCMe_3$), which is possibly 5-coordinate, gives the neutral compound $Mn(Me_3COCHCOCMe_3)_2$ which is monomeric and possibly tetrahedral[573]. Addition of tropolone to a solution of manganese(II) acetate gives $Mn(C_7H_5O_2)_2$, which appears to be polymeric[574].

---

[563] P. W. N. M. van Leeuwen, *Rec. Trav. Chim.* **86** (1967) 247.

[564] G. W. A. Fowles, D. A. Rice and R. A. Walton, *J. Chem. Soc.* (1968) 1842.

[565] B. F. G. Johnson and R. A. Walton, *Spectrochim. Acta* **22** (1966) 1853.

[566] P. W. N. M. van Leeuwen and W. L. Groeneveld, *Rec. Trav. Chim.* **86** (1967) 721.

[567] R. Paetzold and P. Vordank, *Z. anorg. allgem. Chem.* **347** (1966) 294.

[568] W. E. Bull, S. K. Madan and J. E. Willis, *Inorg. Chem.* **2** (1963) 303.

[569] W. Schneider, *Helv. Chim. Acta* **46** (1963) 1842.

[570] B. C. Stonestreet, W. E. Bull and R. J. Williams, *J. Inorg. Nucl. Chem.* **28** (1966) 1895.

[571] J. P. Fackler, Jr., *Progress in Inorganic Chemistry* (edited by F. A. Cotton), Interscience, Vol. 7 (1966), p. 361.

[572] C. Reichert and J. B. Westmore, *Inorg. Chem.* **8** (1969) 1012.

[573] D. H. Gerlach and R. H. Holm, *Inorg. Chem.* **8** (1969) 2292.

The anion of picolinic acid *N*-oxide gives the yellow complex $Mn[(C_5H_4CO_2^-)NO]_2\cdot 2H_2O$ [350], and dipyridyl *N,N'*-dioxide also gives an octahedral complex ion, $Mn(dipyO_2)_3^{2+}$ [350].

Manganese(II) bromide reacts with phenanthrenequinone and chrysenequinone to give black or violet complexes of the type $MnBr_2[(o)\text{-quinone}]$ of unknown structure[350].

Metathesis of anhydrous $MnCl_2$ with LiOMe in methanol gives $Mn(OMe)_2$ [575]. Reflectance spectra and magnetic measurements suggest that the compound is polymeric with an MnO_6 octahedra. Other alkoxides of manganese(II) are also known[132].

Bidentate (O–N) Donors

Manganese(II) gives the complexes $Mn(oxine)_2\cdot 2H_2O$ and $Mn(oxine)_2$ with 8-hydroxyquinoline. The former complex is presumably octahedral, but the structure of $Mn(oxine)_2$ is not known although it has been considered to be square planar[576]. The thermal dissociations of the complexes have been investigated[577]. In addition to $Mn(oxine)_2$ an adduct $Mn(oxine)_2\cdot 2oxine\text{-}H$ has also been described which is possibly 8-coordinate[578].

A number of Schiff base complexes of manganese(II) exist and many of these complexes are sensitive to air oxidation[579]. Bis(*N*-methylsalicylaldimine) manganese(II) has been shown to exist as a dimer in the solid state in which the manganese is bound to three oxygen and two nitrogen atoms to give a distorted trigonal bipyramidal geometry[580]. The magnetic properties of *N,N'*-ethylenebis(salicyldeneiminato) manganese(II), $Mn(salen)_2$ and substituted derivatives have been studied over a temperature range. These measurements, together with X-ray powder data, suggest that these complexes are also dimeric and that there is antiferromagnetic exchange[581]. Some of these Schiff base adducts crystallize with a molecule of solvent, e.g. Mn(5 chlorosalen)·EtOH, and it is possible that these complexes contain 5-coordinate spin-free manganese(II) in the solid state[581]. If Mn(salen) is wet with an organic solvent it is readily oxidized in air to a product of stoichiometry, Mn(salen)OH. However, since this complex exhibits appreciable antiferromagnetic interaction it has been suggested that it may be better formulated as $[Mn(salen)]_2O\cdot H_2O$ [581]. Attempts to obtain a mononitrosyl adduct of Mn(salen) also lead to an oxidized product, Mn(salen)OAc [582]. In general the properties of the Schiff base and *β*-ketoamine complexes of manganese have not been studied extensively. However, the recent observation that *N,N*-disalicylaldehyde-1,3-propanediiminemanganese(II) can apparently add N_2, O_2, CO and SO_2 reversibly[515] suggests that further studies on these complexes could be very interesting.

The reaction of solid $MnCO_3$ with ethylenediaminetetra-acetic acid, H_4Y, proceeds according to the equation

$$3MnCO_3+2H_4Y \rightarrow Mn_3(HY)_2+3H_2O+3CO_2$$

and from the solution $Mn_3(HY)_2\cdot 10H_2O$ can be crystallized[583]. This compound contains

---

[574] E. L. Muetterties, H. Roeskey and C. M. Wright, *J. Am. Chem. Soc.* **88** (1966) 4856.

[575] R. W. Adams, E. Bishop, R. L. Martin and G. Winter, *Australian J. Chem.* **19** (1966) 207.

[576] J. E. Tackett and D. T. Sawyer, *Inorg. Chem.* **3** (1964) 692.

[577] W. W. Wendlandt and G. R. Horton, *Anal. Chem.* **34** (1962) 1098.

[578] Yu. A. Bankovskii, A. F. Ievin'sh, M. R. Buka and E. A. Luksha, *Zh. Neorg. Khim.* **8** (1963) 110.

[579] R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progress in Inorganic Chemistry* (edited by F. A. Cotton), Interscience, Vol. 7 (1966), p. 83.

[580] L. Sacconi, *Coord. Chem. Revs.* **1** (1966) 192.

[581] J. Lewis, F. E. Mabbs and H. Weigold, *J. Chem. Soc.* (1968) 1699.

[582] A. Earnshaw, E. A. King and L. F. Larkworthy, *J. Chem. Soc.* (1968) 1048.

[583] S. Richards, B. Pederson, J. V. Silverton and J. L. Hoard, *Inorg. Chem.* **3** (1964) 27.

7-coordinate ions, $Mn(H_2O)Y^{2-}$ (NbF_7^{2-} geometry), in addition to octahedrally coordinated manganese. The $Mn(H_2O)Y^{2-}$ ions are linked together by very strong hydrogen bonds[583].

The complexes MnPG, $MnPG_2^-$ and $MnP_2G_2^{2-}$ (P^- = pyruvate and G^- = glycinate) are formed in solution, and their stability constants have been determined[584]. Adducts of glycine and $MnCl_2$ are also known[25].

Sulphur Donor Ligands

Bis-(*N*,*N*-diethyldithiocarbamate)manganese(II), $Mn(S_2CNEt_2)$, forms as a bright yellow complex when NaS_2CNEt_2 is added to an aqueous solution of manganese(II) chloride. The compound is pyrophoric and is very sensitive to traces of oxygen. It is probably 5-coordinate since it is isomorphous with $Cu(S_2CNEt_2)_2$ [585]. The action of sodium diethyldithiocarbamate on the manganese(II) ion in the presence of air gives the manganese(III) complex $Mn(S_2CNEt_2)_3$ [350]. Other manganese(II) dithiocarbamate complexes are known[350], and some of these are not as oxygen-sensitive as $Mn(S_2CNEt_2)_2$. The complex (ethylenebis-dithiocarbamato)manganese(II) (common name maneb) is used as a fungicide[221]. $Mn(S_2CNEt_2)_2$ and the related complexes of diethydithiophosphate and butylxanthate do not apparently give e.s.r. signals[586]. The anion of the phosphorus monothio acid $(EtO)_2POS^-$ also coordinates to manganese(II) [587].

(*o*)-Aminobenzenethiol gives the complex $Mn(NH_2C_6H_4S)_2$ which is probably polymeric and octahedral with sulphur bridges[588]. In addition to $Mn(thiooxine)_2$ an adduct, $Mn(C_9H_6NS)_2 \cdot 2C_9H_6NSH$, has been described which possibly contains 8-coordinate manganese(II) [578].

Manganese(II) chloride reacts readily with thiourea to give $MnCl_2[S{=}C(NH_2)_2]_4$ which probably has a *trans*-octahedral structure[25]. However, the action of thiourea on the complexes MnX_2py_2 gives the adducts $MnX_2py_2tu_4$ (X = Cl or Br; tu = thiourea), which possibly contain 8-coordinate manganese(II) [589].

Passage of hydrogen chloride and hydrogen sulphide through a solution of $MnCl_2$ and acetylacetone gives 3,5-dimethyldithiolium tetrachloromanganate(II) instead of the complex $Mn(C_5H_7S_2)_2Cl_4$ as previously reported[25].

Complexes of Manganese(III)

The majority of manganese(III) complexes are octahedral and high spin. Very few low-spin octahedral complexes are known, and they appear to be restricted to the species $Mn(CN)_6^{3-}$ and the dimethylaminotroponiminato complex, $Mn(Me_2ATI)_3$ [556]. The $MnCl_5^{2-}$ anion in the salt $[DipyH_2][MnCl_5]$ contains 5-coordinate manganese(III) with a square-based pyramidal arrangement of chloride ligands[300].

Some of the interest in high spin octahedral manganese(III) complexes results from the possibility that they might be distorted due to the so-called Jahn–Teller effect. X-ray studies on tris(acetyacetonato)manganese(III) reveal that all the Mn–O bond lengths are identical, and it is suggested that an angular distortion is used to remove the degeneracy. However,

---

[584] D. L. Leussing and D. C. Shultz, *J. Am. Chem. Soc.* **86** (1964) 4846.

[585] J. P. Fackler, Jr. and D. G. Holah, *Inorg. Nucl. Chem. Letters* **2** (1966) 251.

[586] N. S. Garif'yanov, S. E. Kamenev, B. M. Kozyrev and I. V. Ovchinnikov, *Chem. Abs.* **68** (1968) 82425h.

[587] M. I. Kabachnik, T. A. Mastryukova, E. I. Matrosov and B. Fisher, *Zh. Strukt. Khim.* **6** (1965) 691.

[588] L. F. Larkworthy, J. M. Murphy and D. J. Phillips, *Inorg. Chem.* **7** (1968) 1436.

[589] K. C. Dash and D. V. R. Rao, *Z. anorg. allgem. Chem.* **350** (1967) 207.

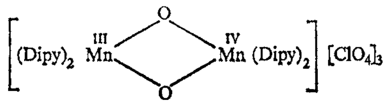
acetylacetonatobis-(*N*-phenylaminotroponiminato) manganese(III) is distorted and possesses four short and two long bonds[588].

The chemistry of manganese(III) in aqueous solution has been reviewed[300]. Complex halides and oxalates, etc., have been discussed in previous sections.

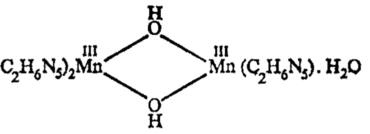
Nitrogen Donor Ligands

Manganese(III) chloride reacts with amines and other similar ligands to give moisture-sensitive adducts such as $MnCl_3 \cdot 3NH_3$, $MnCl_3 \cdot 3RNH_2$, $MnCl_3 \cdot 2NH_2CH_2CH_2NH_2$, $MnCl_3 \cdot py$ and $MnCl_3 \cdot 3py$. 2,2′-dipyridyl and (*o*)-phenanthroline give water-soluble adducts of the type $MnCl_3 \cdot dipy$ and $MnCl_3 \cdot (o)$-phen [25], which are possibly dimeric. The somewhat similar complexes $MnCl_3(dipy)(H_2O)$ and $MnCl_3\{(o)\text{-phen}\}(H_2O)$ are formed when 2,2′-dipyridyl or (*o*)-phenanthroline in hydrochloric acid are added to the brown solution obtained from $KMnO_4$ and hydrochloric acid[591]. Addition of these ligands to the purple solution prepared by treating a suspension of MnO_2 in carbon tetrachloride with hydrogen chloride gas gives the complexes $MnCl_3 \cdot dipy$ and $MnCl_3 \cdot (o)$-phen which may be dimeric since they have anomalously low magnetic moments[591].

A fluoro complex, $MnF_3\{(o)\text{-phen}\}(H_2O)$, has been obtained by addition of (*o*)-phenanthroline to Mn_2O_3 in 40% HF [591]. Oxidation of $[Mn^{II}(dipy)_3][ClO_4]_2$ with persulphate leads to the interesting binuclear complex which appears to contain manganese(III) and manganese(IV) [592].



A somewhat similar complex results when a mixture of $MnSO_4$ and a strongly alkaline solution of biguanide sulphate is oxidized by a current of air[593]. This complex, however, is formulated with hydroxy bridges and two manganese(III) ions:



Ethylenedibiguanide gives dark red crystals of $[Mn(OH)(H_2O)\{C_2H_4(C_2H_5N_5)\}] \cdot 0.5H_2O$ [593] and the reaction of biguanide with $Mn(acac)_3$ results in the hydroxy complex $Mn(OH)(H_2O)(acac)(bigu)$ [594]. Air oxidation of $Mn(acac)_2\{(o)\text{-phen}\}$ gives a manganese(III) complex $(Mn^{III}O_2)_3acac_3(o)$-phen of unknown structure[595].

Arsenic Donor Ligands

No tertiary phosphine complexes of manganese(III) exist but the high spin complexes of (*o*)-phenylenebis(dimethyl)arsine, $[MnX_2(diars)(H_2O)][ClO_4]$, X = Cl or Br, have been obtained via $Mn(OAc)_3$ [559].

[590] M. Bartlett and G. J. Palenik, *Chem. Communs.* (1970) 416.

[591] H. A. Goodwin and R. N. Sylva, *Australian J. Chem.* **18** (1965) 1743; **20** (1967) 629.

[592] R. S. Nyholm and A. Turco, *J. Chem. Soc.* (1962) 1121.

[593] P. Ray, *Chem. Revs.* **61** (1961) 313.

[594] M. M. Ray, J. N. Adhya, D. Biswas and S. N. Poddar, *Australian J. Chem.* **19** (1966) 881, 1737.

[595] D. P. Graddon and G. M. Mockler, *Australian J. Chem.* **17** (1964) 1119.

Oxygen Donor Ligands

The hydrated manganese(III) ion is oxidizing and unstable with respect to manganese(II) and manganese(IV). However, aqueous solutions of manganese(III) can be stabilized by increasing the acidity or increasing the concentration of manganese(II), and these solutions have been studied in some detail[300]. The spectrum of the aquomanganese(III) ion in perchlorate media shows that the solution contains the hexa-aquo ion and the hydroxypenta-aquo ion[417] and the addition of primary alcohols to hydrated manganese(III) ions gives alcoholaquomanganese(III) complexes[596].

Addition of dimethylsulphoxide or dimethylformamide to $Mn(OAc)_3 \cdot 2H_2O$ gives the octahedral complex ions $Mn(DMSO)_6^{3+}$ and $Mn(DMF)_6^{3+}$ [597]. Octahedral complexes have also been isolated with dipyridyl *N,N'*-dioxide[592] and the anion of picolinic acid *N*-oxide[350].

$Mn(acac)_3$ is readily prepared by oxidation of manganese(II) by potassium permanganate in the presence of acetylacetone. The complex is a dark black–brown material which is less stable thermally than the corresponding complexes of chromium(III), iron(III) or cobalt(III). A number of other β-ketoenolate complexes are known, and the ease by which the complexes of manganese(III) can be prepared by oxidation decreases with increase of acidity of the β-diketone[571]. An X-ray study on $Mn(acac)_3$ reveals that all the Mn–O bond lengths are equal, and it has been suggested that an angular distortion is used to remove the degeneracy[571, 590]. The standard heat of formation of $Mn(acac)_3$ is -332.1 ± 0.7 kcal $mole^{-1}$ and the Mn–O heterolytic and homolytic bond energies are 246 and 44 kcal $mole^{-1}$ respectively[598]. The reaction of thiocyanogen with $Mn(acac)_3$ results in cleavage of the Mn–O bonds to give 3-thiocyanato-2,4-pentanedione[599].

$Mn(acac)_3$ resembles the tris-oxalato and tris-malonato manganese(III) complexes in as much that one of the bidentate ligands may be reversibly replaced by two water molecules[350] and the complexes $[Mn(acac)_2(H_2O)_2][ClO_4] \cdot 2.5H_2O$ and $MnCl(acac)_2 \cdot 3H_2O$ have been isolated via the aqueous solution. Mixed chloro complexes, $MnCl_2acac$ and $MnCl(acac)_2$, have also been prepared using $MnCl_3$ [25].

The dialkyl and diaryl aminotroponimate complexes $Mn(acac)_2(N–N)$ and $Mn(acac)(N–N)_2$ have been prepared from $Mn(acac)_3$ [556]. The acetylacetonatobis-(*N*-phenylaminotroponiminato) manganese(III) complex is distorted with four short and two long bonds[590].

Chloroform, methanol and other alcohols hydrogen bond to $Mn(acac)_3$ and greatly affect the visible spectrum of the complex[571].

The addition of tetrahydrofuran to $MnCl_3$ under various conditions gives the adducts $MnCl_3 \cdot 4THF$ and $MnCl_3 \cdot 2THF$ which are unstable at room temperature[25]. Tropolone reacts with manganese(III) acetate to give tris(tropolonato)manganese(III) [119].

Bidentate (O–N) Donors

Picolinic acid and 8-hydroxyquinoline displace acetyacetone from $Mn(acac)_3$ to give the complexes $Mn(oxine)_3$ and $Mn(pic)_3$ [594].

Ethylenediaminetetraacetic acid (EDTA), hydroxyethylethylenediaminetriacetic acid (HEDTA), and *trans*-1,2-diaminocyclohexanetetraacetic acid (CyDTA) coordinate to

---

[596] C. F. Wells and C. Barnes, *J. Chem. Soc.* (1968) 1626.
[597] C. P. Prabhakaran and C. C. Patel, *J. Inorg. Nucl. Chem.* **30** (1968) 867.
[598] J. O. Hill and R. J. Irving, *J. Chem. Soc.* (1968) 3116.
[599] D. N. Sen and N. Thankarajan, *Indian J. Chem.* **4** (1966) 94.

manganese(III) to give the complexes KMn(EDTA)·2.5H_2O, KMn(HEDTA)·2.5H_2O and KMn(CyDTA)·2.5H_2O [600]. The complexes are reasonably stable in the crystalline state and decompose only slowly in aqueous solution. These complexes may contain 7-coordinate manganese(III), but as yet their structures are unknown. All three complexes are equally good oxidizing agents and the reaction of the CyDTA complex with oxalate has been studied[600]. Azide reacts with KMn(EDTA)·2.5H_2O to give a complex which may be 7-coordinate, $K_2[Mn(EDTA)(N_3)]\cdot H_2O$, and in solution it decomposes by an electron transfer step to N_2 and $Mn^{II}(EDTA)(OH_2)^{2-}$ [600]. Electron transfer between $Mn(CyDTA)^-$ and $Mn(EDTA)^{2-}$ and $Mn(CyDTA)^-$ and other complexes has been studied[601].

Certain Schiff base complexes of manganese(II) are oxidized by air to complexes such as Mn(salen)OH which are probably better formulated as $[Mn(salen)]_2O\cdot H_2O$ [581, 582].

Manganese(III) complexes of triethanolamine, diethanolaminemonoacetic acid, ethanolaminediacetic acid and nitriloacetic acid are known[336, 350].

Sulphur Donor Ligands

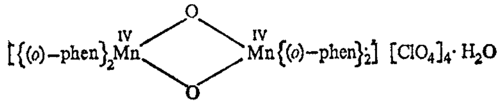
The manganese(II) ion is readily oxidized by air in the presence of $Na_2S_2C_2(CN)_2$ or sodium diethyldithiocarbamate to give $Mn[S_2C_2(CN)_2]^{3-}$ and $Mn(dtc)_3$ [350, 535].

Manganese(IV) Complexes

Most manganese(IV) complexes possess octahedral geometries. Tetrahedral manganese(IV) is probably present in 12-tungstomanganic(IV) acid, and its salts, e.g. $2K_2O\cdot MnO_2\cdot 12WO_3\cdot 20H_2O$ [350]. The 9-molybdomanganate(IV) anion $[MnMo_9O_{32}]^{6-}$, however, contains a trigonally distorted MnO_6 octahedron, and the spectrum of the heteropoly-12-niobomanganate(IV) anion suggests that the trigonal distortion in the niobate is even more pronounced[602]. Complex fluorides, chlorides, oxalates periodates, and other complexes of manganese(IV) have been discussed in previous sections.

Addition of dipyridyl to the brown solution prepared from $KMnO_4$ and hydrochloric acid leads to the high-spin complex $MnCl_4$dipy. The complex slowly looses chlorine at room temperature, and when heated to about 150–155°C the manganese(III) complex $MnCl_3$dipy results. Higher temperatures give a pale yellow product which is probably $MnCl_2$dipy [591].

Perchloric acid and $MnCl_3(H_2O)$\{(*o*)-phen\} react to give a complex of stoichiometry $[MnO\{(o)\text{-phen}\}_2][ClO_4]_2 0.5H_2O$. The antiferromagnetic nature of the complex[591] suggests that it may possibly have a structure such as



This species is similar to the hydroxy bridged biguanide manganese(III) complex[593] and the oxy bridged dipyridyl Mn(III)–Mn(IV) complex[592], but since the structures of none of these complexes is known with any certainty, the relationship between them is not clear.

Dihydroxybis(biguanide) manganese(IV) dihydroxide, $[Mn(OH)_2(C_2H_7N_5)_2][OH]_2$, is reported to be formed as dark red crystals by the action of $KMnO_4$ on biguanide sulphate,

---

[600] R. E. Hamm and M. A. Suwyn, *Inorg. Chem.* 6 (1967) 139, 142, 2150.
[601] R. G. Wilkins and R. E. Yelin, *Inorg. Chem.* 7 (1968) 2667.
[602] B. W. Dale, J. M. Buckley and M. T. Pope, *J. Chem. Soc.* A (1969) 301.

and similar complexes of ethylenedibiguanide and hexamethylenedibiguanide are known[593]. These complexes also have low magnetic moment at room temperature and may be dimeric with either oxy or hydroxy bridges.

In alkaline solution the manganese(II) formaldoxime complex $[Mn(CH_2NO)_6]^{2-}$ is oxidized by air to the manganese(IV) complex, $Mn(R_3)_2^{2-}$, where R is the trimeric form of formaldoxime[603].

Manganese(IV) is stabilized by tellurate ligands in the complexes, $Na_7H_7Mn(TeO_6)_3 \cdot 5H_2O$ and $K_6H_8Mn(TeO_6)_3 \cdot 5H_2O$ [604]. The complexes are not very stable in solution and decompose mainly as follows:

$$H_7Mn(TeO_6)_3^{7-} + H_2O \rightarrow H_4Mn(TeO_6)_2^{4-} + H_4TeO_6^{2-} + OH^-$$

It has been reported[605] that $Mn(dtc)_3$ (dtc = diethyldithiocarbamato) is oxidized slowly in air to $Mn(dtc)_4$, but the nature of this species is not known.

Some odd glycerol complexes of manganese(IV) such as $Na_2Mn(C_3H_5O_3)_2$ are also known[606].

---

[603] M. Bartusek and A. Okac, *Collection Czechoslav. Communs.* **26** (1961) 883, 2174.

[604] M. W. Lister and Y. Yoshino, *Can. J. Chem.* **40** (1962) 1490.

[605] Y. I. Usatenko and N. P. Fedash, *Chem. Abs.* **59** (1963) 13397g.

[606] P. Pascal, *Nouveau Traité de Chimie Minérale* (edited by P. Pascal), Masson et Cie, Vol. 15 (1960), p. 676.

38. TECHNETIUM

R. D. PEACOCK
The University, Leicester

1. DISCOVERY, ISOLATION AND GENERAL PROPERTIES

1.1. DISCOVERY AND ISOLATION

At the time of the discovery of rhenium in 1925 claims were also made for the discovery of element 43, but subsequent work has shown that these must be incorrect. In 1937 Perrier and Segré[1] identified some radiations from a molybdenum plate which had been bombarded with deuterons as being due to isotopes of the missing element. Later they suggested the name "technetium" for the element from the Greek word meaning artificial, since it was the first new element to be prepared artificially[1]. The first isotopes isolated were

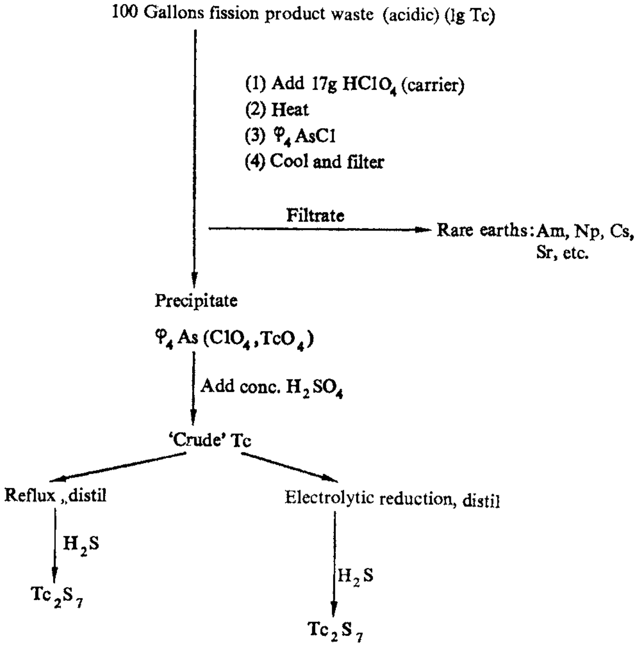


FIG. 1. Extraction of technetium from fission product waste. (G. W. Parker and W. J. Martin, Unclassified Document, ORNL 1116 (1952) **26** (see also G. E. Boyd, *J. Chem. Educ*. **36** (1959) 4.)

---

[1] C. Perrier and E. Segré, *J. Chem. Phys*. **5** (1937) 712; *Nature*, **159** (1947) 24.

TABLE 1. ISOTOPES OF TECHNETIUM*

Isotope	Preparation	Half-life†	Decay	Reference
^{92}Tc	Mo (p, n)	^{92m}Tc 4.3 m	β^+, EC, γ	a
	Mo (d, $2n$)			
^{93}Tc	Mo (d, n)	^{93m}Tc 43.5 m	i.t., EC, γ	a
	Mo (d, n)	^{93}Tc 2.7 h	EC, β^+, γ	
	Mo (p, γ)			
^{94}Tc	Mo (d, $2n$)	^{94m}Tc 52.5 m	β^+, i.t., EC, γ	a, b
	Nb (α, $3n$)			c
	Mo (p, n)	^{94}Tc 293 m	EC, β^+, γ	d
	Mo (d, $2n$)			
	^{94}Ru $\xrightarrow{\beta^+}$ Nb (α, $3n$)			c
^{95}Tc	Mo (d, $2n$)	^{95m}Tc 60 d	i.t., EC, γ	e, f, g
	Mo (d, $2n$)	^{95}Tc 20 h	EC, γ	a, f
^{96}Tc	Mo (p, n)	^{96m}Tc 52 m	i.t., γ	
	Mo (d, $2n$)			
	Nb (α, n)	^{96}Tc 4.3 d	EC, γ	f, g, h
	Mo (d, $2n$)			
	Mo (d, n)			
	Mo (p, n)			
	Ru (n, p)			
^{97}Tc	Mo (d, $2n$)	^{97m}Tc 90.5 d	EC, γ	f
	Mo (p, n)			
	Mo (d, n)			
	Ru (EC)			
	Mo (d, $2n$)	^{97}Tc 2.6×10^6 y	EC	f, i
	^{97m}Tc (i.t.)			
^{98}Tc	Ru (n, p)	^{98}Tc 1.5×10^6 y	β^-, γ	i, j
	Mo (p, n)			
	Mo (d, n)			
^{99}Tc	^{99}Mo $\xrightarrow{\beta^-}$ Ru (n, p)	^{99m}Tc 6.0 h	i.t., γ	j
	Th (φ)			
	U(φ)Mo $\xrightarrow{\beta}$ Tc (i.t.)	^{99}Tc 2.12×10^5 y	β^-	k
	^{99}Mo $\xrightarrow{\beta^-}$			
^{100}Tc	Mo (n, p)	15.8 s	β^-, γ	l, m
	U (φ) Mo $\xrightarrow{\beta^-}$			
	Tc (n, γ)			
	^{103}Ru (n, α)			
^{101}Tc	Mo (d, n)	14.3 m	β^-, γ	m, n, o
	Ru (γ, p)			
	U (φ) Mo $\xrightarrow{\beta^-}$			
	Ru (n, np)			
	U (d, φ)			
^{102}Tc	Ru (n, p)	4.5 m	β^-, γ	n
	U (d, φ)	(5 s)	(β^-)	
^{103}Tc	Ru (n, np)	50 s	β^-, γ	b, n, o
	U (φ)			
^{104}Tc	Mo (d, xn)	18 m	β^-, γ	b, q
	Ru (d, xn)			
	Mo (d, αxn)			
	^{104}Ru (n, p)			
	U (φ) Mo $\xrightarrow{\beta^-}$			

TABLE 1—(*cont.*)

Isotope	Preparation	Half-life†	Decay	Reference
^{105}Tc	U (φ)	7.7 m	β^-, γ	r
	U (φ) Mo $\xrightarrow{\beta^-}$	(10 m)		
^{106}Tc	U (φ)	37 s	(β^-)	
^{107}Tc	U (φ)	29 s	(β^-)	

* Adapted, with modifications, from C. O. Lederer, J. Hollander and I. Perlman, *Table of Isotopes*, 6th edn., Wiley (1967).

† s, seconds; m, minutes; h, hours; d, days; y, years.

[a] G. B. Vingiani *et al.*, *Nuovo Cimento* **23** (10) (1962) 729.

[b] P. Kienk *et al.*, *Z. Physik* **176** (1963) 226.

[c] I. M. Mauszer and T. T. Sugihara, *Nucl. Phys.* **42** (1963) 582.

[d] S. Monaro *et al.*, *Nuovo Cimento*, **28** (10) (1962) 33.

[e] G. Chioliro and P. Ricci, *Nuovo Cimento* **19** (10) (1961) 1121.

[f] I. P. Unik and J. O. Rasmussen, *Phys. Rev.* **115** (1959) 1687.

[g] B. S. Dzhelepov *et al.*, *Izvest. Akad. Nauk. SSSR Sev. Fiz.* **17** (1963) 172.

[h] S. Monaro *et al.*, *Physica*, **28** (1962) 52.

[i] S. Katcoff, *Phys. Rev.* **111** (1958) 575.

[j] G. E. Boyd *et al.*, *Phys. Rev.* **99** (1955) 1030.

[k] R. P. Sullivan, *Natl. Nucl. Energy Ser.*, Div. IV, **9** (1951) 783.

[l] G. E. Boyd and Q. V. Larson, *J. Phys. Chem.* **60** (1956) 707.

[m] J. Csikai *et al.*, *Nucl. Phys.* **41** (1963) 316.

[n] J. Flegenheimer and D. Geithoff, *Z. Naturforsch.* **12a** (1957) 351.

[o] J. Flegenheimer and W. Sulmann-Eggebert, *Z. Naturforsch.* **11a** (1956) 678.

[p] P. Kienk *et al.*, *Radiochim. Acta* **1** (1963) 84.

[q] P. Kienk *et al.*, *Naturwissenschaften* **49** (1962) 294.

[r] J. Flegenheimer *et al.*, *Naturforsch.* **10a** (1955) 708.

^{95}Tc and ^{98}Tc, which had respective half-lives of 60 and 90 days (Table 1), and the long lived isotope, ^{99}Tc, on which most of the chemistry is based, was isolated soon afterwards[2].

Before long it was realized that with the possible exception of ^{98}Tc the isotopes were all too short-lived for any remaining primordial technetium to be detectable on the earth. The half-life of this isotope remained unknown for some time, and claims were made for its detection in nature. Subsequently it was shown that ^{98}Tc has a half-life of about 10^6 years, and it has been concluded that the existence of primordial technetium is very unlikely. Natural technetium, formed by the spontaneous fission of uranium, has, however, been identified and isolated.

The spectral lines of technetium have been observed in certain stars (*S* class and *N* class)[3]; the discovery of the element in the stars has influenced theories of element synthesis and of stellar evolution.

Although the first weighable amounts of technetium were produced by the neutron irradation of molybdenum, this method is unsuitable for the production of large amounts of the element, and the chief source is from uranium fission products—about 6% of the total yield of fission products is technetium. The technetium follows the majority of the other fission products into the waste solutions during the recycling of the irradiated fuel—after storage for several years the level of radioactivity in the waste solutions has fallen sufficiently (because of the decay of the short-lived fission products) to allow the extraction of the longer-lived fission products, including technetium. In Fig. 1 the process adopted for

---

[2] G. T. Seaborg and E. Segrè, *Phys. Rev.* **55** (1939) 808.

[3] P. W. Merrill, *Astrophys. J.* **116** (1952) 21; *Pub. Astron. Soc. Pacific* **68** (1956) 70.

the isolation of the first gramme of the element is indicated[4]. Solvent extraction and ion exchange procedures are presently used in the extraction of technetium, and several kilograms of the element are produced each year. At the present rate of formation of technetium in nuclear power stations it has been estimated that it will not be long before the amount of the element available to man will exceed that of rhenium.

A number of reviews and books on technetium and its chemistry have appeared in recent years[5–9]; frequent reference will be made to these.

Technetium metal has been obtained by the hydrogen reduction of the heptasulphide at 1100° and by the hydrogen reduction of ammonium pertechnetate[4, 8]; the latter method gives a pure product (cf. Chapter 39, Rhenium). More recently, the metal has been obtained by heating $(NH_4)_2TcCl_6$ to red heat[10], and it is evident that a number of the methods applicable to rhenium may be used, *mutatis mutandem*, for technetium, provided the necessary safety precautions are strictly adhered to (p. 884). The element has also been electroplated from solution by electrolysis of a solution of ammonium pertechnetate in 1 M sulphuric acid[10].

TABLE 2. PHYSICAL PROPERTIES OF TECHNETIUM

Property	Value	Reference
Melting point	2250±50°	a
Boiling point	(4700° est.)	
Density	11.50 g/cm³	b
Atomic weight (^{99}Tc)	98.913 (mass spectrographic)	c
	98.8±0.1 (chemical)	d
Ionization potential	7.28 eV	e
Entropy of crystal	7.4±0.2 e.u.	f
of gas (298°K)	43.3 e.u.	g
Magnetic moment (nuclear magnetons)	5.6572	h
Magnetic susceptibility	270×10^{-6} cgs units	i
Metallic radius (12-coordination)	1.358 Å	j
Critical temperature (super conducting)	7.7°K	k
Electronic description of ground state	$4s^2\ 4p^6\ 4d^6\ 5s^1$ (S 9/2)	l

[a] E. Anderson, R. E. Buckley, A. Hellawell and W. Hume-Rothery, *Nature* **188** (1960) 48.
[b] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY (1960) p. 403.
[c] H. G. Inghram, D. C. Hess and R. J. Hayden, *Phys. Rev.* **72** (1947) 1269.
[d] J. W. Cobble, *J. Am. Chem. Soc.* **74** (1952) 1952.
[e] C. E. Moore, *Atomic Energy Levels*, Vol. III, NBS Circular 467 (1958).
[f] G. E. Boyd. *J. Chem. Ed.* **36** (1959) 3.
[g] J. .W Cobble *et al.*, *J. Am. Chem. Soc.* **76** (1953) 5777.
[h] *Chemists Handbook*, Vol. 1, Goskhimizdat, Moscow–Leningrad (1962).
[i] C. M. Nelson, G. E. Boyd and W. T. Smith, *J. Am. Chem. Soc.* **76** (1954) 348.
[j] R. E. L. Mooney, *Phys. Rev.* **72** (1947) 1269; *Acta Cryst.* **1** (1948) 161.
[k] C. C. Koch and G. R. Love, *J. Less-Common Metals* **12** (1967) 79.
[l] D. O. van Ostenberg *et al.*, *Phys. Rev.* **126** (1962) 938.

---

[4] J. W. Cobble, C. N. Nelson, G. W. Parker, W. T. Smith Jr. and G. E. Boyd, *J. Am. Chem. Soc.* **74** (1952) 1852.
[5] R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier (1966) p. 8.
[6] R. Colton, *The Chemistry of Rhenium and Technetium*, Interscience (1965) p. 6 *et seq.*
[7] K. V. Kotegov, O. N. Pavolv and V. P. Shvedov, *Adv. Inorg. and Radiochem.* **11** (1968) 1.
[8] G. E. Boyd, *J. Chem. Ed.* **36** (1959) 3.
[9] K. Schwochau, *Angew. Chem.* **79** (1964) 9.
[10] J. D. Eakins and D. G. Humphries, *J. Inorg. Nuclear Chem.* **25** (1963) 737.

1.2. ISOTOPES

The principal isotopes are listed in Table 1, together with methods of preparation. The short-lived isotopes of greatest practical importance are ^{95m}Tc (60 days), ^{97m}Tc (90.5 days) and ^{99m}Tc (6 hr)[7]. Of the long-lived isotopes, only ^{99}Tc is readily available, and the chemistry refers to this element. A full account of the nuclear chemistry of Tc has been given[7].

1.3. PHYSICAL AND CHEMICAL PROPERTIES

The physical properties of the element are displayed in Table 2. Technetium is a bright silvery-grey metal which is said to tarnish in a moist atmosphere[6]. It crystallizes in a hexagonal close-packed arrangement with the metal atoms in twelve-coordination (cf. Chapters 36 and 43, Molybdenum and Ruthenium). The element, like rhenium, is weakly paramagnetic.

Massive technetium is resistant to oxidation, but in sponge or powder form it burns readily to the volatile heptaoxide. The sponge dissolves in nitric acid (dilute and concentrated) and in concentrated sulphuric acid, but not in hydrochloric acid. Technetium also dissolves in neutral or acid 5% hydrogen peroxide but does not appear to dissolve in ammoniacal hydrogen peroxide. The rate of solution depends on the past history of the metal. In all cases the element is oxidized to the colourless pertechnetate ion.

TABLE 3. ION EXCHANGE SEPARATIONS OF TECHNETIUM FROM MOLYBDENUM AND RHENIUM

Separation	Resin (and form)	Eluent	Efficiency	Reference
TcO_4^- from MoO_4^{2-} (0.5 M HCl)	Dowex-1 Anion (Cl^-)	(a) Mo in 1 M HCl (b) Tc in 4 M HNO_3	Quantitative	a
TcO_4^- from MoO_4^{2-} (weakly alkaline)	Amberlite IRA-400 (ClO_4^-)	(a) Mo in 10% NaOH (b) Tc in 0.5 M NH_4CNS	Quantitative	b
TcO_4^- from ReO_4^- (neutral)	Dowex-1 (ClO_4^-)	0.2 M $HClO_4$	Poor	c
TcO_4^- from ReO_4^- (neutral)	Dowex-2 (SO_4^{2-})	(a) Re in 0.1M $(NH_4)_2SO_4+NH_4CNS$ in NaOH; pH 8.3 (b) Tc by increasing salts to 1 M	Moderate	d
TcO_4^- from ReO_4^- (1 M HCl)	Amberlite IRA-400 (Cl^-)	(a) Re with 5% NH_4CNS (b) Tc with 4 M HNO_3	Quantitative	e

[a] E. H. Huffman, R. L. Oswalt and L. A. Williams, *J. Inorg. Nucl. Chem.* **3** (1956) 49.
[b] N. F. Hall and D. H. Johns, *J. Am. Chem. Soc.* **75** (1953) 5787.
[c] R. V. Sen Sarma, E. Anders and J. Miller, *J. Phys. Chem.* **63** (1951) 559.
[d] R. W. Atterbury and G. E. Boyd, *J. Am. Chem. Soc.* **72** (1950) 4805.
[e] M. Pirs and R. J. Magee, *Talanta* **8** (1961) 395.

Technetium burns in fluorine to a mixture of the penta- and hexafluorides. At one time the element was thought to be nearly inert towards chlorine, but more recently it has been shown that reaction does take place with the formation of the tetrachloride and other chlorine-containing compounds. Sulphur combines at elevated temperatures to give the disulphide, and carbon to give a carbide, TcC.

1.4. ANALYTICAL CHEMISTRY

1.4.1. Separation

Technetium, like rhenium, may be precipitated from hydrochloric acid solution as sulphide, and the early workers therefore used rhenium as a carrier[1]. It was discovered that technetium could be separated from rhenium by distillation from sulphuric acid in a stream of hydrogen chloride; the rhenium distilled (presumably as ReO_3Cl) but the technetium did not (presumably owing to reduction). In the presence of an oxidizing agent it has since been shown that technetium may also be distilled from sulphuric acid[11].

Much of the progress in the analytical chemistry of technetium has been closely linked with the separation procedures used in its isolation; the chief techniques have included ion exchange, solvent extraction and electrical methods. The conventional ion exchange techniques are illustrated in Table 3. Ion exchange paper chromatography has also been used to separate TcO_4^- from $TcCl_6^{2-}$ and Tc(V) species in dilute hydrochloric acid[12].

Most of the solvent exchange processes involve pertechnetate, although more recently the extraction of ions in lower valence states has been studied. Pertechnetate may be efficiently extracted by pyridine from alkaline ($NaOH/Na_2CO_3$) solutions[13] and from potassium carbonate solutions by methyl ethyl ketone[13]. Tetraphenylarsonium pertechnetate has been extracted from alkaline solutions by chloroform[14]. The extraction of pertechnetate from acid solutions into alcohols, esters, ketones, ethers, amines and hydrocarbons has been extensively investigated[15]; that the extracted species is the TcO_4^- ion was shown by the characteristic absorption at 2875 Å, both in the aqueous and organic phases. The presence of a basic oxygen or nitrogen in the organic solvent and the possession by the extracting solvent of an appreciable dielectric constant were shown to be essential conditions for efficient extraction; various other correlations were also noted[15]. More recently the extraction of quaternary ammonium salts of neutral and alkaline pertechnetate by benzene and chloroform has been studied[16].

Chloride complexes of Tc(V) in 12 M hydrochloric acid have been partially extracted ($E_\alpha{}^\circ$ 3) into 0.1 M trioctylphosphine oxide, into cyclohexane, but not into ether[17]. The hexachlorotechnetate(IV) ion, $TcCl_6^{2-}$, may be extracted efficiently from 6 M hydrochloric acid by trioctylphosphine oxide in cyclohexane[17].

Technetium has been separated from both molybdenum and rhenium by electrolysis at a controlled potential[18], and paper electrophoresis has been used to separate the same three elements[19]. Methods of separating technetium have recently been reviewed in detail[7].

1.4.2. Determination of Technetium

Methods include determination from radioactivity, gravimetric, colorimetric, spectrophotometric, polarographic and mass-spectrometric methods, neutron activation and X-ray fluorescence.

---

[11] M. Koyama, *Bull. Chem. Soc. Japan*, **34** (1961) 1766.

[12] S. K. Shukla, *J. Chromatog.* **20** (1965) 580.

[13] S. J. Rimshaw and G. F. Malling, *Anal. Chem.* **33** (1961) 751.

[14] S. Tribalat and J. Beydon, *Anal. Chem. Acta* **8** (1953) 22.

[15] G. E. Boyd and Q. V. Larson, *Unclassified Document* ORNL 2386 (1957) 26; *Unclassified Document* ORNL 2384 (1958) 5; *J. Chem. Phys.* **64** (1960) 988.

[16] R. Shanker, K. S. Venkateswarlu and J. Shankar, *J. Less-Common Metals*, **15** (1968) 311.

[17] G. E. Boyd and Q. V. Larson, *Unclassified Document* ORNL 2782 (1959) 12.

[18] L. B. Rogers, *J. Am. Chem. Soc.* **71** (1949) 1507.

[19] R. A. C. de Carvallo, *Proc. Intern. Conf. Peaceful Uses Atomic Energy*, **28** (1956) 97.

Early methods for the determination of technetium were based upon the radioactivity of ^{99}Tc[1]. The method is sensitive as the specific activity of ^{99}Tc is 37,800 disintegrations/min μg (16.8 μC/mg). However, the β-particles have only low energy ($E_{\max} = 0.29$ MeV) and errors arise due to self-absorption, reflection from the substrate, etc., and counting techniques are now used as a method of detection rather than determination. An ordinary end-window counter with a micro window can detect about 0.1 μg of ^{99}Tc [8]; for the short-lived isotopes ^{99m}Tc, ^{95m}Tc and ^{97m}Tc the sensitivity reaches approximately 10^{-16} g [20].

Gravimetric methods are similar to those used for rhenium, and are not specific. Technetium may be estimated as tetraphenylarsonium pertechnetate[21], nitron pertechnetate[22] and, perhaps less satisfactorily, as the sulphide Tc_2S_7[23]. Tetraphenylarsonium pertechnetate has been precipitated and weighed on the micro-scale[24]. Tetraphenylarsonium and nitron pertechnetate are more soluble than their rhenium analogues.

The simplest spectrophotometric method is to measure the characteristic peaks of the pertechnetate ion at 2460 Å and 1890 Å ($\varepsilon = 6220$ and 2360 respectively)[25]. Rhenium, which absorbs at 2350 Å in perrhenate, does not interfere, and the method may be used to determine the elements simultaneously.

Other spectrophotometric or colorimetric methods depend upon the formation of a coloured complex, usually with the technetium in a lower valency state. Reagents include thiocyanate[26], thio-compounds such as toluene–3,4-dithiol[27], thioglycollic acid[28], thiourea[29] and thiocresol[29], α-furildioxime[30], potassium ferricyanide[31], sulphosalicylic acid[31], α-picolinic acid[31] and diphenyl carbohydrazide[32]. Several spot-reagents have also been proposed[29], of which the reaction of pertechnetate with potassium ethylxanthate appears to be promising. A number of these colorimetric reagents have also been used for the determination of rhenium.

The existence of several oxidation states of technetium has made it possible to use a polarographic method for its quantitative determination[8, 33].

A mass-spectrometric method of determining ^{97}Tc, ^{98}Tc and ^{99}Tc has been developed by Boyd[8], and neutron activation analysis has been used in an effort to detect naturally occurring ^{98}Tc [34]. The X-ray fluorescence technique has been used; it is claimed that 4γ of the element can be detected[35].

---

[20] See ref. 7, p. 71.

[21] G. W. Parker and W. J. Martin, *Unclassified Document*, ORNL 820; S. Tribalat, *Anal. Chim. Acta* **6** (1952) 96.

[22] C. Perrier and E. Segré, *J. Chem. Phys.* 7 (1939) 155.

[23] C. L. Rulfs and W. W. Meinke, *J. Am. Chem. Soc.* 7 (1952) 235.

[24] F. Jasin *et al.*, *Mikrochim. Acta*, Nos. 5–6 (1950) 721.

[25] J. Wolkowitz, *Unclassified Document*, ORNL 1880; G. E. Boyd and Q. V. Larson, *J. Phys. Chem.* **60** (1956) 707.

[26] O. H. Howard and C. W. Weber, *Anal. Chem.* **34** (1962) 530.

[27] F. J. Miller and P. F. Thompson, *Anal. Chem.* **33** (1961) 404.

[28] F. J. Miller and P. F. Thompson, *Anal. Chem.* **32** (1960) 1429.

[29] F. Jasin, R. J. Magee and C. L. Wilson, *Talanta* **2** (1959) 93.

[30] R. Colton and H. Morley, *UKAEA Document AERE-R*3746 (1961); ref. 6, p. 27; A. F. Kuzina, *Zh. Anal. Khim.* **17** (1962) 489.

[31] M. Al-Kayssi *et al.*, *Talanta* **9** (1962) 125.

[32] F. J. Miller and H. E. Zittol, *Anal. Chem.* **34** (1962) 1349.

[33] R. Colton, J. Dalziel, W. P. Griffith and G. Wilkinson, *J. Chem. Soc.* (1960) 71.

[34] E. Alperovitch and J. M. Miller, *Nature*, **176** (1955) 299.

[35] F. Lux, F. Ammentorp-Schmidt and W. Opavsky, *Z. anorg. und allgem. Chem.* **341** (1965) 172.

1.5. SAFETY, HEALTH HAZARDS, BIOLOGICAL ACTIVITY

The handling of technetium (^{99}Tc) on a small scale (< 0.05 g) does not present a serious health hazard provided some elementary precautions are taken. The weak β emission ($\beta_{max} = 0.3$ MeV) is effectively stopped by glass and there is no associated γ-radiation, but with larger amounts of the element the secondary X-rays may become important. A well-ventilated fume cupboard, an effective means of monitoring the working area and strict precautions against loss of the element or its compounds by volatility, dust or spray, are essential requirements. Intending workers should consult the appropriate publications of the International Atomic Agency; in Great Britain safety regulations are included in a Ministry of Labour Code[36].

The physiological effects of technetium have been little studied[37], but it appears that, although injected technetium is eliminated relatively quickly from most organs, the greater concentration in the thyroid gland (13–24% of the activity introduced) may lead to damage from the β-radiation. Data are not available on the chemical toxicity of technetium compounds.

1.6. USES

It is possible, using the isotope ^{99}Tc, to prepare standard sources of β-radiation with an energy of 0.292 MeV[38]; because of the long half-life of the isotope these are practically invariant. The ^{99m}Tc isomer has been used for the study of the chemical and physical state of the isotope on the radioactive decay constant[7]. This isotope has also found applications in medicine, since the energy of its γ-radiation (140 keV) may be satisfactorily collimated by diagnostic apparatus, making it possible to localize damaged tissue in the body exactly[39, 40]. The use of technetium for controlling the burn-up of fuel in nuclear reactors has been proposed[9].

In addition to radiochemical and nuclear uses dependent on the nuclear properties of the element, the normal and chemical properties also have actual or potential value, though their application must be limited, not only by the radiochemical properties, but also by the high cost of the element (a nominal £35 per g). It has been established that ammonium pertechnetate is a good corrosion inhibitor[41], even in negligibly small concentrations (about 5×10^{-5} M). The element and its molybdenum alloys have promising superconducting properties (critical temperature up to at least 13.4°K)[42].

1.7. ALLOYS AND INTERMETALLIC COMPOUNDS

Considerable interest has been shown in part because of the possible superconducting properties mentioned above (especially Mo–Tc, Zr–Tc and Nb–Tc), but also on account of anti-corrosion properties and possible uses in nuclear power engineering and in catalytic processes.

---

[36] *Code of Practice for the Protection of Persons Exposed to Ionizing Radiation in Research and Teaching*, HMSO, London (1964).

[37] Ref. 7, p. 84, and references therein.

[38] N. Matsura and H. Yumoto, *Radioisotopes* (*Tokyo*), **8** (1959) 32.

[39] K. E. Sheer and W. Maier-Borst, *Nucl.-Med.* **3** (1962) 214.

[40] P. V. Harper *et al.*, *Nucleonics*, **22** (1964) 50.

[41] G. H. Cartledge, *Proc. Conf. Use Radioisotopes Phys. Sci. Ind. Copenhagen*, 1961, Vol. 3, p. 549 (1962); *Corrosion*, **15** (1959) 469.

[42] J. B. Darby and S. T. Zegler, *J. Phys. Chem. Solids*, **23** (1962) 1825.

TABLE 4. ALLOYS OF TECHNETIUM

System	Phase	Composition of alloy (at. % Tc)	Intermetallic compounds	Reference
Sc–Tc	α-Mn	88.5	—	a, b
Ti–Tc	$MnZn_2$	66.7	—	a, b
	α-Mn	87.5, 85.7	—	
	CsCl	66.7, 50	—	
Zr–Tc	α-Mn	85.7	$ZrTc_6$	c, d
	$MgZn_2$	66.7	—	
Hf–Tc	α-Mn	87.5, 85.7		a, b
	$MgZn_2$	66.7		
	CsCl	50.0		
V–Tc	bbc	10, 25, 30, 40	TcV_3	a, b, e, f, h
	CsCl	50	TcV	
	bbc+hcp	75		
	hcp	95		
Nb–Tc	bcc	5, 10, 20, 30, 40, 50		a, b, c, g, h
	bcc+α-Mn	60		
	α-Mn	75	$NbTc_3$	
	α-Mn	85		
	hcp	97, (100)		
Ta–Tc	α-Mn	83.4, 80.0		a, b
	CsCl	50.0		
Cr–Tc	σ	75, 60		a, b
Mo–Tc	σ-βTc	75		
	σ	70		
	Cr_3O	60, 56, 53		a, b, c, g, i
W–Tc	σ	75		a, b
Mn–Tc	σ	60		a, b
Fe–Tc	σ	60, 50, 40		j, k
Rh–Tc Pd–Tc Pt–Tc				r
Zn–Tc	—		Zn_2Tc_{11} Zn_6Tc	l
Al–Tc	Ni_2Al_3	—	Tc_2Al_3	m, n, o, p
	Monoclinic		$TcAl_4$	
	$MnAl_6$		$TcAl_6$	
	WAl_{12}		$TcAl_{12}$	
Gd–Tc	—		$GdTc_2$	q
Tb–Tc	—		$TbTc_2$	q
Dy–Tc	—		$DyTc_2$	q
Ho–Tc	—		$HoTc_2$	q
Er–Tc	—		$ErTc_2$	q
Tu–Tc	—		$TuTc_2$	q
Lu–Tc	—		$LuTc_2$	q
Y–Tc	—		YTc_2	q
Th–Tc	—			s
U–Tc	—			s

[a] D. J. Lam, J. B. Darby, J. W. Downey and L. J. Norton, *Nature* **192** (1961) 744.

[b] J. B. Darby, D. J. Lam, L. J. Norton and J. W. Downey, *J. Less-Common Metals* **4** (1962) 558.

[c] V. B. Compton, E. Corazwit, J. B. Maita, B. T. Matthias and F. J. Morin, *Phys. Rev.* **123** (1961) 1567.

[d] J. B. Darby and S. T. Zegler, *J. Phys. Chem. Solids* **23** (1962) 1825.

[e] D. O. van Ostenberg *et al.*, *Phys. Rev. Letters*, **11** (1963) 352.

[f] D. O. van Ostenberg *et al.*, *Phys. Rev.* **128** (1962) 550.

[g] D. O. van Ostenberg and D. J. Lam, *J. Phys. Soc. Japan* **18** (1963) 1744.

[h] C. C. Koch and G. R. Love, *J. Less-Common Metals* **15** (1968) 43.

[i] F. J. Morin and J. P. Maita, *Phys. Rev.* **129** (1963) 1115.

[j] J. B. Darby, L. J. Norton and J. W. Downey, *J. Less-Common Metals* **5** (1963) 397.

[k] R. Buckley and W. Hume-Rothery, *J. Iron Steel Inst.* (*London*) **201** (1963) 121.

[l] *Argonne National Laboratory*, Reports ANL–6739 (1963), ANL–6780 (1963); M. G. Chasonov, I. Johnson and R. Schablaske, *J. Less-Common Metals* **7** (1964) 127.

[m] L. M. d'Alte de Veiga, *Phil. Mag.* **7** (1962) 1247.

[n] L. M. d'Alte de Veiga, *Phil. Mag.* **8** (1963) 349.

[o] L. K. Welford, *Acta Cryst.* **17** (1964) 57.

[p] J. B. Darby, J. W. Downey, and L. J. Norton, *J. Less-Common Metals* **8** (1965) 15.

[q] J. B. Darby, L. J. Norton and J. W. Downey, *J. Less-Common Metals* **6** (1964) 165.

[r] J. Miemiec, *Bull Acad. Polon. Sci., Serv. Sci. Chim.* **11** (1963) 665.

[s] J. B. Darby, A. F. Berndt and J. W. Downey, *J. Less-Common Metals* **9** (1965) 466.

It has been established that technetium forms a continuous series of solid solutions with Re, Ru and Os[43]. In alloys with Sc, Ti, Zr, Hf, Nb and Ta an x-phase isostructural with α-Mn has been found[43]. The presence of a CsCl-type phase in certain alloys distinguishes technetium from rhenium, and its behaviour during the formation of the σ-phase also distinguishes it from rhenium and manganese. A number of systems and alloys are summarized briefly in Table 4 (see also ref. 7).

Technetium has been shown to form amalgams with mercury[10]. Other studies of binary systems have been made with cobalt and nickel[44] and with the platinum metals[45]. Aspects of the binary systems U–C–Tc[46] and V–Al–Tc[47] have been investigated, and the effect of technetium in alloys of uranium and uranium fission products has been studied[48].

2. HYDRIDIC COMPOUNDS, HALIDES, OXIDE HALIDES, CYANIDE AND THIOCYANATE COMPLEXES

2.1. HYDRIDIC COMPOUNDS

From the little that has been reported it has been shown that pertechnetate, like perrhenate, may be reduced polarographically[49] in a non-complexing medium to a state approximating to Tc^{-1}. The TcO_4^- ion is reduced at a potential of about 0.4 V less negative than ReO_4^-, indicating that, as expected, Tc(VII) is more easily reduced than ReO_4^-.

TABLE 5. PROPERTIES OF POTASSIUM ENNEAHYDRIDOTECHNETATE(VII)[51]

Unit cell	Hexagonal	a_0 = 9.64 Å c_0 = 5.56 Å
Tc–H stretch Tc–H bend	IR	1869, 1795, 1779 cm^{-1} 689 cm^{-1}

The reduction of potassium perrhenate, labelled with ^{99}Tc, by a solution of potassium in ethylenediamine gives a complex hydride; the hydridorhenate precipitate contained 90%

---

[43] J. B. Darby, D. J. Lam, L. J. Norton and J. W. Downey, *J. Less-Common Metals*, **4** (1962) 558.

[44] J. B. Darby, L. J. Norton and J. W. Downey, *J. Less-Common Metals*, **5** (1963) 397.

[45] L M d'Alte da Veiga, *Phil. Mag.* **7** (1962) 1247.

[46] I. D. Farr and M. G. Bowman, Los Alamos Sci. Lab., CONF–206–3 (1963).

[47] D. O. van Ostenberg *et al.*, *Phys. Rev. Letters* **11** (1963) 352.

[48] R. W. Bohl, *J. Nucl. Matter* **7** (1962) 99.

[49] R. Colton, J. Dalziel, W. P. Griffith and G. Wilkinson, *J. Chem. Soc.* (1960) 71.

of the radioactivity of the technetium[50]. It was concluded that a complex technetium hydride $KTcH_4 \cdot 2H_2O$, isomorphous with $KReH_4 \cdot 2H_2O$, had been formed[50]. The reduction of pertechnetate to a complex hydride has been confirmed by Ginsberg[51], but the formulation has been corrected to K_2TcH_9, paralleling that of the corresponding rhenium compound.

Potassium enneahydridotechnetate(VII) is more reactive and less stable than K_2ReH_9. It is formed by reducing a dilute 4:1 ethylene-diamine–absolute ethanol solution of ammonium pertechnetate with potassium metal under anhydrous, non-oxidizing conditions[51]. Crystallographically (Table 5) and physically it is similar to the rhenium analogue.

Chemically, K_2TcH_9 is stable in strong aqueous alkali only when in dilute solution; such solutions reduce thallous nitrate directly to the metal without the formation of the white intermediate observed in the rhenium case[51].

Compounds analogous to the hydrido-phosphine derivatives of rhenium have not so far been reported, but the resemblances between the two elements are sufficiently close to expect their ultimate isolation.

2.2. HALIDES

Bromides and iodides of technetium have not so far been isolated; attempts to prepare a heptafluoride have been unsuccessful and it seems that this absence will prove to be one of the real differences between technetium and rhenium. Rather surprisingly, tervalent halides of technetium analogous to the "cluster" compounds of rhenium are not known, though there is mass spectrometric evidence[52] for $Tc_3Cl_9^+$ and the quadrivalent $Tc_3Cl_{12}^+$ ion. The structure of technetium tetrachloride, too, is quite different from that of β-rhenium tetrachloride and does not include metal–metal bonding. The evidence for technetium hexachloride is incomplete.

TABLE 6. HALIDES AND OXIDE HALIDES

Fluorides	Chorides	Bromides
	$TcCl_4$	
TcF_5		
TcF_6	$(TcCl_6)$	
	$TcOCl_3$	$TcOBr_3$
$TcOF_4$	$(TcOCl_4)$	
$TcOF_3$	TcO_3Cl	

2.2.1. Technetium Tetrachloride

This is the only stable chloride of the element which has yet been isolated. It has been synthesized from its elements[53] and by the interaction of technetium heptaoxide with carbon tetrachloride at about 400° in a sealed tube[54].

Technetium tetrachloride forms red crystals which may be easily purified by sublimation

---

[50] J. G. Floss and A. V. Grosse, *J. Inorg. Nuclear Chem.* **16** (1960) 44.

[51] A. P. Ginsberg, *Inorg. Chem.* **3** (1964) 567.

[52] K. Rinke, M. Klein and H. Schäfer, *J. Less-Common Metals*, **12** (1967) 497.

[53] R. Colton, *Nature*, **193** (1962) 872.

[54] K. Knox, S. Y. Tyree, R. D. Srivastava, V. Norman, J. Y. Bassett and J. H. Holloway, *J. Am. Chem. Soc.* **79** (1957) 3358.

in nitrogen or chlorine at about 300°. The structure[55] is very different (Fig. 2) from that of β-$ReCl_4$, and metal–metal bonding is not involved. The technetium atoms are octahedrally coordinated to chlorine, and the slightly distorted $TcCl_6$ octahedra are linked to form a polymeric chain. The repeating Tc_2Cl_8 unit is made up of two $TcCl_4$ planar asymmetric groups related by a glide plane. There are three distinct metal to chlorine distances: metal to nonbridging chlorine atoms (4 and 5), 2.24 Å; metal to bridging chlorine atoms aligned perpendicularly to the chain length (2 and 3), 2.49 Å; metal to the remaining bridging chlorine atoms (2′ and 3′) parallel to the chain length, 2.38 Å. The bond angles lie between about 85° and 95°; with an angle of 94° between the two short bonds and 86.5° between the two long bonds. This structure should be compared with the Nb_2Cl_{10} type and also with that of NbI_4.

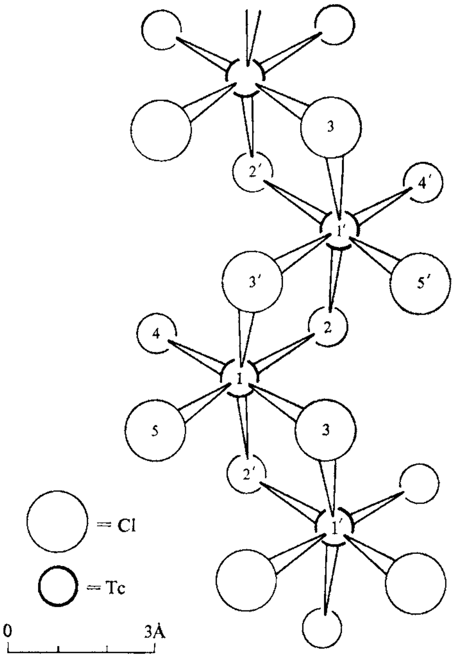


FIG. 2. The $(TcCl_4)_n$ unit. (Reproduced from M. Elder and B. R. Penfold, *Inorg. Chem.* **5** (1966) 1197. Copyright 1966 by the American Chemical Society, reprinted by permission of the copyright owner.)

The few magnetic data recorded for technetium tetrachloride have been taken to ndicate a Curie–Weiss relationship with $\mu = 3.14$ BM and $\alpha = 57°$[56].

Technetium tetrachloride dissolves in water with some hydrolysis, and in hydrochloric acid the yellow hexachlorotechnetate(IV) ion is formed (contrast $ReCl_4$).

2.2.2. Technetium Tetrabromide

Treatment of pertechnetic acid with concentrated hydrobromic acid leads, after evaporation to dryness, to an unstable brown–red compound analysing approximately to

---

[55] M. Elder and B. R. Penfold, *Inorg. Chem.* **5** (1966) 1197.

[56] K. Knox and C. E. Coffey, *J. Am. Chem. Soc.* **81** (1959) 5.

$TcBr_4$ (cf. ReI_4)[77]. The tetrabromide is rapidly hydrolysed in moist air and looses bromine even in a dry, inert atmosphere[77]. With triphenyl phosphine it reacts readily to give the bright orange–red complex $TcBr_4(PPh_3)_2$ (cf. $TcCl_4{\cdot}(PPh_3)_2$—p. 901)[77].

2.2.3. Technetium Pentafluoride

When technetium metal burns in fluorine the pentafluoride is one of the minor products of the reaction[57]. The compound is a yellow solid which melts at 50° to a yellow viscous liquid. In glass it decomposes at about 60°; there are some indications that disproportionation occurs at this temperature as one of the products is $TcOF_4$. Technetium pentafluoride seems to be more stable than its rhenium analogue[57].

Technetium pentafluoride is isostructural with vanadium pentafluoride[49]. The TcF_6 units are therefore linked in endless chains through *cis* fluorine bridges; there is no evidence of metal–metal bonding.

Like rhenium pentafluoride, technetium pentafluoride is moisture-sensitive and is readily hydrolysed[57]. The reaction, however, is not simple, and there is evidence that TcF_6^{2-} ions are formed in aqueous solution besides the expected pertechnetate and technetium dioxide.

TABLE 7. PHYSICAL PROPERTIES OF TECHNETIUM HEXAFLUORIDE[61]

Melting point	37.4°
Boiling point	55.3°
Transition temperature	−4.54° (extrap.)
Vapour pressure (solid)	$\log p_{mm} = 41.1252 - 10.787 \log T - 3564.8/T$ (−16.32° to −5.3°)
Vapour pressure (solid)	$\log p_{mm} = 15.33427 - 2.295 \log T - 2178.0/T$ (−5.2° to 37.4°)
Vapour pressure (liquid)	$\log p_{mm} = 24.8087 - 5.8036 \log T - 2404.9/T$ (37.4° to 51.67°)
ΔH_{sub} (cubic) (kcal mole^{-1})	8.555 (at 37.4°)
ΔH_{sub} (orthorhombic)	10.577 (at −5.3°)
ΔH_{sub} (cubic)	8.750 (at −5.3°)
ΔH_{vap} (kcal mole^{-1})	7.427
ΔH_{fus} (kcal mole^{-1})	1.128
ΔH_{trans} (kcal mole^{-1})	1.827
ΔS_{fus} (e.u.)	3.63
ΔS_{trans} (e.u.)	6.82
ΔS_{vap} (e.u.)	22.0

2.2.4. Technetium Hexafluoride

The reaction of fluorine with technetium powder, either in a static system at 400° [59], or in a flow system at 350° [60], yields volatile technetium hexafluoride. A heptafluoride does not appear to be formed.

Technetium hexafluoride forms a golden yellow solid[61], a yellow liquid and a colourless monomeric vapour[53] (Table 7). There is a phase transition in the solid associated with a change from a low temperature orthorhombic form to a high temperature cubic form. The

---

[57] A. J. Edwards, D. Hugill and R. D. Peacock, *Nature* **200** (1963) 672.

[58] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (A) (1969) 1651.

[59] H. Selig, C. H. Chernick and J. G. Malm, *J. Inorg. Nuclear Chem.* **19** (1961) 377.

[60] D. Hugill and R. D. Peacock, *J. Chem. Soc.* (A) (1966) 1339.

[61] H. Selig and J. G. Malm, *J. Inorg. Nuclear Chem.* **24** (1962) 641.

orthorhombic form has cell constants of $a_0 = 9.55$; $b_0 = 8.74$; $c_0 = 5.02$ Å at $-19°$, and the cubic form has a cell edge of 6.16 Å at 10° [62]. The fundamental frequencies in the vibrational spectra (ν_1, 712; ν_2, 639; ν_3, 748; ν_4, 265; ν_5, 297; ν_6, 174 cm^{-1}) indicate O_h symmetry for the molecule[63]; force constants and mean square amplitudes of vibration have been calculated[64]. The magnetic moment of 0.45 BM at 300°K is low[65].

Technetium hexafluoride dissolves in liquid hydrogen fluoride; the solubility has been estimated to be 0.89 moles for 1000 g. HF at room temperature[66]. In liquid HF hydrazinium fluoride reduces technetium hexafluoride to TcF_6^- and TcF_6^{2-} [66]. Technetium hexafluoride dissolves in iodine pentafluoride; addition of alkali metal chlorides to the solution result in reduction to quinquevalent complex fluorides[60]. Like rhenium hexafluoride, technetium hexafluoride is extremely sensitive to moisture. The first product of hydrolysis, formed with traces of moisture, is probably the oxide tetrafluoride (cf. $ReOF_4$) though this has not been prepared directly in this way. Ultimately, with excess of water, complete decomposition to technetium dioxide, pertechnetate and hydrofluoride takes place.

Quite recently it has been shown that technetium hexafluoride combines with NOF and NO_2F to give complex salts $(NO)_2TcF_8$ and NO_2TcF_7 respectively[67].

2.2.5. Technetium Hexachloride

The chlorination of technetium metal at moderate temperatures results in the formation of two products[53]. The less volatile of these is the tetrachloride, but a volatile green material also appears which on analytical evidence was identified as a hexachloride[53]. It was shown that the green material, which melted at 25°, hydrolysed in the expected manner for a Tc(VI) compound[53], and it was observed that care was required to free it from chlorine. The hexachloride was stated to be extremely unstable, decomposing to the tetrachloride on gentle warming; samples sealed in an atmosphere of chlorine gas decomposed completely to the tetrachloride in 24 hr[53]. Unfortunately this material has not been characterized in any other way, and in particular it has not been shown to be oxygen-free. An oxychloride $TcOCl_4$ might well have a number of the properties described for $TcCl_6$, though it would be difficult to account for the decomposition to $TcCl_4$ unless some TcO_3Cl or another oxygenated compound were also formed together with free chlorine. However, the formula $TcOCl_4$ has been assigned to a quite different material[70].

2.3. OXIDE HALIDES

The certain compounds (see Table 6) include the two oxide fluorides, $TcOF_4$ and TcO_3F, and the oxide chlorides, TcO_3Cl and $TcOCl_3$. Less certain is $TcOCl_4$.

The reaction between technetium dioxide and chlorine has been observed to give two products, a blue material, subliming at 80–90°, and a brown compound, subliming at 500° [68].

---

[62] S. Siegel and D. A. Northrop, *Inorg. Chem.* **5** (1966) 2187.

[63] H. Kim, P. A. Soulev and H. H. Claassen, *J. Mol. Spec.* **26** (1968) 46.

[64] O. N. Singh and D. K. Rai, *Canad. J. Phys.* **43** (1965) 378; G. Nagarajan, *Ind. J. Pure Appl. Phys.* **4** (1966) 237.

[65] H. Selig and J. G. Malm, personal communication (1962).

[66] B. Frlec and H. H. Hyman, *Inorg. Chem.* **6** (1967) 1775.

[67] J. H. Holloway and H. Selig, *J. Inorg. Nuclear Chem.* **30** (1968) 473.

[68] C. M. Nelson, G. E. Boyd and W. T. Smith, *J. Am. Chem. Soc.* **76** (1954) 348.

It was suggested that the brown compound is the oxide trichloride, $TcOCl_3$[69], and this hypothesis has recently been confirmed[70]. The blue material has therefore been tentatively identified as the oxide tetrachloride, $TcOCl_4$[70]. Bromine reacts similarly with technetium dioxide at 350° to give a black sublimate which is said to be the oxide tribromide, $TcOBr_3$[70].

Technetium oxide tetrafluoride, like the pentafluoride, appears as a minor product when technetium metal is treated with fluorine in a flow system[60]. It is separated from the pentafluoride by fractional sublimation under a vacuum.

TABLE 8. PHYSICAL PROPERTIES OF TECHNETIUM OXIDE TETRAFLUORIDE[a]

Melting point	133°
Boiling point (extrapolated)	165°
Vapour pressure: (solid)	$\log p_{mm} = 16.65–5556/T$ (25–84.5°)
(solid)	$\log p_{mm} = 12.30–4000/T$ (84.5–133°)
(liquid)	$\log p_{mm} = 10.12–2538/T$ (133–150°)
ΔH_{sub} (kcal mole^{-1})	25.4 (below 84.5°)
ΔH_{trans} (kcal mole^{-1})	18.3 (above 84.5°)
	7.1
ΔH_{fus} (kcal mole^{-1})	6.7
ΔH_{vap} (kcal mole^{-1})	11.6
ΔS_{vap} (e.u.)	26.5

[a] A. J. Edwards, private communication (1969).

Technetium oxide tetrafluoride exists in two crystalline modifications. The stable form is a pale blue crystalline solid which melts at 134° to a blue liquid (cf. $ReOF_4$). There is a phase change at 84.5° in the solid (Table 8), though it is not yet clear whether the high temperature form is the same as the green crystalline phase metastable at room temperature.

TABLE 9. PHYSICAL PROPERTIES OF TECHNETIUM TRIOXIDE FLUORIDE[73]

Melting point	18.3°
Boiling point	~ 100°
Vapour pressure (solid)	$\log p_{mm} = 12.448–3239.4/T$ (– 8.78° to 18.28°)
(liquid)	$\log p_{mm} = 8.417–2064.6/T$ (18.28° to 51.82°)
Heat of sublimation (ΔH_{sub}) (kcal mole^{-1})	14.83
Heat of vaporization (ΔH_{vap}) (kcal mole^{-1})	9.452
Heat of fusion (ΔH_{fus}) (kcal mole^{-1})	5.377

The blue technetium oxide tetrafluoride is isostructural with $ReOF_4$[23] and $MoOF_4$ and is hence similar in structure to the pentafluoride. The structure consists of distorted octahedral groups linked into endless chains parallel to the *c*-axis by *cis*-bridging fluorine atoms.

The second, metastable form of the oxide tetrafluoride is a green volatile solid which also results from the fluorination of technetium. The structure has been shown to be based on a trimeric $[TcOF_3F_{2/2}]$ unit with *cis*-bridging fluorine atoms[72]. The angle at the bridging fluorine atoms, 161°, is the same as in the stable form. It has been shown that the MOF_4 units can be linked either as endless chains or as trimeric units without disturbing the geometry around the metal atom[72].

---

[69] G. E. Boyd, *J. Chem. Ed.* **36** (1959) 7.

[70] R. Colton and I. B. Tomkins, *Australian J. Chem.* **21** (1968) 1981.

[71] A. J. Edwards, G. R. Jones and B. R. Steventon, *Chem. Communs.* (1967) 462.

[72] A. J. Edwards, G. R. Jones and R. J. C. Sills, *Chem. Communs.* (1968) 1177.

[73] H. Selig and J. G. Malm, *J. Inorg. Nuclear Chem.* **25** (1963) 349.

Both forms of technetium oxide tetrafluoride are moisture sensitive and are hydrolysed completely by water to hydrofluoric acid, technetium dioxide and pertechnetic acid.

Technetium trioxide fluoride (Table 9) has some analogy with the corresponding derivatives of manganese and rhenium. It is formed by the action of fluorine on the heated dioxide[73]; presumably another product richer in fluorine must also be formed (compare the reaction of ReO_2 with fluorine).

The trioxide fluoride forms a yellow crystalline solid and a yellow liquid, which is stable in nickel or Monel metal at room temperature, but which attacks Pyrex glass. Water causes complete hydrolysis. With excess of fluorine at 400° and 4 atm pressure reduction takes place and the hexafluoride is formed[73].

Technetium trioxide chloride was originally identified spectroscopically in chloroform solution, but it has since been synthesized by heating the tetrachloride gently in a stream of oxygen[70], and is said to be a colourless liquid, less stable than its rhenium analogue; gentle heating caused some decomposition to a red solid (?TcO_3)[70].

2.4. CYANIDE COMPLEXES

There appears to be some difference between the cyanide complexes of technetium and rhenium both in oxidation state and in composition. In the presence of cyanide ligand the stable oxidation states of rhenium are : 1, 3, 5, 6 and 7, but those of technetium are 1, 4 and 7 only. This conclusion is supported by polarographic studies[49], which indicate the absence of a stable Tc(V) state in aqueous potassium cyanide. However, the preparative work on technetium compounds is somewhat limited; data are summarized in Fig. 3.

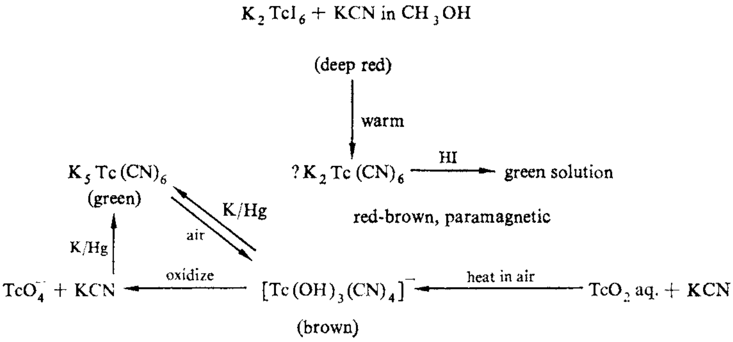


FIG. 3. Reactions of technetium cyanide complexes. (Reproduced, with permission, from R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier, 1966.)

Potassium hexacyanotechnetate(I) has been prepared by reducing potassium pertechnetate with potassium amalgam in the presence of excess of potassium cyanide and in the absence of air. The grey–green residue is purified by recrystallizing from water[74]. The salt has a face-centred cubic lattice (cf. $K_5Mn(CN)_6$ and $K_5Re(CN)_6$) with $a_0 = 12.160 \pm 0.001$ Å; the presence of cyanide ligands was established by infrared spectroscopy[74]. On exposure to air the light green crystals darken, and in solution in the presence of air oxidation to trihydroxytetracyanotechnetate(IV) ion occurs[74].

This hydroxy ion is also formed by the action of hot potassium cyanide solution on

---

[74] K. Schwochau and W. Herr, *Z. anorg. und allgem. Chem.* **319** (1962) 148.

freshly precipitated technetium dioxide, which leads to the formation of a brownish yellow solution from which the slightly soluble thallium salt may be precipitated. The crystals are of low symmetry[74]. Although formulated as $Tl_3[Tc(OH)_3(CN)_4]$ the infrared spectrum was shown to be not inconsistent with the alternative formulation as $Tl_3[TcO(OH)(CN)_4]$[74], as there is an absorption at 905 cm^{-1} which could be due to a Tc–O double bond (cf. $Tl_3[ReO_2(CN)_4]$).

The evidence for the hexacyanotechnetate(IV) ion is slender, since it rests on the equivalent weight of a potassium salt compared with the starting material, potassium hexaiodotechnetate(IV)[75]. The reddish brown precipitate was shown to be paramagnetic and to hydrolyse readily, properties to be expected for $K_2Tc(CN)_6$ (cf. $K_3Re(CN)_8$).

2.5. THIOCYANATE COMPLEXES

Although the production of a colour by the action of thiocyanate on pertechnetate ion is used as the basis of a colorimetric determination of the element, the nature of the complex remained unknown until very recently. By analogy with rhenium, one would expect the $Tc(NCS)_6^-$ ion to be formed, and this has now been isolated as the violet black tetramethylammonium or thallous salts[76].

The reduction of pertechnetate by thiocyanate ion or the reaction of $TcO_2{\cdot}nH_2O$ with alkali thiocyanate in the presence of atmospheric oxygen gives a mixture of complex thiocyanates which is preciptated by the tetramethylammonium ion. The oxidation of this complex salt by TcO_4^- ion leads to the isolation of the $Tc(NCS)_6^-$ ion, to which the absorption peak used in the spectrophotometric determination is due. Tetramethylammonium hexathiocyanotechnetate(V), $(CH_3)_4N[Tc(NCS)_6]$, dissolves readily in acetone or acetonitrile, and with more difficulty in dilute sulphuric or perchloric acids. The absorption spectrum of the violet solutions gives a strong band at 495 mμ. In acid aqueous solution the $Tc(NCS)_6^-$ ion is in a redox equilibrium with another thiocyanate complex in a lower oxidation state; this second thiocyanate complex ion, which has not yet been fully characterized, is that formed by the action of thiocyanate on $TcO_2{\cdot}nH_2O$ in the absence of air. This ion yields brown tetramethylammonium salt; the solution gives an absorption peak at 403 mμ.

3. OXIDES, OXOACIDS AND SALTS, CHALCOGENIDES, REFRACTORIES

3.1. BINARY OXIDES

The existence of two oxides of technetium, the dioxide and the heptaoxide, is now firmly established. There is some sparse evidence for a trioxide (from the action of oxygen on technetium at 400–1000°[78] and by the decomposition of technetium trioxide chloride, TcO_3Cl[79]) but proof is lacking. X-ray evidence has also been adduced in favour of a lower oxide or oxides, but the composition of these is not yet known[80].

---

[75] R. Colton, Ph.D. thesis, University of London, 1960.

[76] K. Schwochau and H. H. Pieper, *Inorg. Nucl. Chem. Letters* **4** (1968) 711.

[77] J. E. Fergusson and (Miss) J. H. Hickford, *Australian J. Chem.* **23** (1970) 453.

[78] S. Fried and N. P. Hall, *Phys. Rev.* **81** (1951) 741.

[79] R. Colton and I. B. Tomkins, *Australian J. Chem.* **21** (1968) 1981.

[80] O. Muller, W. B. White and R. Roy, *J. Inorg. Nuclear Chem.* **26** (1964) 2075.

3.1.1. Technetium Dioxide

This oxide is similar in appearance and behaviour to its rhenium analogue. The dihydrate, $TcO_2 2H_2O$, is readily precipitated by the reduction of a pertechnetate solution with zinc and hydrochloric acid[81], or by the hydrolysis of a warm solution of halogenotechnetate with sodium bicarbonate or ammonium carbonate. The decomposition of ammonium pertechnetate at 700–750° in a nitrogen stream[80, 84], or the dehydration of the dihydrate in a vacuum at 300° [81], leads to the anhydrous oxide.

Technetium dioxide is slightly volatile at 900° and does not decompose even up to 1100°. The heat of formation of the hydrate has been estimated at -103.7 kcal mole^{-1} [82], but this figure was based on an early measure of the TcO_2–TcO_4^- couple of 0.782 V. The anhydrous oxide has the molybdenum dioxide structure[83]; there is some slight doubt about the precise unit cell parameters[80].

Technetium dioxide may be reduced to the metal at 500° by hydrogen; heating in oxygen gives a heptaoxide. The compound reacts with fluorine, chlorine and bromine to give oxide halides.

3.1.2. Technetium Heptaoxide (Ditechnetium Heptaoxide)

This is the only product formed when the element is burnt in an excess of oxygen at 400° [86]. The pale yellow solid melts (Table 10) to a viscous yellow liquid. The entropy of fusion (Table 10, ref. a), as calculated directly from the vapour pressure equations, is 42 e.u.; this value is held to be unreasonable, consequently the figures given by the authors concerned have been estimated from assumed heat capacities. The liquid range of technetium heptaoxide is much greater than that of rhenium heptaoxide, a point which is probably related to the differing solid structures.

TABLE 10. PROPERTIES OF TECHNETIUM HEPTAOXIDE

Property	Value	Reference
Melting point	119.5°	a
Boiling point	310.6°	a
Vapour pressure (solid)	$\log p_{mm} = 18.279–7205/T (\pm 8\%)$	a
Vapour pressure (liquid)	$\log p_{mm} = 8999–3571/T (\pm 1\%)$	a
ΔH°_{fus} (kcal mole^{-1})	16.6 ± 0.5	a
ΔH°_{vap} (kcal mole^{-1})	16.3 ± 0.2	a
ΔS°_{fus}(e.u.)	29 (estimated)	a
ΔS°_{vap}(e.u.)	24 (estimated)	a
ΔH°_{form}(kcal mole^{-1})	-266 ± 2.6	b
Heat of solution (to $HTcO_4$aq.) (kcal mole^{-1})	11.59 ± 0.08	b

[a] W. T. Smith, J. W. W. Cobble and G. E. Boyd, *J. Am. Chem. Soc.* **75** (1953) 5773.
[b] J. W. Cobble, W. T. Smith and G. E. Boyd, *J. Am. Chem. Soc.* **75** (1953) 5777.

The application of X-ray structural methods to technetium heptaoxide indicates that the compound has a molecular structure[85], so that each technetium atom is in an approximately tetrahedral environment of oxygen atoms. The Tc–O bridge bonds (1.840 ± 0.001 Å) are

---

[81] C. M. Nelson, G. E. Boyd and W. T. Smith, *J. Am. Chem. Soc.* **76** (1954) 348

[82] J. W. Cobble, W. T. Smith and G. E. Boyd, *J. Am. Chem. Soc.* **75** (1953) 5777.

[83] W. H. Zachariasen, quoted by A. Magnéli and G. Anderson, *Acta Chem. Scand.* **9** (1955) 1378.

[84] S. Fried and N. F. Hall, Chemistry of Technetium, Am. Chem. Soc., Spring Meeting (1960).

[85] B. Krebs, *Angew. Chem.* (*Int. Ed.*) **8** (1969) 381.

[86] W. T. Smith, L. E. Line and W. A. Bell, *J. Am. Chem. Soc.* **74** (1953) 4964.

comparable in length to the Re(IV)–O and Ru(IV)–O bridge lengths in $[Cl_5Re\text{–}O\text{–}ReCl_5]^{4-}$ (1.86 Å) and $[Cl_5RuORuCl_5]^{4-}$ (1.80 Å). The average value for the Tc–O terminal bond lengths (1.673 Å)[85] corresponds to the Re–O distance in the tetrahedra of ReO_3Cl (1.702 Å), Re_2O_7 (1.70 Å) and $Re_2O_7(OH_2)_2$ (1.73 Å). It is interesting to note that although solid technetium heptaoxide conducts electricity and the liquid does not, for rhenium heptaoxide the reverse is true (see Table 10, ref. a). Technetium heptaoxide is weakly paramagnetic[81].

Chemically, technetium heptaoxide is a stronger oxidizing agent than rhenium heptaoxide. It is equally moisture sensitive and dissolves readily in water to form a solution of pertechnetic acid. The oxide also dissolves in dioxane, presumably to form a complex[81].

3.2. TERNARY OXIDES

Though only a few studies have been made, it is evident that the ternary oxides of technetium fall between those of manganese and rhenium in their properties. There are a number of differences from the corresponding rhenium chemistry in composition, crystallography, and chemical behaviour.

3.2.1. Tervalent

The reaction of appropriate proportions of TcO_2, Tc, and Na_2O or of $NaTcO_4$, TcO_2, Tc and Na_2O at 600° for 10 hr leads to the formation of deep violet $NaTcO_2$. This compound is not formed from the reaction of the dioxide alone with sodium oxide (contrast $LiReO_2$)[87]. The manganese equivalent, $NaMnO_2$, exists, but not the corresponding sodium derivative of rhenium, $NaReO_2$.

3.2.2. Quadrivalent

The reaction of lithium pertechnetate with the element and lithium oxide, or of technetium dioxide and lithium oxide at elevated temperatures[87], leads to water stable, black Li_2TcO_3 (Li_2SnO_3 structure). Similar reactions involving sodium oxide[87] lead to olive green Na_2TcO_3 (Na_2ReO_3 structure) and rust-brown, very hygroscopic Na_4TcO_4 (Na_4SnO_4 structure). The sodium salts disproportionate at high temperatures. These types of compound, Li_2XO_3 and Na_4XO_4, exist for manganese but not for rhenium.

Technetium-containing spinels, in which the technetium occupies the octahedral sites, have been synthesized from technetium dioxide and the appropriate metal oxide (MgO, CoO, MnO, (Co,Mn)O, (Co,Ni)O, (Ni,Mn)O, (Ni,Zn)O, (NiCd)O) but not from CuO, NiO, FeO or ZnO[88]. Some of the experiments were probably unsuccessful because of the development of leaks in the apparatus used[88]. A material with an undistorted rutile structure was obtained in the TiO_2/TcO_2 system at a composition $Ti_{0.6}Tc_{0.4}O_2$ ($a_0 = 4.636$, $c_0 = 2.974$ Å). Similar reactions with the alkaline earth oxides[88] give ABO_3 systems; $SrTcO_3$ has a slightly distorted perovskite structure with $a_0 = 3.95$ Å and $BaTcO_3$ has a hexagonal $BaTiO_3$ structure with $a_0 = 5.758$, $c_0 = 14.046$ Å. The corresponding $PbTcO_3$ has the pyrochlore structure with $a_0 = 10.361$ Å. Rare earth pyrochlores[88] of the more usual composition $Sm_2Tc_2O_7$, $Dy_2Tc_2O_7$ and $Er_2Tc_2O_7$ are sensitive indicators of ionic sizes, and from the unit cell edges a Goldschmidt radius of 0.67 Å has been assigned to Tc^{4+}.

---

[87] C. Keller and B. Kenellakopulos, *J. Inorg. Nuclear Chem.* **27** (1965) 787.

[88] O. Muller, W. B. White and R. Roy, *J. Inorg. Nuclear Chem.* **26** (1964) 2075.

Attempts to prepare the rhenium analogues of the spinels and pyrochlores have not been successful[88].

3.2.3. Quinquevalent

By the reaction of the appropriate pertechnetate with technetium metal and an alkali metal oxide, the compounds Li_3TcO_4 (2 forms) and $NaTcO_3$ have been isolated[87]. Like the quadrivalent derivatives, these disproportionate at high temperatures. The formula type $NaMO_3$ has not been isolated for either manganese or rhenium.

3.2.4. Sexivalent

Only the lithium compounds $\alpha+\beta$ Li_4TcO_5 and $\alpha+\beta$ Li_6TcO_6 have been isolated (Li_4TcO_5 with some difficulty); compounds could not be obtained for sodium[87]. These salts or mixed oxides are blue black or dark green, and isostructural with the corresponding rhenium derivatives. They dissolve in water; the initially rose-coloured solutions soon disproportionate quantitatively to pertechnetate, hydroxide ion and technetium dioxide[87].

TABLE 11. PROPERTIES OF PERTECHNETIC ACID AND THE PERCHETNETATE ION

Property	Value	Reference
ΔH°_{form} (TcO_4^- aq.) (kcal mole^{-1})	-173.0 ± 1.7	a
S° (TcO_4^- aq.) (e.u.)	-47.9 ± 0.3	b
ΔG°_{form} (TcO_4^-) (kcal mole^{-1})	-150.6	a
For the equation $HTcO_4(c) \rightleftharpoons \frac{1}{2}H_2O(g) + \frac{1}{2}Tc_2O_7(c)$, $\log p_{mm} = 8.207–2395/T$		c

[a] J. W. Cobble, W. T. Smith and G. E. Boyd, *J. Am. Chem. Soc.* **75** (1953) 5777.

[b] R. H. Busey and R. Bevan, Unclassified Document ORNL (1960) 2983.

[c] W. T. Smith, J. W. Cobble and G. E. Boyd, *J. Am. Chem. Soc.* **75** (1953) 5773.

The aqueous chemistry of these compounds is particularly interesting, since it is connected with the problem of lower oxidation states of technetium in aqueous solution. Compounds of the TcO_4^{2-} ion are apparently absent (cf. Chapters 39, Rhenium and 37, Manganese), and in this oxidation state technetium evidently behaves like rhenium.

3.2.5. Septavalent

Attempts to prepare mesopertechnetate(VII), TcO_5^{3-}, from aqueous solution have not been successful[89], but the synthesis of mixed oxides formally containing this ion (Na_3TcO_5, K_3TcO_5) and of the ternary oxides Li_5TcO_6 and Na_5TcO_6 has been achieved by dry methods[87].

These are brown compounds which are isostructural with the corresponding rhenium oxides, though they appear to be less stable thermally.

---

[89] S. K. Majumdar, R. A. Pacer and C. L. Rulfs, *J. Inorg. Nuclear Chem.* **31** (1969) 33.

3.3. PERTECHNETIC ACID AND THE PERTECHNETATES

The "per" acid, technetic(VII) acid, is formed in solution when the heptaoxide is dissolved in water, or when the metal or the freshly precipitated dioxide is treated with dilute hydrogen peroxide. Careful evaporation results in the solution first becoming pink, then red and finally dark red crystals of the free acid of the composition $HTcO_4$ appear[90]. The origin of the colour is puzzling; technetium heptaoxide, (Tc_2O_7) is yellowish, and the pertechnetate ion is colourless. It has been noted above that the sexivalent ternary oxides of technetium dissolve in water to give a transient rose-coloured solution; a red coloration has also been observed during the reduction of pertechnetate ion[89]. Some properties of pertechnetic acid and the pertechnetate ion are recorded in Table 11, and an oxidation-reduction diagram for pertechnetate ion in acid solution has been proposed (Fig. 4).

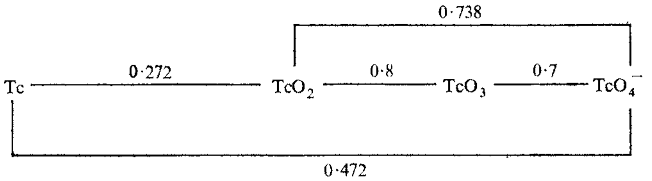


FIG. 4. Oxidation-reduction potentials of technetium (in volts) in acid solution (estimated). (G. H. Cartledge and W. T. Smith, *J. Phys. Chem.* **59** (1955) 1111.)

Pertechnetic acid is a strong acid and may be titrated with the aid of indicators such as methyl red. The solubility of $KTcO_4$ is compared with those of $KReO_4$ and of other salts of MO_4^- ions in Table 24 of Chapter 39, Rhenium; it lies between that of $KMnO_4$ and that of $KReO_4$. In general the solubilities of the pertechnetates seem to be somewhat higher than those of the corresponding perrhenates.

The behaviour of pertechnetate towards reducing agents has been investigated[89]. In addition to the transient existence of Tc(VI) and Tc(V)[89], there is also evidence for Tc(IV) and Tc(III) in the polarographic reduction of pertechnetate in the presence of suitable supporting electrolytes[91]. There is evidence for the Tc(III) state besides that provided by the polarographic work, both from the reduction of the $TcCl_6^{2-}$ ion[92] and from the controlled potential electrolysis of pertechnetate solution at pH 7 in a phosphate buffer[93]. The green solutions of Tc(III) appear to be unstable and are readily oxidized to Tc(IV). It is important to note that, in contrast to perrhenic acid, pertechnetic acid is reduced by concentrated hydrochloric acid without the addition of another reducing agent.

Potassium pertechnetate is a white crystalline solid. It undergoes a reversible colour change on heating, becoming brilliant yellow by 500°. The salt melts at 540° and boils (or sublimes) at about 1000° without decomposition[94]. The first absorption peak of TcO_4^- ion is at 2865 Å; the edge of this lies close to the visible region of the spectrum, and perhaps only a small disturbance from the tetrahedral symmetry of the anion is necessary to cause the strong colour to be shown by the free acid. It is interesting to note that a persistent reddish violet colour, resembling that of the free acid, is sometimes found in solid pertechnetates

[90] G. E. Boyd, J. W. Cobble, C. M. Wilson and W. T. Smith, *J. Am. Chem. Soc.* **74** (1952) 556.

[91] R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier (1966) p. 35; R. Colton, *The Chemistry of Rhenium and Technetium*, Interscience (1965) p. 150.

[92] J. D. Eakins D. G. Humphries and C. E. Mellish *J. Chem. Soc.* (1967) 6012.

[93] P. F. Thomason, Unclassified Document ORNL 2453 (1958) 7.

[94] R. H. Busey and Q. V. Larson, Unclassified Document ORNL 2584 (1958).

which have been dried under the infrared lamp, and a definite absorption band at about 5000 Å was actually recorded by some of the earlier workers[95]. The absorption peaks of pertechnetate ion have been recorded, 2865(m), 2457(s) and 2020(w) Å[96].

Potassium pertechnetate adopts the scheelite structure; the unit cell of $KTcO_4$[97] (a_0 = 5.654; c_0 = 13.030 Å) is larger than that of $KReO_4$ (a_0 = 5.615; c_0 = 12.50 Å), but the metal–oxygen bond lengths are nearly the same (Tc–O = 1.75 Å[98]; Re–O = 1.77 Å). The Na, NH_4, Cs[98] and Ag[99] salts are also isostructural with their rhenium analogues.

Ammonium pertechnetate decomposes on heating to technetium dioxide, but the scheelite structure may persist[88] up to nearly 700°, although the unit cell size of the intermediate decomposition product is considerably smaller. All the alkali metal salts are reduced by heating in hydrogen. Carbon monoxide reacts with potassium pertechnetate at high temperatures and pressures to yield $Tc_2(CO)_{10}$.

3.3.1. Substituted Pertechnetates (cf. ReO_3S^-, ReO_3N^{2-})

There is some slight evidence of the TcO_3S^- ion in solution[100], but apart from this the formation of substituted perrhenates does not appear to have been investigated.

4. CARBONYLS AND ORGANOMETALLIC COMPOUNDS, COMPLEXES

4.1. CARBONYLS

Aspects of the chemistry of technetium carbonyl have recently been reviewed[101]. In carbonyl derivatives, the three Group (VII) elements show close relationships although the properties of the technetium derivatives are closer to those of rhenium than those of manganese.

4.1.1. Ditechnetium Decacarbonyl

The action of carbon monoxide (about 300 atm at 220°) on technetium heptaoxide for 20 hr yields the carbonyl $Tc_2(CO)_{10}$, which may be purified by extraction and recrystallization from ether followed by sublimation at 50° under a vacuum[102]. The colourless compound m.p. 159–160° appears to decompose slowly in air. The vibrational spectra of $Tc_2(CO)_{10}$ indicate that its structure is very similar to that of $Mn_2(CO)_{10}$ and of $Re_2(CO)_{10}$, and X-ray studies confirm this conclusion[103]. From the X-ray studies it has been shown that $Tc_2(CO)_{10}$ is isostructural with $Mn_2(CO)_{10}$; the Tc–Tc distance is 3.036 ± 0.006 Å.

A tetracarbonyl is said to be formed (Fig. 5) as a by-product during the preparation of the carbonyl hydride. The material is reported to be air-stable and appears to be trimeric in cyclohexane solution. It reacts with carbon monoxide to give the pentacarbonyl, and with

---

[95] C. W. Parker J. Reed and J. W. Ruch, Unclassified Document AECD 2043 (1948).
[96] A. Carrington and M. C. R. Symons. *Chem. Rev.* **63** (1963) 443.
[97] B. J. McDonald and G. J. Tyson, *Acta Cryst.* **15** (1962) 87.
[98] W. H. Zachariasen (1952), quoted by G. E. Boyd, *J. Chem. Educ.* **36** (1959) 8.
[99] K. Schwochau, *Z. Naturforsch.* **174** (1962) 630.
[100] A. Mueller, B. Krebs and E. Diemann, *Z. anorg. und allgem. Chem.* **353** (1967) 259.
[101] E. W. Abel and F. G. A. Stone, *Quart. Rev.* **23** (1969) 325.
[102] J. C. Hileman, D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.* **83** (1961) 2953.
[103] M. F. Bailey and L. F. Dahl, *Inorg. Chem.* **4** (1965) 1140.

bromine to give the tetracarbonyl bromide. It was suggested that the structure could be similar to that of the osmium carbonyl $Os_3(CO)_{12}$.

4.1.2. Carbonyl Cations and Anions

These are very similar to the rhenium analogues, and the preparative methods are also similar (Fig. 5). The carbonyl cation, $Tc(CO)_6^+$, forms stable salts with large anions. The carbonyl anion, $Tc(CO)_5^-$, has been identified by spectroscopic techniques. It does not actually appear to have been analysed, but solutions containing it undergo all the expected reactions.

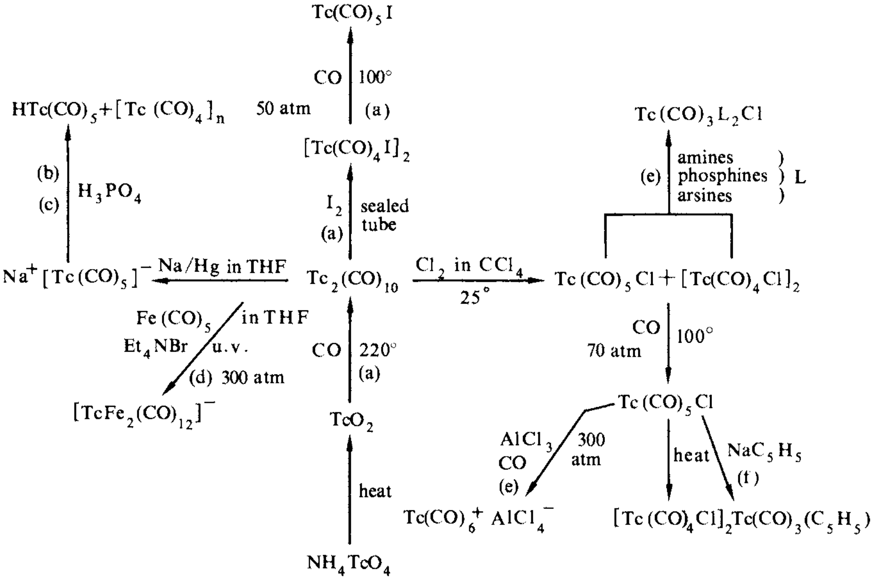


FIG. 5. Reactions of carbonyl compounds of technetium. (Reproduced, with additions, from R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier (1966) p. 102.)

[a] J. C. Hileman, D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.* **83** (1961) 2953.

[b] J. C. Hileman, D. K. Huggins and H. D. Kaesz, *Inorg. Chem.* **1** (1962) 933.

[c] H. D. Kaesz and D. K. Huggins, *Canad. J. Chem.* **41** (1963) 1250.

[d] M. W. Lindauer, G. O. Evans and R. K. Sheline, *Inorg. Chem.* **7** (1968) 1249.

[e] W. Hieber, F. Lux and C. Herget, *Z. Naturforsch.* **20b** (1965) 1159.

[f] E. Fischer and W. Fellmann, *J. Organometal Chem.* **1** (1963) 191.

4.1.3. Carbonyl Hydrides

Spectroscopic evidence has been produced for the existence of the hydride $HTc(CO)_5$. The compound may be distilled from the mixture resulting when solutions containing the anion $Tc(CO)_5^-$ are acidified with phosphoric acid (Fig. 5); the spectrum is very similar to the spectra of $HMn(CO)_5$ and $HRe(CO)_5$.

4.1.4. Carbonyl Halides

These are of two types, the monomeric, $Tc(CO)_5X$, and the dimeric, $[Tc(CO)_4X]_2$ (X = Cl, Br, I). They are prepared (Fig. 5) in much the same way as the corresponding rhenium derivatives, and are similarly stable to the atmosphere. Substitution reactions occur

(Fig. 5) in a similar manner to those of the rhenium derivatives. If the substituting ligand (L) is an amine, phosphine, phosphine oxide, arsine or stibine, the product has the formula $\mathrm{Tc(CO)_3L_2X}$ ($\mathrm{X = Cl, I, CO_2R}$), but if a sulphur ligand is involved the dimeric type $\mathrm{[Tc(CO)_4L]_2}$ (L = SPh, SEt, SMe) is formed, presumably with bridging suphur atoms, through the reaction

$$\mathrm{Tc(CO)_5Cl + 2RSH \longrightarrow [Tc(CO)_4SR]_2 + 2CO + 2HCl}$$

4.2. CYCLOPENTADIENYL DERIVATIVES

Treatment of technetium tetrachloride with sodium cyclopentadienide, $\mathrm{NaC_5H_5}$, in tetrahydrofuran at 50° in the absence of oxygen gives a reddish purple solution which, after the addition of sodium borohydride, yields sensitive, diamagnetic yellow crystals[104] of the composition $\mathrm{Tc(C_5H_5)_2}$, m.p. 150°. The first workers who prepared this compound suggested[105] that it was the dimeric molecule $\mathrm{[Tc(C_5H_5)_2]_2}$, but later work has shown that the material is almost certainly the hydride $\mathrm{Tc(C_5H_5)_2H}$, analogous to the rhenium derivative[106]. In contrast to $\mathrm{Re(C_5H_5)_2H}$, the metal hydrogen frequency in the infrared (at 1984 $\mathrm{cm^{-1}}$) is weak, and this, and the proton n.m.r. signal due to the Tc–H bond, was probably not observed by the first workers. The hydride is basic, and reacts with acids to form salts, e.g.

$$\mathrm{Tc(C_5H_5)_2H} \underset{\mathrm{NaOH}}{\overset{\mathrm{HCl}}{\rightleftharpoons}} \mathrm{[Tc(C_5H_5)_2H_2]Cl}$$

The dihydrodicyclopentadienyl technetium cation may be precipitated as the rather insoluble white hexafluorophosphate, $\mathrm{[Tc(C_5H_5)_2H_2]PF_6}$.

4.3. OTHER AROMATIC DERIVATIVES

The reaction of benzene with technetium tetrachloride in the presence of aluminium trichloride and aluminium yields the $\mathrm{[Tc(C_6H_6)_2]^+}$ cation[104], which is stabilized by $\mathrm{PF_6^-}$ anion. The reduction of this cation with lithium aluminium hydride gives the yellow, diamagnetic, mixed aromatic–Tc(I)–cyclohexadienyl complex $\mathrm{(C_6H_6)Tc(C_6H_7)}$. The $\mathrm{(Tc[C_6(CH_3)_6]_2)^+}$ cation is similarly formed and is reduced to $\mathrm{[C_6(CH_3)_6]Tc[C_6(CH_3)_6H]}$.

The carbonyl derivative $\pi\text{-}\mathrm{C_5H_5Tc(CO)_3}$ (m.p. 87°), analogous to the manganese and rhenium derivatives, has been formed by the action of sodium cyclopentadienide on technetium pentacarbonyl chloride (Fig. 5):

$$\mathrm{Tc(CO)_5Cl + NaC_5H_5 \rightarrow C_5H_5Tc(CO)_3 + NaCl + 2CO}$$

4.4. COMPLEX COMPOUNDS

Apart from the hydrides, cyandies and thiocyanates already discussed, complex compounds of technetium are limited to a few amine, phosphine and arsine derivatives, and the complex halides. Evidence has also been obtained for thiocomplexes in solution[107], and

---

[104] E. O. Fischer and M. W. Schmidt, *Chem. Ber.* **102** (1969) 1954.

[105] D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.* **83** (1961) 4474.

[106] E. O. Fischer and M. W. Schmidt, *Angew. Chem.* (*Inter. Ed.*) **6** (1967) 93.

[107] V. Shvedov and K. Kotegov, *Tr. Gas. Inst. Prikl. Khim.* No. 52 (1964) 76, through *Chem. Abs.* **63** (1965) 15526e.

several compounds containing oxygen ligands have been coprecipitated with the analogous rhenium derivatives[108].

4.4.1. Nitrogen Ligands

The action of dipyridyl upon technetium tetrachloride in ethanol leads to the formation of the quadrivalent complexes $[TcCl_2(dipy)_2]Cl_2$ and $TcCl_2(dipy)$[109] (contrast the behaviour of $ReCl_4$). The reduction of ammonium hexachlorotechnetate by hydroxylamine hydrochloride leads to a number of products, including an apparently bivalent, pink complex, $[Tc(NH_2OH)_2(NH_3)_2]^{2+}2Cl^-$[110].

4.4.2. Phosphorus and Arsenic Ligands

The tervalent technetium complex $(TcCl_2[C_2H_4(PPh_2)_2])Cl$ is formed by the action of the diphosphine $C_2H_4(PPh_2)_2$ on technetium tetrachloride in ethanolic solution. It is isostructural with the corresponding rhenium compound[109]. The reaction between technetium tetrachloride and triphenylphosphine leads to the quadrivalent complex $[TcCl_4(PPh_3)_2]$; the corresponding arsine derivative $[TcCl_4(AsPh_3)_2]$ is formed similarly[109].

The action of *o*-phenylenebisdimethylarsine and halogen acid on pertechnetic acid in aqueous alcohol leads to tervalent complexes of composition $[TcD_2X_2]ClO_4$ (X = Cl, Br, I; D = diarsine). From the tervalent compounds the divalent complexes $[TcD_2X_2]$ may be obtained by hypophosphite reduction, and the quinquevalent complexes by halogen oxidation[111]. The experimental work associated with these diarsine reactions was a remark able demonstration of careful technique involving only a few milligrams of material.

TABLE 12. MAGNETIC PROPERTIES OF SOME HALOGENOTECHNETATES[a]

Compounds	Magnetic moment μ (BM)	Curie constant θ (degrees)
K_2TcF_6	3.55	28
K_2TcCl_6	4.05	68
K_2TcBr_6	4.06	75
K_2TcI_6	4.20	81
Rb_2TcI_6	4.24	126

[a] K. Schwochau, A. Knappwost, E. Bukaul and R. S. B. Navasin Raju, *Z. Naturforsch.* **19a** (1964) 1128.

4.4.3. Complex Halides

These are known for Tc(II–III), Tc(IV) and Tc(V); some solution evidence is also available for oxide halides of Tc(V) and Tc(VI).

The reduction of ammonium chlorotechnetate, $(NH_4)_2TcCl_6$, by zinc and hydrochloric acid leads to a mixture of compounds from which the ammonium or yttrium salts of the

---

[108] J. Ziolkowski, M. Baluka and B. J. Trzebiatowska, *Theory and Structure of Complex Compounds*, Wroclaw, Poland, Pergamon (1962) p. 419.

[109] J. E. Fergusson and J. H. Hickford, *J. Inorg. Nuclear Chem.* **28** (1966) 2293.

[110] J. D. Eakins, D. G. Humphreys and C. E. Mellish, *J. Chem. Soc.* (1963) 6012.

[111] J. E. Fergusson and R. S. Nyholm, *Chem. and Ind.* (1960) 347.

$Tc_2Cl_8^{3-}$ ion, $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$ and YTc_2Cl_8, may be crystallized[110]. The structure of the ammonium salt has been determined[112], and it has been shown that the $Tc_2Cl_8^{3-}$ ion has virtually D_{4h} symmetry (cf. $Re_2Cl_8^{2-}$) with a Tc–Tc distance of 2.13±0.013 Å and Tc–Cl distances of 2.34–2.36±0.03 Å. There is one unpaired electron per Tc_2Cl_8 unit, so the average oxidation state of the technetium is 2.5. The resemblance to the $Re_2Cl_8^{2-}$ ion is close to both in stereochemistry and in bond length (Re–Re = 2.24 Å), and it has been suggested that there is a family of $M_2Cl_8^{n-}$ ions.

Quadrivalent complex halides of technetium are known for all four halogens. The fusion of K_2TcCl_6[113] or of K_2TcBr_6[114] with potassium hydrogen fluoride leads to a yellow melt from which, after leaching with water, the pink salt K_2TcF_6 may be isolated. This salt may be crystallized from water; the free acid, as well as other salts, may be obtained by ion exchange. The sodium and ammonium salts are very soluble in water, as are the corresponding sodium and ammonium salts of the ReF_6^{2-}, IrF_6^{2-}, OsF_6^{2-} and PtF_6^{2-} ions. The fluorotechnetate(IV) ion is even more resistant to hydrolysis than ReF_6^{2-}, and decomposition is only brought about by concentrated alkali. Ammonium fluorotechnetate is said to be decomposed by heat to the nitride fluoride TcNF[115].

The alkali metal and ammonium hexafluorotechnetates (excepting Na_2TcF_6) adopt the trigonal K_2GeF_6 structure[116]. The principal features of the absorption spectra have been assigned[117]; the magnetic moment of the K salt is in line with those of the other halogenotechnetates (Table 12). The infrared spectrum of the K salt shows an absorption of 574 cm^{-1} which has been assigned[113] to the metal–fluorine stretch ν_3. The ligand field stabilization energy is given as 97.5 kcal $mole^{-1}$[119].

The hexafluorotechnetate(IV) ion is also formed as a decomposition product when technetium pentafluoride or the TcF_6^- ion is treated with water[118].

Evidence for a TcF_5^- ion has been presented[118], but the structure is unknown.

Pertechnetate ion is reduced by concentrated hydrochloric acid, and the ultimate product is the hexachlorotechnetate(IV) ion. However, the usual preparative method for the chlorotechnetates follows that of rhenium, and iodide ion is added to the hydrochloric acid solution of potassium pertechnetate to aid the reduction. Initially red crystals of the salt $K_2TcCl_5(OH)$, which is isostructural with K_2TcCl_6, are formed[120] (there does not appear to be a technetium analogue of $K_4Re_2OCl_{10}$) which redissolve with some difficulty in hydrochloric acid to give the yellow K_2TcCl_6. This hydroxy-species is not isolated if hydrochloric acid alone is used to effect the reduction. The other alkali metal hexachlorotechnetates(IV) (Na, Rb, Cs) are prepared similarly. The corresponding red hexabromo- and deep purple hexaiodo-derivatives are formed by the action of the appropriate halogen acid on the chlorotechnetate.

The alkali salts of the chloro- and bromo-complex ions have the cubic K_2PtCl_6 structure, either undistorted (K, Rb, Cs), or with a tetragonal modification (Na). Rubidium hexaiodotechnetate(IV) is also cubic, but the K salt has a monoclinic or orthorhombic

[112] F. A. Cotton and W. K. Bratton, *J. Am. Chem. Soc.* **87** (1965) 921.

[113] K. Schwochau and W. Herr, *Angew. Chem.* **73** (1963) 95.

[114] R. H. Busey, Unclassified Document ORNL 3176 (1961).

[115] D. E. La Valle, R. M. Steele and W. T. Smith, *J. Inorg. Nuclear Chem.* **28** (1966) 260.

[116] K. Schwochau, *Z. Naturforsch.* **19a** (1964) 1237.

[117] C. K. Jørgenson and K. Schwochau, *Z. Naturforsch.* **20a** (1965) 65.

[118] D Hugill and R. D. Peacock, *J. Chem. Soc.* (1966) 1340.

[119] K. Schwochau, *Z. Naturforsch.* **20a** (1965) 1286.

[120] M. Elder, J. E. Fergusson, C. J. Gainsford, J. H. Hickford and B. R. Penfold, *J. Chem. Soc.* (A) (1967) 1423.

distortion[116]. In K_2TcCl_6 the Tc–Cl separation in a regular octahedral structure[120] is 2.35 Å (Re–Cl in K_2ReCl_6 is 2.37 Å), from which, assuming a value of 0.99 Å for the Cl covalent radius, a value for the octahedral covalent radius of technetium of 1.36 Å is obtained. Magnetic moments (K salts) are given in Table 12. The electronic spectra of these hexahalogenotechnetates(IV) have been assigned[117, 120].

The hexachlorotechnetates appear to be more soluble in aqueous solution than the corresponding hexahalogenorhenates, and they are certainly less stable. The hexachlorotechnetates are hydrolysed in 1 M HCl, and it has not proved possible to make the silver salt by precipitation (contrast Ag_2ReCl_6). Quantitative measurements in solution have indicated that the $TcCl_6^{2-}$ and $TcBr_6^{2-}$ ions are markedly less stable thermodynamically and more labile kinetically than their Re analogues[119]; these results have been compared with the ligand field parameters. In contrast to the TcF_6^{2-} ion, the TcX_6^{2-} ions (X = Cl, Br, I) are all rapidly hydrolysed by water or alkali to the hydrated dioxide $TcO_2 \cdot 2H_2O$. The $TcCl_6^{2-}$ ion absorbs at 242 and 240 mμ; this has been taken advantage of as the basis of a spectrophotometric method of determining the element[121].

Quinquevalent complex halides are restricted to the fluorides, although there is evidence for an oxide chloride species.

When technetium hexafluoride, dissolved in iodine pentafluoride, is treated with an alkali-chloride, reduction to the quinquevalent state takes place and the complex fluorides $MTcF_6$ (M = Na, K, Re, Cs) crystallize from solution[118] (with Re, iodide is required to effect a corresponding reduction). The salts are bright yellow, have magnetic moments close to those required by the Kotani theory (e.g. for $NaTcF_6$, μ_{eff} (25°) = 2.25 BM; θ = 130°); the Na and K salts (rhombohedral) are isostructural with the corresponding ruthenium and osmium derivatives but not with the rhenium salts.

The hexafluorotechnetates(V) are air sensitive and are hydrolysed by water with the formation of pertechnetate, hydrated technetium dioxide and hexafluorotechnetate(IV).

The reduction of pertechnetate in hydrochloric acid yields at least one intermediate species before the formation of the $TcCl_6^{2-}$ ion, but the evidence is unclear. Spectrophotometric evidence[122] suggests strongly that the intermediate is a Tc(VI) species, which disproportionates to Tc(VII) and Tc(IV), but, on the other hand, it is claimed that green, diamagnetic $(NH_4)_2TcOCl_5$, a Tc(V) species, is formed by the action of concentrated hydrochloric acid on ammonium pertechnetate[123]. These results are not necessarily in conflict, since the isolation of a Tc(V) salt does not presume the existence of more than a small concentration of the necessary anion in solution at any one time; nevertheless the matter requires investigation.

[121] A. A. Pozdnyakov *Zhur. Analyt. Khim.* **26** (1965) 473.

[122] D. I. Ryabchikov and A. A. Pozdnyakov, *Dokl. Akad. Nauk. SSSR.* **155** (1964) 153.

[123] J. B. Trzebiatowska and M. Baluka, *Bull. Acad. Polon. Sci. Soc. Sci. Chem.* **13** (1965) 1.

39. RHENIUM

R. D. PEACOCK
The University, Leicester

1. DISCOVERY, ISOLATION, PHYSICAL AND CHEMICAL PROPERTIES, MISCELLANEOUS

1.1. DISCOVERY AND ISOLATION

Rhenium, the dvi-manganese of Mendeléev, and the least abundant of the natural chemical elements, was the last of the elements to be identified by conventional chemical methods. The credit for its discovery is usually given to Noddack, Tacke (later Frau Noddack) and Berg, who in 1925 obtained the X-ray spectrum of element 75 from a gadolinite concentrate and also from platinum mineral concentrates[1, 2]. The element, named "rhenium" by the Noddacks, was discovered independently by Loring and Druce[3] in manganese compounds. The first gram of rhenium had been isolated by 1928, and by 1933 the element was being produced commercially from molybdenum residues recovered from copper schists.

The average concentration of rhenium in the earth's crust has been estimated to be 0.027 ppm by Ahrens and Taylor[4], and even in iron meteorites, where the concentration is 0.6 ppm, it is less abundant than osmium, iridium and gold[5]. The element is mainly concentrated in the pegmatites and in pneumatalytic rocks, and especially in molybdenites associated with copper. In the latter rhenium may attain a concentration of 0.3%, and these provide the commercial source[6, 7]. A specific mineral, dzhezkazganite, has been identified in copper deposits[8, 9]; this was originally given the composition $CuReS_4$, but more recent work suggests that the copper is not a mineral-forming component and that the rhenium mineral may be a solid solution of ReS_2 and MoS_2 [10]. The disulphide may occur in Mansfield copper shales[10]. In sedimentary rocks it appears that rhenium is dispersed in molybdenum sulphides when these are rich in molybdenum, but otherwise it crystallizes out as "$CuReS_4$" [11].

---

[1] W. Noddack, I. Tacke and O. Berg, *Naturwissenschaften* **13** (1925) 567.

[2] I. Noddack and W. Noddack, *Das Rhenium*, Vars, Leipzig (1933).

[3] F. H. Loring and J. F. G. Druce, *Chem. News* **131** (1925) 273.

[4] L. H. Aller, *The Abundance of the Elements*, Interscience, New York (1961).

[5] H. Brown and E. Goldberg, *Phys. Rev.* **76** (1949) 1260.

[6] K. B. Lebedev, *The Chemistry of Rhenium* (translated by L. Ronson and A. A. Woolf), Butterworths, London (1962).

[7] S. Tribalat, *Rhénium et Technétium*, Gauthier-Villars, Paris (1957).

[8] E. M. Poplauko, I. D. Marchukova and S. Sh. Zak, *Dokl. Akad. Nauk SSSR* **146** (1962) 433.

[9] D. F. C. Morris and E. L. Short, *Miner. Mag.* **35** (274) (1966) 871.

[10] D. F. C. Morris and E. L. Short, *Handbook of Geochemistry*, Springer-Verlag (1969).

[11] V. N. Gorokhova, *Chem. Abs.* **62** (1965) 14379d.

The extraction processes have been extensively reported by Soviet chemists and are summarized in a recent volume[6], and more briefly in other volumes[12, 13].

The primary step during molybdenum manufacture is to convert molybdenum concentrates into molybdate by roasting in air, when the rhenium is converted to volatile oxides (mainly Re_2O_7) or to calcium perrhenate. Both rhenium heptaoxide, which becomes concentrated in the flue dust, and calcium perrhenate dissolve readily in water, so that by suitable leaching techniques the rhenium may be concentrated in aqueous solution. Rhenium is subsequently extracted from the solution (a) by precipitating a sparingly soluble compound such as potassium perrhenate or the perrhenate of an organic base, (b) by the cementation of the metal or oxide on to iron filings or sponge in acid solution, (c) by absorption, ion exchange or solvent extraction, (d) by electrolytic deposition. The rhenium is recovered finally as potassium perrhenate, which may be readily recrystallized.

At one time the element was obtained from purified potassium perrhenate by direct reduction by hydrogen, first at 520° and then at 1000°.

$$2KReO_4 + 7H_2 = 2Re + 2KOH + 6H_2O$$

However, even after repeated leaching with water or dilute acid, some potassium (about 0.4 %) is retained, and although for many purposes this may not be important the recent use of rhenium filaments in mass spectrometers requires potassium-free rhenium. This has been achieved by converting potassium perrhenate or the contaminated metal to ammonium perrhenate and reducing this in hydrogen instead of the potassium salt. Other methods have also been described[12], and a comprehensive review on the purification of rhenium has been published[14].

On the laboratory scale, rhenium has been prepared by a number of methods. Residues may be converted either to ammonium perrhenate[15] or to $(NH_4)_2ReCl_6$ [16]; these are easily reduced by hydrogen. Crude rhenium may be chlorinated to the pentachloride, which in turn is converted through hydrolysis to the dioxide and hence by hydrogen reduction to the metal[17]. In addition, a number of halogen compounds of rhenium are either thermally unstable or are easily reduced by hydrogen to afford a ready source of the element[12, 13]. The electroplating of rhenium has been extensively investigated, and it is clear that the best results are obtained from sulphuric acid[18, 19]. The reduction of K_2ReCl_6 solution with hydrazine and formaldehyde in the presence of gum arabic yields a colloidal rhenium which is said to have catalytic properties and to be stable for several months[20].

Rhenium has been fabricated using cold working and powder techniques[21].

1.2. ISOTOPES

Apart from the two natural isotopes ^{185}Re and ^{187}Re, these have been synthesized with mass numbers from 177 to 192[22]. The longest lived of the artificial isotopes appears to be

---

[12] R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier, London (1966).
[13] R. Colton, *The Chemistry of Rhenium and Technetium*, Wiley, Interscience, London (1965).
[14] V. I. Bibikova, *Transaction Bull.* 04231.
[15] A. A. Woolf, *J. Less-Common Metals* **1** (1959) 420.
[16] R. D. Peacock, unpublished observation (1957).
[17] D. M. Rosenbaum, R. J. Runch and I. E. Campbell, *J. Electrochem. Soc.* **103** (1956) 516.
[18] R. Colton, *The Chemistry of Rhenium and Technetium*, Interscience, London (1965) p. 8.
[19] N. V. Phillips, Dutch Patent 72568 (1963).
[20] C. Zenghelis and K. Stathis, *Compt. Rend.* **209** (1939) 797.
[21] Batelle Development Corporation, Brit. Patent 768795 (1957).

^{189}Re, which may have a half-life of *ca.* 5 years. The natural isotope ^{187}Re has a half-life of *ca.* 10^{11} years and is a feeble β-emitter ($\beta^{-}_{\max}$ = 0.003 MeV). Chemically, only the isotopes ^{185}Re and ^{187}Re, which are found in the natural element in the ratio 1 : 1.62, are significant.

Table 1. Physical Properties of Rhenium

		Ref.
Atomic weight	186.22 (physical)	a
	186.31 (chemical)	b
Atomic radius (12-coordination) (Å)	1.373	c
Density (g cm^{-3})	21.02	d
Melting point (°C)	3100	d
Boiling point (°C)	5870	d
Critical point (°K)	2.42	d
Ionization potential (eV) (1st)	7.87	d
(2nd)	16.6	d
(3rd)	(26)	d
$\Delta H_{(\mathrm{sub})}$ (kcal mole^{-1})	189	e
$S°$ (crystal) (cal mole^{-1} deg^{-1})	8.89 ± 0.3	f
Paramagnetic susceptibility (e.s.u.)	(1) $\chi_g \times 10^6 = 0.280 + 0.0000075T$	g
	(2) $\chi_g \times 10^6 = 0.310 + 0.000017T$	g
Electronic work function (eV)	4.8	d

[a] L. Friedman, A. P. Irsa and G. Wilkinson, *J. Am. Chem. Soc.* **77** (1955) 3689.
[b] O. Honigschmidt and R. Sachtlebon, *Z. anorg. allgem. Chem.* **191** (1930) 301.
[c] R. C. L. Mooney, *Phys. Rev.* **72** (1947) 1269; *Acta Cryst.* **1** (1948) 161.
[d] *Chemists' Handbook*, Vol. 1, Goskhimizdat, Moscow–Leningrad (1962).
[e] Nat. Bur. Stnd. (US), Circular 500, Washington (1952).
[f] W. T. Smith, Jnr., G. D. Oliver and J. W. Cobble, *J. Am. Chem. Soc.* **75** (1953) 5785.
[g] R. W. Asmussen and H. Soling, *Acta Chem. Scand.* **8** (1954) 563.

1.3. PHYSICAL AND CHEMICAL PROPERTIES

The physical properties (Table 1) indicate that rhenium has the highest melting point of all the transition elements with the exception of tungsten. Analysis of the data from the first emission spectrum indicates that the atom, like manganese, has five *d*-type and two *s*-type valency electrons in outer orbitals.

Rhenium forms a silvery grey metal (particularly noticeable in the electrolytically deposited coatings or in mirrors produced by the decomposition of the halides or of $Re_2(CO)_{10}$) which is said to tarnish in a moist atmosphere. It is isostructural with technetium, crystallizing in a hexagonally close-packed lattice. The element is weakly paramagnetic; there is some variation in the recorded susceptibilities[23].

Massive rhenium resists oxidation, but in sponge or powder form it is very reactive, and burns to the heptaoxide (cf. osmium). The sponge dissolves in oxidizing acids (nitric and concentrated sulphuric) but not in hydrochloric acid. Rhenium dissolves readily in dilute hydrogen peroxide, giving perrhenic acid; the rate of reaction depends upon previous history and particle size[23, 24].

---

[22] C. M. Lederer, J. M. Hollander and I. Perlman, *Table of Isotopes*, 6th edn., Wiley (1967).

[23] R. Colton, *The Chemistry of Rhenium and Technetium*, Interscience, London (1965), p. 7.

[24] R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier, London (1966), p. 22.

Rhenium burns in fluorine, giving a mixture of the hexa- and heptafluorides. It combines readily with chlorine and bromine, but does not react appreciably with iodine. The sponge combines with sulphur at elevated temperatures to give the disulphide.

1.4. ANALYTICAL CHEMISTRY

Separation. Rhenium may be precipitated from hydrochloric acid solution as sulphide. Quadrivalent rhenium gives the disulphide, ReS_2, and perrhenate solutions give the heptasulphide, Re_2S_7, and these may be converted by dilute hydrogen peroxide to perrhenic acid. Separation from the other elements of the sulphide group is fairly readily achieved, especially as perrhenic acid may be distilled at 270–290° from 80% sulphuric acid[25].

TABLE 2. SOLVENT EXTRACTION OF RHENIUM

Extraction	Extracting solvent	Efficiency	Ref.
ReO_4^- from MoO_4^{2-} (4 M NaOH)	Pyridine	Quantitative	a, b
ReO_4^- from MoO_4^{2-} (acid with H_2SO_3)	Triisooctylamine	Good	c
ReO_4^- (acid with H_2SO_4)	Tributylphosphate in kerosene	Fair	d
ReO_4^- (acid with H_2SO_4)	Butanol, isoamyl alcohol	Fair	e
ReO_4^- from MoO_4^{2-}	Tetraphenylarsonium chloride in $CHCl_3$	Quantitative	f

[a] D. T. Meshri and B. C. Haldar, *J. Sci. Ind. Res. (India)* **20B** (1961) 551.
[b] S. J. Rimshaw and G. F. Malling, *Anal. Chem.* **33** (1961) 751.
[c] A. S. Kertes and A. Beck, *J. Chem. Soc.* (1961) 1926.
[d] R. Colton, UKAEA Document AERE-R3823 (1961).
[e] A. S. Kertes and A. Beck, *J. Chem. Soc.* (1961) 5046.
[f] S. Tribalat, *Anal. Chim. Acta* 4 (1950) 258.

Since rhenium is generally obtained from molybdenum ores, good methods of separating the two elements are called for on the analytical scale. Solvent extraction (Table 2), ion exchange (Table 3) and absorption chromatographic techniques have been used. In the last, the acid (0.98 M H_2SO_4) solution was passed down a column of activated charcoal. Separation was achieved by eluting first with further quantities of 0.98 M sulphuric acid, which served to remove the weakly held molybdic acid, and then with boiling 0.1 M sodium hydroxide, by which the rhenium was removed quantitatively[26].

Determination of rhenium. Rhenium has been estimated by gravimetric, volumetric, calorimetric and spectrophotometric methods, by polarography, amperometric titration and by neutron activation analysis.

The two common gravimetric procedures depend upon the precipitation of an insoluble salt of the perrhenate ion, as either nitron perrhenate[27] or as tetraphenyl arsonium per-

---

[25] W. Geilmann and H. Bode, *Z. anal. Chem.* **132** (1951) 250; **130** (1950) 320.
[26] G. B. Alexander, *J. Am. Chem. Soc.* **71** (1949) 3043.
[27] W. Geilmann and A. Voight, *Z. anorg. allgem. Chem.* **193** (1930) 311.

rhenate[28]. Both procedures, which are described in standard analytical textbooks, are subject to interference by a number of common ions, in particular perchlorate, halides, and in the case of the nitron reagent, nitrate itself. Other slightly soluble perrhenates such as thallous[29] and silver have also been used to precipitate rhenium, but, in addition to interfering ions, the solubility of the salts is a drawback.

The hexachlororhenate(IV) ion has been estimated directly by precipitation with tetron (*N*,*N*-tetramethyl-*o*-toluidine)[30], but this procedure is seldom used. At one time rhenium was also determined by weighing as the heptasulphide, Re_2S_7, and it is still useful to know for separation purposes that this compound may be precipitated quantitatively, even though the sulphide is no longer considered a suitable weighing form.

TABLE 3. ION EXCHANGE SEPARATIONS OF RHENIUM FROM MOLYBDENUM AND TUNGSTEN

Separation	Resin (and form)	Eluent	Efficiency	Ref.
ReO_4^- from MoO_4^{2-} (2.5 M NaOH)	Amberlite IRA-400 (OH^-)	(a) Mo in 10% NaOH (b) Re by acidifying with 0.2 M HCl and eluting with 7 M HCl	Good but slow	a
ReO_4^- from MoO_4^{2-} (alkaline)	Amberlite IRA-400 (OH^-)	(a) Mo in 1 M $K_2C_2O_4$ (b) Re in 1 M $HClO_4$	Quantitative	b
ReO_4^- from MoO_4^{2-} (0.1–1.0 M HCl)	Dowex-50 Anion (Cl^-)	(a) Mo not absorbed (b) Re in 10% NaOH	Quantitative	b
ReO_4^- from WO_4^{2-} (1.5 M HCl)	Dowex-1 Anion	(a) W by 1.5 M HCl (b) Re by 4.0 M HNO_3		c

[a] S. A. Fisher and V. M. Meloche, *Anal. Chem.* **24** (1952) 1100.
[b] V. M. Meloche and A. F. Preuss, *Anal. Chem.* **26** (1954) 1911.
[c] E. F. Huffman, R. L. Oswalt and L. A. Williams, *J. Inorg. Nucl. Chem.* **3** (1956) 49.

Volumetric methods of estimation depend either on the strong acid behaviour of perrhenic acid, which allow it to be titrated against alkalis directly, or on the reducing properties of the lower oxides of rhenium, such as the dioxide. Lower oxides are oxidized in dilute sulphuric acid solution by ferric sulphate[31], potassium dichromate and by ceric sulphate[32].

A number of spectrophotometric methods are summarized in Table 4. Apart from the direct determination of perrhenate itself in the ultraviolet region, nearly all depend upon the reduction of perrhenate to some lower valency state, usually Re(IV) or Re(V). Generally a reducing agent such as stannous chloride in acid solution is required (with the very similar procedures used for technetium the reagent itself is often sufficiently reducing to develop the colour). Some of the methods were developed to allow small proportions of rhenium to be determined in the presence of molybdenum. The precise nature of the complexes responsible for the colours has not always been elucidated, e.g. evidence concerning the nature of

---

[28] H. H. Willard and G. M. Smith, *Ind. Eng. Chem.* **11** (1939) 305.
[29] F. Kraus and H. Steinfeld, *Z. anorg. allgem. Chem.* **197** (1931) 52.
[30] W. Geilmann and L. C. Hurd, *Z. anorg. allgem. Chem.* **213** (1933) 336.
[31] W. Geilmann and L. C. Hurd, *Z. anorg. allgem. Chem.* **210** (1932) 350.
[32] W. Geilmann and L. C. Hurd, *Z. anorg. allgem. Chem.* **222** (1935) 56.

the complexes responsible for the thiocyanate colour was not available until very recently (see p. 936).

Rhenium has been determined polarographically making use of the three electron reduction wave of the perrhenate ion in 4 M perchloric or 4 M hydrochloric acids[33], and amperometrically by reduction with chromium(II) salts[34]. In the neutron activation method rock samples are irradiated to induce (n, γ) reactions in the rhenium forming ^{186}Re and ^{188}Re. After allowing the ^{188}Re, which has a short half-life, to decay, the rhenium is extracted from the rocks, and a rhenium carrier is added to determine the chemical yield of the separation. The radioactivity of the ^{186}Re is then estimated[35].

TABLE 4. THE DETERMINATION OF RHENIUM BY SPECTROPHOTOMETRIC METHODS

Reagents	Method	Ref.
ReO_4^-	Absorption peaks of ReO_4^- at 228 mμ ($\varepsilon = 3610$) and 206 mμ ($\varepsilon = 6060$)	a
$ReCl_6^{2-}$	Absorption at 281.5 mμ	b
$ReO_4^-/HCl/SnCl_2 + NaSCN$	Ether extraction of complex, absorption at 420 mμ	c
$ReO_4^-/HCl/SnCl_2+$furil-α-dioxime in acetone	Colour developed in aqueous solution at 532 mμ	d
ReO_4^-/reducing agent + various oximes	Extraction into organic solvents	e
$ReO_4^-/HCl/SnCl_2+$ 4-methylnioxime	Extraction into $CHCl_3$, measure at 436 mμ	f
$ReO_4^-/SnCl_2+$ diethyldithiophosphoric acid	Extraction into benzene, measure at 436 mμ	g
$ReO_4^-/HCl+$o-chloro-8-mercaptoquinoline	Extraction into $CHCl_3$, measure at 430 mμ	h
ReO_4^-/H_2SO_4+diphenylthiosemicarbazide	Extraction into $CHCl_3$, measure at 510 mμ	i
ReO_4^-/antipyridine dyestuffs		j

[a] J. B. Headridge, *Analyst* **83** (1958) 690.
[b] V. M. Meloche and R. L. Martin, *Anal. Chem.* **28** (1956) 1671.
[c] E. F. Malouf and M. G. White, *Anal. Chem.* **23** (1951) 497.
[d] V. M. Meloche, R. L. Martin and W. H. Webb, *Anal. Chem.* **29** (1957) 527.
[e] V. M. Peshcova and M. I. Gromova, *Vestn. Mosk. Univ. Ser. I Fiz. Nat. i Estesteven Nauk* **85** (1952) (see ref. 12, p. 25).
[f] J. L. Kassner, S. F. Ting and E. L. Grove, *Talanta* **7** (1961) 269.
[g] A. L. Lazarev and V. V. Rodzaevskii, *Zh. Analit. Khim.* **16** (1961) 243.
[h] H. Bankovskis and E. Labauova, *Latvijas PSR Zinatnu Akad. Vestis* **1** (1960) 97 (see ref. 12, p. 25).
[i] W. Geilmann and R. Neeb, *Z. anal. Chem.* **151** (1956) 401.
[j] A. Busev and M. Ogareva, *Zh. Analit. Khim.* **21** (1966) 574.

1.5. MISCELLANEOUS

Uses. The uses and potential uses of rhenium are mostly small scale and they are limited by the price of the element which is near that of the more expensive platinum metals.

---

[33] R. Colton, J. Dalziel, W. P. Griffith and G. Wilkinson, *J. Chem. Soc.* (1960) 71.
[34] Z. Gallai and T. Rubinskaya, *Zh. Analit. Khim.* **21** (1966) 584.
[35] D. F. C. Morris and F. W. Fifield, *Talanta* **8** (1961) 612.

Rhenium is the most refractory of the metals which can be precipitated from aqueous solution or electroplated. It is superior to tungsten in wet resistance to attack resulting from transfer by water (corrosion). It does not appear to form stable carbides and has good thermoelectric properties[36], hence the pure element has been used in filaments for mass spectrometers. The corrosion resistance of rhenium is carried over into its alloys with tungsten which also retain the refractory properties of the metals. They have been used in make-and-break devices[37], and a tungsten wire containing 3 % rhenium is an article of commerce. Other uses have included heating windings in furnaces (W–Re + Mo–Re) and thermocouples (Pt–Re [38], Mo–Re, W–Re) [39]. The superconductivity of alloys of rhenium has been extensively studied in recent years.

Alloys. Most of the alloys of rhenium with the transition metals retain the corrosion resistance of the mass of element and some are very hard especially when small amounts of boron silicon or beryllium are added. A number of detailed phase studies have been reported in recent years including the binary systems with aluminium[41], scandium[42], iron[43], cobalt[44], nickel[44], hafnium[45, 46], niobium[47, 48], molybdenum[49], the platinum metals[50], and studies of intermetallic compounds formed between rhenium and bismuth[51], uranium[52] and the rare earths[53, 54]. Some of the work has been summarized[55].

Catalysts. In recent years the interest in rhenium catalysts has increased[40]; one such catalyst is prepared by impregnating silica with a solution of perrhenic acid and reducing in hydrogen at 500°. Rhenium catalysts have been used in dehydrogenation reactions (e.g. of alcohols), in hydrogenation reactions and to promote the decomposition of ammonia. The compounds of rhenium also have catalytic activity[56], and the heptasulphide[57] and heptaselenide have been found to catalyse the hydrogenation of double bonds.

Biological activity. This has been little studied. The available evidence suggests that perrhenate is only fixed by organs to a small extent, e.g. little of the radioactive isotope

---

[36] I. E. Campbell, D. M. Rosenbaum and B. A. Gönser, *J. Less-Common Metals* **1** (1959) 185.

[37] E. M. Sherwood, *Ind. Eng. Chem.* **47** (1955) 2044.

[38] R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier, London (1966), p. 84.

[39] F. Schoenig and J. Kadlecek, *Nucl. Sci. Abstr.* **20** (1966) 1602.

[40] W. M. Davenport, V. Kellonitsch and C. H. Kline, *Ind. Eng. Chem.* **60** (1968) 10.

[41] G. Samsonov and V. Sinel'nikova, *Izv. Akad. Nauk SSSR, Neorgan. Materialy* **1** (1965) 1071.

[42] E. M. Savitskii, M. Tylkina and O. Kh. Khasnidov, *Izv. Akad. Nauk SSSR, Metally* (1966) 116.

[43] N. V. Ageer and V. S. Shekhtman, *Dokl. Akad. Nauk SSSR* **143** (1962) 1091.

[44] K. B. Lebedev, *The Chemistry of Rhenium* (tr. A. A. Woolf), Butterworths, London.

[45] E. M. Savitskii, M. A. Tylkinov, I. A. Tsyganova, E. I. Gkidyshevskii and M. P. Mblyava, *Zh. Neorgan. Khim.* **7** (1962) 1608.

[46] R. D. Blaughes, A. Taylor and J. K. Hulm, *Chem. Abs.* **51** (1962) 221e.

[47] A. G. Knapton, *J. Less-Common Metals* **1** (1959) 480.

[48] E. Zedler, D. Kraut, K. Schlaubitz and D. Muller, *J. Less-Common Metals* **4** (1962) 547.

[49] A. G. Knapton, *J. Inst. Metals* **87** (1958–9) 62.

[50] M. A. Tylkina, T. A. Tsyganova and Z. M. Savitskii, *Zh. Neorgan. Khim.* **7** (1962) 1917.

[51] B. Matthias and A. Jayaraman, *Phys. Rev. Letters* **17** (1966) 640.

[52] A. Berndt and A. Dwight, *Trans. AIME* **233** (1965) 2075 through *Chem. Abs.* **64** (1966) 7629f.

[53] E. M. Savitskii *et al., Izv. Akad. Nauk SSSR, Neorgan. Materialy* **1** (1965) 1621, 1873; *Krystellogrefiya* **10** (1965) 917.

[54] R. P. Elliott, *Proc. Conf. Rare Earth Res. 4th Phoenix Arizona, 1964*, (1965), pp. 215–45 through *Chem. Abs.* **65** (1966) 12942e.

[55] E. M. Savitskii, M. Tylkina and K. Povarova, *Alloys of Rhenium*, Moscow (1965); see *Chem. Abs.* **64** (1966) 13879f.

[56] R. Colton, *The Chemistry of Rhenium and Technetium*, Interscience, London (1965), p. 170.

[57] H. S. Broadbent, G. C. Campbell, W. J. Bartley and J. H. Johnson, *J. Org. Chem.* **76** (1954) 1847.

^{186}Re carried by ammonium perrhenate stays in the thyroid gland of hens[58]. Other work has been summarized by Tribalat[59].

2. HYDRIDIC COMPOUNDS, HALIDES AND OXIDE HALIDES

2.1. HYDRIDIC COMPOUNDS

Like the platinum metals, rhenium in a dispersed state readily absorbs hydrogen, but there is no evidence of discrete compound formation[60]. However, under suitable conditions, viz. the presence of a π-bonding ligand such as a phosphine or by stabilization in a complex, compounds containing rhenium–hydrogen bonds may be isolated.

Indications that unusual reduced rhenium species may be formed originally came from the polarographic reduction of perrhenate and other rhenium-containing anions under various conditions[61]; evidence was obtained for the rhenide (Re^{-1}) state, in acid, neutral (KCl) and in alkaline solution. The nature of the reduced rhenium species in the acid solutions has still not been resolved, partly because they appear only to be stable in dilute solution. But from alkaline solutions it has proved possible to isolate solid compounds, e.g. by the reduction of potassium perrhenate by potassium in a water–ethylenediamine mixture. These materials were at first formulated as compounds containing the square planar $[Re(H_2O)_4]^-$ ion (by analogy with the isoelectronic square planar Pt(II) compounds), but it was shown by n.m.r. spectroscopy that the solutions contained a rhenium–hydrogen bond[62]. Subsequent proposals formulated the potassium salt successively as $KReH_4 \cdot 2H_2O$ ($x = 2$–4), $K_6Re_2H_{14} \cdot 6H_2O$ and as K_2ReH_8. Infrared absorption frequencies in the solid at 1846 and 735 cm^{-1} were assigned to the Re–H bond. A preliminary X-ray analysis demonstrated that the rhenium atoms were 5.5 Å apart, which suggested the presence of discrete monomeric ions, but did not account for the observed diamagnetism of the compound[63]. The question was finally resolved by a neutron diffraction study which located the hydrogen atoms and proved the formula to be K_2ReH_9 [64]; the composition was confirmed by chemical analysis on carefully purified material.

Potassium enneahydridorhenate(VII) forms colourless hexagonal crystals (Table 5). The anion has D_{3h} symmetry; the metal atom lies at the centre of a trigonal prism of hydrogen atoms with three additional hydrogen atoms beyond the centres of the prism faces. The n.m.r. spectrum shows only a single high field peak, indicating equivalence or vibrational deformation of the hydrogen atoms[64]. The metal–hydrogen distances are in accord with the sum of the Pauling radii.

This hydrido compound is stable in potassium hydroxide solution and may be recrystallized from it, but the solid decomposes slowly in moist air to perrhenate and carbonate. Oxidizing agents such as hypochlorite oxidize the compound rapidly. Thallous ion initially causes a white precipitate to appear in an aqueous solution of the compound, but this soon deposits black thallium metal.

---

[58] J. Roche, R. Michel, E. Volopont and B. Sanz, *Compte rend. soc. biol.* **151** (1957) 1098.
[59] S. Tribalat, *Rhénium et Technétium*, Gauthier-Villars, Paris (1957), p. 36.
[60] D. J. C. Yates and J. H. Sinfelt, *J. Catalysis* **14** (1969) 182.
[61] R. Colton, *The Chemistry of Rhenium and Technetium*, Interscience, London (1965), p. 154.
[62] R. Colton, J. Dalziel, W. P. Griffith and G. Wilkinson, *Nature* **183** (1959) 1755.
[63] K. Knox and A. P. Ginsberg, *Inorg. Chem.* **1** (1962) 945; **3** (1964) 555.
[64] S. C. Abrahams, A. P. Ginsberg and K. Knox, *Inorg. Chem.* **3** (1964) 558.

The preparation of the ReH_9^{2-} ion has undoubtedly caused a reassessment of the status of hydrogen as a ligand in transition metal chemistry.

TABLE 5. PROPERTIES OF POTASSIUM ENNEAHYDRIDORHENATE(VII)[63–65]

Unit cell	hexagonal	$a_0 = 9.607 \pm 0.065$ Å $c_0 = 5.508 \pm 0.005$ Å
Re–Re (closest)		5.51 Å
Re–K (average)		3.83 Å
Re–H (average)		1.68 ± 0.01 Å
Angle H–Re–H		$93.6 \pm 0.6°$
$\left.\begin{array}{l}\text{M–H stretch}\\ \text{M–H bend}\end{array}\right\}$ i.r.		1931; 1846; 1814 cm^{-1} 735 cm^{-1}
U.v. absorption		46,080 cm^{-1} $(e'^{(1)}) \rightarrow (a_1'^{(1)})$

TABLE 6. RHENIUM–HYDRIDO–PHOSPHINE COMPOUNDS†

Compound	ν(Re–H) (cm^{-1})	Notes	Ref.
$ReH_3(Ph_3P)_2$	2000	Reinterpreted as $[ReH_x(Ph_3P)_2]_n$	a–c d
$ReH_3(Ph_3P)_4$	2050		a–c
$ReH_5(Ph_3P)_2$	1875	Reinterpreted as $ReH_7(Ph_3P)_2$	d, e
$ReH_5(R_3P)_3$	1900, 1970	$R_3 = EtPh_2, Ph_3$	d, e
$ReH_5(Ph_3P)(Ph_3As)$	In region	$R_3 = Et_2Ph, EtPh_2, Ph_3$;	d
$ReH_7(R_3P)_2$	1800–2000	$(R_3)_2 = Ph_2PC_2H_4PPh_2$	d
$[ReH_x(R_3P)_2]_n$		$R_3 = Et_2Ph$, $n=2$	d
		$R_3 = Ph_3$, n unknown, x approx. 4	
$[ReH_8(R_3P)]^-$	In region	$R_3 = Ph_3, Et_3, Bu_3^n$	f
$[ReH_8(R_3As)]^-$	1850–1980	$R_3 = Ph$	
$ReD_7(PEt_2Ph)_2$	1351 (Re–D)		d

† Adapted, with additions, from J. E. Fergusson, *Coord. Chem. Rev.* **1** (1966) 459, with permission.

[a] L. Malatesta, M. Freni, and V. Valenti, *Angew. Chem.* **73** (1961) 273.

[b] M. Freni and V. Valenti, *Gazz. Chim. Ital.* **91** (1961) 1357.

[c] L. Malatesta in S. Kirscher (ed.), *Advances in the Chemistry of Coordination Compounds*, Macmillan (1961), p. 475.

[d] J. Chatt and R. S. Coffey, *Chem. Communs.* (1966) 545; *J. Chem. Soc.* A (1969) 1963.

[e] L. Malatesta, M. Freni, and V. Valenti, *Gazz. Chim. Ital.* **94** (1964) 1278.

[f] A. P. Ginsberg, *Chem. Communs.* (1968) 857.

The remaining compounds with Re–H links are all stabilized by π-bonding ligands. The majority of these, which are characterized by the presence of one or at the most two rhenium to hydrogen bonds (e.g. $(C_5H_5)_2ReH$; $Re_3H_3(CO)_{12}$; $[(C_5H_5)_2ReH_2]^+Cl^-$; $HRe(CO)_5$), are discussed in the appropriate sections under other ligands, but those incorporating a phosphine ligand call for separate treatment.

The neutral phosphine complexes have been obtained in admixture by reducing the rhenium(V) compounds $ReOCl_3(R_3P)_2$ and $ReO(OR')Cl_2(Pr_3)_2$, the rhenium(IV) complex $ReCl_4(R_3P)_2$, or the rhenium(III) complex $ReCl_3(PR_3)_3$ with either sodium borohydride or

---

[65] A. P. Ginsberg, *Inorg. Chem.* **3** (1964) 567.

with lithium aluminium hydride[66–68]. There has been disagreement over the number of hydrido ligands in some of the complexes, which is an indication of the experimental difficulties (Table 6). The compounds are non-electrolytes and are diamagnetic. Like the ReH_9^{2-} anion, they give rise to only one principal n.m.r. signal, but the splitting by the phosphorus nuclei often enables the number of hydridic hydrogen atoms to be estimated[66]. The anionic complexes $[ReH_8R_3P]^-$ are obtained by treating the salt $(Et_4N)_2ReH_9$ with the phosphine (or appropriately the arsine) and refluxing under nitrogen in propan-2-ol solution[69]. They may be considered as derivatives of ReH_9^{2-}, as may, indeed, the 9-coordinate $ReH_7(R_3P)_2$ compounds.

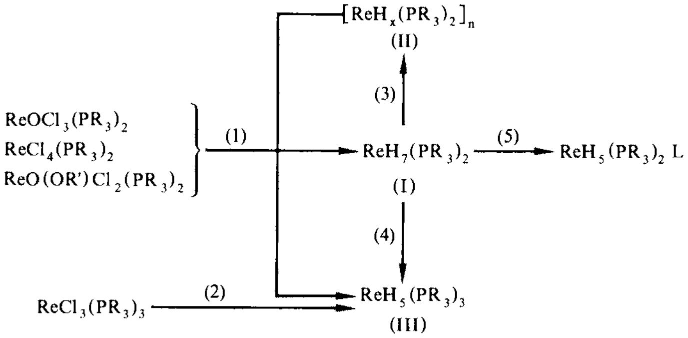


FIG. 1. Preparation and reactions of rhenium hydride complexes. R = alkyl or aryl groups. Solvent for all reactions, tetrahydrofuran. Reagents for (1) and (2), $LiAlH_4$; for (4), PR_3; for (5), ligands. L = AsR_3, PR_3 and amines. Reaction (3) was effected by heat. (Reproduced, with permission, from J. Chatt and R. S. Coffey, *J. Chem. Soc.* A (1969) 1963.)

Treatment of certain of these hydrido complexes with halogenating agents yields the Re(IV) complexes $ReX_4(Ph_3P)_2$ (X = Cl, Br) [68]. With hydrochloric acid all the hydridic hydrogen is displaced from complexes of the types (I) and (III) [66] (Fig. 1), though with the phosphine 1,2-bisdiphenylphosphinoethane as ligand, halogenohydride complexes of rhenium(III) have been reported[68], e.g. $ReH_2X(dpe)_2$ (X = Cl, Br or I) and $ReH_2I(PPh_3)_2(dpe)$.

2.2. HALIDES

The status of the halides of rhenium (Table 7) has changed considerably in the last few years, largely through the recognition of the existence of metallic "clusters" in the trihalides and in certain of the tetrahalides also. Nevertheless, a number of problems remain, including the properties of the highest chloride, $ReCl_6$. Rhenium heptafluoride is unique in being the only septavalent binary halide of a transition metal stable at ordinary temperatures. Of compounds in low oxidation states, the absence of a trifluoride is noteworthy, and the precise composition of the two lower iodides, ReI and ReI_2, remains to be decided.

---

[66] J. Chatt and R. S. Coffey, *Chem. Communs.* (1966) 545; *J. Chem. Soc.* A (1969) 1963.
[67] L. Malatesta, M. Freni and V. Valenti, *Gazz. Chim. Ital.* **94** (1964) 1278.
[68] M. Freni, R. Demichelis and D. Giusto, *J. Inorg. Nucl. Chem.* **29** (1967) 1433.

2.2.1. Trihalides

Although the trichloride and tribromide have been known since the 1930's, it is only recently that their structures have been elucidated, and some of the earlier chemistry, reported in Sidgwick[70], must now be reinterpreted.

TABLE 7. BINARY HALIDES OF RHENIUM

Fluorides	Chlorides	Bromides	Iodides
			(ReI)
			(ReI_2)
	$ReCl_3$	$ReBr_3$	ReI_3
ReF_4	$ReCl_4$	$ReBr_4$	ReI_4
ReF_5	$ReCl_5$	$ReBr_5$	
ReF_6	($ReCl_6$)		
ReF_7			

Brackets denote compounds whose existence is uncertain.

(a) *Rhenium Trichloride*

This was originally prepared by the thermal decomposition of silver hexachlororhenate(IV) Ag_2ReCl_6. The reaction proceeds according to the equation

$$2Ag_2ReCl_6 \rightarrow 4AgCl + ReCl_5 + ReCl_3$$

The tetrachloride, which might be expected to be the product of decomposition, is not formed. Probably the best method of preparation is to decompose the pentachloride thermally in nitrogen[71],

$$ReCl_5 \rightarrow ReCl_3 + Cl_2$$

but small amounts are formed by other reactions, e.g. the reaction of rhenium powder with sulphuryl chloride.

Rhenium trichloride is a dark red crystalline solid which on strong heating gives a green vapour and may be sublimed in a vacuum at 500°. Decomposition to the metal and chlorine is said to begin at 360° [72]. Some physical properties are displayed in Table 8. Rhenium trichloride is less reactive after resublimation at high temperatures, and it has been supposed that different forms exist. Magnetic measurements have lent support to this view; the low-temperature form has a temperature independent molar susceptibility of about 20×10^{-6} c.g.s. units at 25°, and the high temperature form of about 495×10^{-6} c.g.s. units[73]. However, the X-ray evidence does not distinguish the two forms.

The crystal structure of the sublimed trichloride[74] (Fig. 2) indicates that the compound is a trimer, $Re_3(Cl_3)Cl_3Cl_{6/2}$. The internal bridging chlorine atoms (labelled Cl_3 in Fig. 2) are

---

[69] A. P. Ginsberg, *Chem. Communs.* (1968) 857.

[70] N. V. Sidgwick, *The Chemical Elements and their Compounds*, Vol. II, Oxford (1951).

[71] *Inorganic Syntheses*, Vol. I (1939) 182.

[72] L. E. Wilson, NASA Doc. N63-13435 (1963).

[73] D. Brown and R. Colton, *Austral. J. Chem.* **18** (1965) 441.

[74] F. A. Cotton and J. T. Mague, *Inorg. Chem.* **3** (1964) 1402.

coplanar with the triangle of rhenium atoms. The unit is linked to the next cluster by bridging through the in-plane (Cl_4) and out-of-plane chlorine (Cl_1) atoms, one of each to each rhenium atom in the cluster. The (Cl_1) atoms of one cluster become the (Cl_4) of the next. The (Cl_2) atoms which lie below the plane of the triangle are terminal and non-bridging. Hence there

TABLE 8. PHYSICAL PROPERTIES OF RHENIUM TRIBROMIDE AND RHENIUM TRICHLORIDE

	$ReCl_3$	$ReBr_3$	Ref.
Vapour pressure equation	$\log P_{(atm)} = -\frac{(10.87 \pm 0.39)}{T} + 12.83 \pm 0.72$	—	b
$\triangle H_{sub}$ (kcal mole^{-1})†	48.7±1.5	47.6±1.5	b
$\triangle S_{sub}$ (583°) (e.u.)†	58		b
C_p (gibbs)	22.08		a
$\triangle H^\circ_{form}$(crystal) (kcal mole^{-1})	−63.0±0.8	−39.3±0.8	c
†$\triangle H^\circ_{form}$ (gas) (kcal mole^{-1})†	−140±3	−70±4	b
S° (gibbs)	29.61	35±2	a
$\triangle G^\circ$ (kcal mole^{-1})	−45.4±0.8	−31±1.5	a
$\triangle H^\circ_{hydr}$ (kcal mole^{-1})	−54.29±0.14		d

† Figures refer to the trimeric unit.

[a] R. B. Bevan, R. A. Gilbert and R. H. Busey, *J. Phys. Chem.* **70** (1966) 147.

[b] A. Buchler, P. E. Blackbirn and J. L. Stauffer, *J. Phys. Chem.* **70** (1966) 685.

[c] J. P. King and J. W. Cobble, *J. Am. Chem. Soc.* **82** (1960) 2111.

[d] R. H. Busey, E. D. Sprague and R. B. Bevan, *J. Phys. Chem.* **73** (1969) 1039.

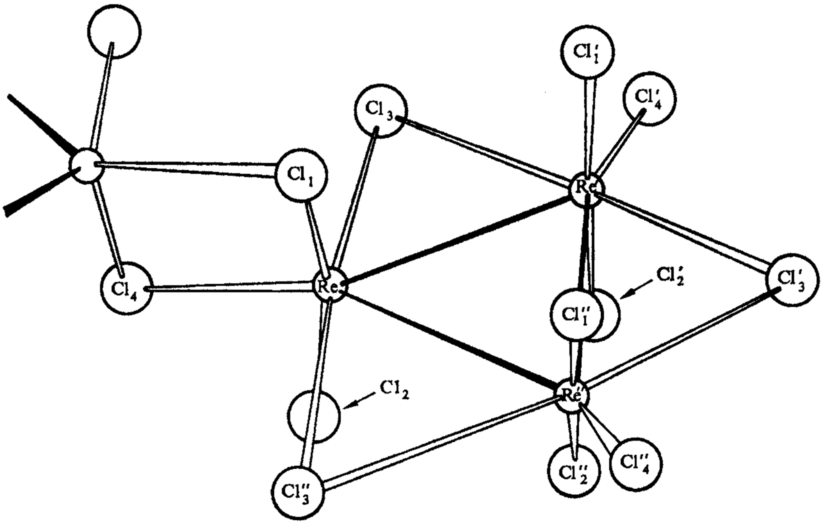


FIG. 2. The Re_3Cl_9 cluster in rhenium trichloride. (Reproduced from F. A. Cotton and J. T. Maghee, *Inorg. Chem.* 3 (1964) 1402; copyright 1964 by the American Chemical Society; reprinted by permission of the copyright owner.)

are three internally bridging chlorine atoms, three terminal out-of-plane chlorine atoms, three externally bridging in-plane chlorine atoms and three externally bridging out-of-plane chlorine atoms associated with each cluster. The relationship between this structure and the compounds derived from rhenium trichloride is discussed in section 7, Complex Compounds (see also Fig. 3). It has been shown, as evidence of the thermal stability of the Re_3Cl_9 units, that they constitute more than 90% of the gaseous compounds at *ca.* 650° [75]. Note that the entropy of the solid ($S°$) is markedly lower than that estimated by summing the atomic contributions from the elements (36 e.u.).

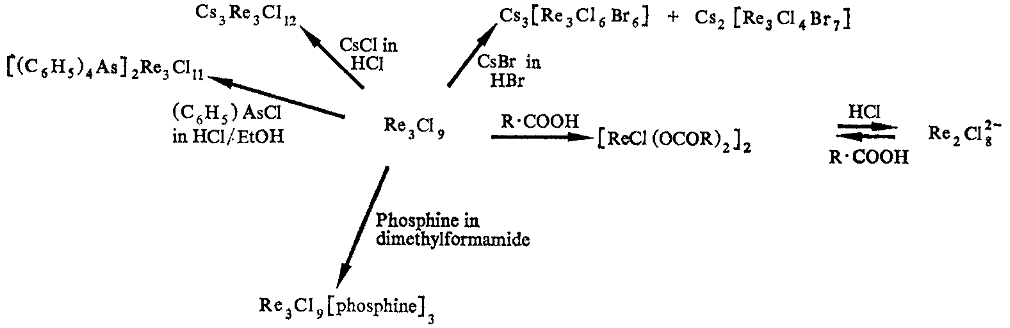


FIG. 3. Some reactions of rhenium trichloride.

The trichloride is reduced to the metal at 250–300° by hydrogen. On being heated in oxygen it gives the oxide tetrachloride, $ReOCl_4$, and perrhenyl chloride, ReO_3Cl. It dissolves in water to give a red solution which slowly hydrolyses; the final product is the hydrated sesquioxide $Re_2O_3 \cdot xH_2O$ [76]. The compound is also soluble in acetone, methanol and acetic acids. In tetrahydrothiophene the molecular weight is 885 (calculated for trimer 887)[74]. Rhenium trichloride dissolves in hydrochloric acid to form a stable red solution which is not easily oxidized. Upon the addition of suitable cations, complex chlorides may be isolated which were at first thought to be derivatives of the $ReCl_4^-$ anion, but recent work has shown that these complexes are polymeric like trichloride itself. Some reactions of the trichloride are summarized in Fig. 3. In the earlier work published in the 1930's it was shown that rhenium trichloride dissolves in liquid ammonia; vapour pressure isotherms suggested the presence of compounds of the composition $ReCl_3 \cdot 14NH_3$, $ReCl_3 \cdot 7NH_3$ and $ReCl_3 \cdot 6NH_3$ [77].

(b) *Rhenium Tribromide*

This is prepared by the thermal decomposition of the pentabromide[78] or of Ag_2ReBr_6 [79]. It has also been prepared by treating rhenium with liquid bromine at 500°, dissolving the resultant mixture of bromides at room temperature in benzene and evaporating to dryness at 80° [80].

---

[75] A. Buchler, P. E. Blackburn and J. L. Stauffer, *J. Phys. Chem.* **70** (1966) 685.
[76] W. Geilmann, F. W. Wrigge and W. Biltz, *Z. anorg. allgem. Chem.* **214** (1933) 248.
[77] W. Klemm and G. Frischmuth, *Z. anorg. allgem. Chem.* **230** (1937) 209.
[78] R. Colton, *J. Chem. Soc.* (1962) 2072.
[79] *Inorganic Synthesis*, Vol. X (1967) 58.
[80] V. C. Tronev and R. A. Dovlyatshina, *Azerb. Khim. Zh.* (1965) 116.

Early reports described the tribromide as red or green, but it is now described as a red-brown crystalline solid. Physical properties are indicated in Table 8. The crystal structure has not been determined in detail, but is said to be very similar to that of the chloride[81]. The Re_3Br_9 unit has been recognized in the tribromide vapour [75] and, curiously, in the mixed complex salt (quin $H)_2$ Re_4Br_{15} [82].

Rhenium tribromide dissolves in acetone, alcohol and ethers to give stable solutions, but in water it is hydrolysed more readily than the trichloride. It reacts with liquid ammonia to give a 1 :4 ammoniate[80]; the nature of this material has not been fully elucidated (see also ref. 79).

(c) *Rhenium Triiodide*

This is not formed directly from the elements. It has been prepared by the decomposition of the tetraiodide in a sealed tube at 350° and by the thermal decomposition of ammonium hexaiodorhenate(IV) at 325° in a vacuum; the residue is subsequently heated with iodine in a sealed tube at 200° to complete the iodonation[83]. A more recent method involves the reduction of perrhenic acid with hydriodic acid and alcohol at elevated temperatures, the crystals being washed with alcohol and carbon tetrachloride[84].

Rhenium triiodide forms a lustrous black solid. It loses iodine on warming, especially under a vacuum. It is slightly soluble in water and in dilute acids, but is almost insoluble in alcohol and ethers[83].

The crystal structure shows that like $ReCl_3$ and $ReBr_3$, the triiodide is trinuclear[85]. The system is similar to that in the trichloride excepting that the bridging is incomplete, inasmuch that in Re_3I_9 only two out of the three rhenium atoms are involved, i.e. $Re_3(I_3)I_4I_{4/2}$ instead of $Re_3(Cl_3)Cl_3Cl_{6/2}$. Not surprisingly, since one rhenium atom is not equivalent to the other two, there are two metal–metal distances in each unit.

2.2.2. Tetrahalides

These are formed with all four halogens but the tetraiodide is unstable.

(a) *Rhenium Tetrafluoride*

This is formed by disproportionation of the pentafluoride[86], but has also been prepared by the reduction of rhenium hexafluoride with rhenium at 550° in a static system[87]. The tetrafluoride forms a blue solid which may be sublimed under a vacuum at about 300°. The X-ray powder photograph has been indexed[87] on the basis of a tetragonal unit cell with unit-cell parameters $a_0 = 10.12$ and $c_0 = 15.95$ Å.

Rhenium tetrafluoride is hydrolysed by water to the dioxide and hydrofluoric acid[86].

Earlier work on the tetrafluoride by Ruff and his co-workers[88], which has been summarized by Sidgwick, appears to refer to a mixture of the tetrafluoride and the pentafluoride,

---

[81] M. J. Bennett, F. A. Cotton and B. M. Foxman, *Inorg. Chem.* **7** (1968) 1563.

[82] F. A. Cotton and S. J. Lippard, *Inorg. Chem.* **4** (1965) 59.

[83] R. D. Peacock, A. J. E. Welch and L. F. Wilson, *J. Chem. Soc.* (1958) 2901.

[84] *Inorganic Synthesis*, Vol. VII (1963) 185.

[85] M. J. Bennett, F. A. Cotton and B. M. Foxman, *Inorg. Chem.* **7** (1968) 1563.

[86] G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.* (1960) 1099.

[87] D. E. LaValle, R. M. Steele and W. T. Smith, *J. Inorg. Nucl. Chem.* **28** (1966) 260.

[88] O. Ruff and W. Kwasnik, *Z. anorg. allgem. Chem.* **220** (1934) 96.

though it should be noted that his experiments, which involved the reduction of hexafluoride by hydrogen, carbon monoxide or sulphur dioxide, have not been repeated.

(b) *Rhenium Tetrachloride*

This compound, which has only recently been synthesized, may occur in two forms, one of which is very much better attested than the other. These forms have been designated α- and β-$ReCl_4$, though it is just possible they refer to the same material.

The action of thionyl chloride on freshly precipitated rhenium dioxide yields[89] a black material analysing to $ReCl_4$. This material (α-$ReCl_4$) is readily attacked by moist air, and on hydrolysis yields some rhenium dioxide. It gives a poor X-ray powder pattern, and the structure has not been determined. The magnetic moment, allowing for a substantial temperature independent contribution of 230×10^{-6} c.g.s. units, is about 1.0 BM per rhenium atom[90]; these results have been interpreted on the assumption that α-$ReCl_4$ consists of a trimeric Re_3Cl_{12} species[90]. It has been stated[90], that the hydrolysis of α-$ReCl_4$ in dilute alkali gives a 25% release of chloride ion, which would be in accordance with the reaction scheme

$$(Re_3Cl_9)Cl_3 + 3OH^- \rightarrow (Re_3Cl_9)(OH)_3 + 3Cl^-$$

Objections have been raised to this formulation, and indeed also to the preparative method and the composition of α-$ReCl_4$ [91, 92]. It has been shown that the use of thionyl chloride as a reagent in preparing anhydrous chlorides from metal hydroxides or hydrated oxides leads to impure materials—successful preparations involve a resublimation which has not been undertaken with α-$ReCl_4$ (presumably owing to thermal decomposition). Sulphur and oxygen have been shown to be present in some supposed specimens of α-$ReCl_4$ [91, 92]. It has also been shown qualitatively[92] that α-$ReCl_4$ gives at least some of the chemical reactions of the β-form, and the interpretation of the magnetic evidence which led to the trimeric formulation has been challenged[92], partly on the basis that similar predictions made[90] about the structures of $MoCl_3$, $MoCl_4$ and WCl_5 have already proved incorrect. Nevertheless, it has been established that materials close to the correct composition for $ReCl_4$ can be prepared by the thionyl chloride method[92], and there is some slight evidence from X-ray powder photography to suggest that α-$ReCl_4$, if it proves to be a true compound, may adopt the $NbCl_4$ structure.

Evidence for the second form of rhenium tetrachloride, β-$ReCl_4$, is much clearer, though the structure of the compound was determined[93] before a deliberate preparative method was discovered.

β-rhenium tetrachloride has been prepared by the reaction of the trichloride with a slight excess of the pentachloride in a sealed tube at 300° [94, 95], by the action of antimony pentachloride on rhenium and by the reaction between rhenium pentachloride and antimony trichloride[95]. This form of the tetrachloride is reported to be a black or dark purple crystalline solid stable indefinitely in a vacuum at room temperature[94]. The compound decomposes to $ReCl_5$ and $ReCl_3$ in a vacuum at 300° [94]. Earlier reports suggested that it

---

[89] D. Brown and R. Colton, *Nature* **193** (1963) 300; *J. Chem. Soc.* (1964) 714.

[90] R. Colton and R. L. Martin, *Nature* **205** (1965) 239.

[91] K. Rinke, M. Klein and H. Schäfer, *J. Less-Common Metals* **12** (1967) 497.

[92] I. R. Anderson and J. C. Sheldon, *Inorg. Chem.* 7 (1968) 2602.

[93] M. J. Bennett, F. A. Cotton, B. M. Foxman and P. F. Stokely, *J. Am. Chem. Soc.* **89** (1967) 2759.

[94] J. H. Canterford and R. Colton, *Inorg. Nucl. Chem. Letters* **4** (1968) 711.

[95] P. W. Frais, A. Guest and C. J. L. Lock, *Canad. J. Chem.* **47** (1969) 1069.

could be metastable[96]. β-$ReCl_4$ is variously stated to have a temperature independent paramagnetism of 580×10^{-6} c.g.s. units[94] or of 1010×10^{-6} c.g.s. units[95].

The structure of β-$ReCl_4$ indicates the compound to be dimeric; i.e. $[Re_2Cl_8]^0$ is analogous to the tervalent $Re_2Cl_8^{2-}$ anion[93]. Structurally the unit may be written $Re_2(Cl_3)Cl_4Cl_{2/2}$; the two rhenium atoms are linked by three chlorine atoms and a metal–metal bond (Re–Re = 2.73 ± 0.03 Å). Each Re_2Cl_8 unit is linked by a single chlorine bridge to the next, so that chains of Re_2Cl_8 units are formed[93]. There is a close resemblance to the $W_2Cl_9^{3-}$ structure.

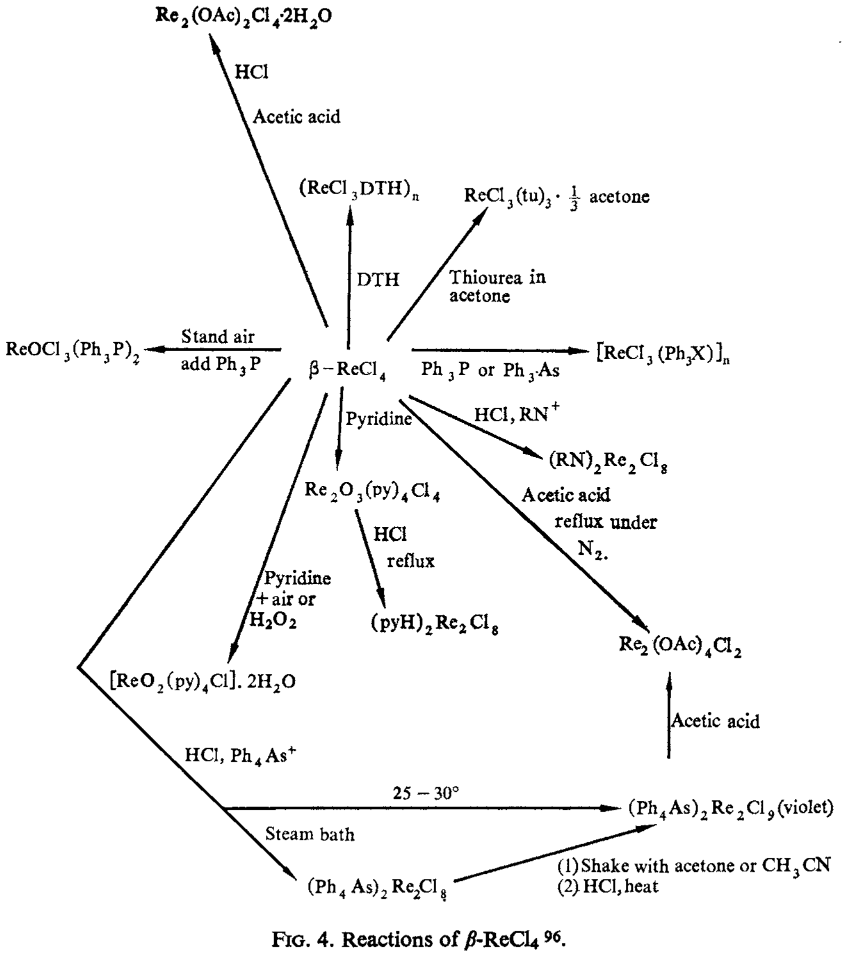


FIG. 4. Reactions of β-$ReCl_4$ [96].

The nature of the β-$ReCl_4$ structure was strongly suspected from the chemical properties (Fig. 4). In many of the reactions a dimeric rhenium unit is retained with reduction to the tervalent state; in others oxidation takes place to quinquevalent Re–O or O–Re–O compounds. In one case the Re(IV) state is stabilized in the violet salt $(Ph_4As)_2Re_2Cl_9$. This has a

---

[96] F. A. Cotton, W. R. Robinson and R. A. Walton, *Inorg. Chem.* **6** (1967) 223.

magnetic moment of 1.1 BM and apparently has rhenium in both the tervalent and quadrivalent states (p. 968).

Rhenium tetrachloride is quite different from the corresponding technetium compound (Chapter 38) in structure and behaviour, and it is particularly interesting to find that hexachlororhenate ion has not been prepared directly by the addition of the β-tetrachloride to aqueous hydrochloric acid.

(c) *Rhenium Tetrabromide*

This has been prepared by the reduction of perrhenic acid with hydrobromic acid, the dissolution of rhenium dioxide in hydrobromic acid and by the treatment of rhenium tetraiodide with successive portions of hydrobromic acid with evaporation to small volume between each addition. In each case the solution of bromorhenic acid which results is finally evaporated to small volume and dried in a desiccator containing potassium hydroxide and phosphorus(V) oxide (cf. osmium and iridium bromides)[97]. The chemistry has not been investigated.

(d) *Rhenium Tetraiodide*

The original claim by the Noddacks to have prepared this compound by passing iodine vapour over rhenium metal has not been substantiated[98]. The tetraiodide may, however, be prepared by reducing perrhenic acid with hydroiodic acid at room temperature[83]. An intermediate compound is first formed (possibly a hydrate on hexaiodorhenic acid); this loses water and hydroiodic acid when kept over alkali and phosphorus(V) oxide in a desiccator, giving the tetraiodide.

Rhenium tetraiodide loses iodine slowly on standing in a vacuum at room temperature, and more rapidly on heating. It is hygroscopic and dissolves readily in water, giving a brown solution which is rapidly hydrolysed[83]. The compound also dissolves in acetone and ether to give rather more stable brown solutions. The magnetic moment has been reported to be 0.9 BM [98a].

2.2.3. Pentahalides

A fluoride, a chloride and a bromide are known. In view of the instability of the tetraiodide, it is not expected that a stable pentaiodide would be formed.

(a) *Rhenium Pentafluoride*

This is formed, together with the blue oxide tetrafluoride $ReOF_4$ and the tetrafluoride ReF_4, when tungsten hexacarbonyl is treated with a slight excess of rhenium hexafluoride, either alone, or preferably in tungsten hexafluoride solution[86]. It is also formed by the reduction of rhenium hexafluoride by tungsten wire at 600° [99]; the pentafluoride is collected on a cold surface at −75°.

---

[97] R. Colton and G. Wilkinson, *Chem. and Ind.* (1959) 1314; R. Colton, unpublished observations quoted in R. Colton, *The Chemistry of Rhenium and Technetium*, Interscience (1965), p. 76.

[98] C. L. Rulfs and P. J. Elving, *J. Am. Chem. Soc.* 72 (1950) 3304.

[98a] J. E. Fergusson, B. H. Robinson and W. R. Roper, *J. Chem. Soc.* (1962) 2113.

[99] I. Haigh and R. D. Peacock, unpublished observation (1969).

Rhenium pentafluoride forms a green or yellow–green solid which melts at 48° to a yellow viscous liquid which readily supercools. Above 140° it undergoes disproportionation to the tetrafluoride and hexafluoride[100], apparently irreversibly,

$$2ReF_5 \rightarrow ReF_4 + ReF_6$$

Some physical properties have been determined[100] and are displayed in Table 9. The magnetic susceptibility has been determined over a range of temperature[86], but the magnetic behaviour is complicated and has not been interpreted.

Rhenium pentafluoride is isostructural with vanadium, chromium and technetium pentafluorides[101]. Its structure has not been determined in detail but is very near to that of molybdenum oxide pentafluoride, so that rhenium pentafluoride must have a chain structure made up of ReF_6 octahedra linked through *cis* fluorine bridges.

TABLE 9. PHYSICAL PROPERTIES OF RHENIUM PENTAFLUORIDE[100]

Melting point	48°
Boiling point (extrapolated)	221.3°
ΔH_{evap} (kcal mole^{-1})	13.88
ΔS_{evap} (e.u.)	28.1
Vapour pressure equation	$\log P_{mm} = 9.024 - 3037/T$ (48–140°)

Rhenium pentafluoride is a very reactive compound. It is hydrolysed by water, but the reaction is complicated by the appearance of ReF_6^{2-} ion as well as the expected perrhenate and hydrated rhenium dioxide (cf. OsF_5) [99].

(b) *Rhenium Pentachloride*

This is formed as the major product when chlorine reacts with rhenium[102], but its properties are surprisingly little known. The compound may be purified by distillation in a chlorine stream or by vacuum sublimation.

Rhenium pentachloride forms a deep brown or black solid, melting at 220°. It volatilizes easily to give a reddish-brown vapour, but the boiling point has not been determined. The magnetic properties have been investigated several times, but there has not been complete concordance, presumably because of the presence of impurities in the samples. The most recent determination[89] gives a paramagnetic susceptibility of 1457×10^{-6} c.g.s. units at 302°K with a θ value of 266°. At low temperatures the paramagnetism diverges from the Curie–Weiss law.

The structure of rhenium pentachloride, determined by single crystal X-ray analysis[103], indicates the presence of the dimeric Re_2Cl_{10} unit ($Cl_4Re(Cl)_2ReCl_4$). The chlorine atoms are double-hexagonal close packed (contrast $NbCl_5$ and UCl_5) with the metal atoms occupying one-fifth of the octahedral holes. The Re–Re bond distance of 3.74 Å indicates the absence

---

[100] G. H. Cady and G. B. Hargreaves, *J. Chem. Soc.* (1961) 1568.

[101] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* A (1969) 1651.

[102] W. Gilmann, F. W. Wrigge and W. Biltz, *Z. anorg. allgem. Chem.* **214** (1933) 248; *Inorganic Syntheses*, Vol. I (1939) 180.

[103] K. Mucker, G. S. Smith and Q. Johnson, *Acta Cryst.* **1324** (1968) 874.

of metal–metal bonding[103]. Other distances within the dimeric unit are Re–Cl (terminal) = 2.244±0.012 Å and Re–Cl (bridging) = 2.465±0.013 Å. The rhenium atoms are displaced from the centre of the octahedra of chlorine atoms in such a way that they appear to repel one another (cf. $NbCl_5$). The absorption and vibrational spectra have been assigned[103a].

Rhenium pentachloride is very reactive. It is hydrolysed immediately by water, and disproportionation to Re(IV) and Re(VII) occurs:

$$3ReCl_5 + 8H_2O \rightarrow 2ReO_2 + HReO_4 + 15HCl$$

When heated with potassium chloride, potassium hexachlororhenate(IV) is formed[104], and with oxygen it can give oxide chlorides. With phosphorus trichloride a complex of composition $RePCl_8$ is formed[105], which has a magnetic moment of 2.37 BM. This has been formulated as $ReCl_5 \cdot PCl_3$[105]. Other chemical reactions have been classified[103a].

(c) *Rhenium Pentabromide*

It has been claimed that this is the major product when bromine vapour is carried in a stream of nitrogen over rhenium at 650° [106], but a better method of preparation is the exchange reaction between rhenium hexafluoride and boron tribromide[107].

Rhenium pentabromide was first stated to be a dark blue solid which melts a little above room temperature to give a bluish-green liquid, the vapour also being blue[106]. However, in the more recent publication it is described as a dark brown solid which begins to decompose to the tribromide at 110° in a vacuum. The magnetic moment falls from 1.28 BM at 295°K to 1.00 BM at 105°K; the Curie–Weiss law is not obeyed.

2.2.4. Hexahalides

Of these the hexafluoride is well known, but many of the properties of the hexachloride remain to be elucidated in spite of recent work.

(a) *Rhenium Hexafluoride*

This is formed, together with the heptafluoride, when heated rhenium powder reacts with fluorine[108]. To obtain the hexafluoride pure the product is heated with an excess of rhenium metal, either in a static[108] or in a flow system[109], at about 400°. Earlier work[88] on the hexafluoride must refer to mixtures of hexa- and heptafluorides. This compound has also been made by fluorinating other rhenium compounds such as the heptasulphide, but the only other good preparative method appears to be the action of chlorine trifluoride on rhenium metal at 300° [110].

Rhenium hexafluoride forms a yellow solid and liquid and a colourless vapour (Table 10). As in the other transition metal hexafluorides, there is a clearly visible phase transition in the solid from a low-temperature orthorhombic form to a high temperature cubic form. The cubic crystals have a glassy appearance; they are large and usually not well formed.

[103a] D. A. Edwards and R. T. Ward, *J. Chem. Soc.* A (1970) 1617.
[104] H. V. A. Briscoe, P. L. Robinson and C. M. Stoddart, *J. Chem. Soc.* (1951) 2263.
[105] P. Machmer, *Inorg. Nucl. Chem. Letters* 4 (1968) 91.
[106] R. Colton, *J. Chem. Soc.* (1962) 2708.
[107] J. H. Canterford, T. A. O'Donnell and A. B. Waugh, *Austral. J. Chem.* **24** (1971) 243.
[108] J. G. Malm and H. Selig, *J. Inorg. Nucl. Chem.* **20** (1961) 189.
[109] R. D. Peacock, unpublished observation (1962).
[110] N. S. Nikolaev and E. G. Ippolitov, *Dokl. Akad. Nauk SSSR* **134** (1960) 358.

The low value of the magnetic moment of rhenium hexafluoride (see Table 11) has been attributed to spin–orbit coupling.

The vibrational spectra of rhenium hexafluoride[111] accord with an octahedral molecule. The chief infrared absorption frequency (ν_3) lies at 715 cm^{-1}; other fundamentals lie at 775 (ν_1), 671 (ν_2), 257 (ν_4), 295 (ν_5) and 193 (ν_6) cm^{-1}. Force constants have been calculated by a number of workers[112]. The Raman spectrum in liquid hydrogen fluoride[113] is similar to the gaseous spectrum; anomalies are attributed to a dynamic Jahn–Teller distortion.

TABLE 10. PHYSICAL PROPERTIES OF RHENIUM HEXAFLUORIDE

		Ref.
Melting point	18.5°	a, b
Boiling point	33.7°	a, b
Solid transition	−3.45°	a
Vapour pressure (solid)	$\log P_{mm} = 12.70721 - 0.8327 \log T - 2303.6/T$ (−10.47° to −3.45°)	a
	$\log P_{mm} = 9.12298 - 0.1790 \log T - 1765.4/T$ (−3.45° to 18.5°)	a
Vapour pressure (liquid)	$\log P_{mm} = 18.20814 - 3.599 \log T - 1956.7/T$ (18.5°–48.06°)	a
ΔH_{trans} (kcal $mole^{-1}$)	2.027	a
ΔH_{fus} (kcal $mole^{-1}$)	1.107	a
$\Delta H_{(vap)}$ (kcal $mole^{-1}$)	6.867	a
ΔS_{trans} (e.u.)	7.52	a
ΔS_{fus} (e.u.)	3.80	a
χ_m (14–296°K)	$0.87 \times 10^{-4} + (78 \times 10^{-4}/T)$ c.g.s. units	c
Magnetic moment	$\mu_{calc} = 0.25$ BM	
Unit cell size (cubic high temperature form) in Å	$a_0 = 6.26$	d
Solubility in liquid HF (moles per 1000 g)	1.75	e

[a] J. G. Malm and H. Selig, *J. Inorg. Nucl. Chem.* **20** (1961) 189.
[b] G. H. Cady and G. B. Hargreaves, *J. Chem. Soc.* (1961) 1563.
[c] H. Selig, F. A. Cafasso, D. N. Gruen and J. C. Malm, *J. Chem. Phys.* **36** (1962) 3440.
[d] S. Siegel and D. A. Northrop, *Inorg. Chem.* **5** (1966) 2187.
[e] B. Frlec and H. H. Hyman, *Inorg. Chem.* **6** (1967) 1596.

Rhenium hexafluoride is very reactive. It hydrolyses in the atmosphere giving a black fume of the dioxide, and in water is decomposed quantitatively:

$$3ReF_6 + 6H_2O \rightarrow 2HReO_4 + ReO_2 + 12HF$$

In some experiments an unstable green solution is first formed which quickly darkens and becomes opaque; this rhenium species has not been identified. With a little moisture only, the oxyfluoride, $ReOF_4$ is formed[115].

---

[111] H. H. Claassen, J. G. Malm and H. Selig, *J. Chem. Phys.* **36** (1962) 2890.
[112] H. Kim, P. A. Sondev and H. A. Claassen, *J. Mol. Spec.* **26** (1968) 46.
[113] B. Frlec and H. H. Hyman, *Inorg. Chem.* **6** (1967) 1596.
[114] N. Bartlett, S. P. Beaton and N. K. Jha, *Chem. Communs.* (1966) 168.
[115] R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier (1966), p. 47.

Rhenium hexafluoride does not react with oxygen at 500° [108] but is reduced by nitric oxide to the complex salt $NOReF_6$ [114]. With nitrosyl fluoride it forms the sexivalent salt $(NO)_2ReF_8$ [114]; the similar salt, K_2ReF_8, is formed by interaction with potassium fluoride[116]. In liquid hydrogen fluoride solution rhenium hexafluoride is reduced by hydrazinium fluoride, $N_2H_6F_2$, to $N_2H_6^{2+}$ salts of either the ReF_6^{2-} or the ReF_6^- ion, depending which reagent is in excess[117]. In liquid sulphur dioxide solution, rhenium hexafluoride is reduced by alkali–metal iodides to the complex salts $MReF_6$ [118] (M = Na, K, Rb, Cs).

(b) *Rhenium Hexachloride*

The reaction of a chlorine–nitrogen mixture at 650° with a rhenium film, specially prepared by absorbing ammonium perrhenate solution into dry, porous brick and reducing to the metal at 600° with hydrogen, yields a crystalline material analysing to $ReCl_6$ [119]. It appears that this material is also frequently present in samples of the pentachloride prepared from hydrogen-reduced rhenium powder[119]. Rhenium hexachloride has also been apparently prepared from the exchange reaction of rhenium hexafluoride or rhenium heptafluoride with boron trichloride; by this method it is claimed that batches of up to 5 g may be formed[107]. The reaction goes below room temperature; similar exchange reactions occur between rhenium fluorides and phosphorus trichloride or carbon tetrachloride[107].

Rhenium hexachloride, whose preparation was also claimed by early workers in the field[119], is said to form long dichroic needles, appearing red–brown by transmitted light and dark green by reflected light. The crystals melt at 29° (29.5±0.5° from vapour pressure measurements)[107] to give a dark brown liquid which volatilizes on gentle heating. The compound is said to be thermally stable in nitrogen and in chlorine. The magnetic moment, measured over the range 105–300°K, is 1.88 BM at 297°K, and the θ value is given variously as 28° [120] and 75° [107] (contrast ReF_6). The infrared spectrum of the material indicates the absence of $ReOCl_4$ [107]; this is an important observation since there is little doubt that confusion has occurred with the latter, which has a melting point (cf. ref. 121) and volatility. Nevertheless, the evidence for $ReCl_6$ is not yet completely conclusive (the reported properties are out of line with those of WCl_6), and a full structural determination is called for.

Hydrolysis of the hexachloride yields perrhenic acid and rhenium dioxide in the correct ratio of 2:1 [119]. With oxygen the only product observed is ReO_3Cl [119].

(c) *Rhenium Heptafluoride*

If the mixture of ReF_6 and ReF_7, prepared by treating rhenium with fluorine, is heated with 3 atm of pressure of fluorine at 400° for several hours, the hexafluoride is converted quantitatively to the heptafluoride[108].

Rhenium heptafluoride, like the hexafluoride, forms a yellow solid, and in many ways has a similar appearance. The physical properties (Table 11) emphasize the similarities to the transition metal hexafluorides, extending even to the transition at low temperatures into an orthorhombic form. The chief interest in this compound lies perhaps in its possible structure.

---

[116] E. G. Ippolitov, *Russ. J. Inorg. Chem.* 7 (1962) 485.

[117] B. Frlec, H. Selig and H. H. Hyman, *Inorg. Chem.* **6** (1967) 1775.

[118] R. D. Peacock, *J. Chem. Soc.* (1957) 467.

[119] R. Colton, *Nature* **193** (1962) 872.

[120] D. Brown and R. Cotton, *J. Chem. Soc.* (1964) 714.

[121] D. D. Edwards and A. A. Woolf, *J. Chem. Soc.* A (1966) 91.

The vibrational spectra suggest the molecule to be a pentagonal bypyramid[122], but neither this evidence, nor that of the ^{19}F n.m.r. spectrum, which shows only a single frequency at 510 ppm downfield from silicon tetrafluoride[123], is quite conclusive.

TABLE 11. PHYSICAL PROPERTIES OF RHENIUM HEPTAFLUORIDE

		Ref.
Triple point	48.3°	a
Boiling point	73.72°	a
Vapour pressure (solid)	$\log P_{mm} = 13.043 - 1.470 \log T - 2206/T$ (−14.47–48.3°)	a
(liquid)	$\log P_{mm} = -21.584 + 9.908 \log T - 2243/T$ (48.3–74.61°)	a
ΔH_{fus} (kcal mole^{-1})	1.799	a
ΔH_{vap} (kcal mole^{-1})	9.154	a
ΔS_{fus} (e.u.)	5.60	a
Density (liquid) at 52° (g cm^{-3})	3.65	a
Unit cell size (high temperature form) in Å	6.26	b

[a] J. G. Malm and H. Selig, *J. Inorg. Nucl. Chem.* **20** (1961) 199.
[b] S. Siegel and D. A. Northrop, *Inorg. Chem.* **5** (1966) 2187.

Rhenium heptafluoride is hydrolysed immediately by water to perrhenic acid and hydrogen fluoride. Unlike ReF_6, it does not combine with alkali metal fluorides even under pressure, nor does it react with oxygen at 500° [108]. Its solution in anhydrous hydrogen fluoride indicates little evidence of ionization[124] to ReF_6^+, but, as has been pointed out, the experiment was not performed in the presence of acids in the hydrogen fluoride system[125].

2.3. OXIDE HALIDES

No oxide iodide of rhenium has so far been isolated, and the absence of compounds for oxidation states of rhenium below V is noteworthy. With the exception of $ReOF_3$ and $ReOBr_3$, for which the evidence is at present incomplete, it appears that all the oxide halides are appreciably volatile either at the ordinary temperature or a little above (Table 12).

2.3.1. Rhenium Oxide Trifluoride

This compound apparently results from the decomposition of the oxide tetrafluoride on Pyrex glass at 250°. It is a black, non-volatile solid, which is very hygroscopic, and dissolves in water to give a blue solution[126].

---

[122] H. H. Claassen and H. Selig, *J. Chem. Phys.* **43** (1965) 103.

[123] N. Bartlett, S. Beaton, L. W. Reeves and E. J. Wells, *Canad. J. Chem.* **42** (1964) 2531.

[124] H. Selig and E. L. Gasner, *J. Inorg. Nucl. Chem.* **30** (1968) 658.

[125] B. M. Chadwick, J. R. Chipperfield, P. G. Nelson and C. F. Stoneman, *Annual Reports Chem. Soc.* **65** A, (1968) 321.

[126] G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.* (1960) 1099.

2.3.2. Rhenium Oxide Tetrafluoride

The original claim by Ruff to have prepared this compound is incorrect, and it seems likely that the properties ascribed by him to $ReOF_4$ actually refer to the oxide pentafluoride.

TABLE 12. OXIDE HALIDES OF RHENIUM

Fluorides	Chlorides	Bromides
($ReOF_3$)		($ReOBr_3$)
$ReOF_4$	$ReOCl_4$	$ReOBr_4$
ReO_3F	ReO_3Cl	ReO_3Br
ReO_2F_3		
$ReOF_5$		

Rhenium oxide tetrafluoride is one of the major products when tungsten or rhenium carbonyls are treated with rhenium hexafluoride[126]. It is also formed by the action of rhenium trioxide on rhenium hexafluoride[127] and by the slow hydrolysis of rhenium hexafluoride in Pyrex glass[126].

Rhenium oxide tetrafluoride forms a blue crystalline solid, a blue liquid and a colourless vapour (Table 13). The magnetic moment is in accord with that expected for a Re(VI) compound. Like the hexafluoride, the oxide tetrafluoride is readily hydrolysed to perrhenic acid, rhenium dioxide and hydrofluoric acid[126].

TABLE 13. PHYSICAL PROPERTIES OF RHENIUM OXIDE TETRAFLUORIDE

		Ref.
Melting point	108°	a
Boiling point	171°	a
Vapour pressure (solid)	$\log P_{mm} = 11.88 - 3888/T$	a
(liquid)	$\log P_{mm} = 10.09 - 3206/T$	a
ΔH_{sub} (kcal mole^{-1})	17.82	a
ΔH_{vap} (kcal mole^{-1})	14.59	a
ΔS_{vap} (e.u.)	32.7	a
χ_m (c.g.s. units)	748.5×10^{-6} (294.6°K)	b
	1762×10^{-6} (106.4°K)	
Curie–Weiss constant, θ	34°	b

[a] G. H. Cady and G. B. Hargreaves, *J. Chem. Soc.* (1961) 1568.
[b] G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.* (1960) 1099.

From single crystal X-ray measurements it has been shown that $ReOF_4$ has the $MoOF_4$ type of structure[128]; the unit may be written $ReOF_3F_{2/2}$. The rhenium atoms are linked through *cis* fluorine bridges to form infinite chains with a Re–F–Re bridging angle of 139°.

---

[127] H. Selig, private communication quoted in R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier (1966), p. 49.

[128] A. J. Edwards, G. R. Jones and B. R. Steventon, *Chem. Communs.* (1967) 462.

A metastable form of the solid which is trimeric like the similar $TcOF_4$ and $MoOF_4$ phases has recently been recognized[129]. In this the rhenium atoms lie at the corners of a triangle, linked through bridging fluorine atoms. The bridging fluorine atoms are again *cis* to one another as in the normal form.

2.3.3. Rhenium Oxide Tetrachloride

Though of similar composition to the corresponding fluoride, this has very different properties. It is formed, together with the trioxide chloride, ReO_3Cl, when rhenium heptaoxide reacts with the rhenium chloride[130] or when rhenium trichloride is treated with oxygen[131]. Separation from ReO_3Cl is achieved by fractional distillation. Recently, a more satisfactory preparative method, viz. the action of sulphuryl chloride in excess on the metal at 300°, has been described[132].

Rhenium oxide tetrachloride forms a brownish crystalline solid which melts to give a brown liquid. The vapour is greenish brown and has been shown to be monomeric[133]. Physical properties are indicated in Table 14 (compare $MoOCl_4$ and $WOCl_4$).

TABLE 14. PHYSICAL PROPERTIES OF RHENIUM OXIDE TETRACHLORIDE

		Ref.
Melting point	29–30.5°; 34°; 30.0±0.1°	a, b, f
Boiling point	228° (extrap)	c
Vapour pressure (liquid)	$\log P_{mm} = 7.63 - 2380/T$	c
ΔH_{vap} (kcal mole^{-1})	10.9	c
Magnetic moment, μ (BM)	1.5	d
Density of liquid (g/cm^3)	$p = 3.3090 - 0.23 \times 10^{-2}T - 0.114 \times 10^{-5}T^2$	e

[a] A. Bruckel and K. Ziegler, *Chem. Ber.* **65** (1932) 916.

[b] O. W. Kolling, *Trans. Kansas Acad. Sci.* **56** (1953) 378.

[c] N. V. Baryshnikov, A. N. Zelikman and M. V. Teslitkaya, *Russ. J. Chem.* **7** (1962) 1368.

[d] W. Schuth and W. Klemm, *Z. anorg. allgem. Chem.* **220** (1934) 193.

[e] L. A. Nisel'son, R. K. Nikolaev and Z. N. Orshanskaya, *Zh. Neorg. Khim.* **12** (1967) 860.

[f] D. Edwards and A. A. Woolf, *J. Chem. Soc.* A (1966) 91.

Rhenium oxide tetrachloride is readily hydrolysed by water to the dioxide, perrhenate and hydrochloric acid. It was said by the original workers to dissolve in cold concentrated hydrochloric acid to give a brown solution from which a red complex salt K_2ReOCl_6 could be isolated (see p. 977). The oxide tetrachloride also reacts with ammonia[134], and is said to give the complex $ReO(NH_2)_2Cl_2$.

---

[129] A. J. Edwards, private communication (1969).

[130] A. Bruckl and K. Ziegler, *Chem. Ber.* **65** (1932) 916.

[131] G. W. Kolling, *Trans. Kansas Acad. Sci.* **56** (1953) 378.

[132] D. Edwards and A. A. Woolf, *J. Chem. Soc.* A (1966) 91.

[133] N. V. Baryshnikov, A. N. Zelikman and M. V. Teslitkaya, *Russ. J. Inorg. Chem.* **7** (1962) 1368.

[134] A. Bruckl and A. E. Pettinger, *Chem. Ber.* **65** (1933) 971.

2.3.4. Rhenium Oxide Tetrabromide

This was originally formulated as the dioxide dibromide. It may be prepared in a number of ways, e.g. by heating rhenium in a stream of bromine carried in oxygen, by heating rhenium heptaoxide with bromine vapour or from rhenium dioxide and bromine vapour[135]. It is a blue solid with a low melting point which is said to decompose to the oxide tribromide, $ReOBr_3$, on heating.

2.3.5. Rhenium Trioxide Fluoride

The existence of the trioxide fluoride was suspected by Ruff, but he was unable to isolate the compound. It has been prepared by two methods; firstly, the interaction of the trioxide chloride, ReO_3Cl, with anhydrous hydrogen fluoride[136], and, secondly, the action of iodine pentafluoride on finely divided potassium perrhenate[137].

Rhenium trioxide fluoride forms a deep yellow solid, melting at 147° to a very viscous, yellow liquid, which in turn boils with slight decomposition at 164°. The liquid compound readily supercools, but crystals may be obtained by slow sublimation in a vacuum. The microwave spectrum of the vapour has been observed[138], and the molecule has been shown to be a symmetric top with the following parameters: $Re–O = 1.692$ Å; $Re–F = 1.859$ Å; angle $F–Re–O = 109° 31'$. The dipole moment was calculated to be 0.85 *D*.

Rhenium trioxide fluoride is decomposed in a moist atmosphere, and is hydrolysed by water to perrhenic and hydrofluoric acids.

This compound is noticeably less volatile than its technetium analogue; the viscosity of the liquid and the colour suggest that the rhenium atoms in the solid and liquid phases are likely to be in six coordination with oxygen and fluorine. The boiling point is somewhat higher than that of the isoelectronic osmium tetroxide, which is known to retain a molecular structure in the solid and liquid phases.

2.3.6. Rhenium Trioxide Chloride

This compound has been prepared by a number of methods, none of which gives a quantitative yield. They involve the interaction between a rhenium chloride and a rhenium heptaoxide[130] or the action of oxygen on either a rhenium chloride[131, 139] or on the oxide tetrachloride[140]. The trioxide chloride is also formed by chlorinating rhenium trioxide at 160–190°; this method gives a pure product after the dissolved chlorine has been pumped off[141]. The action of a chlorine–oxygen mixture on sulphides of rhenium also leads to the compound[139, 141].

Rhenium trioxide chloride is a colourless compound which melts at 4.5°; the boiling point has been given variously as 131° [130] and 128° [141]. The molecule, like that of ReO_3F, is a symmetric top; the structure, determined by microwave spectroscopy[142], gives the molecular parameters $Re–O = 1.761$ Å, $Re–Cl = 2.230$ Å, angle $Cl–Re–O = 108° 20'$. A strong

---

[135] R. Colton, *J. Chem. Soc.* (1962) 2078.

[136] A. Engelbrecht and A. V. Grosse, *J. Am. Chem. Soc.* **76** (1954) 2042.

[137] E. E. Aynsley and M. L. Hair, *J. Chem. Soc.* (1958) 3747.

[138] J. F. Lotspeich, A. Javan and A. Engelbrecht, *J. Chem. Phys.* **31** (1959) 633.

[139] W. Geilmann, F. W. Wrigge and W. Biltz, *Z. anorg. allgem. Chem.* **214** (1933) 248.

[140] R. Colton, unpublished observations quoted in *Halides of Transition Metals*, by R. Colton and J. H. Canterford, Wiley, Interscience (1968).

[141] C. J. Wolf, A. F. Clifford and W. H. Johnston, *J. Am. Chem. Soc.* **79** (1957) 4257.

[142] E. Amble, S. L. Miller, A. L. Schawlaw and C. H. Townes, *J. Chem. Phys.* **20** (1952) 192.

absorption frequency at 960 cm^{-1} in the infrared spectrum is attributed to the rhenium oxygen double bond[141]. The early work[139] suggested the compound to be light sensitive, since a purple colour appears which is also often noticed during the preparation[141]; but this has not been confirmed[141].

The compound is immediately hydrolysed by water to perrhenic and perchloric acids.

2.3.7. Rhenium Trioxide Bromide

The action of bromine vapour on potassium perrhenate[143], or of liquid bromine on the trioxide[144], yields colourless rhenium trioxide bromide, ReO_3Br. On heating this decomposes apparently to the trioxide[143], but otherwise little seems to be known of its chemical properties. The infrared spectrum has been measured and assigned[145]; there is a strong infrared frequency at 963 cm^{-1} (cf. ReO_3Cl) attributable to the rhenium–oxygen double bond.

2.3.8. Rhenium Dioxide Trifluoride

This is probably the compound reported as the dioxide difluoride by Ruff. It is formed by the action of fluorine on rhenium dioxide or on potassium perrhenate, or by the action of mixtures of fluorine and oxygen on the metal[146, 147].

TABLE 15. PHYSICAL PROPERTIES OF RHENIUM DIOXIDE TRIFLUORIDE[147]

Melting point	90°
Boiling point	185.4°
Vapour pressure (liquid)	$\log P_{mm} = 10.36 - 3437/T$ (90–170°)
ΔH_{vap} (kcal mole^{-1})	15.7
ΔS_{vap} (e.u.)	34.3

Rhenium dioxide trifluoride forms a creamy yellow solid and liquid. The liquid readily supercools to a glass which slowly crystallizes on standing (Table 15). In some ways the compound behaves as a transition metal pentafluoride in which two fluorine atoms have been replaced by oxygen, e.g. in the very high Trouton constant and in the high viscosity, both of which suggest association in the liquid.

Rhenium dioxide trifluoride is stable in glass to its boiling point. Like the other septavalent oxide fluorides, it is immediately hydrolysed by water to perrhenic and hydrofluoric acids.

2.3.9. Rhenium Oxide Pentafluoride

This is probably the compound referred to by Ruff as the oxide tetrafluoride. It is formed[146, 147] in the reactions used to prepare the dioxide trifluoride, and appears as the minor product. The difference in volatility allows an easy separation from the dioxide trifluoride.

[143] R. Colton and G. Wilkinson, *Chem. and Ind.* (1959) 1314.

[144] A. Bruckl and K. Ziegler, *Monatsh. Chem.* **63** (1933) 329.

[145] F. A. Miller and J. L. Carlson, *Spectrochim. Acta* **16** (1960) 1148.

[146] E. E. Aynsley, R. D. Peacock and P. L. Robinson, *J. Chem. Soc.* (1950) 1622.

[147] G. H. Cady and G. B. Hargreaves, *J. Chem. Soc.* (1961) 1568.

In physical properties (Table 16), rhenium oxide pentafluoride closely resembles the transition metal hexafluorides, and, like ReF_6 and ReF_7, has a low temperature solid form. At room temperature $ReOF_5$ forms a cream-coloured crystalline solid. It melts to a colourless liquid and forms a colourless vapour.

TABLE 16. PHYSICAL PROPERTIES OF RHENIUM OXIDE PENTAFLUORIDE[147]

Melting point	43.8°
Boiling point	73.0°
Transition temperature (solid)	30.0°
Vapour pressure (solid)	$\log P_{mm} = 9.581 - 2250/T$ (0–30°)
(solid)	$\log P_{mm} = 8.620 - 1958.9/T$ (30–41°)
(liquid)	$\log P_{mm} = 7.727 - 1678.6/T$ (41–73°)
ΔH_{trans} (kcal mole^{-1})	1.339
ΔH_{vap} (kcal mole^{-1})	7.720
ΔH_{sub} (below 30°) (kcal mole^{-1})	8.940
ΔH_{sub} (above 30°) (kcal mole^{-1})	10.280
ΔS_{trans} (e.u.)	3.868
ΔS_{vap} (e.u.)	22.3

The ^{19}F n.m.r. spectrum consists of a weak quartet at 159.6 ppm due to the axial fluorine atom and a strong doublet at 361.9 ppm due to the four equatorial fluorine atoms, measured downfield relative to silicon tetrafluoride[148]; this indicates the molecule to possess the expected C_{4v} symmetry.

2.3.10. Rhenium Chloride Pentafluoride

The action of fluorine on rhenium pentachloride at 30° in a flow system yields the chloride pentafluoride[149]; other solid chloride fluorides are also formed but have not been identified.

Rhenium chloride pentafluoride forms a red solid, melting at −2° to a red liquid. The yellow vapour is monomeric, and the vapour pressure at 25° is about 300 mm. The compound is unstable (much more unstable thatn $WClF_5$), decomposing rapidly at room temperature and slowly at −30°. The compound is paramagnetic with a θ value of 203° and $\mu_{calc} = 1.11$ BM. The infrared spectrum has been recorded[149], and is similar to that of $WClF_5$. Rhenium chloride pentafluoride, like ReF_6 itself, is rapidly hydrolysed by water giving perrhenic acid, rhenium dioxide, hydrofluoric and hydrochloric acids.

3. CYANIDE AND THIOCYANATE COMPLEXES

3.1. CYANIDE COMPLEXES

The cyanide ligand stabilizes rhenium in both high and low oxidation states, and complex cyanides have been claimed for every oxidation state of the element between zero and six. The quinquevalent state, which is normally labile with rhenium, is markedly stabilized by

---

[148] N. Bartlett, S. Beaton, L. W. Reeves and E. J. Wells, *Canad. J. Chem.* **42** (1964) 2531.

[149] R. D. Peacock and D. F. Stewart, *Inorg. Nucl. Chem. Letters* **3** (1967) 285.

cyanide, and in this and the 6-valent state there is a tendency for the rhenium atom to increase its normal coordination number of six to seven or eight. The relationship between the molybdenum and tungsten ions $Mo(CN)_8^{4-}$, $W(CN)_8^{4-}$ and $MoO_2(CN)_4^{4-}$ and the rhenium anions $Re(CN)_8^{3-}$ and $ReO_2(CN)_4^{3-}$ is very evident, and in particular the ease with which $Re(CN)_8^{3-}$ undergoes a single electron change to $Re(CN)_8^{2-}$ is strikingly reminiscent of the oxidation of $Mo(CN)_8^{4-}$ to $Mo(CN)_8^{3-}$. Except in low oxidation states, the resemblance to the corresponding chemistry of manganese and technetium is not very marked. The chemistry of the rhenium cyanide compounds is summarized in Fig. 5; it is, however, apparent that a number of the compounds reported warrant further investigation.

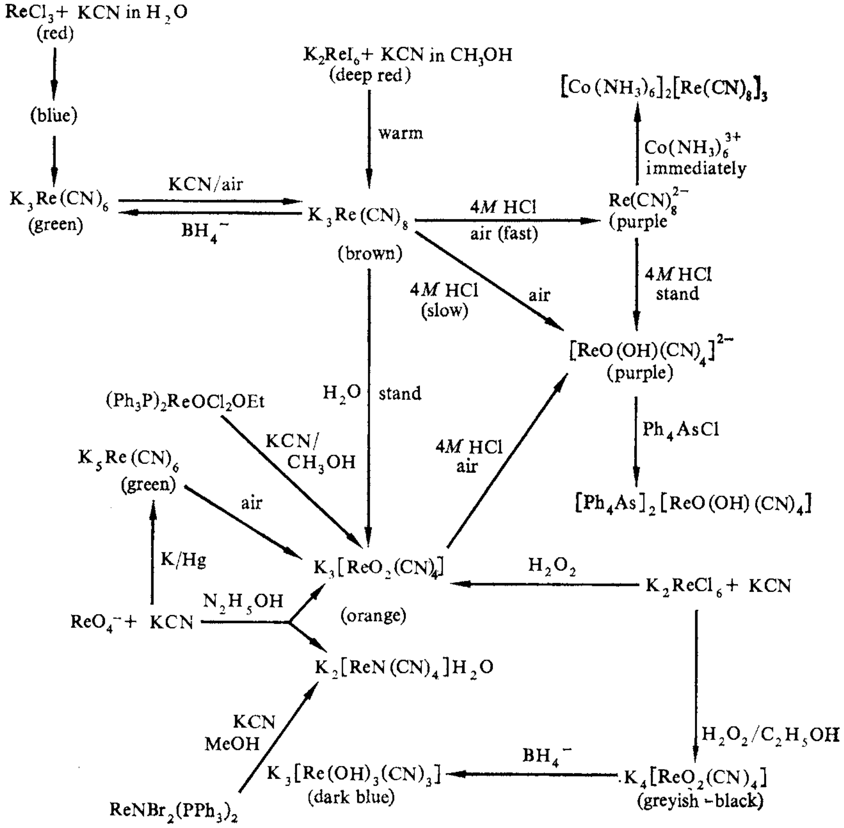


FIG. 5. Reactions of rhenium cyanide complexes.

A zerovalent rhenium complex, $K_6Re(CN)_6$, has been claimed; the evidence, which is incomplete, has been discussed by Colton[150].

The reduction of perrhenate or hexachlororhenate(IV) in the presence of potassium cyanide by potassium amalgam in the absence of air or oxygen leads to the formation of

---

[150] R. Colton, *The Chemistry of Rhenium and Technetium*, Interscience (1965), p. 140.

potassium hexacyanorhenate(I)[151, 152], $K_5Re(CN)_6$. The compound, which crystallizes either with $3H_2O$[151] or in the anhydrous state[152], is a green, slightly paramagnetic material (compare $K_3Re(CN)_6$), whose face-centred unit cell (a_0 = 12.033 ± 0.001 Å) contains four molecules. The infrared spectrum (NaCl region) shows several cyanide stretching frequencies just below 2000 cm^{-1}. The same compound is said to result from the reduction of either $K_2ReO_2(CN)_4$ or K_2ReCl_6 by potassium borohydride in the presence of excess of potassium cyanide[153], but the evidence is incomplete. The stabilization of the rhenium(I) state by cyanide ligand has been demonstrated by polarographic studies[154].

There is some evidence that the rhenium(II) state can be stabilized by cyanide ion. The reduction of sodium perrhenate by sodium amalgam in the presence of excess of sodium cyanide is said to lead to the formation of the $[Re(CN)_5H_2O]^{3-}$ ion, isolated as a sodium salt[155]. Treatment of this with excess of cyanide under reflux is said to yield the $Re(CN)_6^{4-}$ anion (isolated as the K salt)[156], while with carbon monoxide at 140° the anion $[Re(CN)_5CO]^{3-}$ is formed[157]. The reaction of $[Re(CN)_5H_2O]^{3-}$ with 6 M nitric acid is claimed to give the $[Re(CN)_5NO]^{2-}$ anion, isolated as a pink silver salt[158], whilst with bromine oxidation to the green $[Re(CN)_5H_2O]^{2-}$ ion, isolated as the sodium salt, is said to occur[159].

Meier and Treadwell observed that when potassium cyanide reacts with rhenium trichloride in aqueous solution, a complex series of colour changes takes place[160]; the initial red solution of the trichloride turns blue on warming, quickly changes to green, and, finally, after several days, becomes brownish yellow. These results have since been confirmed[161], and it has been shown that the final brownish-yellow solution contains $Re(CN)_8^{3-}$. The reduction of potassium octacyanorhenate(V) with potassium borohydride also yields green hexacyanorhenate(III) ion, which may be precipitated as the insoluble hexamminecobaltic salt[161]. This salt has a magnetic moment of 2.6 BM at 298°K, consistent with the two expected unpaired electrons in the anion. The infrared spectrum shows a peak at 730 cm^{-1} which was attributed to the Re–C stretching frequency[161], but is more likely to be due to rhenium–oxygen containing impurity (cf. the supposed $[Re(CN)_5H_2O]^{2-}$).

Another tervalent compound, potassium tricyanotrihydroxyrhenate(III), has been made from the tetracyanodioxorhenate(IV) ion by treatment with potassium borohydride[153]. It forms a dark blue crystalline powder. Physical data have not been recorded, and doubts have been expressed about the nature of this compound[150].

The action of aqueous potassium cyanide solution on potassium hexachlororhenate(IV) yields an initially white precipitate which rapidly disappears as the solution turns black[153]. Addition of ethanol precipitates a greyish-black solid, which after extraction of potassium cyanide with methanol has the composition $K_4[ReO_2(CN)_4]$, i.e. the salt is a derivative of

---

[151] D. Clauss and A. Lisner, *Z. anorg. allgem. Chem.* **297** (1958) 300.
[152] K. Schwochau and W. Herr, *Z. anorg. allgem. Chem.* **319** (1962) 148.
[153] P. H. L. Walton, J. Kleinberg and E. Griswold, *Inorg. Chem.* **1** (1962) 10.
[154] R. Colton, J. Dalziel, W. P. Griffith and G. Wilkinson, *J. Chem. Soc.* (1960) 71.
[155] S. Sen, *Sci. Cult. Calcutta* **27** (1961) 404.
[156] S. Sen, *Sci. Cult. Calcutta* **26** (1960) 139.
[157] P. Bandyopadhyay, *Sci. Cult. Calcutta* **25** (1959) 278.
[158] B. K. Sen and P. B. Sarkar, *Sci. Cult. Calcutta* **27** (1961) 404.
[159] S. Sen, *Sci. Cult. Calcutta* **25** (1959) 272.
[160] J. Meier and W. D. Treadwell, *Helv. Chim. Acta* **38** (1955) 1679.
[161] R. Colton, R. D. Peacock and G. Wilkinson, *J. Chem. Soc.* (1960) 1374.

rhenium(IV). This result is in marked contrast to the formation of the octacyanorhenate(V) ion from the hexaiodorhenate and potassium cyanide, and it is difficult to see why aerial oxidation should not take place. It has been suggested by Colton[150] that the second stage of the reaction, the appearance of the black solution, could be due to the initial formation of hydrated rhenium dioxide (presumably colloidal). He has pointed out that, although rhenium dioxide is known to dissolve in potassium cyanide solution in the presence of an oxidizing agent (to form $K_3[ReO_2(CN)_4]$), observations do not appear to have been made on the solubility of the dioxide in potassium cyanide solution in the absence of an oxidizing agent.

Brown potassium octacyanorhenate(V) is obtained from the reaction of potassium hexaiodorhenate, K_2ReI_6, with potassium cyanide in hot methanol solution[161, 162]. The compound is diamagnetic and crystallizes with one molecule of water. The oxidation of the rhenium from Re(IV) to Re(V) is a good example of the loss of an electron from a high-lying orbital (cf. Co^{2+}). From the potassium salt the zinc salt, $Zn_3[Re(CN)_8]_2$, and the cobalt hexammine salt are obtained by precipitation, and the sodium, calcium, strontium and barium salts by ion exchange[161].

Potassium octacyanorhenate(V) is stable in alkaline solutions, but is unstable in acid in the presence of air, and nitric acid reacts with it to give a nitrosyl complex[161]. The infrared spectrum in Nujol shows three cyanide stretching frequencies at 2140, 2100 and 2050 cm^{-1}, a spectrum very similar to those of the complex molybdenum and tungsten octacyanide complexes. In aqueous solution, however, the compound shows only one peak (as does $[Mo(CN)_8^{4-}]$ at 2100 cm^{-1}, suggesting that the splitting in the solid-state spectrum is due to crystal interactions. It seems, therefore, that $Re(CN)_8^{3-}$ has the same dodecahedral structure as $Mo(CN)_8^{4-}$. In the KBr region the original samples of octacyanorhenate showed a strong peak at 780 cm^{-1} which has since been shown[162] to be due to $K_3[ReO_2(CN)_4]$ impurity, and indeed it appears that aqueous solutions of $K_3Re(CN)_8$ are less stable than was originally supposed.

Salts of the tetracyanodioxorhenate(V) ion were the first known cyanide complexes of rhenium. The potassium salt is made by treating the quadrivalent potassium hexachlororhenate with excess of potassium cyanide and oxidizing with hydrogen peroxide; the solution is extracted with alcohol (to remove the excess of cyanide), the aqueous layer is evaporated in the cold and the residue is recrystallized from water[163, 164]. An alternative, and perhaps better, method of preparation is to reduce an aqueous solution of potassium perrhenate with hydrazine hydrate in the presence of potassium cyanide[163, 164].

Potassium tetracyanodioxorhenate(V) forms orange crystals easily soluble in water; alkalis have no action on the salt, but acids turn it violet [cf. $Re(CN)_8^{3-}$]. The only slightly soluble salt appears to be that of thallium. The X-ray structure of $K_3ReO_2(CN)_4$ indicates that the oxygen atoms are *trans* to one another in the octahedral anion[165]. The infrared spectrum indicates that in addition to the cyanide stretching frequency at 2000 cm^{-1}, there is a metal–oxygen absorption at 780 cm^{-1} (Table 17). The infrared spectrum of the corresponding thallous salt differs from that of the potassium salt sufficiently to suggest that the anions are not identical.

---

[162] C. J. T. Lock and G. Wilkinson, *J. Chem. Soc.* (1964) 2281.

[163] W. Klemm and G. Frischmuth, *Z anorg. allgem. Chem.* **230** (1937) 215.

[164] G. T. Morgan and G. R. Davis, *J. Chem. Soc.* (1938) 1858.

[165] K. Lukaszewicz and T. Glowiak, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **9** (1961) 613.

Some confusion has been caused by the existence of another Re(V) species which is rather easily formed from the $[ReO_2(CN)_4]^{3-}$ anion, especially in the presence of acid. This is the $[ReO(OH)(CN)_4]^{2-}$ ion, of which a number of salts have been prepared, notably those of large organic cations and of barium[162]:

$$[ReO_2(CN)_4]^{3-} + H^+ \rightleftarrows [ReO(OH)CN)_4]^{2-}$$

The preparative method calls for the addition of cyanogen as well as the acid.

TABLE 17. INFRARED FREQUENCIES IN CYANIDE COMPLEXES (cm^{-1})

Complex	CN stretch	HOH bend	M≡N	M=O	H_2O	OH
$K_3Re(CN)_8$	2140 2100 2050			(780)		
$K_3[ReO_2(CN)_4]$	2000			780		
$Tl_3[ReO_2(CN)_4]$	2125	1620		780	3460	
$[Ph_4As]_2[ReO(OH)(CN)_4]$	2190 2150			956		
$K_2[ReN(H_2O)(CN)_4]$	2160	1620	997 974			3720 3625
$[dipy\ H_2][ReO(OH)(CN)_4]$	2090			950		

Treatment of potassium octacyanorhenate(V) solution with dilute hydrochloric, acetic or perchloric acids in the presence of air yields a purple solution[161]; this colour change occurs only at a pH of less than 5. Oxidation does not occur in alkaline solution. A potassium salt has not been obtained from the purple solution, but immediate addition of hexammine cobaltic chloride gives insoluble, purple $[Co(NH_3)_6]_2[Re(CN)_8]_3$ [161]. This salt, as expected, is paramagnetic ($\mu = 2.0$ BM). However, the behaviour of the $Re(CN)_8^{2-}$ anion in solution is most unusual. When aqueous potassium octacyanorhenate(V) in air is acidified, the purple solution formed is at first paramagnetic as expected, but rapidly becomes diamagnetic without further colour change[161]. The change in susceptibility is exponential with a half-life of 5 ± 2 sec. A log plot allows extrapolation back to zero time (addition of acid), and the moment at zero time is 2.0 BM, agreeing with the moment of the hexamminecobaltic salt[161]. When the hexamminecobaltic chloride is added to the Re(V) solution immediately after acidification, the whole of the purple species is precipitated. When, however, the solution is kept until it is diamagnetic before the hexamminecobaltic chloride is added, only a small precipitate (about 5%) is formed[161]. Tetraphenylarsonium chloride, Ph_4AsCl, gives precipitates with both fresh and aged solutions of the $Re(CN)_8^{2-}$ ion; the fresh purple precipitate is paramagnetic ($\mu = 2.0$ BM), but the precipitate from the aged diamagnetic solution is largely diamagnetic itself[161]. On the basis of analytical and n.m.r. evidence it was supposed that the aged, diamagnetic solution and precipitates were derived from the $[Re(OH)(CN)_8]^{2-}$ ion[161], but the evidence has since been re-examined by Lock and Wilkinson[162], and it is concluded that the supposed $Re(OH)(CN)_8^{2-}$ anion is actually $[ReO(OH)(CN)_4]^{2-}$. (Presumably in the original investigation adventitious Ph_4AsCN was present in the aged precipitate.)

Lock and Wilkinson[162] have explained the various reactions on the basis of the following scheme:

$$\mathrm{Re(CN)_8^{3-}} \xrightarrow[\text{air}]{4\,\text{M HCl}} \mathrm{Re(CN)_8^{2-}} \qquad \text{(a) very fast, complete within 30 sec}$$

$$\mathrm{Re(CN)_8^{3-}} \xrightarrow[4\,\text{M HCl}]{} \mathrm{[ReO(OH)(CN)_4]^{2-}} \qquad \text{(b) slow}$$

$$\mathrm{Re(CN)_8^{2-}} \longrightarrow \underset{\text{(unstable)}}{\mathrm{[ReO_2(CN)_4]^{2-}\ \text{or}\ [ReO(OH)(CN)_4]^{-}}} \qquad \text{(c)}$$

$$\left.\begin{array}{l}\mathrm{[ReO_2(CN)_4]^{2-}}\\ \mathrm{[ReO(OH)(CN)_4]^{-}}\end{array}\right\} \longrightarrow \mathrm{[ReO(OH)(CN)_4]^{2-}} \qquad \text{(d) fast}$$

$$\mathrm{Re(CN)_8^{2-}} \longrightarrow \mathrm{[ReO(OH)(CN)_4]^{2-}} \qquad \text{(e)}$$

The Re(VI) species $[ReO_2(CN)_4]^{2-}$ and $[ReO(OH)(CN)_4]^-$ are not isolated.

The nitrido-species $K_2[ReN(CN)_4] \cdot H_2O$ appears as a by-product during the preparation of $K_3[ReO_2(CN)_4]$ from perrhenate and KCN in the presence of hydrazine[162]. It was identified, apart from analytical evidence, by the characteristic Re–N absorption frequency in the infrared, and by comparison with known derivatives of osmium. The X-ray crystal structure, recently determined, indicates that the rhenium and nitride nitrogen atoms lie in infinite chains with alternating rhenium and nitrogen, in a similar fashion to the tungsten and oxygen chains in $WOCl_4$. The nitrogen is asymmetrically placed between the rhenium atoms (Re–N = 1.53 and 2.44 Å). On the available data it is considered that the cyanide groups are linked to the rhenium atoms through the nitrogen atoms[166]. In solution, however, it appears from infrared data that the composition of the ion is $[ReN(CN)_4H_2O]^{2-}$ [167].

The complex $ReNBr_2(PPh_3)_2$ reacts with potassium cyanide in methanol to give yellow $K_3[ReN(CN)_5]$ when the cyanide is in excess, and pink $K_2[ReN(CN)_4] \cdot H_2O$ when cyanide is not in excess[167]. (See also p. 960.)

Several other Re(V) species have recently been described, e.g. salts of the $[ReO(OH)(H_2O)(CN)_3]^-$ ion[168], but the evidence for these is incomplete.

3.2. THIOCYANATE COMPOUNDS

Simple thiocyanates of rhenium have not yet been isolated, and indeed the whole position over the neutral complexes is confusing. The addition of thiocyanate to an acidified perrhenate solution containing a reducing agent produces a red coloration which has been used for many years as the basis of a colorimetric method of rhenium analysis, but little is known of the nature of the complex. It has been supposed at various times that complexes of Re(IV), Re(V) or Re(VI) are produced; the most recent firm suggestion, which is supported by strong evidence[169], is that the colorations are due to the $Re(NCS)_6^-$ and $Re(NCS)_6^{2-}$ ions described below.

3.2.1. Complex Thiocyanates

Derivatives of three complex ions, tervalent $Re_2(NCS)_8^{2-}$, quadrivalent $Re(NCS)_6^{2-}$, and quinquevalent $Re(NCS)_6^-$, have recently been described.

---

[166] M. C. Chakravorti, *J. Indian Chem. Soc.* **43** (1966) 381.

[167] N. P. Johnson, *J. Chem. Soc.* A (1969) 1843.

[168] W. O. Davies, N. P. Johnson, P. Johnson and A. J. Graham, *Chem. Communs.* (1969) 736.

[169] R. A. Bailey and S. L. Kozak, *Inorg. Chem.* **6** (1967) 2155.

The action of sodium thiocyanate on $[(C_4H_9)_4N]_2Re_2Cl_8$ in methanol solution and in the presence of acetic acid and acetic anhydride leads to the formation of $[(C_4H_9)_4N]_2[Re_2(NCS)_8]$ as a red crystalline material[170]. Salts of the $(C_6H_5)_4As^+$ and $(C_6H_5)_3CH_3As^+$ cations have also been prepared as orange and dark red crystals respectively.

The $Re_2(NCS)_8^{2-}$ anion is diamagnetic (supporting an eclipsed configuration; cf. $Re_2Cl_8^{2-}$), and spectroscopic and conductivity data have been reported. The infrared measurements indicate the thiocyanate groups to be bonded to the rhenium through the nitrogen atoms. Salts containing $Re_2(NCS)_8^{2-}$ react with triphenylphosphine to give a green complex anion which apparently has the formula $[Re_2(NCS)_8(P(C_6H_5)_3)_2]^{2-}$, and it is suggested that a rhenium–rhenium bond is not present in this complex. Polarographic reduction of $Re_2(NCS)_8^{2-}$ ion shows that one-electron changes to $Re_2(NCS)_8^{3-}$ and $Re_2(NCS)_8^{4-}$ occur (cf. $Re_2Cl_8^{2-}$) [171].

Salts of the quadrivalent $Re(NCS)_6^{2-}$ ion have been synthesized by two methods. The reaction of $Re_2Cl_8^{2-}$ with sodium thiocyanate in an acetone solution results in oxidation to Re(IV) and the isolation of $Re(NCS)_6^{2-}$ salts of $(n\text{-}C_4H_9)_4N^+$ and $(C_6H_5)_4As^+$ cations as red–brown salts; the curious salt $[(n\text{-}C_4H_9)_4N]_3[Re_2(NCS)_8(CO)_2]$ was isolated as a by-product[170]. Potassium hexachlororhenate(IV) reacts with fused potassium thiocyanate at 225° to give an almost black mixture from which, after cooling and extracting with absolute alcohol (to free from solid KCl), the caesium salt $Cs_2Re(NCS)_6$ may be isolated by addition of caesium chloride solution[172]. The Tl^+ salt has also been prepared[172].

Salts of $Re(NCS)_6^{2-}$ are red–brown or dark brown. The Cs salt dissolves in ethanol, water, ether, dilute acids and alkalis but is insoluble in chloroform or in petroleum ether (b.p. 60–90°) [172]. The thallous salt is only slightly soluble in water and in ethanol[172]; the salts of the large cations dissolve in tetrahydrofuran[170]. The infrared spectra have been held to show that the thiocyanate groups are bonded to the rhenium through the nitrogen atoms[170], though this view has been challenged[169]. The magnetic moments of the $Re(NCS)_6^{2-}$ compounds vary with the cation[170, 172] (μ_{eff}(298°K) 3.3– 3.5 BM); with the large organic cations the θ values are much lower than with K^+, Ag^+ or Tl^+ [170]. It is curious to note that magnetic measurements were made[173] on salts of the $Re(NCS)_6^{2-}$ ion long before their preparation was described; the original synthetic method has still not been published.

The quinquevalent complex $CsRe(NCS)_6$ has been prepared by fusing rhenium pentachloride with potassium thiocyanate; the rest of the procedure is similar to that described for $Cs_2Re(NCS)_6$, except that advantage is taken of the reduced solubility of $CsRe(NCS)_6$ in ethanol[169].

The salt $CsRe(NCS)_6$ is a medium-brown powder. The infrared evidence is held to favour attachment of the thiocyanate group to the rhenium through the sulphur atom, and the magnetic moment of 1.38 BM is in the range reported for other Re(V) compounds at 25°.

Recently cyanates containing the $[Re(OCN)_6]^{2-}$ and $[Re(OCN)_6]^-$ ions have been synthesized by methods analogous to the foregoing[172a].

3.2.2. Other Thiocyanato-complexes

Only a few have been reported in the literature: $ReO(NCS)_3L_2$ [L = $(C_2H_5)_2(C_6H_5)P$ or

---

[170] F. A. Cotton, W. R. Robinson, R. A. Walton and R. Whyman, *Inorg. Chem.* **6** (1967) 929.

[171] F. A. Cotton, W. R. Robinson and R. A. Walton, *Inorg. Chem.* **6** (1967) 1257.

[172] R. A. Bailey and S. L. Kozak, *Inorg. Chem.* **6** (1967) 419.

[172a] R. A. Bailey and S. L. Kosak, *J. Inorg. Nucl. Chem.* **31** (1969) 689.

[173] G. E. Boyd, C. M. Nelson and W. T. Smith, *J. Am. Chem. Soc.* **76** (1954) 348.

[174] J. Chatt and G. A. Rowe, *J. Chem. Soc.* (1962) 4010.

[175] L. I. Evteev, *Zh. Neorg. Khim.* **10** (1965) 2573.

$(C_6H_5)_3P]$ [174], the alleged rhenium(IV) complex $ReO(NCS)_2(py)_3$ [175], the alleged salt $K_3ReO_2(NCS)_4$ [176], the rhenium(III) carboxylates $Re_2(O_2CR)_4(NCS)_2$ [177], the trinuclear $Re_3Cl_3(NCS)_{6+n}]^{n-}$ ions[178], and various carbonyl derivatives[178a].

4. OXIDES

4.1. BINARY OXIDES

Rhenium forms three anhydrous oxides: the dioxide, the trioxide and the heptaoxide. There is good evidence also for a hydrated sesquioxide, $Re_2O_3 \cdot 3H_2O$; rhenium dioxide also forms hydrates, and it has been shown recently that solid perrhenic acid is structurally a hydrate of the heptaoxide (p. 945). Oxides of univalent and bivalent rhenium have been claimed to exist, but definite evidence of their identity is lacking.

4.1.1. Rhenium Sesquioxide

The alkaline hydrolysis of rhenium trichloride in the absence of air yields a black oxide of composition $Re_2O_3 \cdot xH_2O$, which is readily oxidized to the hydrated dioxide[179]. This hydrated oxide has recently been re-investigated, and it has been found that rhenium trichloride is hydrolysed by water alone at 100° in the absence of air to yield the oxide, and that the same material is also formed by the reduction of aqueous ammonium perrhenate with sodium borohydride[180]. The composition of the dried material is $Re_2O_3 \cdot 3H_2O$ [180]. At 200° in the absence of air one molecule of water is lost, and complete decomposition to Re and ReO_2 takes place at 500° [180]. The enthalpy of hydrolysis of rhenium trichloride in alkaline solution at 25° has been measured[181] and from the result (-54.29 ± 0.14 kcal mole^{-1}) the enthalpy of formation of dirhenium trioxide (hydrate) is calculated to be -119.2 kcal mole^{-1}, and the free energy of formation is estimated to be -101.6 ± 0.6 kcal mole^{-1}. Although Hurst *et al.*[180] claimed to have observed the release of oxygen during the thermal decomposition of the sesquioxide, it has been pointed out by Busey *et al.* that the simple disproportionation $Re_2O_3 \cdot 3H_2O \rightarrow \frac{1}{2}Re + \frac{3}{2}ReO_2 + 3H_2O$ is more favourable; these authors also noted that in aqueous solution the reaction: $Re_2O_3 + 5H_2O \rightarrow 2ReO_2 \cdot 2H_2O + H_2$ is favoured ($\triangle G^\circ = -19.8$ kcal mole^{-1}) and occurs at a very slow but measurable rate.

4.1.2. Rhenium Dioxide

The anhydrous oxide has been prepared[182, 183] by a number of methods; the partial reduction of ammonium perrhenate, the reduction of rhenium heptaoxide with hydrogen at 300°, the reaction of the heptaoxide with metallic rhenium at 600° and the thermal dissociation of the trioxide in a vacuum at 300°. The hydrated dioxide, $ReO_2 \cdot 2H_2O$, obtained from the aqueous hydrolysis of the hexahalogenorhenates(IV), the hydroysis of rhenium pentachloride, the action of reducing agents on perrhenates, or by the electrolysis of neutral or

---

[176] D. I. Ryabchilov, V. A. Zarinskii and I. I. Nazarenko, *Zh. Neorg. Khim.* **6** (1961) 647.
[177] F. Taha and G. Wilkinson, *J. Chem. Soc.* (1963) 5406.
[178] B. H. Robinson and J. E. Fergusson, *J. Chem. Soc.* (1964) 5683.
[178a] P. M. Treichel and W. M. Douglas, *J. Organometal. Chem.* **19** (1969) 221.
[179] W. Geilmann, F. W. Wrigge and W. Blitz, *Z. anorg. allgem. Chem.* **214** (1950) 239.
[180] F. Hurst, P. Gibart and K. Traore, *Compt. Rend.* **236C** (1966) 97.
[181] R. H. Busey, E. D. Sprague and R. B. Bevan, *J. Phys. Chem.* **73** (1969) 1039.
[182] R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier (1966), p. 28.
[183] R. Colton, *The Chemistry of Rhenium and Technetium*, Interscience (1965), p. 44.

aqueous perrhenate solutions at a platinum electrode, loses water under a vacuum at 250–500° to give the anhydrous dioxide.

Rhenium dioxide forms a dark blue or black powder (Table 18), which appears to exist in monoclinic (below 300°) and orthorhombic (300–1500°) forms. The monoclinic form has the MoO_2 structure[184], and the average Re–Re distance, assuming rhenium positions similar to the molybdenum positions in MoO_2, has been estimated to be 2.61 Å, indicative of metal–metal bonding.

TABLE 18. PROPERTIES OF RHENIUM DIOXIDE

		Ref.
Sublimation point (760 mm)	1363° (extrap)	a
Vapour pressure	$\log P_{mm} = 11.65 - 14{,}437/T$ (650–785°)	a
ΔH_{sub} (kcal mole^{-1})	65.6	a
ΔH°_{form} (kcal mole^{-1})	-236.7 [fresh $ReO_2 \cdot 2H_2O(c)$]	c
ΔH°_{form} (kcal mole^{-1})	-241.8 [aged $ReO_2 \cdot 2H_2O(c)$]	c
ΔG°_{form} (kcal mole^{-1})	-197.3 ± 1.5 [fresh $ReO_2 \cdot 2H_2O(c)$]	c
ΔG°_{form} (kcal mole^{-1})	-202.4 ± 1.5 [aged $ReO_2 \cdot 2H_2O(c)$]	b, c

[a] V. I. Deev and V. I. Smirnov, *Dokl. Akad. Nauk SSSR* **140** (1961) 822.
[b] G. E. Boyd, J. W. Cobble and W. T. Smith, *J. Am. Chem. Soc.* **75** (1953) 5783.
[c] R. Busey, K. Gayer, R. Gilbert and R. Bevan, *J. Phys. Chem.* **70** (1966) 2609.

Rhenium dioxide is slightly paramagnetic, with a susceptibility for the anhydrous material of 43.6×10^{-6} e.m.u.[185] and of 139×10^{-6} e.m.u. for the hydrate[186]. The magnetic and electrical properties have recently been discussed in terms of a band model[187]. The hydrate $ReO_2 \cdot 2H_2O$ is reported to have a scheelite lattice[188].

Anhydrous rhenium dioxide is said to decompose above 700° to the metal and the heptaoxide[180], but single crystals have been grown, presumably in closed systems, at much higher temperatures. The anhydrous compound is not attacked by alkalis, water or non-oxidizing acids other than the halogen acids, but the behaviour of the hydrate depends upon its previous history. Alkalis dissolve the hydrate to form easily oxidized brown solutions which are said to contain rhenates(IV), but true rhenates(IV) are only prepared by the dry reactions of the hydrate or the anhydrous compound with fused alkalis. Rhenium dioxide dissolves in the halogen acids to give dark solutions which are said ultimately to give hexahalogenorhenates(IV). Aqueous oxidizing agents such as hydrogen peroxide and nitric acid convert the dioxide to perrhenate, and the anhydrous compound is readily oxidized to the heptaoxide by warming in oxygen.

4.1.3. Rhenium Trioxide

Rhenium trioxide was originally prepared by allowing the heptaoxide to react with powdered rhenium or rhenium dioxide at about 300°; the slight excess of heptaoxide is

---

[184] D. B. Rogers, R. D. Shannon, A. W. Sleight and J. L. Gillson, *Inorg. Chem.* **8** (1969) 841.
[185] W. Schuh and W. Klemm, *Z. anorg. allgem. Chem.* **220** (1934) 193.
[186] C. M. Nelson, G. E. Boyd and W. T. Smith, *J. Am. Chem. Soc.* **76** (1954) 378.
[187] J. Goodenough, P. Gibart and J. Breriet, *Compt. Rend.* **261** (1965) 2331.
[188] G. Coeffier, K. Traore and F. Brenet, *Compt. Rend.* **253** (1961) 103.

sublimed away or washed out of the crystalline trioxide with water. Better methods of preparation are the decomposition of the rhenium heptaoxide–dioxane adduct[189] or the reaction between carbon monoxide and rhenium heptaoxide at 300°.

Rhenium trioxide forms a red solid, though blue and purple specimens have been reported. Certain physical properties are collated in Table 19. The crystal structure is closely related to perovskite, with cubic close packing of the oxygen atoms[190] ($a_0 = 3.734 \pm 0.006$; Re–O = 1.87 Å), and the compound is only slightly paramagnetic[191].

Chemically, rhenium trioxide is inert. It is insoluble in water, in hot hydrochloric acid and in dilute sodium hydroxide, but it dissolves in concentrated nitric acid to give perrhenic acid, and it is reduced by acidified potassium iodide to the dioxide. Concentrated alkali induces dismutation to perrhenate and dioxide, so that it is not possible to prepare rhenates(VI) in aqueous solution–alkali fusion in the absence of air is necessary. Above 300° rhenium trioxide disproportionates in a vacuum to give the heptaoxide and dioxide[192]. (The relation between this observation and the vapour pressure measurements is not very clear.)

TABLE 19. PHYSICAL PROPERTIES OF RHENIUM TRIOXIDE

		Ref.
Sublimation point	614°	a
Vapour pressure	$\log P_{mm} = 15.16 - 10{,}882/T$ (325–420°)	a
ΔH_{sub} (kcal mole^{-1})	49.78	
ΔH°_{sub} (kcal mole^{-1})	146.1 ± 0.8	b
ΔG°_{form} (kcal mole^{-1})	128.1 ± 0.8	b

[a] V. I. Deev and V. I. Smirnov, *Dokl. Akad. Nauk SSSR* **140** (1961) 822.
[b] J. P. King and J. W. Cobble, *J. Am. Chem. Soc.* **79** (1957) 1559.

Recent work has shown that rhenium trioxide, heated at 1000° under 65 kbars pressure, appears to lose oxygen, and the symmetry of the copper-coloured oxide changes from cubic to orthorhombic. At high pressures it appears that a hexagonal oxide with a composition between ReO_2 and ReO_3 also exists. Solid solutions between WO_3 and ReO_3 have also been investigated; in order to avoid loss of oxygen during the experiments, Re_2O_7 was used as an oxidizing flux[193].

4.1.4. Rhenium Heptaoxide (Dirhenium Heptaoxide)

This, the highest oxide of rhenium, is formed when the metal is heated in air or oxygen above 150°. It has been noted that the oxidation proceeds through intermediate stages since the red trioxide has been observed on some faces of a single crystal of the element at lower oxygen pressures[194]. Alternatively, perrhenic acid, prepared *in situ* from the element and hydrogen peroxide, may be heated with phosphorus pentaoxide under vacuum when the

---

[189] C. J. Wolf, A. F. Clifford and W. H. Johnston, *J. Am. Chem. Soc.* **79** (1957) 4257 (see *Inorganic Synthesis*, Vol. III (1950) 187).

[190] K. Meisel, *Z. anorg. allgem. Chem.* **207** (1932) 121.

[191] C. M. Nelson, G. E. Boyd and W. T. Smith, *J. Am. Chem. Soc.* **76** (1954) 348.

[192] H. Nechemkin, A. N. Kurtz and C. F. Hiskey, *J. Am. Chem. Soc.* **73** (1951) 2829.

[193] A. W. Sleight and J. L. Gilson, *Solid State Communs.* **4** (1966) 601.

[194] A. A. Woolf, Reviewer's observation in *Quart. Rev.* **15** (1961) 373.

heptaoxide sublimes away from the reaction mixture[195]; this method obviates the difficulty of collecting the heptaoxide fume from a flowing gas stream. In a static system the formation of the heptaoxide is a convenient way of purifying the element[196].

Rhenium heptaoxide, purified by vacuum sublimation, forms large yellow angular crystals. The solid usually sublimes, but in a confined space melts at about 300° (Table 20).

TABLE 20. PROPERTIES OF RHENIUM HEPATOXIDE

		Ref.
Melting point	300.3°	a
Boiling point	360.3°	a
Vapour pressure (solid)	$\log P_{mm} = 15.010 - 7320/T$	a
(liquid)	$\log P_{mm} = 8.98 - 3868/T$	a
ΔH_{fus} (kcal mole^{-1})	15.81	a
ΔH_{vap} (kcal mole^{-1})	17.7	a
ΔH_{sub} (kcal mole^{-1})	33.5	a
ΔS_{fus} (e.u.)	27.6	a
ΔS_{vap} (e.u.)	28.0	a
ΔS_{sub} (e.u.)	58.4	a
ΔH°_{form} (kcal mole^{-1})	-296.7	b
S° (solid) (e.u.)	49.54	c
S°_{298} (gas) (e.u.)	105.0 ± 0.3	c
ΔG°_{form} (kcal mole^{-1})	-255.0 ± 2.0	c

[a] W. T. Smith, L. E. Line and W. A. Bell, *J. Am. Chem. Soc.* **74** (1952) 4965.

[b] G. E. Boyd, J. W. Cobble and W. T. Smith, *J. Am. Chem. Soc.* **75** (1953) 5783.

[c] R. H. Busey, *J. Am. Chem. Soc.* **78** (1956) 3263.

The crystal structure, recently determined by single crystal X-ray methods[197], involves ReO_6 octahedra and ReO_4 tetrahedra (Fig. 6) linked in such a way that only a little rearrangement is required to produce the gaseous molecule $[O_3ReOReO_3]$ (cf. also the dihydrate). If the partly heteropolar character of the longer (>2.0 Å) Re–O bonds is stressed the lattice can, in an idealized form, be regarded as an arrangement of ReO_4^- (the tetrahedra) and ReO_3^+ ions. The Re–O bond lengths should be compared with those in perrhenate (1.77 Å) and in $La_4Re_6O_{19}$ (1.98–2.01 Å). Observed O–Re–O bond angles are 76–104° in the distorted octahedra, 104–113° in the tetrahedra. Re–O–Re bond angles are found at values from 147.0 to 152.9°.

In the vapour phase Re_2O_7 is monomeric, this implies tetrahedral coordination of the rhenium. The large values of ΔS_{fus} and ΔS_{vap} indicate structural changes between the phases. The Raman spectra of the liquid and vapour have recently been assigned[198].

---

[195] R. D. Peacock, unpublished observation (1954).

[196] *Inorganic Synthesis*, Vol. III (1950) 188; see also A. A. Woolf, *J. Inorg. Nucl. Chem.* **7** (1958) 291.

[197] B. Krebs, A. Müller and H. Beryer, *Chem. Communs.* (1968) 263.

[198] I .R. Beattie and G. A. Ozin, *J. Chem. Soc.* A (1969) 2615.

Chemically, rhenium heptaoxide is extremely sensitive to moisture, and early reports of a peroxide seem to have been occasioned by the presence of traces of water in the heptaoxide. (Interestingly, however, a mass spectrometric study of rhenium surfaces treated with nitric acid produces in addition to $Re_2O_7^+$, the ion ReO_4^+ [199]. The heptaoxide dissolves in ethers, alcohols and amines without reduction, though it is not always clear whether it can be recovered unchanged from such solutions. At 300° hydrogen reduces the heptaoxide to the dioxide, and at 800° to the metal. Carbon monoxide and sulphur dioxide will also reduce the heptaoxide at elevated temperatures. According to the Noddacks, dry hydrogen sulphide interacts with the heptaoxide to give the heptasulphide[200].

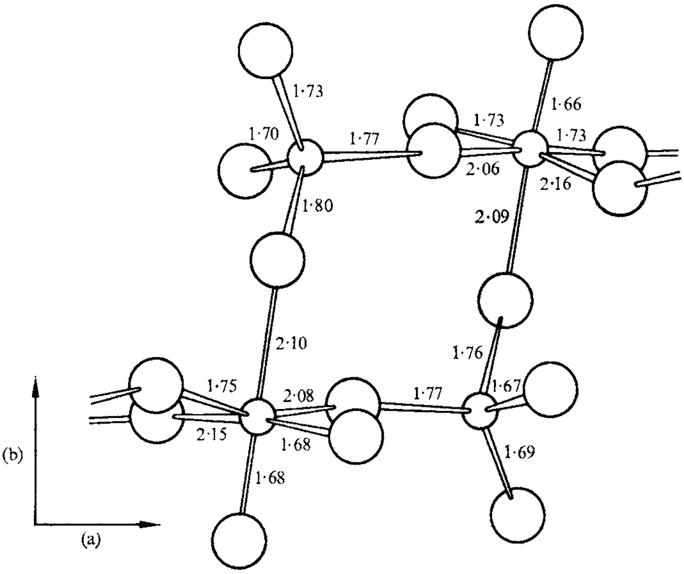


FIG. 6. Asymmetrical unit of the Re_2O_7 structure (bond distances in Å). (Reproduced, with permission, from B. Krebs, A. Müller and H. Beryer, *Chem. Communs.* (1968) 264.)

4.2. TERNARY AND QUATERNARY OXIDES

In these, rhenium is stabilized in every oxidation state from 3 to 7; there is also the mixed oxide $La_4Re_6O_{19}$ with rhenium in a formal oxidation state of $4\frac{1}{3}$.

4.2.1. Tervalent Rhenium

Fusion of rhenium dioxide with lithium monoxide results in disproportionation, and the stabilization of Re(III) in the ternary oxide, $LiReO_2$, which is isostructural with $LiWO_2$ [201]. Curiously, the similar reaction of sodium oxide with rhenium dioxide results only in the formation of Re(IV) compounds.

---

[199] M. H. Studier, *J. Phys. Chem.* **66** (1962) 189.

[200] I. and W. Noddack, *Z. anorg. allgem. Chem.* **181** (1929) 1.

[201] R. Scholder and P. Pfeiffer, *Angew. Chem.* **75** (1963) 376.

4.2.2. Quadrivalent Rhenium

Attempts to synthesize rhenium pyrochlores and spinels by reaction of ReO_2 with rare earth oxides and bivalent transition metal oxides appear to have been unsuccessful[202]. The Re(IV) state in melts is one of the disproportionation products of Re(VI), but few phases have been isolated—one compound established with certainty has the composition Na_2ReO_3; this in turn disproportionates to mesoperrhenate and rhenium metal at sufficiently high temperatures[201].

4.2.3. The Compound $La_4Re_6O_{19}$

This phase has been synthesized from La_2O_3, ReO_3 and Re metal at 1000° in a vacuum[203]. The structure consists of a three-dimensional network of ReO_6 octahedra; the ReO_6 octahedra are linked in pairs by a shared edge, and the pairs themselves are linked through the sharing of corners. There is metal–metal bonding (Re–Re = 2.42 Å in each pair of ReO_6 octahedra) and the average rhenium–oxygen distance is 1.98–2.01 Å.

4.2.4. Quinquevalent

Although Re(V) is not found in simple oxides (Re_2O_5, as reported by the early workers, was almost certainly ReO_3), a number of ternary and quaternary oxides do exist. These include the lithium "salt" Li_3ReO_4, the calcium "salt" $Ca_2Re_2O_7$ and a number of phases including rare earths of the type $Ba_2(RE)ReO_6$ (RE is a rare earth) [201]. The oxide $Cd_2Re_2O_7$, which was originally prepared as a supposed analogue of the ferromagnetic Ca_2ReFeO_6, has the pyrochlore structure with Re–O = 1.90±0.02 Å [204].

4.2.5. Rhenium Bronzes

These mixed oxides, which are similar to the long-known tungsten bronzes, have been produced by the reduction of alkali metal perrhenates with rhenium metal under 65 kbar pressure. The bright gold bronzes A_xReO_3, which are highly resistant to non-oxidizing acids, have metallic properties similar to those of the tungsten bronzes[205].

4.2.6. Sexivalent

The fusion of perrhenate, rhenium metal (or dioxide) in the correct proportions to form Re(VI), with a suitable base oxide[201,206] leads to ternary oxides nominally containing ReO_6^{6-}, ReO_5^{4-} and $Re_2O_9^{6-}$. Those containing the ReO_6^{6-} anion are known for Li^+, Ca^{2+}, Sr^{2+} and Ba^{2+}; others have been made in melts but not isolated[201]. Structurally, they resemble similar compounds of W(VI) and Os(VI). The lithium compound Li_6ReO_6 exists in two crystalline forms, one of which appears to be closely related to the orthoperrhenate Li_5ReO_6. Each has a hexagonal unit cell (for Li_6ReO_6, $a_0 = 5.03$, $c_0 = 14.12$ Å; for Li_5ReO_6, $a_0 = 5.05$, $c_0 = 14.21$ Å) [201,206]. The second form is isostructural with Li_6WO_6 [207]. The lithium rhenate Li_4ReO_5 also exists in α and β forms, which have affinities with the corresponding tungsten

[202] O. Muller, W. B. White and R. Roy, *J. Inorg. Nucl. Chem.* **26** (1964) 2075.

[203] J. Longo and A. W. Sleight, *Inorg. Chem.* **7** (1968); N. L. Morrow and L. Katz, *Acta Cryst.* **24B** (1968) 243.

[204] P. C. Donahue, J. M. Longo, R. D. Rosenstein and L. Katz, *Inorg. Chem.* **4** (1965) 1152.

[205] A. W. Sleight, T. A. Bither and P. E. Bierstedt, *Solid State Communs.* **7** (1969) 299.

[206] R. Scholder and K. L. Huppert, *Z. anorg. allgem. Chem.* **334** (1964) 209.

[207] J. Hauck, *Z. Naturforsch.* **24b** (1969) 455.

and tellurium compounds[201]. The alkaline earth compounds M_3ReO_6 have the perovskite lattice, as do the mixed oxides $(M'M'')_3ReO_6$ and $M_5Re_2O_{11}$ (M, M′, M″ = alkaline earth). Other phases such as Ba_2ReO_5 and $M_2Re_2O_9$ (M = Ca, Sr, Ba) have structural affinities with compounds of tellurium, molybdenum, tungsten, osmium and phosphorus of analogous composition[201]. The vibrational spectra of Li_6ReO_6 have been assigned[207a].

These rhenates decompose, even in alkaline solution, to rhenium dioxide and perrhenate [cf. the Tc(VI) compounds]. Compounds containing the ReO_4^{2-} ion have not been isolated.

Rhenium trioxide, which is the obvious starting material for rhenates(VI), does not dissolve appreciably in fused alkali below 400°, at which temperature these simple ternary Re(VI) compounds dismutate and the trioxide itself is showing signs of instability. However, quaternary oxides of the types $A_2[(M^{II}Re^{VI})]O_6$ and $A_3[(M_2^{II}Re^{VI})]O_9$ (A = Ba or Sr) are formed by heating rhenium trioxide with the appropriate oxides or carbonates to 900°. The former have a perovskite lattice; when the divalent cation M(II) is a transition metal, the compounds have interesting magnetic properties[208]. Most of the latter series have the hexagonal barium titanate lattice[209]. These oxides, which are strongly coloured, resemble rhenium trioxide itself in being resistant to water and to dilute acids. They dissolve in concentrated nitric acid and in acidified 30% hydrogen peroxide to give perrhenate.

TABLE 21. BARIUM PERRHENATES [a]

Salt	Colour	M.p. (°C)	Reaction conditions	Solubility in CH_3OH (g per 100 ml)
$Ba(ReO_4)_2$	Colourless	799		0.37
$Ba_3(ReO_5)_2$	Citron yellow	1200	$BaCO_3$ at 700° (2 h)	0.03
$Ba_5(ReO_6)_2$	Orange yellow	1200	$BaCO_3$ at 850° (20 h)	5.3

[a] R. Scholder, K. L. Hupper and P. P. Pfeiffer, *Angew. Chem.* **75** (1963) 375.

4.2.7. Septavalent

The dry reactions of alkalis or bases with perrhenates at moderate temperatures yield mesoperrhenates of the composition M_3ReO_5 (M = Na, K, ½Ba, ½Sr) [201, 206]. These are citron yellow oxides or salts isostructural with periodates and osmates(VII) of similar formulae[201, 206]. The relation between the various barium perrhenates is shown in Table 21. Fusion of perrhenates with oxides or carbonates at higher temperatures and for longer periods yields orange yellow orthoperrhenates M_5ReO_6 (M = Li, Na, ½Ba, ½Sr, ½Ca) which are again isostructural with the corresponding osmium and iodine compounds.

The infrared spectra of $Ba_5(ReO_6)_2$ and $Ba_3(ReO_5)_2$ have recently been measured[210], and the frequencies for $Ba_5(ReO_6)_2$ have been interpreted in terms of discrete ReO_6^{5-} octahedra. The electronic spectrum of $Ba_5(ReO_6)_2$ shows an absorption at 430 mμ which has been assigned to a $t_{2u} \rightarrow t_{2g}$ transition[210].

[207a] J. Hauck and A. Fadini, *Z. Naturforsch.* **25b** (1970) 422.

[208] J. Longo and R. Ward, *J. Am. Chem. Soc.* **83** (1961) 2816.

[209] R. Ward, *Inorg. Chem.* **1** (1962) 723.

[210] E. J. Baran and A. Müller, *Z. anorg. allgem. Chem.* **368** (1969) 167.

Similar orthoperrhenates, which may be better regarded as quaternary oxides, are formed by the fusion of barium carbonate with sodium or lithium perrhenate[210]. The compounds, which are red when hot and yellow when cold, have an ordered perovskite structure and may be written $Ba(M_{0.5}Re_{0.5})O_3$ (M = Li or Na). A similar set, of lower symmetry, is known for strontium[211], and other quaternary oxides such as Li_3MgReO_6 are also known[212].

4.2.8. Mesoperrhenates from Aqueous Solution

Barium mesoperrhenate, $Ba_3(ReO_5)_2$, is made the wet way by adding alkali or baryta water to an aqueous solution of barium perrhenate[213]. The product is usually contaminated with barium carbonate. The mesosalt separates as a bright yellow powder, apparently without water of constitution. Although it is unnecessary to postulate the existence of an ReO_5^{3-} ion in the solid, since presumably the rhenium retains 6-coordination (perhaps as a mixed metal oxide), the constitution of the ion present in aqueous solution is interesting. On the basis of spectrophotometric data Rulfs[214] has adduced evidence for a monomeric anion formulated either as ReO_5^{3-} or as $ReO_5(\text{hydrated})^{3-}$ (in order to retain 6-coordination of the rhenium). Presumably the latter species would be $[ReO_4(OH)_2]^{3-}$ (cf. osmium tetroxide, which is isoelectronic with the 4-coordinated ReO_4^- ion, yields in alkaline solution salts of the 6-coordinated $[OsO_4(OH)_2]^{2-}$ anion). Rulfs[214] has noted that solid $Ba_3(ReO_5)_2$ has additional absorption peaks in the visible region above those shown by the aqueous meso ion, and, indeed, the solutions of mesoperrhenate ion are colourless. The other mesoperrhenates (Sr, Na, K) which may be prepared in the dry way are not precipitated from aqueous solution; presumably this is only a solubility effect.

5. PERRHENIC ACID AND THE PERRHENATES, CHALCOGENIDES AND REFRACTORY COMPOUNDS

5.1. PERRHENIC ACID AND THE PERRHENATES

An aqueous solution of perrhenic acid is formed when the heptaoxide is dissolved in water or when the metal or dioxide is oxidized by hydrogen peroxide. Anodic oxidation of the consolidated metal in alkaline solution has also been employed; the alkali metal ions are subsequently removed on a cation exchange column.

The perrhenic acid is colourless in dilute solution. On evaporation the solution becomes yellow green; careful drying of a concentrated solution over P_2O_5 yields yellowish, hygroscopic crystals of composition $Re_2O_7\cdot 2H_2O$, which may be recrystallized from nitromethane[215]. That this is a true molecular hydrate of Re_2O_7 with coordinated water has been shown by the single crystal X-ray analysis[215]. The structure is closely related to that of Re_2O_7 itself (see Fig. 6); one rhenium atom is tetrahedrally surrounded by oxygen atoms, while the oxygens lie in a distorted octahedral arrangement around the second rhenium atom, the tetrahedral group being joined to the octahedral group by a common corner.

---

[211] A. W. Sleight and R. Ward, *J. Am. Chem. Soc.* **83** (1961) 1088.

[212] G. Lang, *Z. anorg. allgem. Chem.* **348** (1966) 246.

[213] B. Scharnow, *Z. anorg. allgem. Chem.* **215** (1933) 183.

[214] S. K. Majumdar, R. A. Pacer and C. L. Rulfs, *J. Inorg. Nucl. Chem.* **31** (1969) 33.

[215] H. Beyer, O. Glemser and B. Krebs, *Angew. Chem.* (Int. Edn.) **7** (1968) 295.

The Re–O–Re angle is practically 180°. The positions of the hydrogen atoms, and of the hydrogen bonds, by which one molecular unit is linked to the next, have not been established with certainty. The hydrogen bonds are evidently retained in concentrated aqueous solutions of perrhenic acid, and this is the reason for their high viscosity[215]. Concentrated aqueous solutions of perrhenic acid also show a characteristic Raman spectrum which differs from that of perrhenate. In the vapour phase perrhenic acid has been shown to exist as $ReO_3(OH)$ [206], but the heating of solid perrhenic acid leads to the volatilization of rhenium heptaoxide.

TABLE 22. PHYSICAL PROPERTIES OF PERRHENATES

1. *Solubilities in water and in moles per litre at about* 20°[a–d]

	ReO_4^-	TcO_4^-	ClO_4^-	MnO_2^-	BF_4^-
Na	*ca.* 3.5		v. soluble	17.28 (25°)	v. soluble
K	0.034	0.106 (25°)	0.404	0.121	sl. soluble
Rb	0.031		0.052	0.055	0.027
NH_4	0.227		0.580 (15°)	2.136 (25°)	
Ag	0.0089	sl. soluble	sl. soluble	v. soluble	v. soluble

2. *Thermodynamic properties of perrhenate ion*

		Ref.
ΔH°_{form} (ReO_4^- aq.) (kcal mole^{-1})	−189.2	h
ΔG_{form} (ReO_4^- aq.) (kcal mole^{-1})	−167.1	h
ΔS°_{form} (ReO_4^- aq.) (e.u.)	−74.2	h
S° (ReO_4^- aq.) (e.u.)	48.3 ± 0.3	i

[a] E. Wilke-Dorfürt and T. Gunzart, *Z. anorg. allgem. Chem.* **215** (1933) 369.

[b] E. Neuser, *Z. anorg. allgem. Chem.* **230** (1937) 253.

[c] R. H. Busey and R. B. Bevan, unclassified document, ORNL-2983 (1960) 9.

[d] B. Scharnow, *Z. anorg. allgem. Chem.* **215** (1933) 184. Solubilities and other physical properties of perrhenates have also been recorded, refs. e–g.

[e] W. T. Smith and S. H. Long, *J. Am. Chem. Soc.* **70** (1948) 354.

[f] W. T. Smith and G. E. Maxwell, *J. Am. Chem. Soc.* **73** (1951) 658.

[g] W. T. Smith, *J. Am. Chem. Soc.* **73** (1951) 7.

[h] G. E. Boyd, J. W. Cobble and W. T. Smith, *J. Am. Chem. Soc.* **75** (1953) 5.

[i] J. W. Cobble, G. D. Oliver and W. T. Smith, *J. Am. Chem. Soc.* **75** (1953) 5786.

Perrhenic acid is a strong acid; this is shown by the pH of its aqueous solution, its attack upon metals, metal oxides, carbonates, and hydroxides, the behaviour of perrhenates on ion-exchange resins, and the solubility of its salts. These observations have been confirmed quantitatively by measurement of the dissociation constant (about 40) [217]. The acid may be titrated with the aid of indicators such as methyl red.

---

[216] O. Glemser, A. Müller and H. Schwarzkopf, *Z. anorg. allgem. Chem.* **334** (1964) 21.

[217] N. Bailey, A. Carrington, K. A. K. Lott and M. C. R. Symons, *J. Chem. Soc.* (1960) 290.

The solubilities of some perrhenates and other salts of MX_4^- anions in water are tabulated in Table 22. The perrhenates follow the "strong acid" pattern of the perchlorates and fluoroborates, whose ions are only slightly deformable. The silver salts listed in Table 22 fall into two groups, but since the bonding in ReO_4^- must differ considerably from that in ClO_4^- or in BF_4^-, distinctions of this kind are to be expected.

The perrhenate ion is stable over a wide range of pH, and it is only at very high pH that the concentration of the meso ion, ReO_5^{3-}, becomes appreciable[218]. The action of reducing agents on perrhenate in aqueous solution has been extensively studied[219]. From this work, and by measurements of the polarographic behaviour of perrhenate in the presence of various supporting media[219], it may be concluded that in the majority of cases reduction stops at Re(IV), often with the intermediate formation of Re(V). Strong reducing agents in acid solution may take the rhenium down to lower oxidation states[220]. The oxidation reduction schemes for perrhenate in aqueous solution are indicated in Fig. 7. In non-aqueous solutions the reduction of perrhenate may take place in quite a different manner, and recent work in sulphuric acid had indicated the formation of the coloured species Re(VI) (pink) and Re(V) (blue) by reduction with Fe(II) or Sn(II)[221]. Perrhenate ion has been shown to coordinate more strongly than ClO_4^- or BF_4^-, but less strongly than Cl^- or Br^-.[221a].

The solid perrhenate salts are colourless, except when the cation itself is coloured, and are stable. Potassium perrhenate melts at 555° (ref. e, Table 22), and boils at about 1370° under atmospheric pressure. The absence of colour in the solids at 25° is due to a shift of the first strong electron transfer band of the permanganate ion into the ultraviolet; the absorption of ReO_4^- begins only at 2800 Å, and peaks occur at 2273 Å (m) and 2041 Å (s). The absorption has been ascribed to the transition $(t_1)^6 3t_2;\ {}^1T_2 \leftarrow {}^1A_1$ associated with the tetrahedral symmetry and allowing for some "*d* orbital" character in the metal–oxygen bonds[222].

The vibrational spectra of perrhenate are characteristic of a tetrahedral anion ($\nu_1 = 971$, $\nu_2 = 331$, $\nu_3 = 918$, $\nu_4 = 343$ cm^{-1})[223]. The infrared frequency at 918 cm^{-1} is sufficiently strong to be used for the qualitative detection of the anion.

A number of the perrhenates containing a univalent cation, including those of the alkali metals, ammonium and thallium, adopt a scheelite (tetragonal) or pseudoscheelite (orthorhombic) structure. The rhenium–oxygen distance in $KReO_4$ is 1.77 Å[224] (cf. Tc–O in $TcO_4^- = 1.75$ Å and Ru–O in $RuO_4^- = 1.79$ Å).

Although the potassium and some of the other alkali metal salts may be distilled unchanged, ammonium perrhenate is decomposed on heating, ultimately to ReO_2[225]. It appears, curiously, that the scheelite structure of NH_4ReO_4 is retained even when the weight loss of the sample reaches two-thirds of that attained by complete decomposition to ReO_2[225], though the size of the unit cell is diminished. All the alkali salts are reduced by hydrogen at 400–1000°, but the resulting metals are contaminated with alkali which is difficult to remove completely. Fluorine reacts with potassium perrhenate to give the dioxide trifluoride,

---

[218] S. K. Majumdar, R. A. Pacer and C. L. Rulfs, *J. Inorg. Nucl. Chem.* **31** (1939) 33.

[219] R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier (1966), p. 34; R. Colton, *The Chemistry of Rhenium and Technetium*, Interscience (1965), p. 165.

[220] F. A. Cotton, N. F. Curtis and W. R. Robinson, *Inorg. Chem.* **4** (1965) 1696.

[221] L. V. Porisova, D. I. Ryabchikov and T. I. Yerinowa, *Russ. J. Inorg. Chem.* **13** (1968) 166.

[221a] H. G. Mayfield, Jr. and W. E. Bull, *Inorg. Chim. Acta* **3** (1969) 676.

[222] A. Carrington and M. C. R. Symons, *J. Chem. Soc.* (1957) 659.

[223] L. A. Woodward and H. L. Roberts, *Trans. Faraday Soc.* **52** (1956) 615.

[224] J. C. Morrow, *Acta Cryst.* **13** (1960) 443.

[225] G. Coeffier, K. Traore and F. Brenet, *Compt. Rend.* **253** (1961) 103.

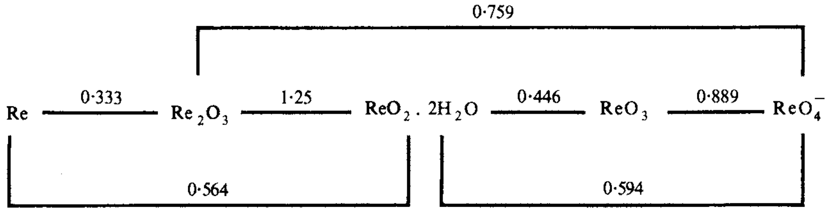
ReO_2F_3. Carbon monoxide acts on potassium perrhenate at high temperatures and pressures to give dirhenium decacarbonyl, $Re_2(CO)_{10}$. Ammonium perrhenate, heated in a nitrogen atmosphere, gives a mixture of rhenium metal and the nitride Re_3N.

The ester $(CH_3)_3SiOReO_3$ has been prepared from the interaction of either Re_2O_7 and trimethylsilyl oxide or silver perrhenate and trimethylchlorosilane[226]. It forms a white solid, m.p. 79.5°, which may be sublimed under a vacuum. The X-ray crystal structure[227] shows a normal Re–O–Si bridging bond to be present in contrast to the Re–O–Re bond in $[Cl_5Re–O–ReCl_5]^{4-}$ ion.

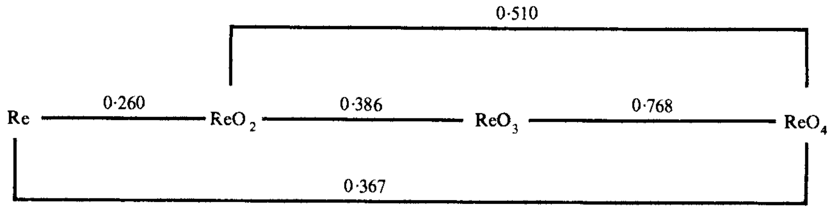
5.2. SUBSTITUTED PERRHENATES

5.2.1. Nitridorhenate(VII)

The potassium salt has been isolated from the action of potassamide on a solution of rhenium heptaoxide Re_2O_7, in liquid ammonia[228]. The nitridorhenate(VII) ion, ReO_3N^{2-}, is isoelectronic with the well-known osmiamate anion, OsO_3N^-, and with the nitridomolybdate anion MoO_3N^{3-} and has intermediate properties; for instance it is hydrolysed by water but is stable to the atmosphere. In the infrared region the ion shows absorption frequencies at 909 and 936 cm^{-1} attributed to the Re–O bond, and at 1025 cm^{-1} attributed to the Re–N bond.



(alkaline solution)



(acid solution)

FIG. 7. Oxidation-reduction potentials of rhenium (in volts) in alkaline[a] and acid[b] solutions.

[a] R. H. Busey, E. D. Sprague and R. B. Bevan, *J. Phys. Chem.* **73** (1969) 1039.

[b] J. P. King and J. W. Cobble, *J. Am. Chem. Soc.* **79** (1957) 1559.

5.2.2. Thiorhenates(VII)

When hydrogen sulphide is passed into a neutral solution of a perrhenate the colourless

---

[226] M. Schmidt and H. Schnidbauer, *Chem. Ber.* **92** (1959) 2667.

[227] G. M. Sheldrick and W. S. Sheldrick, *J. Chem. Soc.* (1969) 2161.

[228] A. F. Clifford and R. R. Olson, *Inorganic Synthesis*, Vol. VI (1960) 167.

solution becomes yellow–green and thioperrhenates are formed according to the equation

$$ReO_4^- + H_2S \rightleftharpoons ReO_3S^- + H_2O$$

The solution also contains dark polythio-compounds, but the slightly soluble yellow thallous thiorhenate(VII) may be obtained by addition of thallous nitrate solution followed by fractional crystallization[229]. Other salts (of ammonium, and the alkali metal cations), which are yellow–green, are more soluble. The silver, lead, cupric and mercury salts were not isolated; instead, a mixture of the perrhenate and sulphide was formed.

The thioperrhenates are more soluble than the perrhenates; they decompose slowly even in netural solution, and upon the addition of acid to the solution rhenium heptasulphide is precipitated[229].

Recent work has shown that $TlReO_3S$ has the $BaSO_4$ structure[230]. The infrared absorption spectrum of the ReO_3S^- ion (absorption peaks at 938 (m); 891 (s, br); 504 (m); 330 (m); 310 (s); 240 (m) cm^{-1}) has been assigned, and the peak at 504 cm^{-1} has been attributed to the Re–S stretching frequency[231].

It was suggested by the early workers that the prolonged action of hydrogen sulphide on perrhenate solutions leads to the replacement of more of the oxygen atoms by sulphur, and recent measurements of the electronic absorption spectra of such solutions suggest strongly that the ReS_4^- ion is present[231]. It has, however, also been shown that addition of Tl^+ to the solutions results, not in the precipitation of $TlReS_4$, but of a mixture of Tl_2S and Re_2S_7 [231].

5.3. CHALCOGENIDES

Rhenium forms the sulphides ReS_2, ReS_3 and Re_2S_7, the selenides $ReSe_2$ and Re_2Se_7, and a telluride $ReTe_2$. The telluride and the trisulphide have only been made by dry methods, but the remaining compounds may be precipitated from aqueous solution. In its chalcogenides rhenium appears to show normal oxidation states.

5.3.1. Rhenium Disulphide

This may be prepared by fusing the elements together or by heating the heptasulphide in nitrogen at 750°, or, in the wet way, by the action of hydrogen sulphide on a quadrivalent rhenium compound such as the hexachlororhenate. The compound (Table 23) as prepared the wet way, is amorphous, but the high-temperature methods of preparation yield a crystalline disulphide which apparently has a disordered version of the molybdenum disulphide structure. Like molybdenum disulphide itself, the compound is a soft black material. Rhenium disulphide is only slightly paramagnetic (μ_{eff} = 0.38 BM at 28°)[232] but is probably not magnetically dilute.

5.3.2. Rhenium Trisulphide

It has recently been claimed[233] that the hydrogen reduction of the heptasulphide at 25° leads to the trisulphide and that it is formed as an intermediate during the thermal decomposition of the heptasulphide in nitrogen[233].

[229] W. Feit, *Z. anorg. allgem. Chem.* **199** (1931) 262.

[230] A. Mueller and B. Krebs, *Z. anorg. allgem. Chem.* **342** (1966) 183.

[231] A. Mueller, B. Krebs and E. Diemann, *Z. anorg. allgem. Chem.* **353** (1967) 259.

[232] W. Klemm and W. Schuth, *Z. anorg. allgem. Chem.* **220** (1934) 193.

[233] K. Traore, G. Coeffier and J. P. Brenet, *Compt. Rend.* **254** (1962) 491; K. Traore, *Bull. Soc. Chim.* (1965) 1284.

5.3.3. Rhenium Heptasulphide (Dirhenium Heptasulphide), Re_2S_7

The heptasulphide is usually prepared by the action of hydrogen sulphide on a solution of a perrhenate in 4 M hydrochloric acid. A pressure of gas is required to complete the precipitation[234]. The compound is also precipitated more slowly from ammoniacal solution, but in neutral solution thioperrhenates appear as intermediates. Sulphur impurity is removed from the heptasulphide, after a preliminary drying at the ambient temperature, by leaching with carbon disulphide. Made in this way, the heptasulphide contains a little moisture which is difficult to remove, but the anhydrous compound may be obtained the dry way through the action of hydrogen sulphide on rhenium heptaoxide[235].

TABLE 23. PHYSICAL PROPERTIES OF THE RHENIUM SULPHIDES

		Ref.
Rhenium disulphide		
Vapour pressure	$\log P_{mm} = 3.214 - 4976/T$ (500–700°)	a
ΔH_{sub} (kcal mole^{-1})	22.66	
ΔH_{form} (kcal mole^{-1})	-42.7 ± 1.2	a
Unit cell (hexagonal)	$a_0 = 3.14$; $c_0 = 12.20$ Å	b
Rhenium heptasulphide		
ΔH_{form} (kcal mole^{-1})	-107.9 ± 1.8	a
Unit cell (tetragonal)	$a_0 = 13.7 \pm 0.3$; $c_0 = 10.24 \pm 0.66$	c

[a] J. E. McDonald and J. W. Cobble, *J. Phys. Chem.* **66** (1962) 791.
[b] K. Meisel, *Angew. Chem.* **44** (1931) 243.
[c] K. Traore, G. Coeffier and P. Bronet, *Bull. Soc. Chim.* (1962) 361.

Rhenium heptasulphide forms a dark brown or black material which dries to a fine powder. It is readily decomposed by heat to lower sulphides, and is reduced by hydrogen, eventually, at 1000°, to the element. In air, the heptasulphide oxidizes readily, sometimes with incandescence, to the heptaoxide, and it dissolves in oxidizing solvents such as nitric acid, bromine water and hydrogen peroxide solution. The heptasulphide is not attacked by hydrochloric acid, potassium sulphide or dilute sulphuric acid. Fluorine reacts with the dry heptasulphide to give rhenium hexafluoride[236]. With chlorine, the heptasulphide eventually yields, at 450–500°, a mixture of chlorides, but at lower temperatures the first products are chloride sulphides of composition $Re_2S_3Cl_4$ (at 120°) and $ReSCl_2$ (at 400°). The chloride sulphide $Re_2S_3Cl_4$ is insoluble in carbon tetrachloride and in alcohol, but is soluble in benzene and dissolves in water with hydrolysis[237].

---

[234] S. Tribalat, M. L. Jungfleisch and V. Collet, *Compt. Rend.* **251** (1960) 718.

[235] J. H. Muller and W. A. Lahande, *J. Am. Chem. Soc.* **55** (1933) 2376.

[236] R. D. Peacock, unpublished observation (1950).

[237] I. A. Glukhov, S. B. Davidyants, M. A. Yunusev and N. A. El'manova, *Zh. Neorgan. Khim.* **6** (1961) 1264.

5.3.4. Selenides

Less is known about these than the sulphides, though they have recently been re-investigated[238]. The structure of the diselenide has been shown to be of the $Cd(OH)_2$ type[239]. The diselenide is formed both directly from the elements and by the decomposition of the heptaselenide at 325°.

5.3.5. Tellurides

Only the ditelluride appears to exist. It has been prepared from the elements, and is not isostructural with the disulphide or diselenide[240].

5.4. REFRACTORY COMPOUNDS

A number of binary and ternary compounds are known. These span the area between covalent compounds and alloys; and many are semiconductors. Most are prepared by dry reactions at high temperatures, especially between the elements.

Several borides exist. They have been prepared by heating the elements together at about 1200° in sealed, evacuated silica tubes, either in the electric arc or by induction heating[241]. They resemble the other transition metal borides in appearance and properties. The diboride, ReB_2, is not isostructural with the diborides of the transition metals of Groups IV, V and VI. The triboride ReB_3 has structural affinities with Mo_2B_5 and with W_2B_5, and Re_7B_3 is isostructural with RuB_3 and Th_7Fe_3. Other phases, such as $Re_{23}B_6$ ($Cr_{23}C_6$ type), have also been identified[242], and certain ternary borides, e.g. $Ni_{11}Re_{12}B_6$ [242], have also been investigated.

From X-ray diffraction patterns of quenched Re–C alloys, the existence of carbides has been suggested, but no definite information is yet known[243].

Silicides of rhenium seem to be less well known than the borides, at least in the open literature. The disilicide, $ReSi_2$, which is a good semiconductor, seems to be the most important, but other phases, Re_3Si, Re_5Si_2 and ReSi, the latter isostructural with other cubic monosilicides, are also known[244].

The action of nitrogen or ammonia upon rhenium does not seem to yield a nitride, but the action of ammonia on the perrhenate NH_4ReO_4 is said to yield the nitride Re_3N [245], and the hydrogen reduction of ammonia perrhenate at 300° yields a mixture of rhenium metal and the same nitride. The nitride Re_3N is insoluble in aqueous hydrogen peroxide, which distinguishes it from the metal. The action of heat on an ammine of rhenium trichloride, $ReCl_3 \cdot 4NH_3$, is said to give the nitride Re_2N as the end product of decomposition.

The only phases in the rhenium–phosphorus system in the region of 0–50% phosphorus at 800–1100° have the composition Re_2P and ReP. The two phosphides resemble the

---

[238] V. Obolonchidi and T. H. Mikhlina, *Ukr. Khim. Zh.* **30** (1964) 1037.

[239] N. W. Alcock and A. Kjekshus, *Acta Chem. Scand.* **19** (1965) 79.

[240] S. Furnseth and A. Kjekshus, *Acta Chem. Scand.* **20** (1966) 245.

[241] S. LaPlaca and B. Post, *Acta Cryst.* **15** (1962) 97.

[242] E. Ganglberger, H. Nowotny and F. Benesovsky, *Monatsch. Chem.* **97** (1966) 101.

[243] W. A. Frail, in *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 11, Academic Press, London (1968), p. 209.

[244] S. Weglowski, *Roozniki Chem.* **39** (1964) 779.

[245] T. S. Verkhoglyadova, T. V. Dubovcho and G. V. Samsonov, *Paroshkovaya Met. Akad. Nauk SSSR* **1** (1961) 9.

phosphides of other transition metals; dirhenium phosphide has an orthorhombic unit cell isostructural with the corresponding ruthenium compound[246]. At higher phosphorus concentrations the phosphide Re_3P_7 is formed.

The rhenium arsenide, Re_3As_7, which has been synthesized (together with the mixed phosphide–arsenides $Re_3As_3P_4$ and $Re_3As_4P_3$) by heating rhenium with the appropriate non-metals, has been the subject of much controversy. It now appears that the structure is of the Ru_3Sn_7 type; the rhenium atoms are in coordination with eight arsenic atoms ($4As_I$; $4As_{II}$) at the corners of a square antiprism (Re–As = 2.60 to 2.55 Å). The As_I atoms are in tetrahedral coordination with rhenium (at 2.60 Å), while the As_{II} atoms are in tetrahedral coordination with three rhenium atoms at 2.55 Å and one arsenic at 2.48 Å (the As–As single bond distance)[247]. The compound is substantially covalent with the rhenium in the nominally Re(VII) state.

The chemistry of these compounds and of other rhenium refractories has recently been reviewed[248]; however, the Re_3As_7 structure set out in this review has been criticized by Kjekshus *et al.*[249] who have confirmed Schnering's work.

Although it does not appear that attempts have been made to obtain these phosphides and arsenides from aqueous solution, there does not seem to be any reason why they should not have an aqueous chemistry like the sulphides and selenides.

6. CARBONYLS AND ORGANOMETALLIC DERIVATIVES

This is one of the most rapidly advancing fields of rhenium chemistry. The resemblance between manganese, technetium and rhenium is closest in those low valency compounds, though in the cyclopentadienide derivatives there are considerable differences between manganese, on the one hand, and technetium and rhenium, on the other. It is perhaps significant that organometallic compounds of rhenium involving σ bonding ligands only do not appear to exist; the early reports of a trimethyl rhenium, $(CH_3)_3Re$, have been shown to be incorrect. Structural aspects of the chemistry of rhenium carbonyl have recently been reviewed[250].

6.1. RHENIUM CARBONYL (DIRHENIUM DECACARBONYL)

Rhenium carbonyl was discovered by Hieber and his coworkers in 1941, and the present method of preparation is still essentially similar. Rhenium heptaoxide is treated with carbon monoxide at 250° under 200 atm pressure (270° and 250 atm pressure are recommended if potassium perrhenate is used as the starting material); the reaction also goes, but more slowly, with Re_2S_7 [251]. The carbonyl is purified by vacuum sublimation.

Dirhenium decacarbonyl, $Re_2(CO)_{10}$, forms white crystals which are stable at the ordinary temperature. It melts in a sealed tube at 177° but volatilizes under atmospheric pressure

[246] S. Rundquist, *Acta Chem. Scand.* **15** (1961) 342.
[247] M. Klein and H. G. von Schnering, *J. Less-Common Metals* **11** (1966) 298.
[248] F. Hulliger, *Structure and Bonding* **4** (1968) 53.
[249] P. Jensen, A. Kjekshus and T. Skansen, *J. Less-Common Metals* **17** (1969) 455.
[250] E. W. Abel and F. G. A. Stone, *Quart. Rev.* **23** (1969) 325.
[251] W. Hieber and H. Fuchs, *Z. anorg. allgem. Chem.* **248** (1941) 256.

at about 140°; above this temperature in nitrogen it decomposes slowly to carbon monoxide and rhenium, but in air it tends to ignite spontaneously. The compound has a slight sweet odour. Rhenium carbonyl dissolves in camphene and in cyclopentanone; in these solvents the molecular weight corresponds to $Re_2(CO)_{10}$. In most solvents, however, including water, rhenium carbonyl is only slightly soluble.

Rhenium carbonyl is diamagnetic. The dimeric formula implies two structural possibilities when 6-coordination of the metal is realized: (i) a metal–metal bond and (ii) bridging carbonyls. Preliminary infrared data was thought to indicate that neither of these possibilities was correct, but X-ray diffraction has shown that the dimeric molecule is linked through a metal–metal bond[252]. The two linked octahedra in the carbonyl molecule are rotated by 45° with respect to one another. The Re–Re bond length (3.02 Å) is longer than the sum of the normal covalent radii (2.56 Å). The strength of the metal–metal bond is a matter of some interest; it has been shown from kinetic measurements[253] that the lower limit for the activation enthalpy required to produce homolytic fission is 38.6±0.4 kcal mole^{-1}. The energetics of ionization and dissociation have been estimated from appearance potentials in the mass spectrometer[254], the value obtained (2.22 eV) does not refer to the same fission process as the

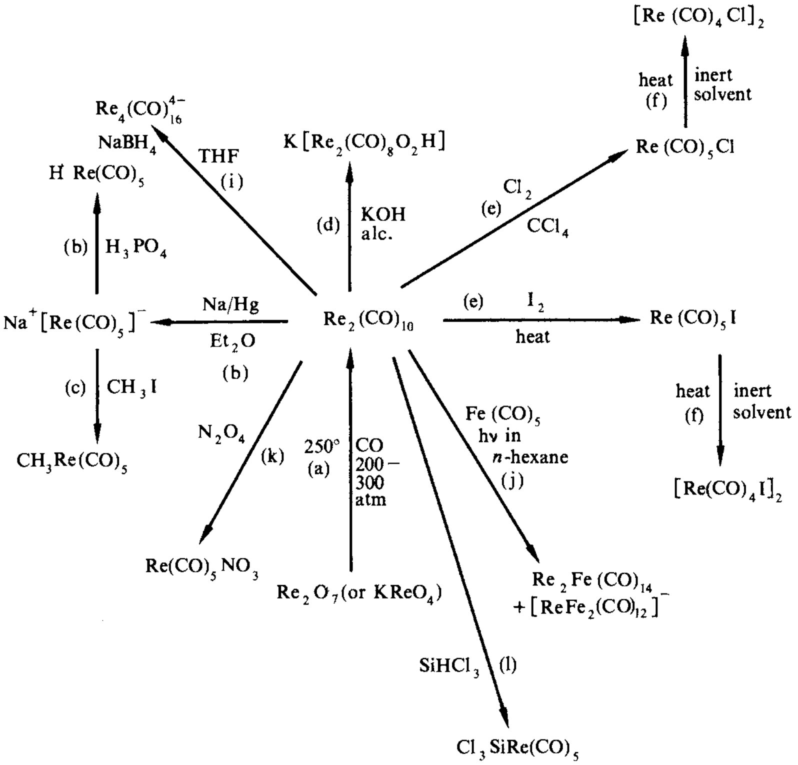


FIG. 8A. Reactions of rhenium carbonyl.

---

[252] L. F. Dahl, E. Ishishi and R. E. Rundle, *J. Chem. Phys.* **26** (1957) 1750.
[253] L. I. B. Haines and A. J. Poë, *Chem. Communs.* (1968) 984.
[254] H. J. Svec and G. A. Junk, *J. Am. Chem. Soc.* **89** (1967) 2836.

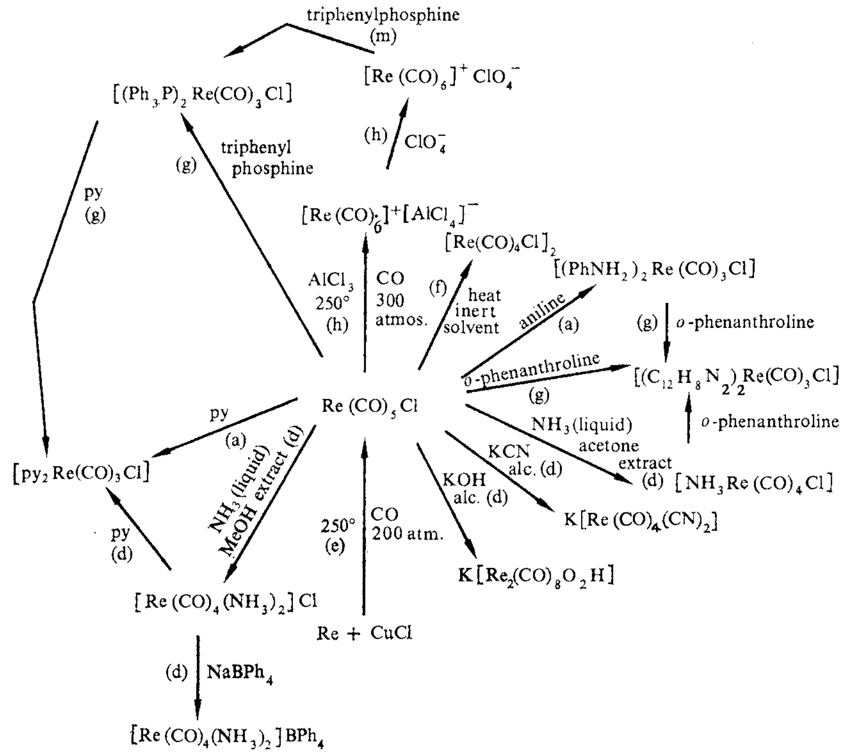


FIG. 8B. Reactions of rhenium carbonyl chloride.

[a] W. Hieber and H. Fuchs, *Z. anorg. allgem. Chem.* **248** (1941) 256, 269.
[b] W. Beck, W. Hieber and G. Braun, *Z. anorg. allgem. Chem.* **308** (1961) 23.
[c] A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, *J. Chem. Soc.* (1962) 3653.
[d] W. Hieber and L. Schuster, *Z. anorg. allgem. Chem.* **287** (1956) 214.
[e] W. Hieber, R. Schuh and H. Fuchs, *Z. anorg. allgem. Chem.* **248** (1941) 243.
[f] E. W. Abel, G. B. Hargreaves and G. Wilkinson, *J. Chem. Soc.* (1958) 3149.
[g] E. W. Abel and G. Wilkinson, *J. Chem. Soc.* (1959) 1501.
[h] W. Hieber and T. Kruck, *Z. Naturforsch.* **16b** (1961) 709; *Angew. Chem.* **73** (1961) 586.
[i] R. Bau, B. Fontal, H. D. Kaesz and M. R. Churchill, *J. Am. Chem. Soc.* **89** (1967) 6374.
[j] G. O. Evans, J. P. Hargaden and R. K. Sheline, *Chem. Communs.* (1967) 186.
[k] C. C. Addison, R. Davis and N. Logan, *Inorg. Chem.* **6** (1967) 1926.
[l] W. Jetz and W. A. G. Graham, *J. Am. Chem. Soc.* **89** (1967) 2773.
[m] E. W. Abel and S. P. Tyfield, *Chem. Communs.* (1968) 465.

kinetic measurements. The relative order of metal–metal dissociation constants in the carbonyls $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ and $ReMn(CO)_{10}$ is Re–Mn > Re–Re > Mn–Mn; approximate force constants calculated from Raman data are in the same order[255]. The infrared and Raman data have recently been completely assigned[256].

Dilute acids and alkalis have no action upon rhenium carbonyl, but the compound is attacked by hot concentrated nitric and sulphuric acids. Certain other reactions are indicated in Fig. 8A. The salt $K[Re_2(CO)_8O_2H]$, formed by the action of alcoholic potassium hydroxide

---

[255] H. M. Gager, J. Lewis and M. J. Ware, *Chem. Communs.* (1966) 616.
[256] I. J. Hyams, D. Jones and E. R. Lippincott, *J. Chem. Soc.* A (1967) 1987.

upon the carbonyl or on the carbonyl chloride $Re(CO)_5Cl$, does not appear to have been investigated since the early work, and confirmation is required. The reaction with iron pentacarbonyl, which leads to the mixed carbonyl $Re_2Fe(CO)_{14}$, has opened routes to a large number of new carbonyls, whilst the reduction of rhenium carbonyl with $NaBH_4$ is similarly important in leading to new "cluster" compounds. A large number of phosphine and arsine derivatives have been isolated[256a] (see also Fig. 9).

6.2. CARBONYL CATIONS AND ANIONS

At high temperatures and pressures rhenium pentacarbonylchloride reacts with aluminium chloride and carbon monoxide to give the salt $[Re(CO)_6]^+[AlCl_4]^-$. Other stable salts of $Re(CO)_6^+$ with large anions may be obtained by exchange, and the perchlorate and tetraphenylborate have been isolated. The hexacarbonylrhenium(I) cation is of the octahedral, inert gas type, and is isoelectronic with $W(CO)_6$. A study of the infrared and Raman spectra has recently enabled twelve of the thirteen fundamental frequencies to be assigned[257]; the results may have important theoretical consequences, since they indicate the force constants for the Re–C bond are near those for the W–C bond in $W(CO)_6$; presumably the loss in π-bonding consequent upon the positive charge is offset by an increase in σ-bonding between the metal and the carbon atom. A number of substituted cations, e.g. [v-triars $Re(CO)_3]^+$ [258] and *trans* $[(Ph_3P)_2Re(CO)_4]^+$ [259], are known.

Alkali salts of the pentacarbonylrhenate(I) anion, $Re(CO)_5^-$, are formed when dirhenium decacarbonyl is reduced in ethereal solution by the appropriate amalgam. They are pyrophoric solids which are irreversibly hydrolysed to the carbonyl hydride $HRe(CO)_5$ in aqueous solution, even at high pH, and it has been shown that the $Re(CO)_5^-$ anion does not exist in aqueous systems[260].

The salts in solution are important intermediates in the preparation of alkyl and other derivatives containing the $Re(CO)_5$ group. In particular the treatment with carbonyls or carbonyl halides of other elements leads to mixed carbonyls or carbonyl ions, e.g. with $Mn(CO)_5Cl$ the carbonyl $MnRe(CO)_{10}$ is formed, and with $W(CO)_6$ the anion $[WRe(CO)_{10}]^-$ [261]. The generation of new compounds of this type has been admirably illustrated by Kruck and his colleagues[262], who have treated the Re cations $Re(CO)_6^+$ and $[Re(CO)_4(PR_3)_2]^+$ with carbonyl anions such as $V(CO)_6^-$, $Mn(CO)_5^-$ and $Fe(CO)_3NO^-$; in many cases a salt is found which then loses CO to yield a mixed carbonyl, e.g. the salt $[Re(CO)_6]^+[V(CO)_6]^-$ is isolated but $Re(CO)_6^+$ with $Mn(CO)_5^-$ gives $MnRe(CO)_{10}$. In a very similar manner, the reaction of $Re(CO)_5^-$ with R_2SnCl_2 yields the tin derivatives[263] $R_2Sn[Re(CO)_5]_2$ (R = alkyl, Cl), which may be regarded as an insertion of SnR_2 into the Re–Re bond in $Re_2(CO)_{10}$. The reaction of $Re(CO)_5^-$ with $2\text{-}B_5H_8Br$ [264] yields the boron derivative $2\text{-}[Re(CO)_5]B_5H_8$, whilst another boron derivative, the anion $[H_3B\cdot Re(CO)_5^-]$, is formed when $Re(CO)_5^-$ is treated with borane etherate $R_2O\cdot BH_3$ [265].

[256a] E. Singleton, J. T. Moelwyn-Hughes and A. W. B. Garner, *J. Organometal. Chem.* **21** (1970) 449.
[257] E. W. Abel, R. A. N. Maclean, M. G. Norton and S. P. Tyfield, *Chem. Communs.* (1968) 900.
[258] R. S. Nyholm, M. R. Snow and M. H. B. Stiddard, *J. Chem. Soc.* (1965) 6564.
[259] T. Kruck and M. Hoeffler, *Chem. Ber.* **96** (1963) 3035.
[260] W. Beck, W. Hieber and G. Braun, *Z. anorg. allgem. Chem.* **308** (1961) 23.
[261] U. Anders and W. A. G. Graham, *J. Am. Chem. Soc.* **89** (1967) 539.
[262] T. Kruck, M. Hoeffler and M. Noack, *Chem. Ber.* **99** (1966) 1153.
[263] J. A. J. Thompson and W. A. G. Graham, *Inorg. Chem.* **6** (1967) 1365.
[264] D. F. Gaines and T. V. Ioris, *Inorg. Chem.* **7** (1968) 1041.
[265] G. W. Parshall, *J. Am. Chem. Soc.* **86** (1964) 361.

The reaction of dirhenium decacarbonyl with sodium borohydride in tetrahydrofuran gives rise to a solution with an intense red coloration. The addition of tetra-*n*-butylammonium iodide to the red solution gives rise to a red crystalline salt, which has been shown[266] to contain the $Re_4(CO)_{16}^{2-}$ ion by X-ray crystallographic measurements. The four rhenium atoms are arranged as two fused, approximately equilateral triangles, with Re–Re distances ranging from 2.956±0.007 to 3.024±0.007 Å. Each rhenium atom is associated with four terminal carbonyl groups.

6.3. CARBONYL HYDRIDES

Treatment of the sodium salt $NaRe(CO)_5$ with phosphoric acid yields the monohydride $HRe(CO)_5$. This is a colourless, air-sensitive liquid; the solid melts at 12.5°. The vapour pressure[260] is given by the equation

$$\log P_{\mathrm{mm}} = 8.598 - 2353.6/T \, (6\text{–}100°)$$

The calculated latent heat of evaporation is 10.76 kcal $mole^{-1}$. The infrared spectrum[260] shows an absorption at 1832 cm^{-1} assigned to the Re–H stretch; the corresponding Re–D stretch is at 1318 cm^{-1}. The spectrum suggests a low molecular symmetry.

Rhenium carbonyl hydride is very weakly acidic and is insoluble in water. It is more stable than the corresponding iron and cobalt carbonyl hydrides, but at 100° it decomposes into dirhenium decacarbonyl and hydrogen.

The polynuclear carbonyl hydrides $HRe_3(CO)_{14}$ and $H_3Re_3(CO)_{12}$ have recently been identified[267] among the products when $Re_2(CO)_{10}$ is reduced with sodium borohydride and the resulting red solution in tetrahydrofuran is acidified. By altering the reaction conditions and the proportions of reagents, the yields of these interesting compounds may be maximized. The mixed hydrides $HMnRe_2(CO)_{14}$ and $HMn_2Re(CO)_{14}$ were also prepared[267], and it is clear that a very large preparative and structural field remains to be investigated. The hydride $HMn_2Re(CO)_{14}$ is interesting inasmuch that the crystal structure involves an L-shaped configuration of metal atoms in which it has been suggested that the hydrogen atom is located between the two rhenium atoms[268]; the evidence is the long Re–Re bond (3.39 Å). The Mn–Re distance is 2.96 Å.

The treatment of $H_3Re_3(CO)_{12}$ with base leads to the formation of the $[H_2Re_3(CO)_{12}]^-$ anion whose structure is based on a triangle of Re atoms[269].

Ultraviolet irradiation of a solution of $Re_2(CO)_{10}$ and $(C_6H_5)_2SiH_2$ in benzene yields the compound $(C_6H_5)_2SiH_2Re_2(CO)_8$. The physical evidence[269a] and X-ray structure[269b] are consistent with the presence of two hydrogen atoms bridging the Re–Si bonds.

In addition to the neutral hydrides, it has been found that the action of carbon monoxide on the salt $(Et_4N)_2ReH_9$ dissolved in alcohol in the presence of Et_4NOH leads to the tetraethylammonium salt of the $[Re_2(CO)_6H_3]^-$ ion being formed along with a number of other compounds. On the basis of n.m.r. and infrared evidence it is concluded that the carbonyl groups are terminal and the two rhenium atoms are linked by three hydrogen bridging atoms[270].

[266] M. R. Churchill and R. Bau, *Inorg. Chem.* **7** (1968) 2606.
[267] W. Fellman and H. Kaesz, *Inorg. Nucl. Chem. Letters* **2** (1966) 63.
[268] M. R. Churchill and R. Bau, *Inorg. Chem.* **6** (1967) 2086.
[269] M. R. Churchill, P. M. Bird, H. D. Kaesz, R. Bau and B. Fontal, *J. Am. Chem. Soc.* **90** (1968) 7135.
[269a] J. K. Hoyano, M. Elder and W. A. G. Graham, *J. Am. Chem. Soc.* **91** (1969) 4568.
[269b] M. Elder, *Inorg. Chem.* **9** (1970) 762.
[270] A. P. Ginsberg and M. J. Hawkes, *J. Am. Chem. Soc.* **90** (1969) 5930.

6.4. CARBONYL HALIDES

These are of several kinds, the monomeric $Re(CO)_5X$ (X = Cl, Br, I), the dimeric $[Re(CO)_4X]_2$ and the highly reactive $[Re(CO)_3Cl]_x$. There is also a fully substituted PF_3 derivative, $ClRe(PF_3)_5$ [271].

As with the carbonyl halides of iron, cobalt and nickel, rhenium pentacarbonyl iodide and bromide are more easily formed than rhenium pentacarbonyl chloride, and it is possible to get them by the passage of CO at atmospheric pressure over the iodorhenate and bromorhenate respectively at 200°. However, this takes several days, but when pressure apparatus is available the reaction time can be shortened very considerably by using 200 atm pressure of carbon monoxide in the presence of a halogen acceptor such as copper powder[272]. For the chloride (from $ReCl_5$ or K_2ReCl_6) a pressure of carbon monoxide is essential. Alternatively, $Re_2(CO)_{10}$ is treated with halogen in a sealed tube (chlorine and bromine in CCl_4, iodine alone), and the reaction product, which is chiefly tetracarbonyl halide, is heated with carbon monoxide under pressure at 100° to give the pentacarbonyl halide.

The rhenium pentacarbonyl halides are colourless, odourless, crystalline compounds which are stable to 400°. They are diamagnetic. Although the structures have not been determined, the vibrational spectra of $Re(CO)_5I$ have been assigned on the basis of C_{4v} symmetry[256].

The pentacarbonyl halides are unreactive towards the atmosphere and sublime readily at 90–140° in a carbon monoxide stream. With amines they undergo substitution reactions (see Fig. 8B). Two of the carbonyl groups are readily displaced but it is not possible to replace more. This has been explained[273] by supposing that the carbonyl groups which are *cis* to the halogen, assuming octahedral coordination about the metal atom, are labile (*trans* effect). The first amine molecule replaces one of the *cis* carbonyl groups; a second carbonyl group *cis* to both halogen and amine ligand is then replaced by a second amine molecule:

$$Re(CO)_5X \rightarrow \underset{\text{(not isolated)}}{[Re(CO)_4(amine)X]} \rightarrow [Re(CO)_3(amine)_2X]$$

Further substitution does not occur since with three essentially non-π electron accepting ligands present the metal carbon multiple bond character is at a maximum and the carbonyl groups have exclusive use of the metal $d\varepsilon$ orbitals for π-bonding. Similar arguments may be used for other derivatives, including those of triphenylphosphine (see Fig. 8B); interestingly, another isomer of $(Ph_3P)_2Re(CO)_3Cl$ was prepared by the action of triphenylphosphine on $[Re(CO)_6]ClO_4$.

In some reactions substitution of the halogen as well as carbonyl may take place[273a]. In the reaction of $Re(CO)_5Br$ with $Me_3S\cdot PPh_2$, cleavage of the Si–P bond takes place and the dimeric $[Re(CO)_4PPh_2]_2$ is formed with bridging P atoms[274]; similar sulphur and selenium compounds are also known.

The existence of bridging non-metal atoms as an alternative to Re–Re bonds is characteristic of the tetracarbonyl halides $[Re(CO)_4X]_2$ (X = Cl, Br, I), which may be formed by refluxing the pentacarbonyl halides in an inert solvent for some time[273]. These tetracarbonyl halides are stable to air, the chloride and bromide are colourless, but the iodide is yellow.

---

[271] T. Kruck, A. Engelmann and W. Long, *Chem. Ber.* **99** (1966) 2473.

[272] W. Hieber, A. Schuh and H. Fuchs, *Z. anorg. allgem. Chem.* **248** (1941) 243.

[273] E. W. Abel, G. B. Hargreaves and G. Wilkinson, *J. Chem. Soc.* (1958) 3149.

[273a] R. J. Angelici and A. E. Kruse, *J. Organometal. Chem.* **22** (1970) 461.

[274] K. Edgar, B. F. G. Johnson, J. Lewis, I. G. Williams and J. M. Wilson, *J. Chem. Soc.* A (1967) 379.

[275] J. C. Hileman, D. K. Huggins and H. D. Kaesz, *Inorg. Chem.* **1** (1962) 933.

The existence of halogen bridges is indicated by the infrared spectra[275]. The tetracarbonyl halides undergo substitution reactions in much the same way as the pentacarbonyl halides, but the rate of reaction is much greater[273].

The remaining neutral halide, $Re(CO)_3Cl$, has been made by the reversible decomposition of $[Re(CO)_3SPh_2Cl]$ under vacuum at 90° [276].

The reaction of the carbonyl halides with halide ions leads to the formation of a number of carbonyl halide anions[277], e.g. $Re(CO)_4I_2^-$, $Re_2(CO)_7Cl_3^-$ and $Re(CO)_4IBr^-$.

6.5. OTHER σ-BONDED CARBONYL DERIVATIVES

The reaction between the $Re(CO)_5^-$ anion and acyl or perfluoroacyl chlorides yields the corresponding carbonyl derivatives $R\cdot CORe(CO)_5$ ($R = CH_3$, C_6H_5, C_2F_5, etc.). These are volatile compounds which have the peculiar property of losing CO above their melting points to form the derivatives $R\cdot Re(CO)_5$ [278]. Some of the alkyl or aryl derivatives may also be prepared by the action of the corresponding halide, e.g. CH_3I, on $Re(CO)_5^-$. It is concluded from physical measurements that the organic substituent occupies one position about an octahedrally coordinated rhenium atom. The $Re(CO)_5^-$ ion also reacts with fluoro-olefins, alicyclic fluorocarbons, polyfluoroaromatic compounds, polyfluoroheterocyclic nitrogen compounds and a number of other organic derivatives to give a variety of derivatives containing the $Re(CO)_5$ moiety. Other derivatives may be formed by direct reaction of $HRe(CO)_5$ with the appropriate organic reagent, e.g. with hexafluorobuta-1,3-diene the adduct $CHF_2\cdot CF_2\cdot CF{:}CF\cdot Re(CO)_5$ is formed[276], and an azobenzene derivative is also known[280].

6.6. CYCLOPENTADIENYL AND RELATED COMPLEXES

Rhenium pentachloride reacts with cyclopentadienyl sodium in tetrahydrofuran to give a yellow compound which has a composition very near to $Re(C_5H_5)_2$. However, instead of displaying magnetic properties associated with either five unpaired electrons [cf. $Mn(C_5H_5)_2$] or a single unpaired electron, which might be expected for a monomeric compound of composition $Re(C_5H_5)_2$, the rhenium cyclopentadienide is diamagnetic. The infrared spectrum is consistent with a sandwich structure such as in ferrocene, and the compound is monomeric in solution. The only acceptable explanation is that the compound is in fact biscyclopentadienylrhenium hydride $[(C_5H_5)_2ReH]$, and this hypothesis has been confirmed by n.m.r. studies and by an investigation of the mass spectrum[281].

Biscyclopentadienylrhenium hydride forms lemon-yellow acicular crystals, m.p. 161–162°, from organic solvents. It is stable to 250°, and sublimes readily in a vacuum about 80°. With CCl_4 chloroform is formed; this reaction is characteristic of metal–hydrogen bonds[281]. The compound is not affected by alkali, but it dissolves without effervescence in

---

[276] W. Hieber and W. Rohn, *Angew. Chem.*, Int. Edn., 7 (1968) 627.

[277] E. W. Abel, I. S. Butler, M. C. Gonarkar, C. R. Jenkins and M. H. B. Stiddard, *Inorg. Chem.* **5** (1966) 25.

[278] H. D. Kaesz, R. B. King and F. G. A. Stone, *Z. Naturforsch.* **15B** (1960) 763.

[279] M. Green, N. Mayne and F. G. A. Stone, *J. Chem. Soc.* A (1968) 902 and preceding papers.

[280] R. F. Heck, *J. Am. Chem. Soc.* **90** (1968) 313.

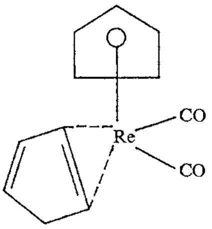
[281] M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.* (1958) 4314.

dilute hydrochloric or sulphuric acids, and absorbs gaseous HCl or HBr to form salts quantitatively as white, hygroscopic powders:

$$(C_5H_5)_2ReH + HCl \rightarrow [(C_5H_5)_2ReH_2]^+X^-$$

In the presence of excess of hydrogen chloride gas the white solid becomes pink, which is held to suggest the presence of $[HCl_2]^-$ ion. Biscyclopentadienylrhenium hydride is a base comparable in strength with ammonia; the p*K* value in 60% dioxan is 8.5 (NH_3 in 60% dioxan has a p*K* value of 8.85). The corresponding deuteride has been prepared by exchange and, as with the carbonyl hydride, this has enabled the Re–H stretching frequency to be unambiguously identified, in the solids the Re–D frequencies are at 1458 and 1432 cm^{-1} and the Re–H frequencies at 2037 and 2000 cm^{-1} [281].

At 250 atm pressure and 100°, $(C_5H_5)_2ReH$ reacts with carbon monoxide to give pale yellow crystals of $C_{10}H_{11}Re(CO)_2$ [282]. From n.m.r. studies, infrared measurements and chemical properties it has been shown that the structure is



with a "half-sandwich" cyclopentadienyl grouping and an olefinic link. The C_5H_6 group may be hydrogenated with the loss of one of the double bonds. This compound is not formed by direct synthesis from rhenium carbonyl and cyclopentadiene; only the diamagnetic π-cyclopentadienylrhenium tricarbonyl, π- $C_5H_5Re(CO)_3$, is thus isolated[282].

The analogy between cyclopentadienyl compounds and metal–carborane derivatives has been emphasized by the synthesis and the structure[283] of the $[(B_9C_2H_{11})Re(CO)_3]^-$ anion. This is synthesized by the reaction between $Na^+B_9C_2H_{11}^-$ and $BrRe(CO)_5$; the anion being isolated as the Cs^+ salt. $(C_5H_5)_2ReH$ gives a dilithiated species with *n*-butyl lithium $(C_5H_4Li)_2ReH$. The lithium atoms can be replaced by HgCl units through treatment with mercuric chloride, but with methyl iodide the compound $(C_5H_5)(CH_3C_5H_4)Re(CH_3)_2$ is formed in which two methyl groups are directly bonded to the rhenium atoms[284].

Rhenium also forms compounds involving olefins [e.g. $ReCl_2(C_{10}H_{12})_2$], and acetylenes [e.g. $ReCl(C_6H_5C{\equiv}CH)_2$] [285]. The $ReAr_2^+$ [286] ion is formed, and the partially substituted carbonyl cation $[C_6(CH_3)_6Re(CO)_3]^+$ is also known[287]. More recently, an interesting paramagnetic compound $Re[C_6(CH_3)_6]_2$ has been obtained which may be converted to a diamagnetic dimer[288].

---

[282] M. L. H. Green and G. Wilkinson, *J. Chem. Soc.* (1958) 4314.
[283] A. Zalkin and T. E. Hopkins, *Inorg. Chem.* **5** (1966) 1189.
[284] R. L. Cooper, M. L. H. Green and J. T. Moelwyn-Hughes, *J. Organometal. Chem.* **3** (1965) 261.
[285] R. Colton, R. Levitus and G. Wilkinson, *Nature* **186** (1960) 233.
[286] E. O. Fischer and A. Wirzmüller, *Chem. Ber.* **90** (1957) 1725.
[287] G. Winkhaus and H. Singer, *Z. Naturforsch.* **18b** (1963) 418.
[288] E. O. Fischer and H. W. Schmidt, *Ber.* **99** (1966) 2206.

7. COMPLEX COMPOUNDS

The complex chemistry of rhenium is large and a number of new developments have taken place in recent years. The work up to 1966 has been reviewed by Fergusson[289].

7.1. NITRIDO AND NITROGEN DERIVATIVES

Rhenium appears to form several stable series of derivatives in which the nitrido group acts as a ligand. The nitrido-rhenate(VII) ion ReO_3N^- (p. 947) and the nitrido-cyanides (p. 936) have already been described; in the remaining neutral derivatives, the nitrido-group is stabilized by phosphine ligands attached to the rhenium.

The reduction of perrhenate by hydrazine hydrochloride in the presence of a phosphine ligand in alcoholic solution, or the action of azide ion on the complexes $[ReCl_3(PR_3)_3]$ yields the red $[ReNX_2(PPh_3)_2]$ and the yellow $[ReNX_2(PR_3)_3]$ ($X = Cl$, Br or I; $R =$ alkyl or aryl groups) complexes[290]. In the former type formed by the more bulky phosphines the nitrogen atom occupies one position in the octahedral complex and is covalently bonded to the rhenium atom by a triple bond. A strong infrared band at about 1050 cm^{-1} has been tentatively associated with the Re–N bond (cf. Re–N in ReO_3N^- at 1025 cm^{-1}). The X-ray structure of the complex $[ReNCl_2(PEt_2Ph)_3]$ indicates that the nitrogen atom is *trans* to chlorine[291] and that the compound is in the *mer* form.

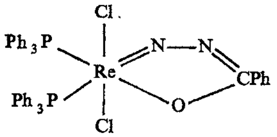
The structure of the compounds $[ReNX_2(PPh_3)_2]$ is not known, but the evidence so far available favours a square pyramidal configuration[290]. The pure compounds $ReNX_2(PPh_3)_2$ have recently been isolated by treating $[ReO(OEt)X_2(PPh_3)_2]$ with PPh_3 and hydrazine sulphate under reflux in ethanol[292].

Mer-$[ReNCl_2(PEt_2Ph)_3]$ shows a close resemblance to acetonitrile and benzonitrile in its electron donor properties, and combines with boron halides (BF_3, BCl_3, BBr_3) to give pale blue to purple adducts. It also combines with the bridged platinum complex $[Pt_2Cl_4(PEt_3)_2]$ to give the donor acceptor compound $[(PEt_2Ph)_3Cl_2Re\ N \rightarrow PtCl_2(PEt_3)]$ [293].

Rhenium has been shown to form complexes with molecular nitrogen as a ligand, and these exist for Re(O), Re(I) and possibly for Re(II).

The reaction of *cis*-$[Re(CO)_4Br(PMe_2Ph)]$ and *trans*-$[Re(CO)_3Cl(PMe_2Ph)_2]$ with hydrazine leads to the formation of compounds having coordinated molecular nitrogen and a σ-NH_2 ligand of composition $[Re(CO)_3(NH_2)(N_2)(PMe_2Ph)]$ and $[Re(CO)_2(NH_2)(N_2)(PMe_2Ph)_2]$ respectively. These are pale yellow–brown crystalline complexes which are unstable in the presence of air[294].

The degradation of the complex[295]



---

[289] J. E. Fergusson, *Coord. Chem. Revs.* **1** (1966) 464.

[290] J. Chatt, C. D. Falk, G. J. Leigh and R. J. Paske, *J. Chem. Soc.* A (1969) 2288.

[291] P. W. R. Corfield, R. J. Doedens and J. A. Ibers, *Inorg. Chem.* **6** (1967) 197; R. J. Doedens and J. A. Ibers, *ibid.*, p. 204.

[292] W. P. Johnson, *J. Chem. Soc.* A (1969) 1843.

[293] J. Chatt and B. T. Heaton, *Chem. Communs.* (1968) 274; *J. Chem. Soc.* A (1971) 705.

[293a] J. Chatt, J. R. Dilworth, G. J. Leigh and R. L. Richards, *Chem. Communs.* (1970) 955.

[294] J. T. Moelwyn-Hughes and A. W. B. Garner, *Chem. Communs.* (1969) 1309.

[295] J. Chatt, J. R. Dilworth, G. J. Leigh and R. J. Paske, in *Progress in Inorganic Chemistry* (ed. M. Cais), Elsevier, Amsterdam (1968), p. 246.

in the presence of tertiary phosphines in methanolic solution leads first of all to tervalent benzoylazo-complexes $ReL_3Cl_2N_2COPh$ and then to the stable *trans* nitrogen complexes $[ReCl(N_2)L_4]$ [L = PMe_2Ph, $\frac{1}{2}(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)$...] [293]. These pale yellow complexes contain Re(I). They may be oxidized by chlorine in chloroform solution to Re(III) or Re(V) derivatives, but oxidation of the compound $[ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$ leads to a purple, paramagnetic, unstable salt thought to be the Re(II) derivative $[ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2]Cl$. The compound $[ReClN_2(PMe_2Ph)_4]$ has also been obtained directly from molecular nitrogen[293]; some of its reactions have recently been described[293a].

7.2. ARYL, ALKYL-IMIDO AND NITRILE COMPLEXES

Strong nitrogen bonds with rhenium are also formed through the action of an arylamine on the complexes $ReOX_3L_2$ and $ReOX_2(OEt)L_2$, which results in the arylimido complexes $ReX_3(NAr)L_2$ [290]. The formal rhenium–oxygen double bond has been replaced by a formal rhenium–nitrogen double bond; the actual rhenium–nitrogen bond order deduced from infrared evidence is nearer 3 than 2. The methylimino-analogue

$$[ReCl_3(NCH_3)P(C_6H_5)_2(C_2H_5)_2]$$

is made by the action of dimethylhydrazine dihydrochloride on $[ReOCl_3(PPh_3)_2]$ followed by phosphine exchange. In this compound, the coordination about the rhenium atom is distorted octahedral, with the phosphine ligands *trans* to one another, two Cl atoms *trans* to one another in the basal plane and the third Cl at one vertex, and the methylimino group (coordinated with the Re atom via the nitrogen atom) at the other[296].

By warming the solution of $ReCl_5$ in the appropriate anhydrous nitrile, greenish-brown paramagnetic crystals of the neutral quadrivalent complexes $ReCl_4L$ (L = MeCN, Pr^nCN, PhCN) may be obtained[297]. By ligand exchange other $ReCl_4L_2$ complexes (L = PPh_3, $AsPh_3$, $SbPh_3$) may be prepared from these nitrile complexes; whereas primary aromatic amines yield orange crystalline derivatives believed to be complexes of *N*-aryl-amidines, $ReCl_4[R\cdot C(:NH)NHR']$.

7.3. COMPLEXES WITH AMMONIA AND AMINES

Although several Re(II) complexes containing amines have been mentioned, none has been confirmed[289]. Similarly, a few complexes of amines with mononuclear Re(III) have been reported.

The early workers reported that the rhenium trihalides combine with ammonia, but the results require confirmation. Other work involving Re(III) halides and amines described before about 1965 generally requires re-interpretation, since the nature of the Re "cluster" compounds was not known until then (see also p. 915).

Rhenium trichloride combines with a number of amines. With pyridine and aniline the red complexes $[Re_3Cl_9L_3]$ are formed, and similar bromide derivatives are also known. The direct reaction of bidentate amines such as *o*-phenanthroline and 2-2′-bipyridyl with a rhenium trihalide has been shown to yield compounds of the composition $Re_3X_9(\text{bidentate})_{1.5}$, which are postulated to be polymeric. With pyridine the trimeric anion $[Re_3Br_{10}(py)_2]^-$ may also be formed under the appropriate conditions.

---

[296] D. Bright and J. A. Ibers, *Inorg. Chem.* **8** (1969) 703.

[297] G. Rouschias and G. Wilkinson, *Chem. Communs.* (1967) 442.

Quadrivalent amino-derivatives of rhenium are not formed directly from the tetrachloride or tetrabromide, but, curiously, have been made by the action of an amine on the tetraiodide (Table 24). The bromo- and chloro-derivatives are prepared by the pyrolysis of the ReX_6^{2-} salt of the appropriate cation, or in the case of the amine anions $[ReX_5(py)]^-$, treatment of the pyridinium salt with pyridine at a high temperature[298].

TABLE 24. QUADRIVALENT RHENIUM COMPLEXES [a]

Compound	Magnetic moment	Comments (preparative)
$ReCl_4(Ph_3P)_2$	3.84	From $ReOX_3(Ph_3P)_2$ or $ReH_3(Ph_3P)_2$
$ReBr_4(Ph_3P)_2$		
$ReI_4(Ph_3P)_2$		ReI_4 + phosphine
$ReCl_4(Ph_3P)(py)$		$ReCl_4(Ph_3P)_2$ + pyridine
$ReCl_4(py)_2$	3.3	pyrolysis of $(pyH)_2ReX_6$
$ReBr_4(py)_2$		
$ReI_4(py)_2$	3.7	ReI_4 + pyridine
$ReCl_4(Et_2PhP)_2$	3.64	pyrolysis of $(Et_2PhPH)_2ReX_6$ or oxidation of $ReX_3(Et_2PhP)_3$
$ReBr_4(Et_2PhP)_2$		
$ReCl_4(bipy)$	3.41, 3.5	pyrolysis of $(bipyH)_2Rex_6$
$ReBr_4(bipy)$	3.48	
$ReI_4(o\text{-phen})$		ReI_4 + *o*-phenanthroline
$[ReCl_5py]^-$	3.76, 3.45	$(pyH)_2ReX_6$ + pyridine at 190°
$[ReBr_5py]^-$	3.66	
$Re(diarsine)Cl_4$	3.46	halogenation of $[Re(CO)_5(diarsine)X]$
$Re(diarsine)Br_4$	3.42	
$Re_2Cl_4(acac)_4$	2.9 (soln)	$[ReCl_4(Ph_3P)_2]$ + acetylacetone or $[ReCl(acac)_2(Ph_3P)]$ + acetylacetone
$[ReOCl(OAc)]_2$	diamag	Re_3Cl_9 + AcOH in air or oxygen
$[Re_2OCl_5(OAc)(Ph_3P)_2]$	diamag	*trans*-$ReOX_3(Ph_3P)_2$ + AcOH at 120° in air
$[Re_2OBr_5(OAc)(Ph_3P)_2]$	diamag	

[a] Reproduced, with permission, from J. E. Fergusson, *Coordination Chemistry Reviews* **1** (1966) 459.

The reaction of rhenium pentachloride with ammonia leads to a number of ammine complexes whose nature is uncertain.

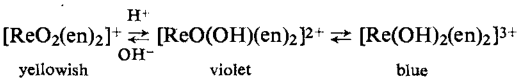
The quinquevalent rhenium derivatives of amines fall into two main classes[289], (a) neutral $ReOX_3L_2$ (X = Cl, Br; L = py, ½bipy), and (b) cationic $[ReO_2L_4]^+$ (L = py, ½en) and related ions. A number of other complexes, particularly of pyridine, have also been isolated. In earlier work, confusion arose because of the ease of oxidation of Re(III) species to Re=O species was not appreciated. The Re=O bonds in these Re(V) compounds are short and the complexes are diamagnetic. The diamagnetism has been explained by supposing that the short Re–O bond reduces the symmetry from O_h to C_{4v} in which a low lying b_2 orbital is available for accommodating two electrons[299] (see also ref. 289, pp. 482 *et seq.*).

---

[298] G. K. Babeshkina and V. G. Tronev, *Dokl. Akad. Nauk SSSR* **152** (1963) 100.

[299] W. J. Kirkham, A. G. Osborne, R. S. Nyholm and M. H. B. Stiddard, *J. Chem. Soc.* (1965) 550; see *Inorganic Synthesis*, Vol. VIII (1966) 176.

The dioxo-compounds with ethylene diamine ligand have been known for some time. Potassium hexachlororhenate dissolves in 90% ethylene diamine at 50°, and from the solution the cation $[ReO_2en_2]^+$ may be separated as the iodide. From the original acidic ethylene diamine solution two other complexes may be obtained[300], which are related according to the reversible reaction



$$\underset{\text{yellowish}}{[ReO_2(en)_2]^+} \underset{OH^-}{\overset{H^+}{\rightleftarrows}} \underset{\text{violet}}{[ReO(OH)(en)_2]^{2+}} \rightleftarrows \underset{\text{blue}}{[Re(OH)_2(en)_2]^{3+}}$$

Further acidification leads to the replacement of the ligand and the formation, according to acidity, of $[Re(en)Cl_2O(OH)]$ and $[Re(en)Cl_2(OH)_2]^+$; ultimately, all of the amine is replaced.

7.4. PHOSPHINE, ARSINE AND STIBINE DERIVATIVES

The action of a phosphine on a perrhenate in ethanolic halogen acid solution leads first of all to reduction of the rhenium(VIII) to rhenium(V) (Fig. 9); if sufficient of an alkyl or alkyl–aryl phosphine is present, further reduction to Re(III) complexes may occur [triphenylphosphine is not a sufficiently strong reducing agent to cause reduction of Re(V) to Re(III)]. The physical evidence indicates that the yellow to orange $[ReCl_3(phosphine)_3]$ compounds which are paramagnetic (μ = 2.0–2.4 BM) exist entirely in the *mer* form. The purple Re(IV) complexes which are formed by dissolving the $[ReCl_3(phosphine)_3]$ complexes in carbon tetrachloride and refluxing (see Fig. 9), exist in the *trans* form (μ = 3.4–3.7 BM).

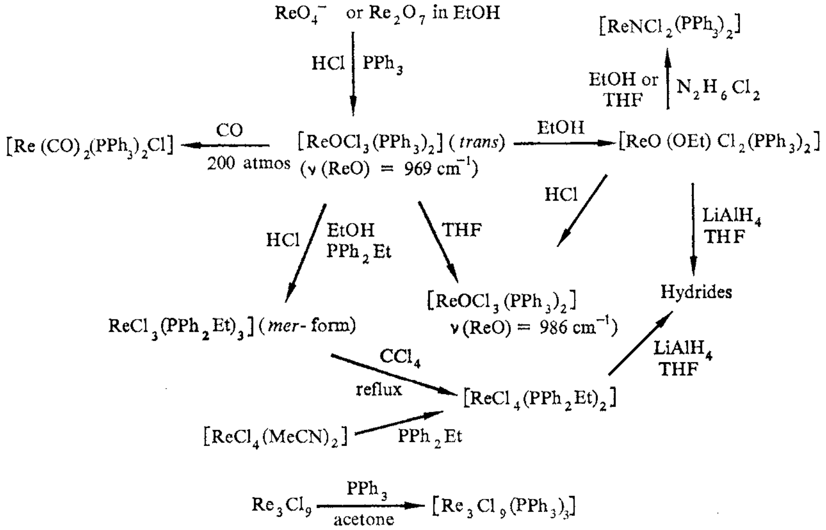


FIG. 9. Phosphine derivatives [a].

[a] *Inorg. Synth.*, Vol. 9, pp. 145, 147. J. Chatt, G. J. Leigh and D. M. P. Mingos, *J. Chem. Soc.* (A) (1969) 1674. J. Chatt, G. J. Leigh, D. M. P. Mingos and R. J. Paske, *J. Chem. Soc.* (A) (1968) 2636. R. Davis and J. E. Fergusson, *Inorg. Chem. Acta* 4 (1970) 16. (see also figs. 1 and 2b).

---

[300] J. H. Beard, J. Casey and R. K. Murmann, *Inorg. Chem.* 4 (1965) 797.

The ethoxy-complexes [ReO(OEt)Cl_2(phosphine)$_2$] are generally formed at the same time as the diamagnetic *trans* [ReOCl_3(phosphine)$_2$] complexes (Fig. 9), but the latter may be converted into the former by the action of ethanol. The action of hydrogen chloride on the ethoxy-complexes leads to the reformation of the [ReOCl_3(phosphine)$_2$] complexes, but apparently in a differing configuration (Fig. 9). The structure of *trans* [ReOCl_3(PEt_2Ph)$_2$] has been determined by X-ray crystallography[301].

The action of a phosphine on rhenium trichloride leads to trimeric [Re_3Cl_9(phosphine)$_3$], very different from the mononuclear Re(III) derivatives. The structure of [Re_3Cl_9($PPhEt_2$)$_3$] has been determined[302] (cf. Re_3Cl_9 and $Re_3Cl_{12}^{2-}$). β-$ReCl_4$ is reduced to an Re(III) derivative by triphenylphosphine[302a].

TABLE 25. DIARSINE DERIVATIVES [a–c]

Compound	Colour	Magnetic moment (BM) at 20°
Re(III) [ReD_2Cl_2]ClO_4	Golden yellow	2.1
[ReD_2Br_2]ClO_4	Orange	2.0
[ReD_2I_2]ClO_4	Red	1.8
Re(II) [ReD_2Cl_2][c]	Yellow–brown	—
[ReD_2Br_2][c]	Green	1.7–1.8
[ReD_2I_2][c]	Green	—
Re(V) [ReD_2Cl_4]ClO_4	Purple	0.7
[ReD_2Br_4]Br_3	Green	

[a] N. F. Curtis, J. E. Fergusson and R. S. Nyholm, *Chem. and Ind.* (1958) 625.

[b] A. Earnshaw, B. N. Figgis, J. Lewis and R. D. Peacock, *J. Chem. Soc.* (1961) 3132.

[c] J. Lewis, R. S. Nyholm and G. A. Rodley, *J. Chem. Soc.* (1965) 1483.

The known arsine and stibine complexes (L = R_3As, R_3Sb) have been prepared in a similar manner to the phosphine derivatives[289]. Polydentate phosphines and arsines, however, appear to be more effective than the unidentate ligands in stabilizing Re(II), and the diarsines in particular may also bring out high coordination numbers with Re(V).

Complexes with the diarsine *o*-phenylenebisdimethylarsine have been extensively investigated (Table 25.) The tervalent compounds are made in aqueous alcoholic solution by heating perrhenic acid with the diarsine, hypophosphorous acid and the appropriate halogen acid under reflux. The divalent compounds are obtained from the tervalent by reduction with sodium stannite, and the quinquevalent compounds by oxidation with a halogen.

7.5. OXYGEN LIGANDS

Complexes are known for Re(III), Re(IV) and Re(V). An acetylacetonate of Re(III) has been isolated by the prolonged refluxing of Re(III) or Re(IV) oxides with acetylacetone[303].

[301] H. W. W. Ehrlich and P. G. Owston, *J. Chem. Soc.* (1963) 4368.

[302] F. A. Cotton, S. J. Lippard and J. T. Mague, *Inorg. Chem.* 4 (1965) 508.

[302a] M. G. B. Drew, D. G. Tisley and R. A. Walton, *Chem. Commun.* (1970) 600.

[303] R. Colton, R. Levitus and G. Wilkinson, *J. Chem. Soc.* (1960) 4121.

This material, which analyses as the *tris*acetylacetonate, $Re(C_5O_2H_7)_3$, forms brown crystals which are monomeric in solution. The magnetic susceptibility follows the Curie–Weiss law with $\mu_{calc} = 2.80$ BM and $\theta = 160°$. The infrared spectrum is similar to that of other *tris*acetylacetonates and the strong band at 1550 cm^{-1} is attributed to the chelated carbonyl group. Other acetylacetone derivatives are formed by the action of the ligand on the phosphine complex $[ReOCl_2(OEt)(PPh_3)_2]$. The final product, in which all the phosphine has been replaced, is the quadrivalent complex $[Re_2Cl_4(acac)_4]$ [304], which must presumably contain acetylacetonate bridging groups.

Rhenium trichloride reacts with the lower carboxylic acids to give brown monomeric complexes $[ReCl_3(R \cdot CO_2H)_2]$ in which the rhenium is supposed to be five-coordinate, and orange binuclear complexes $[ReCl(O \cdot COR)_2]$. Treatment of the complexes with hydrochloric acid[305] yields the $Re_2Cl_8^{2-}$ anion reversibly:

$$Re_2Cl_8^{2-} + 4R \cdot COOH \rightleftharpoons [ReCl(OCOR)_2]_2 + 4HCl + 2Cl^-$$

That the compounds have an Re–Re link has been demonstrated by determination by X-ray analysis of the structure of the complex $ClRe(O_2CC_6H_5)_4ReCl \cdot 2CHCl_3$, which indicates[306] the rhenium–rhenium bond length to be 2.235 Å (cf. 2.24 Å in $Re_2Cl_8^{2-}$). In the presence of air the carboxylato-complexes are oxidized to $[ReOCl(O \cdot COR)_2]_2$ and $[ReO_2(O \cdot CO \cdot R)]_2$, which, like the Re(III) compounds, are diamagnetic.

Aqueous potassium chlororhenate or hydrated rhenium dioxide react with solutions of chelating organic acids to give complex ions of composition $[Re_2O(OH)_6L_2]^{4-}$ (L = oxalate, tartrate, citrate or gallate)[307]; several other complexes of a similar type have been reported. Complexes which contain both organic acid ligands and phosphines, of the general formula $[Re_2Cl_3(CO_2R)_2(PPh_3)_2]$ have been described[308].

A number of the complexes of the type $[Re_2OCl_5(carboxylato)(PPh_3)_2]$ (cf. Table 24) have also been described[308]; the compound $[Re_2OCl_5(C_2H_5CO_2)(PPh_3)_2]$ has been shown to be dimeric with a short Re–Re bond distance of 2.522 Å [309].

Oxo-complexes involving nitrogen or phosphine ligands will be found under the appropriate sections, and the anionic oxo-complexes such as the complex oxo-halides are more conveniently discussed with the complex halides (p. 976).

7.6. SULPHUR LIGANDS

The ligand 2,5-dithiahexane reacts with the $Re_2Br_8^{2-}$ ion to give the divalent $[ReBr_2DTH]_n$. The action of the same ligands on the $Re_2Cl_8^{2-}$ ion gives the mixed valency complex $[Re_2Cl_5(DTH)_2]$ as well as the mononuclear $ReCl_3(DTH)_2$ [310]. The structure of pentachlorobis[1,2-bis(methylthio)ethane]dirhenium has been reported[311], and has been shown to involve a rhenium–rhenium triple bond. Thiourea reacts with the $Re_2Cl_8^{2-}$ ion; the Re–Re bond is broken, and the complex $ReCl_3(thiourea)_3$ is formed.

---

[304] D. E. Grove, N. P. Johnson, C. L. J. Lock and G. Wilkinson, *J. Chem. Soc.* (1965) 490.

[305] F. A. Cotton, C. Oldham and W. R. Robinson, *Inorg. Chem.* **5** (1966) 1798.

[306] M. J. Bennett, W. K. Bralton, F. A. Cotton and W. R. Robinson, *Inorg. Chem.* **7** (1968) 1570.

[307] J. B. Trzebiatowska *et al.*, *Bull. Acad. Polon. Sci.*, Class III, **9** (1961) 57, 65, 685.

[308] G. Rouschias and G. Wilkinson, *J. Chem. Soc.* A (1966) 465.

[309] F. A. Cotton and B. M. Foxman, *Inorg. Chem.* **7** (1968) 1784.

[310] F. A. Cotton, C. Oldham and R. A. Walton, *Inorg. Chem.* **65** (1967) 214.

[311] M. J. Bennett, R. Walton and F. A. Cotton, *J. Am. Chem. Soc.* **88** (1966) 3866.

Perhaps the most interesting of the sulphur ligand complexes is formed by mixing rhenium pentachloride in ethanol with benzoin and P_4S_{10} in xylene. The complex $[Re(S_2C_2Ph_2)_3]$ is isolated as green crystals with a paramagnetism corresponding to one unpaired electron[312]. The structure indicates the six sulphur atoms to lie at the corners of a nearly perfect trigonal prism ($Re-S_{av} = 2.325$ Å; $S\widehat{Re}S = 81.4°$; S–$S = 3.043$ Å) centred on the rhenium atom (cf. ReS_2) [313]. A number of other related sulphur ligands form similar complexes.

7.7. COMPLEX HALIDES AND OXIDE HALIDES

The complex halides of rhenium exist with the element in the oxidation states 3, 4, 5 and 6. From time to time there have been reports of divalent complexes, but careful examination of the evidence would suggest that these refer to tervalent rhenium. The known compounds resemble the analogous types formed by other transition elements of the second and third periods; the quinquevalent fluorine compounds recall the corresponding compounds of molybdenum and tungsten, but the other complex halides are more like those of the platinum metals, and especially of osmium. The structural and physical properties of the quadrivalent salts have been studied extensively, both because of the electronic configuration of the octahedral Re(IV) entity, d^3, and the ease of handling the compounds. Less is known of the thermochemical properties, and only the $ReCl_6^{2-}$ ion has been studied in this connection.

Complex oxide halides have been studied in a more sporadic fashion than the complex halides themselves, and much remains to be done. Since they are generally formed as intermediates during the preparation of the complex halides, or as by-products, or are easily formed from the complex halides, it is convenient to treat the two sets of compounds together.

7.7.1. Tervalent Compounds

Fluorine compounds of Re(III) have not been certainly isolated, and attempts to make the complexes, e.g. by fusing rhenium trichloride with potassium hydrogen fluoride, have not so far met with success. Complex halides are, however, formed in this oxidation state with chlorine, bromine and possibly iodine. Unlike some of the other Re(III) complexes none of these appears to be mononuclear, though, as pointed out by Fergusson[289], it is not unreasonable to expect that the hexahalogeno-anions $[ReX_6]^{3-}$ should exist. On several occasions claims have been made for the isolation of $ReCl_6^{3-}$ by the electrolytic reduction of ReO_4^- and of $ReCl_6^{2-}$ in hydrochloric acid solution, or by the hydrogenation of the perrhenate ion in the presence of hydrochloric acid, but the invariable product appears to be the $ReCl_6^{2-}$ ion, often in a variety of colours and crystal habits[289].

(i) *Binuclear Complexes*

Some of these were formerly supposed to contain Re(II). They are formed by the prolonged action of hypophosphite on perrhenate in the presence of a halogen acid and by the action of hydrogen under pressure on a perrhenate or a hexahalogenorhenate(IV) in the presence of concentrated halogen acid[289, 314].

---

[312] E. I. Stiefel, R. Eisenberg, R. C. Rosenberg and H. B. Gray, *J. Am. Chem. Soc.* **88** (1966) 2956.

[313] R. Eisenberg and J. A. Ibers, *Inorg. Chem.* **5** (1966) 411.

[314] See R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier (1966), p. 69.

The blue potassium salt of the complex chloro-ion crystallizes as the dihydrate $K_2Re_2Cl_8 \cdot 2H_2O$, which contains the $Re_2Cl_8^{2-}$ entity (Fig. 10). There is a very short Re–Re bond (2.24 Å), and the configuration of the chlorine atoms is eclipsed. The Re–Cl distance is shorter than that in $ReCl_6^{2-}$ (2.37 Å). It has been assumed qualitatively that each rhenium atom uses its $d_{x^2-y^2}$, p_xp_y and *s*-orbitals to form the ReX_4 σ bonds, so that the d_{z^2} and p_z orbitals (*dp* hybrid) are available to form the Re–Re σ bond and two non-bonding σ orbitals, centrifugally directed, one from each rhenium atom. The d_{yz} and d_{xz} orbitals have π-symmetry and can form two Re–Re π bonds, and the remaining *d* orbital, the d_{xy}, has δ-symmetry and can form a Re–Re δ bond. Hence the Re–Re bonding should consist of a σ bond, two π bonds and a δ bond, implying a net bond order of 4 and accounting for the short bond distance. (This treatment, however, gives apparently a bond order of only 0.4 for the Re–Cl bond.) The δ bond is held to explain the eclipsed structure, since it erects a barrier against rotation with a minimum energy in the eclipsed configuration[289, 315]. An extended treatment has also been given[316], which leads to a maximum calculated Re–Re bond energy of 366 kcal mole^{-1} and a rotational barrier of 51 kcal mole^{-1}.

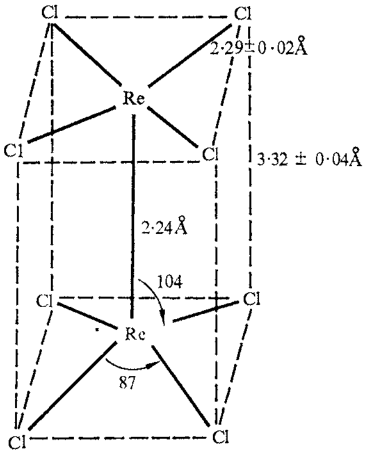


FIG. 10. Structure of the $Re_2Cl_8^{2-}$ ion [a]. (Reproduced, with permission, from R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier, 1966.)

[a] F. A. Cotton and C. B. Harris, *Inorg. Chem.* **4** (1965) 334.

The rhenium–rhenium bond length (2.24 Å) should be compared with values of 3.02 Å in $Re_2(CO)_{10}$, to 2.75 Å in the metal, and the sum of the normal covalent radii (2.56 Å); however, if allowance is made for changes in coordination number the contrast is perhaps less striking. In the bromo-complex, $(pyH)_2Re_2Br_8$, whose structure has also been determined, Re–Re bond distances of 2.207 and 2.27 Å have been recorded in two crystalline forms[317].

---

[315] F. A. Cotton, *Quart. Rev.* **20** (1966) 389.

[316] F. A. Cotton and C. B. Harris, *Inorg. Chem.* **6** (1967) 924.

[317] P. A. Koz'min, V. G. Kuznetsov and Z. Y. Papova, *J. Struct. Chem.* (*USSR*) **6** (1965) 624.

As indicated above, the $Re_2Cl_8^{2-}$ ion undergoes reaction with carboxylic acids to produce the dimeric compounds $[ReCl(OCOR)_2]_2$, with 2,5-dithiahexane to give the mixed valency compound $[Re_2Cl_5(DTH)_2]$, and with sodium thiocyanate to give complex isothiocyanates of the $[Re_2(NCS)_8]^{2-}$ ion. Polarographic reduction[318] gives a conventional two-wave reduction polarogram which has been interpreted in terms of a reversible reduction to $[Re_2Cl_8]^{3-}$ (cf. the existence of $Tc_2Cl_8^{3-}$) and a less simple reduction to $Re_2Cl_8^{4-}$. Oxidation of $Re_2Cl_8^{2-}$ ion by chlorine leads to the $Re_2Cl_9^-$ ion[319].

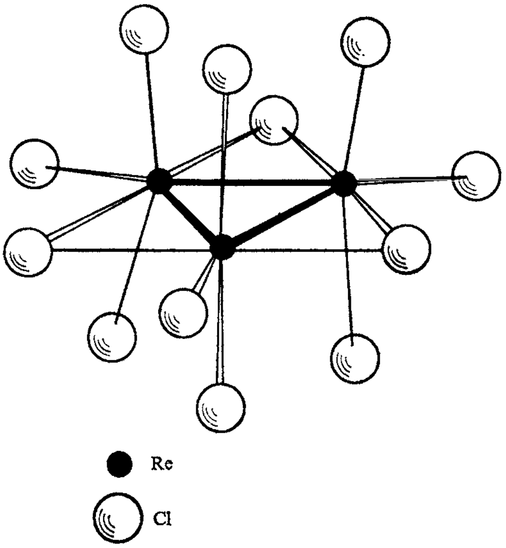


FIG. 11. Structure of the $Re_3Cl_{12}^{3-}$ ion [a,b]. (Reproduced, with permission, from J. E. Fergusson, *Coordin. Chem. Rev.* **1** (1966) 459.)

[a] W. T. Robinson, J. E. Fergusson and B. R. Penfold, *Proc. Chem. Soc.* (1963) 116.
[b] J. A. Bertrand, F. A. Cotton and W. A. Dollase, *Inorg. Chem.* **2** (1968) 1166.

Structural data for $Re_3Cl_{12}^{3-}$

Re–Re	Re–Cl (terminal in-plane)	Re–Cl (terminal out-of-plane)
2.48 Å	2.52 Å	2.36 Å
Re–Cl (bridge)	$\mathrm{Cl}\hat{\mathrm{Re}}\mathrm{Cl}$ (terminal off-plane)	$\mathrm{Re}\hat{\mathrm{Cl}}\mathrm{Re}$
2.39 Å	158°	62°

(ii) *Trinuclear Complexes*

Rhenium trichloride dissolves in hydrochloric acid, and stable, red, diamagnetic salts of composition $MReCl_4$ (M = Rb, Cs) may be readily crystallized or precipitated from the solution upon the addition of the appropriate alkali chloride. Thermal decomposition of the salts leads to rhenium trichloride, rhenium and hexachlororhenate(IV). For some time, it was believed that on the basis of a monomeric formulation, these complexes constituted the

---

[318] F. A. Cotton, W. R. Robinson and R. A. Walton, *Inorg. Chem.* **6** (1967) 1257.
[319] F. Bonati and F. A. Cotton, *Inorg. Chem.* **6** (1967) 1353.

only known examples of tetrahedral spin-paired complexes[320], but subsequent structure determinations have indicated them to be trimeric, a conclusion which was first suspected from the common electronic absorption spectra of $ReCl_4^-$, $Re_3Cl_{11}^{2-}$, $[ReCl_3Ph_3P]$ and of $ReCl_3$ itself in ethanolic solution[289].

In $Re_3Cl_{12}^{3-}$ the fundamental unit includes three rhenium atoms in a strongly bonded regular triangle or "cluster" (cf. Re_3Cl_9, Fig. 2). There are three bridging in-plane chlorine atoms, three terminal in-plane chlorine atoms and six terminal out-of-plane chlorine atoms (Fig. 11).

The rhenium–rhenium bonds are longer than in $Re_2Cl_8^{2-}$; other angles and bond lengths may be rationalized in terms of steric repulsions. The $Re_3Cl_{11}^{2-}$ anion, isolated in the Ph_4As^+ salt, has a related structure, but the rhenium–rhenium bond distances are no longer equal due to the absence of a terminal chlorine[289]. Related $Re_3X_{10}^-$ (X = Cl, Br) ions also exist, and the complex $Re_3Cl_9(Et_2PhP)_3$ also has a related structure.

The trinuclear bromide complexes are similar to the chloride; mixed Re(III)–Re(IV) complexes of composition $M_2Re_4Br_{15}$, containing $Re_3Br_9^{3-}$ and $ReBr_6^{2-}$ anions, are also known[289]. A number of mixed compounds such as $Cs_3[Re_3Cl_6Br_6]$ and salts of the $[Re_3Br_{10}(py)_2]^-$ ion have also been isolated. Bonding theories for these compounds utilizing various molecular orbital treatments have been summarized by Fergusson[289]; the principal conclusion is that the Re–Re bond order is two.

Interestingly, although the structure of rhenium triiodide has been shown in general terms to be of a similar type to that of the trichloride and tribromide, iodide complexes have not yet been isolated. In this connection, the present writer noticed a number of years ago that $(NH_4)_2ReI_6$, partly decomposed by heating under vacuum, may give a red solution in water, which presumably contains an Re(III) anion.

7.7.2. Re(III)–Re(IV) and Binuclear Re(IV) Complexes

The relation between the various binuclear Re halide ions is indicated in Fig. 12. Salts of the $Re_2X_9^{2-}$ and $Re_2X_9^-$ ions have only been isolated for large cations (e.g. $[n\text{-}C_4H_9)_4N]^+$); the $Re_2X_9^{2-}$ compounds have the expected paramagnetism (1.5 and 1.7 BM/formula unit for $Re_2Cl_9^{2-}$ and $Re_2Br_9^{2-}$ respectively). The structure of the $Re_2Cl_9^-$ ion indicates that it is related to that of β-$ReCl_4$, and may be written as $[Cl_3Re(Cl_{6/2})ReCl_3]^-$; the two rhenium atoms (Re–Re = 2.71 Å) are linked by a metal–metal bond and three bridging chlorine atoms[321]; as in $ReCl_4$ the Re–Re bond order is two. The bioctahedral structure is closely related to that of $W_2Cl_9^{3-}$. Other physical data (infrared and electronic spectra) have been discussed briefly[321]. (See also Fig. 12, ref. a.)

7.7.3. Hexahalogenorhenates(IV)

(i) *Hexafluororhenates(IV)*

Potassium hexafluororhenate(IV) K_2ReF_6 is formed when the hexachloro- or hexaiodorhenate(IV) is heated with potassium hydrogen fluoride (best formed *in situ* by evaporating potassium bicarbonate with excess of hydrofluoric acid) at 250–400° or when hydrogen fluoride is passed over potassium hexabromorhenate(IV) at 450°. The salt may be purified

---

[320] L. E. Orgel, *Inst. Intern. Chim. Solvay. 10e Conseil Chim. Brussels*, (1956), p. 289.

[321] F. A. Cotton and P. Stokely, quoted in F. A. Cotton and B. M. Foxman, *Inorg. Chem.* 7 (1968) 1784.

by recrystallization from water; salts of other cations (Na$^+$, NH$_4^+$, Rb$^+$, Cs$^+$, Ba^{2+}, Co(NH$_3$)$_6^{3+}$) and the aqueous acid may be obtained by precipitation or by ion-exchange[322, 323]. A nitrosonium (NO$^+$) salt has also been made. The hexafluororhenates are pale pink, though the sodium salt is bluish.

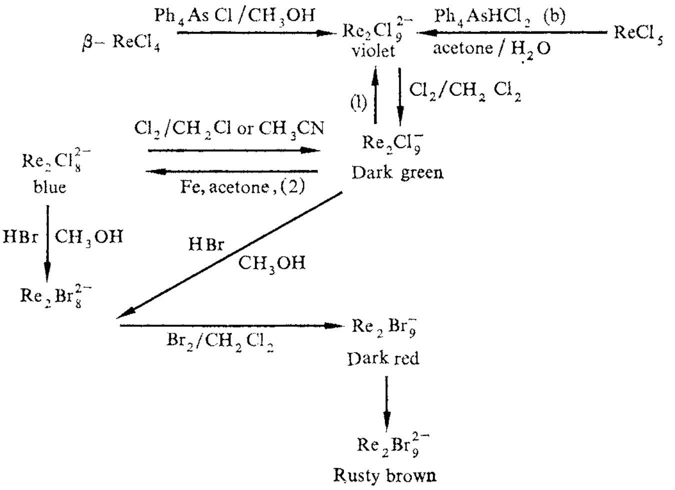


FIG. 12. The Re$_2$X$_8^{2-}$, Re$_2$X$_9^{2-}$ and Re$_2$X$_9^-$ species [a].

(1) Cu, Hg, Sn on acetone solution or Fe on C$_2$H$_5$OCOCH$_3$ solution; heat CH$_3$OH for 10 min.
(2) Heat CH$_3$OH for 35 min.
[a] Adapted from F. Bonati and F. A. Cotton, *Inorg. Chem.* 7 (1967) 1353.
[b] E. A. Allen, N. P. Johnson, D. T. Rosevear and W. Wilkinson, *Inorg. Nucl. Chem. Letters* **5** (1969) 239.

The K, Rb, Cs and NH$^+$ salts have the K$_2$GeF$_6$ structure; the Re–F distance in the nearly regular ReF$_6^{2-}$ anion is reported to be 2.00–2.05 Å [324]. The magnetic moments ($\mu \sim 3.3$ BM at 300°K) are less than the spin-only value for the d^3 octahedral case; the moment of the aqueous solution (3.47 BM) is similarly low. (See also Table 12, under technetium.)

The hexafluororhenates(IV) are resistant to hydrolysis, and may be recrystallized from water. The solubility decreases from the sodium to the caesium salt. The ammonium salt is very soluble [contrast (NH$_4$)$_2$ReCl$_6$]. Barium hexafluororhenate is not precipitated immediately when barium chloride solution is added to a solution of K$_2$ReF$_6$ in water, but a drop of ethanol induces precipitation. The solubility of BaReF$_6$ decreases markedly on ageing. Alkali induces slow decomposition of the ReF$_6^{2-}$ ion to ReO$_2$, but complete breakdown of the hexafluororhenates(IV) requires alkali fusion[322].

---

[322] R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier (1966), p. 62.
[323] J. H. Canterford and R. Colton, *Halides of the Second and Third Row Transition Metals*, Wiley (1968), p. 302.
[324] E. Weise, *Z. anorg. allgem. Chem.* **283** (1956) 377.

Ammonium hexafluororhenate(IV) is said to decompose on heating to the black nitride fluoride, ReNF [325].

(ii) *Hexachlororhenates(IV)*

The usual method of preparation starts from perrhenate, although freshly precipitated rhenium dioxide will dissolve in concentrated hydrochloric acid to give a brown solution which on boiling yields a solution of hexachlororhenic acid.

TABLE 26. PROPERTIES OF HEXACHLORORHENATES(IV)

		Ref.
$\triangle H^{\circ}_{\text{form}}$ ($ReCl_6^{2-}$ aq) (kcal mole^{-1})	-183.0	a
$\triangle G^{\circ}_{\text{form}}$ ($ReCl_6^{2-}$ aq) (kcal mole^{-1})	-141.6	a
$\triangle H^{\circ}_{\text{(hydrolysis)}}$ (K_2ReCl_6(c)) (kcal mole^{-1})	-63.6 ± 0.2	a
$\triangle H^{\circ}_{\text{(soln)}}$ (K_2ReCl_6(c)) (cal mole^{-1})	10,397	b
C°_p (K_2ReCl_6(c)) (cal mole^{-1} deg^{-1})	51.31	b
S° (K_2ReCl_6(c)) (e.u.)	88.84 ± 0.18	b
S° ($ReCl_6$ aq) (e.u.)	59.8	b
$\triangle S^{\circ}_{\text{form}}$ ($ReCl_6^{2-}$ aq) (e.u.)	-140.2	b
Transition temperatures (K_2ReCl_6)	11.9°K (magnetic), 76.05, 103.4, 110.9°K	b
Fundamental vibrational frequencies (K_2ReCl_6)	343 (ν_1), 260 (ν_2), 310 (ν_3), 176 (ν_4), 159 (ν_5), ? 100 cm^{-1} (ν_6)	c
	$\mu_{300°K}$ θ	
Magnetic properties: K_2ReCl_6	3.25 88°	d
Cs_2ReCl_6	3.35 45°	
$(pyH)_2ReCl_6$	3.58 14°	
$(QH)_2ReCl_6$	3.54 13°	
$(TH)_2ReCl_6$	3.50 35°	
Bond distances: Re–Cl(K_2ReCl_6)	2.37 Å; 2.35 Å	e, g
Re–Cl[(*p*-toluidine)$_2ReCl_6$]	2.35 Å	f

[a] R. H. Busey, K. H. Gayer, R. A. Gilbert and R. B. Bevan, *J. Phys. Chem.* **70** (1966) 2609.
[b] R. H. Busey, H. H. Dearman and R. B. Bevan, *J. Phys. Chem.* **66** (1962) 82.
[c] Interpolated from K. Schwochau and W. Krasser, *Z. Naturforsch.* **24a** (1969) 403.
[d] B. N. Figgis, J. Lewis and F. E. Mabbs, *J. Chem. Soc.* (1961) 3138.
[e] B. Aminoff, *Z. Krist.* **94** (1936) 246.
[f] E. Adam and T. N. Marguis, *Inorg. Chem.* **6** (1967) 213.
[g] H. D. Grundy and I. D. Brown, *Canad. J. Chem.* **48** (1970) 1151.

To prepare potassium hexachlororhenate, solutions of potassium perrhenate in 1:1 hydrochloric acid may be reduced by iodide, hypophosphite, chromous chloride or titanous chloride[328]. The first stable product of the iodide reduction is $K_4Re_2OCl_{10}$, which generally separates out and may be redissolved in hot concentrated hydrochloric acid to yield the hexachlororhenate. These reduction reactions are clearly complex and other oxo-salts have

---

[325] D. E. LaValle, R. M. Steele and W. T. Smith, *J. Inorg. Nucl. Chem.* **28** (1966) 260.
[326] *Inorganic Synthesis*, Vol. I (1939) 178; Vol. VII (1963) 189.
[327] H. G. Smith and G. E. Bacon, *J. Appl. Phys.* **37** (1966) 979.
[328] P. B. Dorain, in *Transition Metal Chemistry* (ed. R. L. Carlin), Edward Arnold (1968).

been isolated (see below). Other salts of the hexachlororhenate(IV) ion may be prepared similarly, or by precipitation or ion exchange from the potassium salt; the free acid may be isolated as the hydrate salt $(H_3O)_2ReCl_6$ if its aqueous solution is evaporated slowly under a vacuum. Dry methods for preparing hexachlororhenates have also been reported: treatment of potassium chloride with rhenium pentachloride at 300° gives potassium hexachlororhenate; perrhenates react with carbon tetrachloride in a bomb at 400° to give hexachlororhenates, and other salts have been produced through the interaction of an alkylammonium chloride with $ReOCl_4$ in thionyl chloride solution[322, 323].

Potassium hexachlororhenate(IV) is a green crystalline, air stable salt, which is slightly soluble in cold water. The solubility of the alkali metal chlororhenates increases from caesium to sodium, the silver salt (prepared by precipitation from a cold aqueous solution of potassium hexachlororhenate), and the thallous salt (prepared similarly), are practically insoluble. Ammonium hexachlororhenate is about as soluble as the potassium salt; salts of large organic cations are almost insoluble.

The alkali metal hexachlororhenates (K, Rb, Cs, NH_4) adopt the K_2PtCl_6 structure (Table 26). Neutron diffraction studies on the K salt indicate a primitive lattice below 70°K; at 4.2°K the structure is an ordered antiferromagnetic consisting of ferromagnetic alignment in the 001 planes with adjacent planes aligned antiparallel[327]. A selection of magnetic properties is given in Table 26; all the compounds show antiferromagnetic interactions, and attempts to reduce these by solid solution measurements in a K_2PtCl_6 host or by making salts of large cations (e.g. *p*-toluidine hexachlororhenate) have not been successful[289, 323].

Force constants have been obtained for the $ReCl_6^{2-}$ ion by several groups of workers. (Table 26, ref. c.)

The absorption spectrum of the $ReCl_6^{2-}$ ion has been measured on a number of occasions, and assignments have been made (Table 27). Other bands have been observed in melts and under high pressures; summaries of these measurements have been given by Fergusson[289] and Dorain[328].

The hexachlororhenate(IV) ion is stable in cold aqueous solution but is rapidly hydrolysed on warming the solution or by treating it with alkali. Treatment of the ion in solution with hydrobromic or hydriodic acid leads to the formation of hexabromorhenate(IV) and hexaiodorhenate(IV) ion respectively; there are equilibria in the series

$$ReCl_6 \underset{HCl}{\overset{HBr}{\rightleftarrows}} ReBr_6^{2-} \underset{HBr}{\overset{HI}{\rightleftarrows}} ReI_6^{2-}$$

Although these have not been measured, it is possible to traverse the series either way, though with greater ease towards the right [cf. the halogenoplatinates(IV)].

(iii) *Hexabromorhenates(IV)*

The perrhenate ion is reduced slowly by hydrobromic acid, but in making the bromorhenates(IV) it is preferable to have a reducing agent such as iodide ion or hypophosphite ion present[326]. The alkali metal salts are red; the K, Rb, Cs and NH_4 salts have the cubic K_2PtCl_6 structure (Table 28). The vibrational spectra of the K and Cs salts are in accord with octahedral symmetry of the $ReBr_6^{2-}$ anion, and force constants have been calculated (Table 28). Magnetic measurements indicate antiferromagnetic interactions with a Curie temperature of 15.3°K, corresponding to the lowest heat capacity transition at 15.2°K (Table 28)[329, 330]. There is probably a structural change in K_2ReBr_6 below 150° [330], since a

TABLE 27. ULTRAVIOLET AND VISIBLE SPECTRA OF ReX_6^{2-} IONS[a, b]

(Racah parameters A_i, B_i, C_i; ligand-field splitting parameter (33,500 cm^{-1}) and spin–orbit coupling parameter ζ (2300 cm^{-1}))

	$^2T_1(\Gamma_8) \leftarrow {}^4A_2$ $^2E(\Gamma_8)$	$^2T_1(\Gamma_6) \leftarrow {}^4A_2$	$^2T_2(\Gamma_7) \leftarrow {}^4A_2$	$^2T_2(\Gamma_8) \leftarrow {}^4A_2$	$^4T_2(^4\Gamma_5) \leftarrow {}^4A_2$	$^4T_1(^4\Gamma_4) \leftarrow {}^4A_2$	Lig sp pa
F$_6$)$^{2-}$	9080	10,890†	17,670†	18,910	32,800	37,500	3
Cl$_6$)$^{2-}$	7600	9400†	14,140†	15,340	28,010		2
Br$_6$)$^{2-}$	7260	9170†	13,230	14,860			2
$_6$)$^{2-}$	7350	8470					2
Cl$_6$)$^{2-}$ lc.)	7895	8798, 9167	14,653	15,723	34,458	38,546	

† Vibrational structure.

(Reproduced with permission, from J. E. Fergusson, *Coordination Chem. Reviews* **1** (1966) 478.)

[a] J. C. Eisenstein, *J. Chem. Phys.* **34** (1961) 1628.

[b] C. K. Jorgenson and K. Schwochau, *Z. Naturforsch.* **20a** (1965) 65.

spontaneous though anomalous evolution of heat occurs at this temperature when the compound is cooled, and a colour change from reddish purple to orange also takes place.

Potassium hexabromorhenate dissolves in hydrobromic acid to give red or deep yellow solutions, but in water alone the compound suffers rapid hydrolysis. In nitric acid solution the ion is sufficiently stable to allow the silver salt to be precipitated.

TABLE 28. PROPERTIES OF POTASSIUM HEXABROMORHENATE(IV)

		Ref.
C_p° (K_2ReBr_6(c)) (cal mole^{-1} deg^{-1})	54.24	a
S° (K_2ReBr_6(c)) (e.u.)	108.74	a
Fundamental vibrational frequencies (K_2ReBr_6)	20 (ν_1), 170 (ν_2), 240 (ν_3), 123 (ν_4), 117 (ν_5), 75 (ν_6) cm^{-1}	b
Magnetic properties μ_{eff} (300°K)	3.20 BM $\theta = 105^\circ$	c
Bond distance: Re–Br(K_2ReBr_6)	2.50 Å	d
	2.48 Å	e

[a] R. H. Busey, R. B. Bevan and R. A. Gilbert, *J. Phys. Chem.* **69** (1965) 3471.
[b] Interpolated from K. Schwochau and W. Krasser, *Z. Naturforsch.* **24a** (1969) 403.
[c] B. N. Figgis, J. Lewis, R. S. Nyholm and R. D. Peacock, *Discussions Faraday Soc.* **26** (1958) 103.
[d] D. H. Templeton and C. H. Daubon, *J. Am. Chem. Soc.* **73** (1951) 4492.
[e] H. D. Grundy and I. D. Brown, *Canad. J. Chem.* **48** (1970) 1151.

iv) *Hexaiodorhenates(IV)*

Potassium hexaiodorhenate has been prepared by reducing the potassium perrhenate with hydriodic acid in the presence of potassium iodide or hypophosphite, or by evaporating the complex chloride with successive portions of hydriodic acid. The remaining alkali metal and NH_4^+ salts may be prepared similarly[326].

The alkali metal hexaiodorhenates are nearly black crystalline solids. The rubidium and caesium salts adapt the K_2PtCl_6 [331] structure but K_2ReI_6 is of lower, probably monoclinic, symmetry[332]; NQR measurements on K_2ReI_6 suggest that there are three crystallographically non-equivalent iodine atoms present[333].

The whole question of phase changes among the halogenorhenates is extraordinarily interesting. It has been pointed out by Brown[334] that in the K_2PtCl_6 type of structure this phenomenon is associated with a radius ratio effect. If the radius ratio is defined as the ratio of the cation radius to the radius of the cavity formed by the twelve halogen atoms from the four octahedral anions surrounding the cation then:

(i) crystals with a radius ratio < 0.89 will be distorted at room temperature;
(ii) crystals with a radius ratio of between 0.89–0.98 will be cubic at room temperature but will distort at lower temperatures;
(iii) crystals with a radius ratio > 0.98 will not be distorted at any temperature.

---

[329] R. H. Busey and E. Sorder, *J. Chem. Phys.* **36** (1962) 93.
[330] R. H. Busey, R. B. Bevan and R. A. Gilbert, *J. Phys. Chem.* **69** (1965) 3471.
[331] K. Schwochau, *Z. Naturforsch.* **19a** (1964) 1237.
[332] J. Dalziel, N. S. Gill, R. S. Nyholm and R. D. Peacock, *J. Chem. Soc.* (1958) 4012.
[333] R. Ikeda, D. Nikemura and M. Keba, *Bull. Chem. Soc. Japan* **36** (1963) 1056.
[334] I. D. Brown, *Canad. J. Chem.* **42** (1964) 2758.

For K_2ReCl_6 the radius ratio as defined above is 0.97, and distortion occurs at low temperatures.

For K_2ReBr_6 the radius ratio is 0.91, and distortion occurs at about 150°K [330]. For K_2ReI_6, with a radius ratio of less than 0.89, there is distortion at room temperature.

The magnetic moments of the hexaiodorhenates (3.2–3.6 BM) and the high θ values ($\theta \sim 100°$) suggest antiferromagnetic interactions. It has been shown that antiferromagnetism in the ReX_6^{2-} series increases in the order $F < Cl < Br < I$, in line with increasing metal–halogen covalent bonding[335].

Potassium hexaiodorhenate(IV) dissolves in hydriodic acid and also in acetone and methanol to give dark purple solutions of moderate stability. In dilute acid, or in neutral or alkaline aqueous solution, the compound is hydrolysed. The reaction with sulphuric acid is discussed below (section 7.7.6).

7.7.4. Hexafluororhenates(V)

The reduction of rhenium hexafluoride by alkali metal iodides in sulphur dioxide or iodine pentafluoride solution leads to the formation of salts of the ReF_6^- ion[336, 337]. An NO^+ salt is formed by the direct interaction of ReF_6 and nitric oxide[338].

The structural affinities of these salts lie with those of the MoF_6^- and WF_6^- ions rather than with the corresponding technetium and osmium compounds; a number of unit cell parameters have been reported[339]. The infrared spectrum of $KReF_6$ gives an absorption peak at 627 cm^{-1} assigned to the Re–F stretch[340]; the magnetic properties, studied over a temperature range, show deviations from the simple Kotani type of behaviour which have been attributed to antiferromagnetic interactions[337].

Salts of the ReF_6^- ion are moisture sensitive; they react vigorously with water giving hydrated rhenium dioxide, hydrofluoric acid, perrhenate ion and hexafluororhenate(IV) ion[336, 337], but are only broken down completely by fusion with alkali.

The $ReCl_6^-$ ion has recently been isolated as the PCl_4^+ salt[340a].

7.7.5. Fluororhenates(VI)

The reaction between potassium fluoride and excess of rhenium hexafluoride in a Teflon tube at 0° takes place with evolution of heat[341]. After the potassium fluoride has dissolved, the tube is held at 20° for several hours to complete the reaction; and when the excess of hexafluoride is subsequently pumped off an orange or pink residue of potassium octafluororhenate(VI) remains. The Rb and Cs salts may be prepared similarly.

The salt K_2ReF_8 crystallizes in the orthorhombic system. The ReF_8^{2-} ion has been shown from X-ray measurements to adopt a square antiprismatic configuration[342] with Re–F = 1.87–1.93 Å. The magnetic moments of the K, Rb and Cs salts lie in the range 1.6–1.71 BM, in contrast to the low moment of rhenium hexafluoride[341].

The action of more rhenium hexafluoride on the octafluororhenate(VI) gives yellow salts of the composition $MReF_7$ (M = K, Rb, Cs) [341]. The thermal stability of these hepta-

---

[335] B. W. Figgis, J. Lewis and F. E. Mabbs, *J. Chem. Soc.* (1961) 3138.

[336] R. D. Peacock, *J. Chem. Soc.* (1957) 467.

[337] G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.* (1958) 3776.

[338] N. Bartlett, S. P. Beaton and N. K. Jha, *Chem. Communs.* (1966) 168.

[339] R. D. W. Kemmitt, D. R. Russell and D. W. A. Sharp, *J. Chem. Soc.* (1962) 4418.

[340] R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.* (1959) 2762.

[340a] P. W. Frais and C. J. L. Lock, *Chem. Commun.* (1970) 1612.

[341] N. S. Nikolaev and E. G. Ippolitov, *Dokl. Akad. Nauk SSSR* **140** (1961) 129.

[342] P. A. Koz'min, *Zh. Strukt. Khim.* **5** (1964) 70.

fluororhenates lies in the order Cs > Rb > K; they are only weakly paramagnetic ($\mu = 0.6$–0.7 BM). (These results are not entirely in accord with the present writer's experience, which suggests that under dry conditions rhenium hexafluoride does not combine with potassium fluoride, but that combination does occur if traces of an ionizing medium such as iodine pentafluoride or of hydrogen fluoride are present.)

7.7.6. Complex Oxo- and Hydroxy Salts

The first stable product to be isolated during the reduction of potassium perrhenate by iodide in the presence of hydrochloric acid is potassium μ-oxodecachlorodirhenate(IV), $K_4[Re_2OCl_{10}]\cdot H_2O$. This yellowish-brown salt has a small temperature-independent paramagnetism, and X-ray studies show the presence of the $[Cl_5Re{-}O{-}ReCl_5]^{4-}$ anion. The complex oxo-anion consists of two octahedral units linked through the oxygen atom; the Re–O–Re atoms are colinear with a short Re–O distance of 1.86 Å (cf. $K_2Ru_2OCl_{10}$). The Re–Cl bond distance is 2.38 Å [343] (cf. K_2ReCl_6, 2.37 Å). The very weak paramagnetism has been accounted for by a molecular orbital treatment[344].

In solution the $[Re_2OCl_{10}]^{4-}$ ion is in equilibrium with the green $[ReCl_5OH]^{2-}$ ion according to the equation

$$[Re_2OCl_{10}]^{4-} + H_2O \rightleftharpoons 2[ReCl_5(OH)]^{2-}$$

and it appears that the hydroxy-species is more stable below 18° [345]. In the $[ReCl_5(OH)]^{2-}$ ion the spin-pairing mechanism which operates for $[Re_2OCl_{10}]^{4-}$ is no longer present, and $[ReCl_5(OH)]^{2-}$ has a susceptibility near that of $ReCl_6^{2-}$. Other reactions are summarized in Fig. 13.

There is very little information about bromine complexes corresponding to the above, but it has been found that when K_2ReI_6 is dissolved in 20% sulphuric acid the purple colour of the solution may be extracted almost completely by ether, and the ether layer then contains all the rhenium and five-sixths of the iodine. Addition of an alcoholic solution of tetramethylammonium chloride to the extract results in the formation of the tetramethylammonium salt of the $[ReI_5(OH)]^{2-}$ ion[346].

Three types of complex oxohalogenorhenate(V) ions are known: $[ReOCl_5]^{2-}$, $[ReOX_4]^-$ and $[ReOX_4L]^-$ ($L = CH_3CN, H_2O, Ph_3P$) ($X = Cl, Br, I$).

Freshly prepared rhenium pentachloride dissolves in 12 M hydrochloric acid to give a red–brown solution from which salts of the $ReOCl_5^{2-}$ anion may be precipitated by addition of Rb^+, Cs^+, $C_9H_8N^+$ or PPh_3H^+ cations[346, 347]. Other methods of preparation have also been described[347, 348]. Most of the salts are yellow, but that of PPh_3H^+ ion is said to be pink[347]. The tetramethylammonium salt has a small paramagnetism in accordance with the expected spin-pairing mechanism, but the caesium salt appears to be anomalous since the magnetic properties depend on the preparative method[346, 347]; they have been commented upon by Colton[349].

---

[343] J. C. Morrow, *Acta Cryst.* **15** (1962) 851.

[344] B. J. Tzrebiatowska and W. Wojeiechowski, *J. Inorg. Nucl. Chem.* **25** (1963) 1477.

[345] B. J. Tzrebiatowska and S. Wajda, *Bull. Acad. Polon. Sci.*, Class III, **2** (1954) 249.

[346] R. Cotton, *Austral. J. Chem.* **18** (1965) 435.

[347] D. Grove and G. Wilkinson, *J. Chem. Soc.* A (1966) 1224.

[348] B. N. Ivanov-Emin, K. C. Dipek and A. E. Ezhov, *Russ. J. Inorg. Chem.* **11** (1966) 733.

[349] J. H. Canterford and R. Colton, *Halides of the Second and Third Row Transition Metals*, Wiley, London (1968), p. 315.

The complexes of the $[ReOX_4]^-$ ions have been prepared by a variety of methods; some starting from perrhenate and others from the oxidation by air of the Re_3Br_9 solution in hydrobromic acid[289]. The infrared spectra of these and of the closely related $[ReOX_4{\cdot}L]^-$ ions indicate a strong Re–O bond absorbing at 950–1000 cm^{-1} (cf. the $ReOX_3L_2$ complexes)[289, 347]. Structure determinations on two compounds of the $[ReOX_4L]^-$ type indicate (for $Ph_4As[ReOBr_4{\cdot}CH_3CN]$ and $Et_4N[ReOBr_4{\cdot}H_2O]$)[348] a square pyramidal arrangement for the $ReOBr_4$ entity with the oxygen at the apex. The coordinating CH_3CN and H_2O ligands are weakly bonded *trans* to the oxo-ligand. The Re–Br distance (2.48–2.51 Å) is about the same as in $ReBr_6^{2-}$, but the Re–O distance (1.71–1.73 Å) is said to be sufficiently short to be associated with a Re–O triple bond.

Re(VI) complex ions involving oxygen and a halogen are known for fluorine and chlorine.

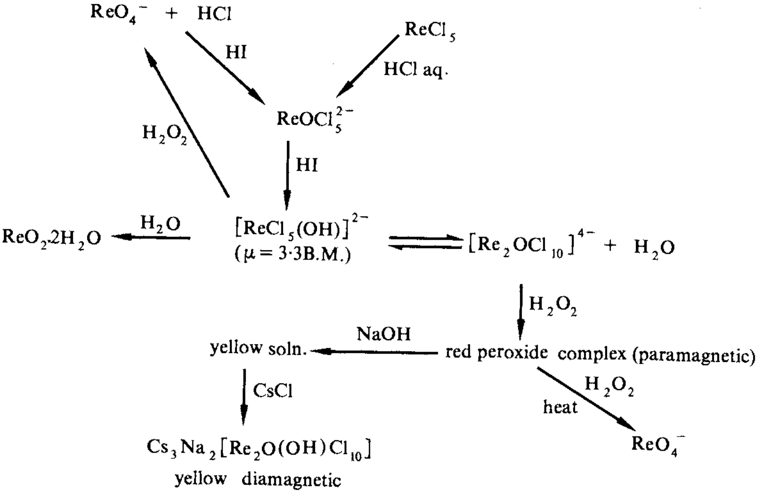


FIG. 13. Reactions of $[Re_2OCl_{10}]^{4-}$ and $[ReCl_5(OH)]^{2-}$ ions. (Adapted, with modification, from R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier, 1966, p. 73.)

The octafluororhenates(VI) become blue in air or in water, and the first hydrolysis products, isolated after suitable treatment, are the $MReOF_5$ salts. These appear to dissolve in ethylmethylketone from which the salts may be obtained crystalline. In the caesium salt the oxidation state of the rhenium was shown to be six, and the magnetic moment is given as 1.48 BM[351]. The colour of these salts recalls that of $ReOF_4$ itself.

Red $ReOCl_6^{2-}$ ion is said to be formed when a solution of rhenium pentachloride in hydrochloric acid is exposed to the air; the potassium salt K_2ReOCl_6 may be precipitated by the addition of potassium chloride. If rhenium pentachloride is dissolved in a mixture of thionyl chloride and iodine monochloride the same ion is said to be formed. Compounds of

[350] F. A. Cotton and S. J. Lippard, *Inorg. Chem.* 5 (1966) 4165; 4 (1965) 1621.

[351] E. G. Ippolitov, *Russ. J. Inorg. Chem.* 7 (1962) 485.

[352] B. J. Brisden and D. A. Edwards, *Chem. Communs.* (1966) 278.

the $ReOCl_5^-$ ion, with large organic cations, have been prepared by the reaction between rhenium oxide tetrachloride and the appropriate cation dissolved in chloroform solution (μ = 1.5–1.6 BM)[352].

Complex oxofluoro- and oxochlororhenates(VII) are known. The former, prepared by the action of bromine trifluoride on the alkali metal perrhenates, have the composition $MReO_2F_4$ (M = K, Rb, Cs, ½Ba). They are creamy-yellow compounds hydrolysed in the air by water[353]. The latter are represented only by the pale yellow salt $Cs_3[ReO_3Cl_3]$, formed by precipitating a solution of perrhenic acid in HCl saturated hydrochloric acid with caesium chloride[354].

---

[353] R. D. Peacock, *J. Chem. Soc.* (1955) 607.

[354] D. E. Grove, N. P. Johnson and G. Wilkinson, *Inorg. Chem.* **8** (1969) 1196.

INDEX

Contents of Comprehensive Inorganic Chemistry

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*

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 VIIIA, 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 AHRLAND *University of Lund*

Master Index

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.*

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 informationabout 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.

Therald 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 subsections 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