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RECENT ADVANCES IN THE COORDINATION CHEMISTRY OF RHENIUM

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CONTENTS

ABBREVIATIONS

acac	acetylacetonate
bipy	bipyridyl
bipyH	bipyridylium cation
diarsine	*o*-phenylenebisdimethylarsine
diphos	1,2-bis(diphenylphosphino)ethane
DMSO	dimethylsulphoxide
DTH	2,5-dithiahexane
EDTA	ethylenediaminetetraacetate anion
en	ethylenediamine
o-phen	*o*-penanthroline

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py	pyridine	sal	salicylate anion
pyH	pyridinium cation	TAS	bis(*o*-diphenylarsinophenyl)phenylarsine
QAS	tris(*o*-diphenylarsinophenyl)arsine	tolH	toluidinium cation
quinH	quinolinium cation		

A. INTRODUCTION

After the discovery of rhenium in 1925 and the initial burst of research the study of its chemistry stagnated in the nineteen forties. Since 1956, and especially in the last five years there have been significant developments in its chemistry which have opened up new fields of investigation.

Rhenium chemistry has been the subject of a number of reviews and books in the short time that it has been studied[1–6]. This review will therefore be restricted to some of the latest developments for the most part not covered by these texts. In particular the chemistry of ter- and pentavalent rhenium and some of the consequences of our improved knowledge of these oxidation states are discussed. In addition certain aspects of rhenium chemistry which at present are, in some respects, unique to rhenium will be reviewed.

The chemistry of the rhenium carbonyls and rhenium π-complexes are best considered in relation to other transition metals, and for this reason have been omitted from the present review. Excellent discussions which include rhenium compounds are available on transition-metal carbonyls and π-complexes.

B. BIVALENT RHENIUM

The divalent oxidation state of rhenium is the most-poorly characterised of its eight oxidation levels. A number of compounds reported in recent years as containing rhenium(II)[7–14] have since been reinterpreted as either rhenium(V) oxo-, nitrido- or oxoethoxy-complexes[15–18] or as dimeric rhenium(III) species[19]. These compounds will be discussed under the appropriate oxidation state.

The rhenium(II) chloride hydrates $ReCl_2 \cdot 2\,H_2O$ and $ReCl_2 \cdot 4\,H_2O$ have been reported[14]. However, their existence needs confirmation in view of the reinterpretation of the chloro-salts $ReCl_4{}^{2-}$ as dinuclear species containing tervalent rhenium[19]. The blue colour of the chlorides suggest that they are at least dinuclear (see under tervalent rhenium).

Rhenium(II) iodide has been reported[20] as a diamagnetic compound prepared by thermal decomposition of the tetraiodide. Compounds of analytical composition ReI_2 have frequently been obtained[20, 21] from attempts to prepare ReI_3 by some of the reported methods[22, 23].

Well-characterised compounds of rhenium(II) are formed with polydentate arsine (Table 1) and phosphine ligands. The diarsine complexes, $[Re(diarsine)_2X_2]$ ($X = Cl, Br, I$)[24], are obtained by reduction of tervalent rhenium compounds with sodium stannite or hydrazine hydrate. The reduction is reversible and proceeds slowly in air when the compounds are in solution. The complexes which are non-electrolytes and monomeric have magnetic moments close to that expected for a d^5 spin-paired configuration in an octahedral field. The stereochemistry of the compounds is most probably *trans*-octahedral.

The complexes of the quadridentate arsine QAS, $\mathrm{ReX_2QAS}$[25], are non-electrolytes and have rather-low magnetic moments. This latter fact has been attributed to a highly-distorted octahedral structure. The triarsine compounds $\mathrm{ReX_2TAS}$[25] are apparently five-coordinate in non-ionizing solvents, but they undergo some ionization in polar solvents. Dissociations of the type;

$$\mathrm{ReX_2TAS} \rightleftharpoons [\mathrm{ReXTAS}]^+ + \mathrm{X}^-$$

or

$$2\,\mathrm{ReX_2TAS} \rightleftharpoons [\mathrm{ReXTAS}]^+ + [\mathrm{ReX_3TAS}]^-$$

may account for the ionization. The QAS and TAS complexes of rhenium(II) decompose on oxidation unlike the complexes of diarsine, a stronger electron donor.

TABLE 1

RHENIUM(II)–ARSINE COMPLEXES

Compound	*Colour*	*Magnetic moment* (B.M.)	*Conductivity* *(Ω^{-1} M^{-1} cm^{-2})*	*Ref.*
$\mathrm{Re(diarsine)_2Cl_2}$[a]	brown	2.13	insoluble	24, 26
$\mathrm{Re(diarsine)_2Br_2}$	yellow	1.99	2.7($\mathrm{PhNO_2}$)	24
$\mathrm{Re(diarsine)_2I_2}$	green	1.82	3.8 ($\mathrm{PhNO_2}$)	24
$\mathrm{Re(QAS)Cl_2}$	orange	1.16	1.3($\mathrm{PhNO_2}$)	25
$\mathrm{Re(QAS)Br_2}$	orange	1.15	2.1($\mathrm{PhNO_2}$)	25
$\mathrm{Re(TAS)Cl_2}$[b]	red	1.60	22.4($\mathrm{CH_3NO_2}$)	25
$\mathrm{Re(TAS)Br_2}$[b]	red	1.67	7.9($\mathrm{PhNO_2}$)	25
			42.0($\mathrm{CH_3NO_2}$)	25
$\mathrm{Re(TAS)I_2}$[b]	purple black	1.74	5.9($\mathrm{PhNO_2}$)	25
			23.9($\mathrm{CH_3NO_2}$)	25

[a] ν(Re–Cl), 279 cm^{-1}. [b] five-coordinate.

A complex of the diphosphine-1,2-bis(diphenylphosphino)ethane, $[\mathrm{ReCl_2(diphos)_2}]^\circ$, has been obtained by a borohydride reduction[17] of the tervalent complex $[\mathrm{ReCl_2(diphos)_2}]\mathrm{Cl}$.

A rhenium(II)–pentacyano-aquo complex, $\mathrm{Na_3Re(CN)_5(H_2O)}$, has been reported and its chemistry studied. It is extracted from the reaction products produced on reducing potassium perrhenate with sodium amalgam in the presence of sodium cyanide[27–29]. The compound is hygroscopic and brown in colour, but gives a violet solution in acid solution. The aquo-ligand can be replaced by a variety of reagents such as, $\mathrm{NOC_6H_4N(CH_3)_2}$[30], CO[31], $\mathrm{SO_3}^{2-}$[32], NO^+[33,34], NO[35],

NO_2^-[33], and CN^-[36–38]. In the latter case the hexacyano-complex, $K_4[Re(CN)_6] \cdot 3\,H_2O$, is obtained as diamagnetic, yellow-brown crystals[36,37]. The electronic-absorption spectrum of $K_3[Re(CN)_6] \cdot 3\,H_2O$ has been recorded and the bands assigned to ligand-field transitions[38].

2,2′-Bipyridyl and *o*-phenanthroline complexes have also been reported as being obtained from the pentacyano-complex; they are: $[Re(CN)_4L]^{2+}$, $Re(CN)_2L_2$ (L = bidentate ligand)[39–41] and the cationic species[41] $[Re(bipy)_2(CH_3CN)_2]^{2+}$.

Brief mention has also been made of the compounds[42,43] $Re(o\text{-phen})_2Cl_2$, $Re(NO)Cl_3 \cdot 4\,H_2O$ and $K_2[Re(NO)Cl_5]$.

A number of the cyano-complexes listed above have been poorly characterised and it would be of interest to have confirmation of their compositions and especially details of physico-chemical measurements. The possibility that the complexes are cyano–hydrido-complexes cannot be excluded. The hexacyanide complex of monovalent rhenium, $K_5Re(CN)_6$, is, on the other hand, well characterised[44,45].

The complex $(ReBr_2DTH)_n$ has been prepared by treating the tervalent complex ion $(Re_2Br_8)^{2-}$ with the ligand. A compound with rhenium in mixed valence states, $Re_2Cl_5(DTH)_2$, can also be isolated[46] (see under tervalent rhenium).

C. TERVALENT RHENIUM

The chemistry of tervalent rhenium was sparse until 1963, and excepting for a few mononuclear octahedral compounds, inadequately characterised. The recent discovery of trimeric and dimeric entities of rhenium(III) has made it possible to reinterpret a considerable amount of earlier work. In addition, investigations of trivalent rhenium have increased at a rapid rate.

The chemistry of rhenium(III) falls into three categories: (a) mononuclear paramagnetic complexes, generally with octahedral coordination; (b) dimeric compounds, based on the $(Re_2X_8)^{2-}$ unit, which have a strong Re–Re bond; and (c) trimeric compounds, based on the Re_3X_9 unit, which contain triangles of strongly-bonded rhenium atoms. Historically, the structure of the trimeric clusters was elucidated before the dimeric compounds, but for uniformity the chemistry will be reviewed in the above order.

The recent work, besides showing that the chemistry of rhenium(III) is extensive and varied, demonstrates that it is closely related to the metal cluster chemistry of molybdenum, tungsten, niobium, and tantalum.

The extensive use of X-ray crystallographic techniques on key compounds has been an important factor in producing order in tervalent-rhenium chemistry. In the short space of four years nine structures have been determined (and one of a related technetium compound), and the investigation of a number of structures is still in progress.

(i) Mononuclear complexes

The mononuclear octahedral rhenium(III) compounds are listed in Table 2. Not all of them have been adequately characterised.

The spin-only value of the magnetic moment for Re^{III}-(d^4) octahedral compounds is 2.83 B.M. However, μ_{eff} is less than this as a consequence of spin–orbit coupling ($\zeta = 2500\ cm^{-1}$ for Re^{III})[47].

The diarsine-[24] and mono- and diphosphine[16,17,50] complexes $[ReL_2X_2]^+$ and ReX_3L_3 are readily obtained by reduction of the perrhenate ion. The diarsine compounds are isomorphous with similar complexes of other metals, some of which are known to have the *trans* configuration[26]. The stereochemistry is con-

TABLE 2

RHENIUM(III) MONONUCLEAR COMPLEXES

Compound	*Magnetic moment (B.M.)*	*Comments*	*Ref.*
$[Re(diarsine)_2Cl_2]ClO_4$[b]	2.14	ν(Re–Cl) 325 cm^{-1}	24, 26, 47
$[Re(diarsine)_2Br_2]ClO_4$[b]	2.02		24, 47
$[Re(diarsine)_2I_2]ClO_4$[b]	1.74		24, 47
$[Re(diarsine)_2Cl_2]Cl$[b]		ν(Re–Cl) 313 cm^{-1}	26
hydrated complex		ν(Re–Cl) 317 cm^{-1}	26
$[ReCl_2(QAS–O)]Cl$[b]	2.34	ν(As–O) 838, 313 cm^{-1}	25
$ReCl_3(Et_2PhP)_3$[c]		C_{3v} symmetry	16, 17, 48, 49
$ReCl_3(Me_2PhP)_3$			
$[ReCl_2(diphos)_2]Cl, ClO_4$[b]			16, 17, 50
$[ReBr_2(diphos)_2]Br, ClO_4$[b]			50
$[ReCl_3(Et_2PhP)\ (diphos)]$			17
$Re(acac)_3$	1.9–2.3	monomeric	51
$ReCl_2(acac)\ (Ph_3P)_2$	1.4		52
$ReBr_2(acac)\ (Ph_3P)_2$	1.6		52
$ReI_2(acac)\ (Ph_3P)_2$			52
$ReCl_2(\beta\text{-diketone})\ (Ph_3P)_2$[a]			52
$ReCl_2(acac)\ (Et_2PhP)_2$			52
$ReCl(acac)_2(Ph_3P)$			52
$Na_2[Re(CN)_5H_2O]$			32, 53
$K_3[Re(CN)_3(OH)_3]$			54
$Co(NH_3)_6[Re(CN)_6]$	2.6		55
$K_3Re(CN)_6$		impure	55
$ReX_3(thiourea)_3$		X = Cl, Br	46
$Re(o\text{-phen})_2Cl_3$	diamag.		42
$ReCl_3(diphos)$[d]			50
$ReCl_3(diarsine)$[d]	diamag.		56
$ReCl_3(Ph_3PO)_2$[d]		ν(P–O) 1137 cm^{-1}	57
$Re[P(OPh)_3]_3I_3$	1.65		22
$Re[P(OC_6H_4Me)_3]_3I_3$	1.65		22

[a] β-diketone = 1,1,1-trifluoropentane-2,4-dione, 1,1,1,5,5,5-hexafluoropentane-2,4-dione or thenoyltrifluoroacetone. [b] 1 : 1 electrolytes. [c] Dipole moment = 6.3 D, non-electrolyte in $PhNO_2$. [d] five-coordinate.

firmed by the existence of a single ν(Re–Cl) stretching frequency in the infrared[26]. The symmetry of the complexes $ReCl_3(PR_2Ph)_3$ (R = Et, Me) is reported as C_{2v} from NMR[48,49] and dipole moment[16,17] measurements.

The tetradentate ligand, QAS, reacts with rhenium(III) chloride to give a complex, $[ReCl_2(QAS–O)]Cl$, in which one arsenic atom has been oxidised[25]. The appearance of two bands in the infrared at 838 and 813 cm^{-1} is used as evidence for the existence of the As–O bond. The magnetic moment of the compound is rather high for tervalent rhenium.

Under certain conditions the dimeric complex, $(Bu_4N)_2Re_2Cl_8$, reacts with diphosphine to give $ReCl_3$(diphos)[50]. Two other compounds $ReCl_3$(diarsine) and $ReCl_3(Ph_3PO)_2$, have been reported[56,57] to contain five-coordinate rhenium(III). Speculation as to their structure would be premature without details of the physical properties of the complexes.

Further study of the cyanide compounds is necessary[32,53,54], before one can be sure that they are formulated correctly. The complex $Co(NH_3)_6[Re(CN)_6]$ is reported to have a magnetic moment of 2.6 B.M.[55]. The complex Re(*o*-phen)$_3$Cl$_3$ is said[42] to be diamagnetic suggesting a more-complex formulation than given.

Seven-coordinate compounds $[ReCO(diarsine)_2X_2]X_3^-$ (X = Br, I) have been isolated. They are 1:1 electrolytes, diamagnetic, and can only be isolated with large anions[58].

In view of the variety of ligands forming mono-nuclear octahedral complexes of rhenium(III) it is not unreasonable to expect that the hexahalogeno-anions $(ReX_6)^{3-}$ should exist. Some early reports of the existence of $(ReCl_6)^{3-}$ have not been confirmed[59–61]. Recent attempts, using electrolytic reduction[60] of $(ReO_4)^-$ or $(ReCl_6)^{2-}$ or by hydrogenation[62] of $(ReO_4)^-$ in hydrochloric acid have not been confirmed[6,63]. The product invariably formed is the hexahalogeno anion, $(ReCl_6)^{2-}$, often in a variety of colours and crystal habits which might suggest different compounds[63].

(ii) Dinuclear complexes

During the nineteen fifties a number of compounds formulated as containing rhenium(II) ($KHReCl_4H_2O$, $KHReCl_4$ and $(pyH)HReCl_4$) were obtained by reduction of the perrhenate ion with hydrogen in a hydrochloric acid medium[14]. The unrefined X-ray crystal structure of the pyridinium salt has been determined; it showed that the anion was dimeric without halogen bridges. The anion, reformulated as $(Re_2Cl_8)^{4-}$, consisted of two approximately square-planar $ReCl_4$ groups united by a short (2.22 Å) Re–Re bond. Equally remarkable was the discovery that the $ReCl_4$ groups were in the eclipsed configuration (Fig. 1)[64].

Recently a dimeric tervalent rhenium entity $(Re_2Cl_8)^{2-}$ (X = Cl, Br) has been obtained by reducing the perrhenate anion with hypophosphite ion[19,67]. In the case of the chloride the reaction proceeds through a green stage, which contains

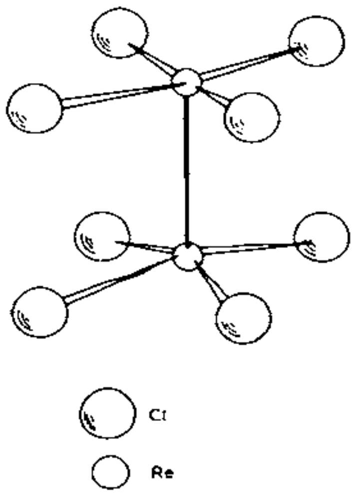


Fig. 1. Structure of $(Re_2Cl_8)^{2-}$ ion.

the $(ReCl_6)^{2-}$ species. Later the colour turns dark brown and from the solution the dinuclear complex anion can be isolated with cations such as[65] K^+, NH_4^+, R_4N^+, Ph_3PH^+, and Ph_4As^+. It is very likely that the two species $(Re_2Cl_8)^{4-}$ and $(Re_2Cl_8)^{2-}$ are in fact the same anion of tervalent rhenium[19], viz., $(Re_2Cl_8)^{2-}$. It therefore appears unnecessary to formulate the "rhenium(II)" compounds as $M_2H_2[Re_2Cl_8]$. A comparison of the products obtained by the two preparative methods is given in Table 3.

The structure of $K_2[Re_2Cl_8] \cdot 2\ H_2O$ has since been determined[66] and the result is in agreement with that of the refined structure of $(pyH)_2Re_2Cl_8$ (Fig. 1). The eight chlorine atoms lie approximately at the corners of a cube with the two rhenium atoms depressed slightly into opposite cube faces. Relevant structural data are as follows:

Re–Cl, 2.29 Å; Re–Re, 2.24; $\widehat{\text{ClReCl}}$, 87°; $\widehat{\text{ClReRe}}$, 103.7°; and Cl....Cl non bonded, 3.32 Å.

The structure of the bromo-complex, $(pyH)_2Re_2Br_8$, has also been determined[67]. Two crystalline forms apparently exist and the Re–Re bond lengths are reported as 2.207 Å and 2.27 Å.

The bonding in the $(Re_2Cl_8)^{2-}$ anion is particularly interesting in view of the very short Re–Re bond and the eclipsed configuration. Qualitatively[19,68] one can assume that each rhenium atom uses its $d_{x^2-y^2}$, p_x, p_y and s-orbitals forming the ReX_4 σ-bonds, leaving the d_{z^2} and p_z-orbitals (dp hybrid) for forming the Re–Re σ-bond and two non-bonding σ-orbitals (σ_n) centrifugally directed, one from each rhenium atom. Of the remaining orbitals, d_{yz} and d_{xz} have π-symmetry and can form two Re–Re π-bonds while d_{xy} has δ-symmetry and can form a δ-bond. The Re–Re bond is therefore quadruple $\sigma^2\pi^4\delta^2\sigma_n{}^0$, and the eight d elec-

TABLE 3

COMPARISON OF $(Re_2Cl_8)^{2-}$ COMPLEXES MADE BY DIFFERENT METHODS

H_3PO_2 reduction			*H_2 reduction*		
Cation	*Colour*	*Electrolyte type*	*Cation*	*Colour*	*Electrolyte type*
n-Bu_4N^+	blue	1:2	$NH_4^+(2\ H_2O)$	very dark green	1:2
pyH^+	dark green	1:2	NH_4^+	dark green	1:2
$C_6H_{11}NH^+$	dark green	1:2	$K^+(2\ H_2O)$	very dark green	1:2
Ph_4As^+	blue	1:2	K^+	dark green	1:2
Ph_3MeAs^+	blue-green	1:2			

trons (Re^{III}-d^4) are adequately accommodated. This scheme satisfactorily accounts for the diamagnetism, short Re–Re bond and the eclipsed configuration. The δ-bond (estimated strength from electronic spectra = 3.7 eV), which can only form in the eclipsed position, must be sufficiently strong to overcome the steric repulsions between halogens of neighbouring ReX_4 groups[68].

The anion $(Re_2Cl_8)^{2-}$ reacts with 2,5-dithiahexane[69,70] to give a complex $Re_2Cl_5(DTH)_2$, which can be considered as having the rhenium atoms in oxidation states II and III. The structure of the compound has been determined[69] and it is found that the entities $ReCl_4$ and ReS_4 are in the staggered configuration, suggesting that the δ-bond has been broken. The nine d-electrons (Re^{II}-d^5, Re^{III}-d^4) are accommodated $\sigma^2\pi^4 d_{xy}{}^2 d_{xy}{}^1$ predicting a paramagnetic compound which is observed experimentally. A small increase in the Re–Re bond to 2.29 Å is reported. The σ_n-orbitals, which are vacant in $(Re_2Cl_8)^{2-}$ are used in $Re_2Cl_5(DTH)_2$ for the axial attachment of chlorine atoms, one strongly and one weakly. The use of the σ_n-orbitals for bonding appears dependent on access of these orbitals to coordinating ligands[70].

Rhenium(III) chloride reacts with carboxylic acids RCOOH (R = CH_3, C_2H_5, n- and iso-C_3H_7) to give[71] dimeric compounds $[ReCl(OCOR)_2]_2$. The chemical evidence suggested that the compounds have a similar structure to that of copper(II) acetate. The compounds are diamagnetic, but a Re–Re bond was not originally invoked to account for this.

However, more recent evidence has shown that treatment of the compounds with hydrochloric acid produces the $(Re_2Cl_8)^{2-}$ species, and in fact the reaction is reversible[65,68]:

$$(Re_2Cl_8)^{2-} + 4\ RCOOH \rightleftharpoons [ReCl(OCOR)_2]_2 + 4\ HCl + 2\ Cl^-$$

The reaction proceeding to the right is the best preparative route[46,65,70] to the carboxylate complexes. The complexes probably have the structure depicted in[68] Fig. 2.

A wide range of similar compounds have now been prepared[46,71] and reports of carboxylic-acid derivatives of rhenium(II)[11-13] have been reinterpret-

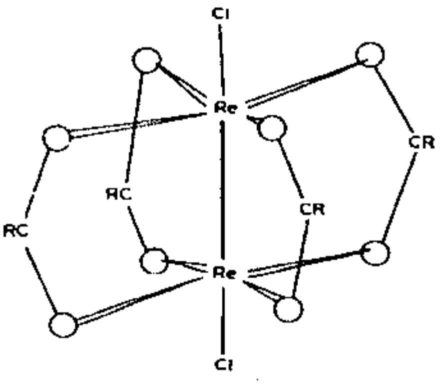


Fig. 2. Structure of $Re_2(O_2CR)_4Cl_2$.

ed[46,70] as dimeric compounds of rhenium(III) (Table 4). The compound[72] $Re_2Cl_3(RCOO)_2(Ph_3P)_2$ may also be one of this class.

The rhenium(III) dimeric compounds are either blue-green or orange-brown in colour. The anion $(Re_2Cl_8)^{2-}$, which is blue, has three electronic-spectral bands at[65,68] 14,000 cm^{-1}, 32,000 cm^{-1}, and 40,000 cm^{-1} which have been assigned to the transitions $\delta \rightarrow \sigma_n$, $\delta \rightarrow \delta^*$ and Cl → Re (charge transfer) respectively. The orange-brown compounds do not possess the 14,000 cm^{-1} band, a fact which can be related to the absence of the vacant σ_n-orbitals due to ligands bonding in the axial positions[68,70].

TABLE 4

RHENIUM(III)–DIMERIC CARBOXYLATE COMPLEXES

Compound	*Colour*	*Comments*
$Re_2(O_2CCH_3)_4X_2$ (X = Cl, Br)	orange-brown	Halogens bonded in terminal positions, along the line of the Re–Re bond.
$Re_2(O_2CC_2H_5)_4X_2$ (X = Cl, Br)	orange-brown	
$Re_2(O_2CC_3H_7)_4X_2$ (X = Cl, Br, I)	orange-brown	
$Re_2(O_2C(CH_3)_3)_4Cl_2$	red-brown	
$Re_2(O_2CC_6H_5)_4X_2$ (X = Cl, Br, SCN)	red-brown	
$Re_2(x\text{-}CH_3C_6H_4CO_2)_4Cl_2$ (*x* = *o*, *m*, *p*)	red	
$Re_2(O_2CCH_2C_6H_5)_4Cl_2$	orange	
$Re_2(O_2CCH_2Cl)_4Cl_2$	orange	
$Re_2(O_2CCH_3)_3Br_3H_2O$	orange	terminal groups Br, H_2O.
$Re_2(O_2CC_3H_7)_4SO_4(H_2O)_2$	blue	Colour suggests SO_4^{2-} and H_2O not coordinated.
$Re_2(O_2CCH_3)_2X_4(H_2O)_2$ (X = Cl, Br)[a]	blue	2 H_2O and 2 py only weakly bonded.
$Re_2(O_2CCH_3)_2Cl_4(py)_2$[a]	blue	
$Re_2(OCCH_3)_2(O_2CCCl_3)_2(H_2O)_2$[a]	blue	
$Re_2(OCC(CH_3)_3)_2(O_2CCCl_3)_2$	blue	
$Re_2(O_2CCCl_3)_2Cl_4$	blue	

[a] non-electrolyte

The position of the intense band at 27,000–36,000 cm^{-1} ($\delta \rightarrow \delta^*$) varies with the ligand X (Cl, Br, I) in the compounds[70] $Re_2X_2(OCOC_3H_7)_4$. It moves to lower energy in the order Cl > Br > I. This may be due to an interaction between the halogen and the (Re–Re) π-bonds weakening the Re–Re bond. The $\delta \rightarrow \delta^*$ transition could well be sensitive to any such change. The Re–Re bond is therefore weakened in the complexes $Re_2X_2(OCOC_3H_7)_4$ in the order Cl < Br < I; this has been likened to a *trans* effect. Shifts in some of the weak bands of the carboxylate complexes have been correlated with the nature of the alkyl or aryl group R[70].

The dimeric anions $(Re_2X_8)^{2-}$, react with triphenylphosphine to give compounds of analytical composition ReX_3Ph_3P which are very insoluble and probably dimeric. However, an infinite polymeric structure cannot be ruled out[50].

Sulphur-donor ligands react with the $(Re_2Cl_8)^{2-}$ anion in a variety of ways[46]. Thiourea and tetramethylthiourea break the Re–Re bond giving octahedral complexes ReX_3(thiourea)$_3$. A measurement of the magnetic moment might confirm that the complexes are mononuclear and octahedral. 2,5-Dithiahexane forms both mononuclear and dinuclear complexes $Re_2Cl_5(DTH)_2$, $ReX_3(DTH)_n$, depending on the reaction conditions; it also either partially or completely reduces the rhenium to the divalent oxidation state $(ReBr_2DTH)_n$. The ligand 1,2-dicyanoethylene-1,2-dithiolate forms the complex $[Ph_4As]_2Re_2[C_2S_2(CN)_2]_4$.

The dimeric species $(Re_2X_8)^{2-}$ (X = Cl, CNS) can be smoothly reduced polarographically in acetonitrile to give[73] in solution the species $(Re_2X_8)^{3-}$ and $(Re_2X_8)^{4-}$. This observation removes the apparent anomaly of the technetium compound[74] $(Tc_2Cl_8)^{3-}$.

(iii) Trinuclear complexes

Rhenium(III) chloride was considered to be dimeric until recently[75]. The chloro-salts, M^IReCl_4, isolated from hydrochloric-acid solutions of rhenium(III) chloride are diamagnetic[76] and on the basis of these data have been quoted as possibly the only known examples of spin-paired tetrahedral complexes[77]. Tervalent rhenium and possibly technetium (d^4) are considered two of the most-likely elements to have a spin-paired tetrahedral stereochemistry.

During an investigation to demonstrate the tetrahedral stereochemistry, a tetraphenylarsonium salt was isolated which was best represented as $(Ph_4As)_2$-Re_3Cl_{11}. It was also noticed that the electronic-absorption spectra of the substances $(ReCl_4)^-$, $(Re_3Cl_{11})^{2-}$, $ReCl_3Ph_3P$, and $ReCl_3$ in ethanol were identical in the range 12,500–20,000 cm^{-1} suggesting a common absorbing species[78].

It was therefore clearly of interest to investigate the $(ReCl_4)^-$ anion in detail. Two independent reports of the structure of the salt $CsReCl_4$ were published almost simultaneously in 1963[79–81]. The anion is trimeric, $(Re_3Cl_{12})^{3-}$ and contains a triangle of strongly-bonded rhenium atoms. There are three types of chlorine

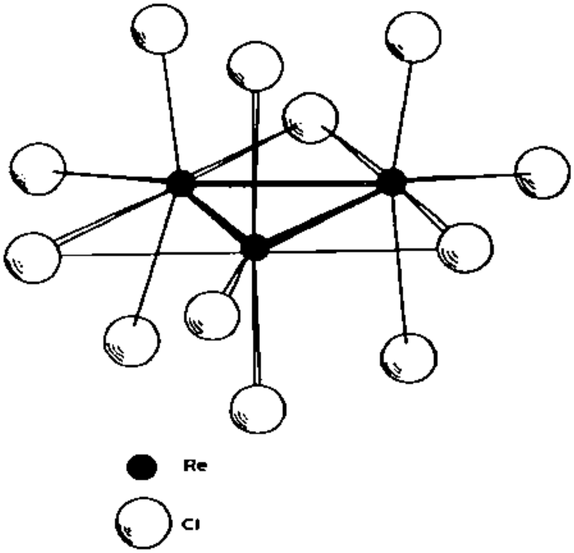


Fig. 3. Structure of $(Re_3Cl_{12})^{3-}$ ion.

atoms: (a) three bridging chlorine atoms, (b) six terminal out-of-plane chlorine atoms, and (c) three terminal in-plane chlorine atoms (Fig. 3). Bond lengths and relevant bond angles are listed in Table 5 together with data on related structures since determined.

The results indicate that the Re–Re bonds are short, but not as short as in $(Re_2Cl_8)^{2-}$. The Re–Cl terminal out-of-plane and bridging bonds appear to be "normal" while the terminal in-plane Re–Cl bonds are long relative to the others. The latter fact can be readily explained in terms of steric interactions: the out-of-plane terminal halogens are splayed outwards due to steric repulsions, and the

TABLE 5

STRUCTURAL DATA ON TRIMERIC RHENIUM(III) COMPOUNDS

	Re–Re	*Re–X terminal in-plane*	*Re–X terminal out-of-plane*	*Re–X bridge*	*$\widehat{XReX}$ terminal off-plane*	*$\widehat{ReXRe}$ bridge*	*Ref.*
$(Re_3Cl_{12})^{3-}$	2.48	2.52	2.36	2.39	158°	62°	79–81
$(Re_3Cl_{11})^{2-}$	2.483, 2.435*	2.56	2.30, 2.29*	2.35	158°, 153°*	63°	82, 83
$(Re_3Br_{12})^{3-}$	2.48	2.75	2.49	2.53	156°	59°	84
$(Re_3Br_{11})^{2-}$	2.49, 2.43*	2.72	2.48, 2.38*	2.54	159°, 134°*	58°	85, 86
Re_3Cl_9	2.49	(2.66)	2.40, 2.29	2.46	163°	61°	87, 88
Re_3Br_9	2.465		2.45	2.54	155°	58°	89
$Re_3Cl_9\ (Et_2PhP)_3$	2.49	2.70**	2.32, 2.30	2.395, 2.371	159°	63°	90

* Bond length and bond angles associated with the halogen-deficient rhenium. ** Re–P.

only way the terminal in-plane chlorines can move is directly outwards from the metal atoms.

The structures of other trinuclear compounds of rhenium (Table 5) are similar to that of $Cs_3Re_3Cl_{12}$ and only points of additional interest will be outlined. The structure of the complex[90] $Re_3Cl_9(Et_2PhP)_3$ confirms that the phosphine ligands are bonded in the terminal in-plane positions and, as expected, the Re–P bonds are long. The Re_3Cl_9 clusters[87,88] in rhenium(III) chloride are interlinked by certain of the terminal halogens acting as intercluster bridges so that each rhenium atom has five chlorines bonded to it as in $(Re_3Cl_{12})^{3-}$. The bromide[89] Re_3Br_9 which occurs as an independent species in the crystal of $(quinH)_2Re_4Br_{15}$ ($(quinH)_2ReBr_6 + Re_3Br_9$) has one unusual feature in that it exists as isolated units in the crystal lattice. The structure has gaps at the positions where one would expect to find the terminal in-plane halogens. This is surprising in view of the fact that the removal of one terminal in-plane halogen in the anions $(Re_3X_{11})^{2-}$ ($X = Cl, Br$)[82,83,85,86] relieves some of the steric strain and the out-of-plane halogens on the deficient rhenium bend down so that the $\widehat{BrReBr}$ angle is 134° rather than the usual 159°. This is not observed for the isolated Re_3Br_9 structure. A further interesting feature of the $(Re_3X_{11})^{2-}$ anions, most noticeable for the bromo-complex where the data are more accurate, is that the three Re–Re bonds are not all equivalent as in the case of the symmetrical structures. The two bonds to the halogen-deficient rhenium atom are shorter by as much as 0.1 Å.

The structure of rhenium(III) iodide is under investigation and preliminary work shows it to be isomorphous with Re_3Br_9, with a triangle of rhenium atoms[11]. It will be of interest to know how the larger iodine atoms affect the length of the Re–Re bonds.

The mass spectrum[91] of Re_3Cl_9 at 280° confirms the existence of the trinuclear structure at higher temperatures. The preparation temperature for Re_3Cl_9 is in the vicinity of 500° and it is very likely that the trimer also exists at that temperature.

(iv) Bonding theories

Three approaches to the bonding in the rhenium cluster have been proposed, each at a different level of sophistication, but agreeing on the broad qualitative features. The first and most-general approach is a delocalised molecular-orbital description[92] of the metal–metal bonding. The two other descriptions consider more localised molecular orbitals[93,94]. The different approaches are compared in Table 6.

The first approach[92] considers the structure as composed of three square-planar $ReCl_4$ units. The rhenium atom orbitals not used in bonding to the halogens are combined by a LCAO, molecular-orbital method to form Re–Re delocalised

TABLE 6

BONDING THEORIES FOR $(Re_3Cl_{12})^{3-}$

Metal orbitals	*Transformation*	*Metal bonding orbitals*	*Comments*
1.Ref. 92			
$d_{x^2-y^2}$, s, p_x, p_y		dsp^2 hybrids	$ReCl_4$ units
p_z		p_z	terminal in-plane halogen
d_{z^2} d_{xy} d_{xz} d_{yz}	A'_1+E' A''_1+E'' A'_2+E' A''_2+E'' in D_{3h}	A'_1, A''_2, E', E'' bonding E'', E', A''_1, A'_2 antibonding	Re–Re bonding
2.Ref. 94			
d_{z^2} d_{xy} d_{xz} d_{yz}		equivalent orbitals A'_1, A''_2, E', E''	Re–Re bonding: bent σ, bent π and bent ξ per Re–Re bond
		A'_1, E' from bridging chloride atoms	Re–Cl–Re bridging three-centre bond
3.Ref. 93			
either			
d_{z^2}, $d_{x^2-y^2}$, d_{xy} s, p_x, p_y, p_z		d^2sp^3 hybrids	$Re(Re_2Cl_5)$ σ-bond framework
or			
s d_{xy}	A_1 B_2	A_1, B_2	$Re(Re_2)$ σ-bonds
p_x, d_{z^2}, $d_{x^2-y^2}$ p_z p_y	A_1 B_1 B_2 in C_{2v} local symmetry around each Re	$3A_1$, B_1, B_2	$ReCl_5$ σ-bonds
d_{yz} d_{zx}	A'_1+E' A'_2+E' in D_{3h}	A'_1, E' bonding A'_2, E' antibonding	Re–Re π-bonding

molecular orbitals (Table 6, 1). The six bonding orbitals, A_1', A_2'', E' and E'', satisfactorily accommodate the twelve d-electrons (Re^{III}-d^4). Hence the Re–Re bond order is predicted to be two.

The above molecular orbitals have been reconsidered in terms of the Equivalent Orbital approach (Table 6, 2). In this case the metal–metal bonding has been resolved into a bent σ, bent π, and bent ξ bond per Re–Re bond[94].

In the third bonding description[93] the local symmetry around each rhenium atom is considered (5 Re–Cl and 2 Re–Re σ-bonds per Re). Orbitals unused in

σ-bonding are employed to form Re–Re π-type bonds. The metals *d*-electrons are accommodated as follows; six in the three Re–Re σ-bonds and six in the three Re–Re π-bonds. This also predicts a bond order of two and as in the other cases, explains the diamagnetism (Table 6, 3).

The inequality of the rhenium–rhenium bonds in the $(Re_3X_{11})^{2-}$ anions may be accounted for by improved overlap in the two short bonds. This may be achieved by incorporating the centrifugally-directed orbital left vacant on the halogen-deficient rhenium atom[93]. The Re–Br (out-of-plane) bonds to the deficient rhenium are also shorter than the other bonds; this may arise from a release of steric pressure at that point in the anion. This can be considered as being assisted by the formation of a Br–Re–Br three-centre bond in which filled *d*-orbitals of the bromine atoms are used.

The bridging chlorine atoms have been considered either to bond through one three-centre bond[94] or two two-centre bonds[92,94]. Each bridging halogen donates two electrons to the three-centre bond and therefore the Re_3X_3 unit can be described as an eighteen-electron structure. The alternative approach suggests a twenty-four-electron structure. An advantage of the three-centre bond is that the bridging angle of 60° is not unusual, whilst it would be in the case of two two-centre bonds which presumably involve the *p*-orbitals of the halogens.

(v) Electronic spectra

One feature common to all compounds containing the triangular rhenium cluster is the presence of two electronic absorption bands in the visible and near-infrared spectra[82,88,90,95–101]. The position of the high-energy band, 17,500–19,400 cm^{-1}, is remarkably constant for ligand changes in the terminal positions. Some variations in the second band, 12,300–13,300 cm^{-1}, have been related to ligand differences, e.g., nitrogen donors shift[97,100] the band to around 11,100 cm^{-1}. The change in the bridging halogens does shift both bands slightly. The two bands also have an intensity ratio of approximately 3:1 (high energy: low energy, molar extinction coefficient 1200–1800:400–600). The position and relative intensity of the bands can be used qualitatively for showing the presence of rhenium triangles in tervalent-rhenium compounds. No quantitative assignments have so far been made for the bands. However, certain chemical facts make it possible to suggest a qualitative assignment. Chlorine exchange and a controlled thiocyanate replacement of chlorine has demonstrated that the basic structural unit is Re_3X_3 (X = bridging halogens)[97]. The isolation[99] of the complex $Re_3Br_3(AsO_4)_2(solvent)_3$ confirms the lability of all the terminal halogens. Also the major shift in the spectral bands to lower energy occur when the bridging halogens are changed from chlorine to bromine[97]. These facts suggest that the two spectral bands are associated with the Re_3X_3 entity and may be assigned to a $X_{bridge} \rightarrow Re(triangle)$ transition.

TABLE 7

TYPICAL RHENIUM(III) TRIMERIC CLUSTER COMPOUNDS[16, 17, 93, 95–103]

Type	
$(Re_3X_{12})^{3-}$	X = Cl, Br; cations, Cs^+, $(Co(en)_3)^{3+}$
$(Re_3Cl_{11})^{2-}$	cations, Ph_4As^+, $Ph_3benzylP^+$
$(Re_3Br_{11})^{2-}$	cations, Cs^+, quinH^+
$(Re_3Br_{10})^-$	cations, Ph_3PH^+, Ph_2EtP^+, quinH^+
$[Re_3Cl_3(CNS)_6]^{3-}$	cation, Ph_3MeAs^+
$[Re_3Cl_3(CNS)_6]^{3-}$	cation, Ph_4As^+
$[Re_3Cl_{11}Ph_3P]^{2-}$	cation, Ph_4As^+
$[Re_3Br_{10}(py)_2]^-$	cation, $Ph_3benzylP^+$, Ph_3PH^+
$(Re_4Br_{15})^{2-}$	$(Re_3Br_9 + ReBr_6{}^{2-})$; cations, quin$H^+$, $(C_2H_5)_4N^+$
$(Re_4Cl_3Br_{15})^{2-}$	$((Re_3Cl_3Br_6)^{2-} + (ReBr_6)^{2-})$; cation, Cs^+
$(Re_3Cl_3Br_7)^{2-}$	cation, Cs^+
$(Re_3Br_6(NO_3)_3)^{3-}$	cation, Cs^+
$Re_3Br_3(AsO_3)_3(DMSO)_3$	
$Re_3X_9L_3$	X = Cl, Br; L = monodentates, Ph_3P, py, Ph_3As, Ph_3PO, DMSO, CH_3CN, Et_2PhP, R_2SO, aniline.
$Re_3Cl_9L_6$	L = monodentates, Ph_3AsO, Ph_3PO
Re_3Cl_6(bidentate)$_3$	acac
Re_3X_9(bidentate)$_{1.5}$	bipy, diphos, DTH
Re_3X_9(bidentate)$_3$	bipy, DTH

(vi) Chemistry of trinuclear complexes

The range of compounds that have been produced is large and Table 7 lists some of the different types.

The halides Re_3Cl_9 and Re_3Br_9 have been prepared in two major ways, viz.; thermal decomposition of ReX_5 or Ag_2ReX_6[98,104,105]. The yields are never very great and attention must be paid to experimental detail to increase them[98]. The bromide has also been reported[106] as resulting through the reaction of rhenium and bromine in a sealed tube at 400–550°.

Complexes of the halides are readily obtained by adding the appropriate ligand to the halide in an organic solvent. The halogeno-complexes are isolated by adding the appropriate cation to an acidic solution of the halide[97,98,100].

The method for obtaining rhenium(III) iodide is less well understood. A number of preparations have been reported[23,107–109], but not always confirmed[20,21]. The product obtained in many cases analyses closer to a composition ReI_2. Recently crystalline rhenium(III) iodide was obtained; preliminary X-ray analysis confirms that it has the trimeric structure[21].

The free energy of formation of the chloride and bromide are given as -47.8 and -33.6 kcal mole^{-1} from oxidation experiments[110], and more recently as -45.4 and -31 kcal mole^{-1} from heat-capacity measurements[111]. Rhenium(III) chloride starts to dissociate irreversibly above 360° according to the reaction[112]:

$$2\,ReCl_3 \rightarrow 2\,Re + 3\,Cl_2$$

The salts of $(Re_3Cl_{12})^{3-}$ disproportionate at 250° to[61] Re^{II}, Re^{IV} and Re^{VII}. The clusters do not have a high stability towards hydrolysis and oxidation. The chloro-compounds are less readily oxidised than the bromo-compounds[103], and the oxidation products are Re^{IV} and Re^{V} depending on conditions[113,114].

Rhenium(III) chloride has an observed molecular weight of 885 (calc. for trimer 887) in tetrahydrothiophene (cryoscopic)[88]. The observed molecular weight of the complexes $Re_3X_9L_3$ (L = neutral monodentate ligand) is low[97]. This is presumably due to a reversible dissociation of the weakly-bonded ligand in solution according to the reaction:

$$Re_3X_9L_3 \rightleftharpoons Re_3X_9L_{3-n} + n\,L.$$

It has been shown[90] independently that the bands in the ultra-violet spectra of the complexes deviate from Beer's Law, and free-ligand (L) absorption bands appear on dilution. A similar type of dissociation does not occur for the halogeno-anions to any appreciable extent[97].

However, under the appropriate experimental conditions the terminal in-plane halogens can be completely removed as demonstrated by the formation of the salt types[97,98], $(Re_3X_{11})^{2-}$ and $(Re_3Br_{10})^-$. The number (0, 1, or 2) of halogens removed from the anions can be correlated with the increasing size of the cation used. The effect is most pronounced for the bromo-anions, where presumably the larger bromine atoms give rise to greater steric pressure in the anion making it easier for terminal halogens to be removed. Whereas $(Re_3Cl_{12})^{3-}$ is the predominant species of the chloro-complexes the predominant bromo-complex is $(Re_3Br_{10})^-$. The anions can cope with neutral ligands as in $[Re_3Cl_{11}(Ph_3P)]^{2-}$ and $[ReBr_{10}(py)_2]^-$ where the number of cations has not been increased[97]. Mixed chloro–bromo complexes can also be obtained by dissolving rhenium(III) chloride in hydrobromic acid and precipitating with caesium, to give $Cs_3[Re_3Cl_6Br_6]$ and $Cs_2[Re_3Cl_4Br_7]$[103].

All of the rhenium(III) cluster compounds, whose magnetic moments have been measured, are slightly paramagnetic[106,111,115,116], and in certain cases this has been shown to be temperature independent[111,115,116]. Two forms of rhenium(III) chloride have been found on the basis of their magnetic susceptibility[116]. One form is prepared at 375° by thermal decomposition of $ReCl_5$ ($\chi_m = 40$–55×10^{-6}) while the other is obtained from this by sublimation at 475° ($\chi_m = 528 \times 10^{-6}$). The forms are apparently similar in all other respects. It is the high-temperature form whose structure has been determined[88,111].

The interesting salts $(cation)_2Re_4Br_{15}$, (cation = $quinH^+$, $(C_2H_5)_4N^+$ or pyH^+)[89,101] and[103] $Cs_5Re_4Cl_6Br_{12}$ have been produced. The crystal lattices contain in each case the $(ReBr_6)^{2-}$ anion (with appropriate cation) as well as a trimeric rhenium structure. The first three compounds contain neutral Re_3Br_9 and the latter the salt $Cs_3Re_3Cl_6Br_6$. The compounds are physical mixtures of the two components as shown from X-ray powder photographs, electronic-absorption spectra and a detailed X-ray analysis of $(quinH)_2Re_4Br_{15}$[89].

Complexes with oxy-ligands have proved interesting, especially the bis-arsenate complex $Re_3Br_3(AsO_4)_2(solvent)_3$[99], where three oxygen atoms of each $(AsO_4)^{3-}$ anion replace the terminal out-of-plane halogens. The ν(Re–O) stretching frequencies, E and A_1, are assigned to bands at 550 and 539 cm^{-1} respectively. Infrared studies on other oxy-ligand complexes, $Re_3X_9L_3$ (L = Ph_3PO, R_2SO[98] or[103] $[Re_3Cl_9(NO_3)_3]^{3-}$, suggest that the Re–L(O) bond is "normal" rather than long as in the case of complexes with other ligands. This may be a feature of the smaller oxygen atom which is not as sterically hindered in the terminal in-plane position as are halogens and other donor ligands. This suggests therefore that the terminal in-plane bonds are not inherently weak[98]. However, it is necessary to be cautious in the interpretation of the infrared data of such complex molecules.

Bidentate ligand complexes of Re_3X_9 have given some difficulty. Complexes of rhenium(III) halides with *o*-phenanthroline and 2,2′-bipyridyl were originally reported to give Re_2X_4(bidentate) (X = Cl, Br)[117] and $Re_2I_4(bidentate)_2$[118]. The chloro- and bromo-compounds have since been found to contain the rhenium triangle[97]. The compounds have been reprepared and appear to have the composition $Re_3X_9(bidentate)_{1.5}$ (bidentate = bipy, DTH, diphos)[100], while the original composition has also been confirmed[97]. The complexes containing 1.5 ligands are postulated as polymeric with the bidentate ligand bridging between clusters. Infrared data suggests that DTH is in the *trans* configuration. A stoichiometric *o*-phenanthroline complex cannot be obtained, which is consistent with the fact that it cannot bridge in the same way[100]. Under more-severe conditions further ligands coordinate. In these cases the bidentates are said to be acting as monodentates[100], however, it is feasible that a bidentate ligand could coordinate to one rhenium atom with a consequential ionisation of the terminal halogens.

A number of other rhenium(III) compounds which have been prepared can in some cases be reinterpreted on the basis of a rhenium triangular cluster, for example, complexes reported in refs. 7–9, 15, 17, 22, 57, 117–126. Tetraammine complexes $ReX_3\cdot 4\,NH_3$, are probably ammonolysis products[109, 119]. The eight-coordinate complex $Ag_3[Re(CN)_7NO]$ said[55] to contain NO^+ has rhenium in a formal oxidation state of three.

The triangular cluster of rhenium-metal atoms has also been postulated for certain carbonyl compounds, viz., $[Re(CO)_3SR]_3$[127, 128], $[Re(CO)_3SeR]_3$[129] and $[HRe(CO)_4]_3$[130]. The two former complexes are thought to contain SR or SeR bridges and the latter compound may or may not have hydride bridges.

D. QUADRIVALENT RHENIUM

A few aspects of the chemistry of rhenium(IV) will be reviewed and in particular the developments that have taken place during the last few years.

(i) *Rhenium(IV) chloride*

An outstanding feature of rhenium(IV) chemistry was for a long time the absence of rhenium(IV) chloride. However, it has recently been prepared[131,132] as the insoluble product of the reaction of rhenium(IV) oxide and thionyl chloride. The product has a low magnetic moment, the value 1.02 BM being obtained after correction for a temperature-independent paramagnetic component[133]. On the basis of the magnetic data the compound is postulated as being trimeric $[Re_3Cl_{12}]^0$ with a structure analogous to the tervalent-rhenium clusters. Since there are three metal *d*-electrons less, per trimer, than in $(Re_3Cl_{12})^{3-}$, it is expected from the bonding theories that the compound would have one unpaired electron per trimer[13].

It is of interest that the structure of rhenium(IV) selenide is based on triangles of bonded rhenium atoms $Re–Re_{Av} = 2.81$ Å[134]. Rhenium dioxide also contains Re–Re bonds of length 2.61 Å[135,136].

A crystalline sample of rhenium(IV) chloride has recently been obtained by a high-temperature decomposition of rhenium(V) chloride[73]. Both chemical and preliminary X-ray evidence suggest that the compound is dimeric $[Re_2Cl_8]^0$ and analogous to the dimeric rhenium(III) species[73] $(Re_2Cl_8)^{2-}$.

The different samples of $ReCl_4$ (α-$ReCl_4$ = Re_3Cl_{12} and β-$ReCl_4$ = Re_2Cl_8) are interesting in that the chemistry of rhenium(IV) chloride is analogous to that

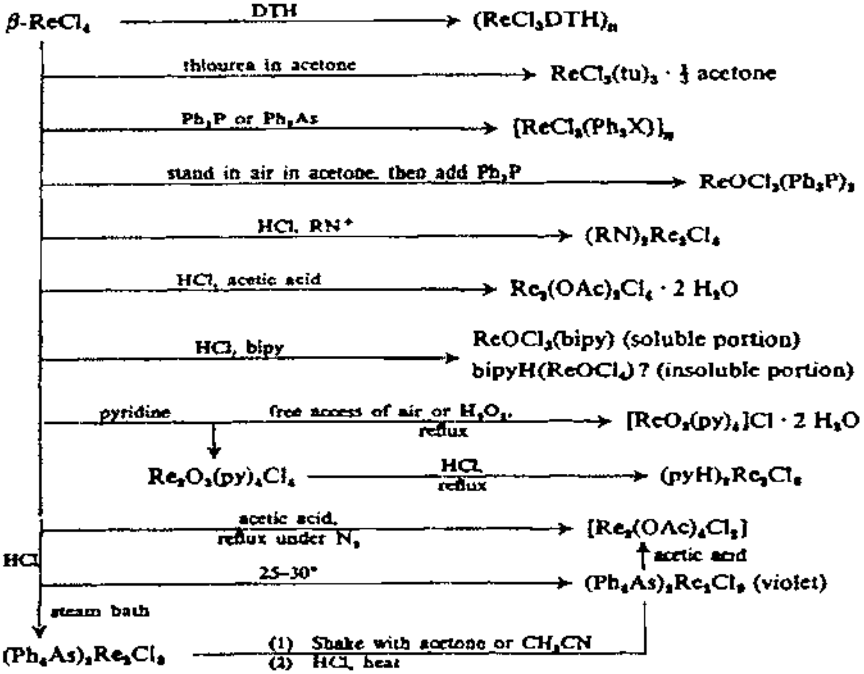


Fig. 4. Reactions of $ReCl_4$[73].

of rhenium(III). Certain of the reactions of β-$ReCl_4$ are summarised in Fig. 4. It is evident that the reaction products are either dimeric rhenium(III) species or rhenium(V) compounds. In only one case is the rhenium(IV) oxidation state stabilised, viz., $(Ph_4As)_2Re_2Cl_9$. The violet compound has a magnetic moment of 1.1 BM and apparently contains rhenium in both the ter- and quadri-valent oxidation states. The structure of the anion is probably similar to that of the dimeric $(Re_2Cl_8)^{2-}$ ion with one electron less in the filled δ-orbital giving rise to one unpaired electron per $(Re_2Cl_9)^{2-}$ ion[73].

It is of interest that, in the only case where comparison is possible, technetium(IV) does not form a metal–metal bonded structure. The halide $TcCl_4$ has an octahedral stereochemistry and is polymeric through halogen bridges[137,138]; its chemistry is typical of mononuclear tetravalent technetium[139].

(ii) Rhenium(IV) hexahalogeno-anions

The familiar rhenium(IV)-hexahalogeno salts $M^I_2ReX_6$ have been known for some time, but it is only recently that accurate spectral and magnetic data have been obtained. The preparative details and chemistry of the complexes have been extensively discussed[5,6,140–146].

Simple ligand-field theory predicts that the stereochemistry of the complex anion $(ReX_6)^{2-}$ $(Re^{IV}\text{-}d^3)$ would be regular octahedral. However, structural and spectral data provide evidence for and against this prediction. The observed magnetic moments are less than the spin-only value (3.86 BM). It is perhaps this fact that is of special interest.

X-ray diffraction studies of the salts $M^I_2ReX_6$ (X = F, Cl, Br) suggest a regular octahedral environment around the metal[140,142,147–149]. The iodo-compounds are less symmetrical and are not isomorphous with analogous chloro- and bromo-compounds[150]. The bond lengths Re–F, 2.00–2.05 Å[142] and Re–Cl, 2.37 Å[151] are reported. The ESR spectrum of the Re^{4+} cation in a K_2PtCl_6 host lattice does not show a resonance that can be attributed to a non-cubic field[152]. This has been confirmed by NQR measurements[153]; both K_2ReCl_6 and K_2ReBr_6 have one resonance line whereas K_2ReI has two (triplets), a fact which is said to

TABLE 8

RAMAN AND INFRARED DATA ON THE $(ReX_6)^{2-}$ ANIONS
$\nu_1(Re\text{–}X)$ = sym. stretch, $\nu_3(Re\text{–}X)$ = asym. stretch

		H+[154]	*Cs*+[154]	*K*+	*Et*$_4$*N*+[154]
$(ReCl_6)^{2-}$	ν_1	346[a]			
	ν_3		313	331.5, 319[155], 321[157]	314, 300
$(ReBr_6)^{2-}$	ν_1	213[a]			
	ν_3		217		

[a] Raman on H_2ReX_6 solutions.

be consistent with three crystallographically non-equivalent iodine atoms. Raman and infrared measurements[154] are consistent with an octahedral symmetry for the chloro- and bromo-compounds. Table 8 lists the reported ν(Re–X) stretching frequencies.

A number of workers have assigned the ligand-field spectral bands of the $(ReX_6)^{2-}$ anions[158–161]. The general features of the spectra are given in Table 9 together with calculated positions of the bands for K_2ReCl_6. Certain of the work has demonstrated that the spin-forbidden bands $^2E_1(\Gamma_8) \leftarrow {}^4A_2$, $^2T_1(\Gamma_6) \leftarrow {}^4A_2$ and $^2T_2(\Gamma_8) \leftarrow {}^4A_2$ have considerable vibrational fine structure with an energy separation of the order 150–300 cm^{-1}. Slight blurring of the vibrational structure is said to be due to deviations from a regular octahedral symmetry[160].

TABLE 9

LIGAND-FIELD BANDS OF THE $(ReX_6)^{2-}$ ANIONS[158,160] (in cm^{-1})

(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})).

	$^2T_1(\Gamma_8) \leftarrow {}^4A_2$	$^2E(\Gamma_8)$, $^2T_1(\Gamma_6) \leftarrow {}^4A_2$	$^2T_2(\Gamma_7) \leftarrow {}^4A_2$	$^2T_2(\Gamma_8) \leftarrow {}^4A_2$	$^4T_2(^4\Gamma_5) \leftarrow {}^4A_2$	$^4T_1(^4\Gamma_4) \leftarrow {}^4A_2$	*ligand-field splitting parameter*
$(ReF_6)^{2-}$	9,080	10,890[a]	17,670[a]	18,910	32,800	37,500	32,800
$(ReCl_6)^{2-}$	7,600	9,400[a]	14,140[a]	15,340	28,010		29,000
$(ReBr_6)^{2-}$	7,260	9,170[a]	13,230	14,860			28,000
$(ReI_6)^{2-}$	7,350	8,470					26,000
$(ReCl_6)^{2-}$ (calc.)	7,895	8,798, 9,167	14,653	15,723	34,458	38,546	

[a] vibrational structure.

When the salt K_2ReCl_6 is subjected to high pressures all the bands shift to lower energy[162,163] a new band appearing at 16,100 cm^{-1}; this was assigned to a $^2T_2(\Gamma_8) \leftarrow {}^4A_2$ transition. An alternative interpretation[164] considers that the two bands in the region 14,200 and 15,700 cm^{-1}, as well as the new band, are all $^2T_2(\Gamma_8) \leftarrow {}^4A_2$ transitions. The third band only arises under pressure as a consequence of a low-symmetry component splitting the $^2T_2$ state. The absence of the 16,100 cm^{-1} band at atmospheric pressure suggests a regular symmetry since only two $^2T_2(\Gamma_8) \leftarrow {}^4A_2$ transitions would be expected in this case. In molten LiCl–KCl, the two bands $^2T_2(\Gamma_8) \leftarrow {}^4A_2$ and $^2T_1(\Gamma_8) \leftarrow {}^4A_2$ are split suggesting some tetragonal distortion. This is said to be due to an anion–cation interaction and is only observed for strongly-polarising cations[165]. It is clear that the spectroscopic evidence provides conflicting information about the regularity of the octahedral stereochemistry.

The magnetic moments and Weiss constants for a number of $M^I{}_2ReX_6$ compounds are listed in Table 10. The main reason suggested for the reduction in the magnetic moment below 3.86 BM is an antiferromagnetic interaction. The Curie

TABLE 10

MAGNETIC DATA FOR M_2ReX_6 COMPLEXES

Compound	*Range of magnetic moments reported B.M. (293–300 °K)*	*θ (°K)*	*Ref.*
K_2ReF_6[a]	2.98–3.32	30–40	141, 142, 166, 167
	3.25, 3.43 (aq. soln.)		166, 167
Rb_2ReF_6	3.17	−25	142
Cs_2ReF_6	3.24, 3.32	20, 24	142, 167
$BaReF_6$	3.41		141
K_2ReCl_6[a]	3.25–3.33	55–88	13, 166–170
	3.5 (dil. HCl soln.)		166, 167
	3.62 (in K_2PtCl_6)		169
Cs_2ReCl_6	3.35	50	167
$(NH_4)_2ReCl_6$	3.32		13
$(Me_4N)_2ReCl_6$	3.66	−20	171
$(Et_4N)_2ReCl_6$	3.62	−1	171
$(pyH)_2ReCl_6$	3.58	14	167
$(quinH)_2ReCl_6$	3.48, 3.54	13	13, 167
$(tolH)_2ReCl_6$	3.50	35	149
$(bipyH)_2ReCl_6$	3.66		13
K_2ReBr_6[a]	3.19, 3.20	105	166, 170
	3.6 (dil. HBr soln.)		166, 167
Cs_2ReBr_6	3.36	80	167
$(pyH)_2ReBr_6$	3.69		13
$(quinH)_2ReBr_6$	3.76		13
$(bipyH_2)ReBr_6$	3.74		13
K_2ReI_6[a]	3.32, 3.57	100	166, 167, 170
	3.55 (9*N* HI soln.)		167
Cs_2ReI_6	3.22	135	167
$(NH_4)_2ReI_6$	3.27		13

[a] High values of the magnetic moments of these compounds and Rb_2ReI_6 are reported in ref. 172.

points[168] for K_2ReCl_6 and K_2ReBr_6 are 12.4 °K and 15.3 °K which correspond with heat-capacity transitions at 11.9 °K and 15.2 °K[168,173,174] respectively. It is possible that a structural change from the K_2PtCl_6-type lattice to one of lower symmetry occurs at low temperatures. This is indicated by a spontaneous heat evolution at 150 °K when K_2ReBr_6 is cooled[174]. Neutron diffraction studies on K_2ReCl_6 indicate a face-centred cubic lattice at 295 °K and a primitive lattice below 70 °K but still retaining an essential octahedral symmetry around the metal atom. At 4.2 °K the structure is an ordered antiferromagnetic consisting of ferromagnetic alignment in the 001 planes with adjacent planes aligned antiparallel[175].

The magnetic moments of the compounds are increased when diluted. Dilution has been achieved by dissolving the compounds in an appropriate solvent[166,167] or in the solid state by placing the compounds in a K_2PtCl_6 lattice[169,176]. The magnetic moments are also increased in compounds containing large cations, due to a similar dilution effect[13,167].

The antiferromagnetism appears to increase in the order $F < Cl < Br < I$ which has been related to an increasing metal–halogen covalent bonding[13,167]. In the case of K_2ReCl_6 the exchange is said to occur through d_π–p_π Re–Cl bonding and also through p_π–p_π interaction between neighbouring chlorine atoms[176]. The type of interaction appears to be the same for the chloro- and bromo-compounds[168]. The high electronegativity of fluorine and the close F–F distance act in opposition in their effect on the super-exchange[168] in K_2ReF_6.

Independent estimates of the spin–orbit coupling parameter ζ of Re^{4+} vary considerably: 1460 cm^{-1}[168] 3,300 cm^{-1}[167], 2,300 cm^{-1}[159] and 2,400 cm^{-1}[177].

(iii) Rhenium(IV) oxo-complexes

The oxy-bridged complex $K_4[Re_2OCl_{10}]$ has been known for some time and is obtained as an intermediate in the reduction of potassium perrhenate[178] to K_2ReCl_6. It is a 4:1 electrolyte and is weakly paramagnetic indicating spin coupling of the rhenium d^3-electrons. The compound undergoes an unusual reaction with hydrogen peroxide leading to a blood-red compound which appears to contain a additional oxygen atom, which can be lost reversibly[179–182]. Spin coupling between the rhenium atoms is removed in the oxygenated complex, the compound $(quinH)_4Re_2O_2Cl_{10}$ having a magnetic moment of 3.5 BM[179].

The structure of $K_4[Re_2OCl_{10}]$ has been determined; it consists of two octahedrons linked through a common oxygen atom[183]. The Re–O bond length is 1.86 Å suggesting double bonding at least, and as expected for maximum stability the Re–O–Re system is collinear[184]. The application of the bonding theory used to explain the diamagnetism of the ruthenium complex[185], $K_4[RuOCl_{10}]$, is not adequate for the rhenium compound as it would leave two unpaired electrons per dimer[178,186]. A different approach allots the rhenium orbitals s, p_x, p_y, $d_{x^2-y^2}$, d_{yz} and d_{xy} for the six σ-bonds to each rhenium. The remaining orbitals d_{z^2}, p_x, d_{xz} can combine with the p_x and p_y orbitals of the oxygen to give the molecular orbitals $E_g^{(b)}$, E_u, A_{1g}, A_{2u}, $E_g^{(a)}$ which accommodate the 10 electrons (3 per Re and 4 from the O) in a spin-paired arrangement. (The scheme will also account for the diamagnetism of the ruthenium complex)[186,187].

A number of dibasic carboxylic-acid complexes of rhenium(IV) also contain the Re–O–Re system. The compounds $M_4[Re_2(OH)_6L_2O]$ (L = oxalate, citrate, tartrate or gallate), $M_4[Re_2(OH)_2(C_2O_4)_4O]$ and $M_4[Re_2(OH)_2(EDTA)O]$ are diamagnetic and molecular-weight data confirms their dimeric structures[188–193]. The electronic-spectral bands of the complexes have been assigned to ligand-field transitions, the ground state being designated as a $^4A_{2g}$ term. It is not clear why this is so as the compounds are diamagnetic and completely spin-paired through Re=O multiple bonding. The position of the bands changes with the number of coordinated hydroxo-ligands[194,195].

An alternative formulation of the compounds could be in terms of tervalent dinuclear rhenium species, i.e., $K_4[Re_2^{IV}(OH)_2(C_2O_4)_4O]$ as $K_4[Re^{III}(OH)_2(C_2O_4)_4]$. However, treatment of the complexes with conc. hydrochloric acid does not give the blue $(Re_2Cl_8)^{2-}$ anion[78].

Salicylic acid forms a monomeric compound $Tl_2[Re(OH)_4(sal)]$ which is parmagnetic, $\mu = 3.56$ BM[191]. The hydroxy complexes, $K_2Re(OH)Cl_5$[178] and $(Et_4N)_2Re(OH)I_5$[196], have also been prepared. The latter compound has a magnetic moment of 3.57 BM.

Other coordination compounds of rhenium(IV) are listed in Table 11 together with magnetic data and preparative details. The compounds, in general, have an octahedral stereochemistry, and have magnetic moments slightly less than the spin-only value. The complexes formed from the tetraiodide are paramagnetic, indicating that the Re–Re interaction, which presumably accounts for the diamagnetism of the halide[20], has been destroyed. The dimeric carboxylic-acid complexes have been formulated with a mixture of oxy-, chloro-, and carboxylate bridges[71,72] but, in view of the common occurrence of dimeric rhenium(III) carboxylate complexes containing a direct Re–Re bond and bridging carboxylate

TABLE 11

RHENIUM(IV) COMPLEXES

Compound	*Magnetic moment*	*Comments (preparation)*	*Ref.*
$ReCl_4(Ph_3P)_2$	3.84	From $ReOX_3(Ph_3P)_2$ or $ReH_3(Ph_3P)_2$	72, 197–200
$ReBr_4(Ph_3P)_2$			197–199
$ReI_4(Ph_3P)_2$	—	ReI_4 + phosphine	117, 121
$ReCl_4(Ph_3P)(py)$		$ReCl_4(Ph_3P)$ + pyridine	72
$ReCl_4(py)_2$	3.3	pyrolysis of $(pyH)_2ReX_6$	10, 201
$ReBr_4(py)_2$			202
$ReI_4(py)_2$	3.7	ReI_4 + pyridine	117, 122
$ReCl_4(Et_2PhP)_2$	3.64	pyrolysis of $(Et_2PhPH)_2ReX_6$ or oxidation of $ReX_3(Et_2PhP)_3$	49, 200
$ReBr_4(Et_2PhP)_2$			200
$ReCl_4(bipy)$	3.41, 3.5	pyrolysis of $(bipyH)_2ReX_6$	13, 203, 204
$ReBr_4(bipy)$	3.48		13, 204
$ReI_4(o\text{-}phen)$		ReI_4 + *o*-phenanthroline	121
$[ReCl_5py]^-$	3.76, 3.45	$(pyH)_2ReX_6$ + pyridine at 190°	13, 205
$[ReBr_5py]^-$	3.66		13, 205
$Re(diarsine)Cl_4$	3.46	halogenation of $Re(CO)_3(diarsine)X$	58
$Re(diarsine)Br_4$	3.42		58
$Re_2Cl_4(acac)_4$	2.9 (soln.)	$ReCl_4(Ph_3P)_2$ + acetylacetone or $ReCl(acac)_2Ph_3P$ + acetylacetone	52, 72
$[ReOCl(OAc)]_2$	diamagnetic	Re_3Cl_9 + AcOH in air or oxygen	71
$Re_2OCl_5(OAc)(Ph_3P)_2$	diamagnetic	*trans*-$ReOX_3(Ph_3P)_2$ + AcOH at 120° in air	72
$Re_2OBr_5(OAc)(Ph_3P)_2$	diamagnetic		72
$ReO(SCN)_2(py)_3$		redn. $KReO_4$ with $SnCl_2$ and then add pyridine	206
$K_4[ReO_2(CN)_4]$		K_2ReCl_6 + KCN	54

ligands it is possible that these are similar compounds of quadrivalent rhenium. Both $Re_2OCl_2(O_2CR)_2$ and $Re_2OX_5(O_2CR)(Ph_3P)_2$ can in fact be reformulated on this basis.

E. QUINQUEVALENT RHENIUM

Until recently the chemistry of pentavalent rhenium was confined to a few compounds. Some of these, such as rhenium(V) chloride and the dioxo-complexes $[ReO_2(SCN)_4]^{3-}$ and $[ReO_2(en)_2]^+$ have been known for some time. Others such as the eight-coordinate cyanide[55,207] $[Re(CN)_8]^{3-}$ and diarsine $[Re(diarsine)_2X_4]^-$ $(X = Cl, Br)$[208] complexes are of more recent origin.

Since 1960 the scene has changed, as a number of pentavelent-rhenium complexes have been isolated in which the rhenium atom is associated with one oxo-ligand. The first examples of these compounds were wrongly interpreted as either rhenium(III) or -(II) complexes, the oxo-ligand not being detected[9,19]. The chemistry will be reviewed according to the various types of compounds known.

(i) Mono-oxo complexes

Complexes of type $ReOX_3L_2$. The reduction of perrhenic acid with triphenylphosphine in ethanol and hydrochloric acid gives rise to the complex $ReOCl_3(Ph_3P)_2$[15-17,57]. It is isolated in two isomeric forms, one green, the other yellow[57]. Diethylphenylphosphine has also been used as a ligand and it gives an analogous compound $ReOCl_3(Et_2PhP)_2$ also in two isomeric forms, blue and green[16,17]. Other preparative routes involve treating the anion $(ReOX_4)^-$ with ligand L (Ph_3P or Ph_3As) in acetonitrile[209] or using the oxo–alkoxide complexes $ReO(OR)X_2L_2$ (see below) as starting materials[57]. The rate of formation of the compounds $ReOX_3(PR_3)_2$ has been related to the electronegativity of the group R attached to the phosphorus[17]. The compounds characterised to date are listed in Table 12.

The complexes are six-coordinate and diamagnetic[57]. The latter property is unexpected for a d^2 configuration in a simple octahedral environment. However, the short Re–O bond reduces the octahedral symmetry to C_{4v} in which a low lying b_2 orbital is available for accommodating the two electrons[58]. The diamagnetism can also be accounted for in terms of Re–O multiple bonding (see below).

The triarsine TAS appears to form seven-coordinate compounds[25] if all the arsenic atoms are assumed bonding. Conductivity studies indicate that the bromo-compound is probably six-coordinate in nitromethane solution.

The number of isomers expected for the complexes $ReOX_3L_2$ is three. The green isomer of $ReOCl_3(Et_2PhP)_2$ is *trans* with a dipole moment of 1.7 D, while

TABLE 12

RHENIUM(V) $ReOX_3L_2$ COMPLEXES

Compound	*Colour*	*Melting point (°C)*	*ν(Re–O)*	*Dipole moment (D)*	*Ref.*
trans-$ReOCl_3(Ph_3P)_2$	yellow	211–214	969	2.5	15–17, 57, 209
$ReOCl_3(Ph_3P)_2$	green		981		57
trans-$ReOBr_3(Ph_3P)_2$	yellow	181–183	981		17, 57, 209
$ReOI_3(Ph_3P)_2$			982		57
$ReO(SCN)_3(Ph_3P)_2$	brown	132–136	958		16, 17
trans-$ReOCl_3(Et_3P)_2$	green	164–174	973	1.7	16, 17
cis-$ReOCl_3(Et_3P)_2$	blue	126–129	982		16, 17
trans-$ReOCl_3(n\text{-}Pr_3P)_2$	green	130–134	985	1.3	16, 17
cis-$ReOCl_3(n\text{-}Pr_3P)_2$	blue	110–115			200
trans-$ReOCl_3(Et_2PhP)_2$	green	166–169	978	1.7	16, 17
cis-$ReOCl_3(Et_2PhP)_2$	blue	157–160	977	10.8	16, 17
cis-$ReOBr_3(Et_2PhP)_2$	green	171–175			200
cis-$ReOI_3(Et_2PhP)_2$	brown	171.5–174	97[illegible]		17
$ReO(SCN)_3(Et_2PhP)_2$	brown	138–142	964		16, 17
$ReOCl_3[P(CH_2Cl)_3]_2$	red	156–161	975		17
$ReOCl_3(diphos)$	blue	257–262	976		17
cis-$ReOCl_3(diphos)$	green		980		50
$ReOCl_3[C_2H_4(PEt_2)_2]$	blue	240–243	984		16, 17
$ReOCl_3(Ph_3As)_2$			967		15, 57
$ReOBr_3(Ph_3As)_2$			980, 974		57, 209
$ReOCl_3(Et_2PhAs)_2$	turquoise	120–122	978		16, 17
cis-$ReOCl_3(Me_2PhAs)_2$	blue	170–175			200
$ReOCl_3(diarsine)$	green		991, 970		58
$ReOCl_3(TAS)$	green	284–285	980	seven-	25
$ReOBr_3(TAS)$	yellow-green	275–276	971	coordinate	
$ReOCl_3(Ph_3Sb)_2$			976		57
$ReOBr_3(Ph_3Sb)_2$			969, 973		57
$ReOCl_3(py)_2$					210
$ReOBr_3(py)_2$ (reported as $ReBr_3(py)_2$)					211
$ReO(CNS)_3(py)_2HF \cdot H_2O$					212
$ReOCl_3(bipy)$	violet				203
$ReOCl_3(bipy)$	green				

the blue isomer is one of the two *cis* forms with a dipole moment of 10.8 D[16, 17]. A violet "isomer" has since been found to be a mixture[200] of violet *trans*-$ReCl_4(Et_2PhP)_2$ and green *trans*-$ReOCl_3(Et_2PhP)_2$. The structure of the *trans*-complex, $ReOCl_3(Et_2PhP)_2$ has been determined by X-ray diffraction techniques[213]. The bond lengths are: Re–Cl, 2.41, 2.47, 2.43 Å; Re–P, 2.45, 2.48 Å, and Re–O, 1.60 Å. The rhenium atom does not lie in the $P_1P_2Cl_3Cl_4$ plane (Fig. 5) but protrudes slightly towards the oxygen atom. The Re–P bond length is said to be "normal" with no evidence for d_π–d_π bonding. On the other hand the Re–O bond is very short suggesting a bond order approaching three. The rhenium atom can bond the six ligands with σ-bonds using its valence orbitals $5d_{z^2}$, $5d_{x^2-y^2}$, $6s$, $6p_x$, $6p_y$, and

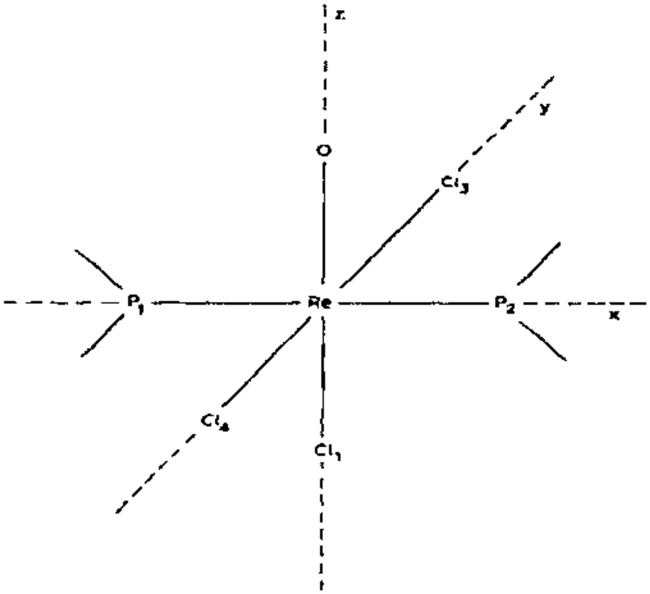


Fig. 5. Stereochemistry of the $ReOCl_3P_2$ entity in $ReOCl_3(R_3P)_2$.

$6p_z$. In addition the rhenium and oxygen atoms can take part in $p_{x\pi}$–$d_{xz\pi}$ and $p_{y\pi}$–$d_{yz\pi}$ bonding giving an effective triple bond, $Re \equiv O$. The unused d_{xy} orbital on the rhenium will accommodate the two *d*-electrons giving a spin-paired complex. It is surprising that the rhenium atom can accept so much charge without some removal by back π-bonding to the phosphorus atoms, especially as the filled $d_{xy}(b_2)$ orbital is correctly placed for such bonding. It is of doubtful validity to argue about bond order from bond length[213], when comparable data are limited or entirely absent, as in the case of the Re–P bond. One can say from the above bonding considerations that Re–P π-bonding is very likely.

The high bond order of the Re–O bond is also indicated by the position of the ν(Re–O) assymetric stretch in the infrared, which is assigned to a sharp intense band in the range [15–17,25,57,58,214] 958–985 cm^{-1}. In addition it is known that the oxo-ligand cannot be protonated whereas protonation is possible for the *trans*-dioxo-complexes where the Re–O bond order is lower[57] (see below).

Complexes of the type $ReO(OR)X_2L_2$ (Table 13). The formation of the pentavalent-rhenium-alkoxo complexes, $ReO(OR)X_2L_2$, is closely related to the formation of the complex type discussed above. The formation of rhenium(V)–alkoxo complexes reflects the strong affinity of pentavalent rhenium for oxygen. The affinity is sufficient to cause cleavage of the hydroxy bond RO–H.

The reduction of perrhenic acid with triphenylphosphine in ethanol in the presence of either hydrobromic or hydroiodic acid gives the complexes

TABLE 13

RHENIUM(V) $ReO(OR)X_2L_2$ COMPLEXES

Compound	*Colour*	*Melting point (°C)*	*$\nu(Re{=}O)$ (cm^{-1})*	*$\delta(OCH_2)$ (cm^{-1})*	*Ref.*
$ReO(OMe)Cl_2(Ph_3P)_2$	grey	200–203	946		16, 17, 57
$ReO(OEt)Cl_2(Ph_3P)_2$	grey	199–203	946	909	16, 17, 57
$ReO(OEt)Cl_2(Ph_3P)_2$	green		953	910	57
$ReO(OCH_2Ph)Cl_2(Ph_3P)_2$	grey	178–182	943	909	16, 17
$ReO(OMe)Br_2(Ph_3P)_2$			944, 933		57
$ReO(OEt)Br_2(Ph_3P)_2$	grey-brown	147–149	940	909	15–17, 57
$ReO(OMe)I_2(Ph_3P)_2$			944, 931		57
$ReO(OEt)I_2(Ph_3P)_2$	green	155–165	946	909	15–17, 57
$ReO(n\text{-}PrO)I_2(Ph_3P)_2$	olive-green	150–160	921	921	17
$ReO(OC_2H_4OMe)I_2(Ph_3P)_2$	olive-green	153–159	932	918 (sh)	17
$ReO(OMe)Cl_2(Et_2PhP)_2$	violet	132–136	937		17
$ReO(OEt)Cl_2(Et_2PhP)_2$	violet	135–139	951	916	17
$ReO(OCH_2Ph)Cl_2(Et_2PhP)_2$	violet	168–172	935	906	17
$ReO(OMe)Br_2(Et_2PhP)_2$	brown-violet	132–136			200
$ReO(OEt)Cl_2(EtPh_2P)_2$	purple	163–167	942	913	17
$ReO(OC_2H_4OMe)Cl_2(n\text{-}Pr_2PhP)_2$	lilac	159–162	958	917	17
$ReO(OMe)Cl_2[P(CH_2Cl)_3]_2$	purple	138–142	943		17
$[ReO(OEt)I(Ph_3P)_2(p\text{-}MeC_6H_4NC)]X$ 1:1 electrolytes formulated as $[ReI(Ph_3P)_2(p\text{-}MeC_6H_4NC)]X$					215

$ReO(OEt)X_2(Ph_3P)_2$ (X = Br, I). The corresponding chloride is obtained when hydrazine hydrochloride is used as the reducing agent in anhydrous conditions[15–17, 57]. Alternatively, preparation is achieved by boiling the complexes $ReOX_3L_2$ in the appropriate alcohol[57]. Certain alkoxo-ligands are replaceable by others, e.g., 2-methoxyethoxide replaces[17] n-PrO$^-$ and EtO$^-$. The compounds are diamagnetic[57], presumably for the same reason as for the $ReOX_3L_2$ complexes.

The complexes $[Re(Ph_3P)_2(p\text{-}MeC_6H_4NC)I]X$ ($X = I^-$, Ph_4B^-, ClO_4^-, and I_3^-), which are 1:1 electrolytes[215] are prepared from "$Re(Ph_3P)_2I_2$" which is in fact $ReO(OEt)(Ph_3P)_2I_2$. Hence they may be reformulated as $[ReO(OEt)(Ph_3P)_2(p\text{-}MeC_6H_4NC)I]X$.

The stereochemical position of the alkoxo-ligand in the complexes is not definitely known as dipole-moment measurements are precluded by rapid interconversion of the isomers[52]. However, infrared data suggest that the oxo- and alkoxo-ligands are *trans* to each other[15–17, 57, 214]. The Re–O stretch is now found at a lower frequency, in the range 930–958 cm^{-1}. The oxo-ligand is said to have a strong *trans*-directing influence[214].

The complexes $ReO(OEt)X_2(Ph_3P)_2$ (X = Cl, Br, I) when treated with acetylacetone give green products $ReO(acac)X_2(Ph_3P)_2$. The diamagnetic compounds have bands in the infrared assignable to a ν(Re–O) stretch and they are apparently seven-coordinate. However, the compounds have not been obtained pure as they react with further acetylacetone to give tervalent-rhenium complexes[52].

Halogeno-salts of rhenium(V) oxo-compounds. Two classes of salts are at present known, viz., $(ReOX_5)^{2-}$ and $(ReOX_4)^-$. The latter type is sometimes associated with a neutral ligand.

The former type have been infrequently studied since the early work on K_2ReOCl_5. Recently the complexes $(quinH)_2ReOX_5$ (X = Br, I) have been prepared by reducing potassium perrhenate with sulphur dioxide[216]. The compounds, like K_2ReOCl_5, are diamagnetic and the bromo-compound has been shown to be mononuclear.

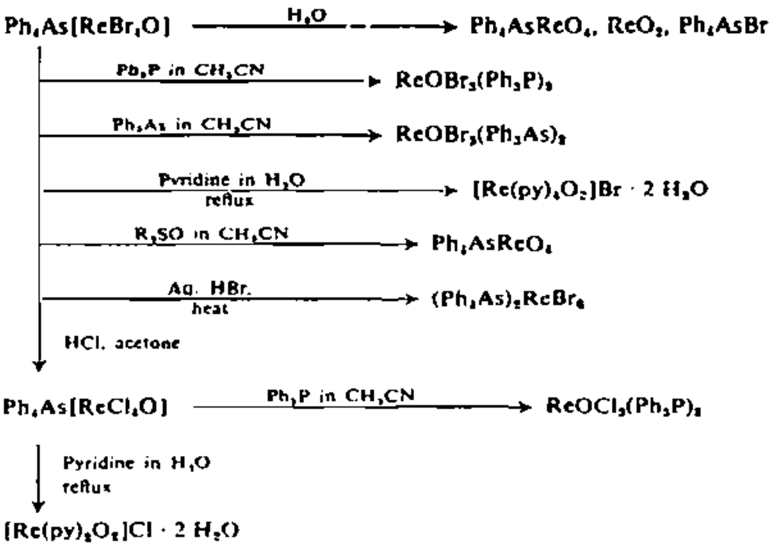
More recently[196] the complex Cs_2ReOCl_5 was isolated from a solution of rhenium pentachloride in hydrochloric acid. This compound is reported to have a magnetic moment of 2.85 BM which is surprising in view of the usual diamagnetic behaviour of rhenium(V) oxo-compounds. A magnetic moment of 1.3 BM is predicted for a regular octahedral rhenium(V) complex; the spin-only value is reduced by spin–orbit coupling. Some distortion from octahedral symmetry would increase the value until a point is reached where the new C_{4v} symmetry would give a change over to a spin-paired complex both electrons being accommodated in a stable b_2 orbital. Either there is an anomaly with the caesium compound or the compound has a different formulation. There is disagreement in the literature as to the existence of the potassium salt[114,217].

The halogeno-complex type $(ReOX_4)^-$ or $(ReOX_4L)^-$ has only recently been isolated. Treatment of $ReOCl_3(Ph_3P)_2$ with hydrogen chloride in benzene gives the salt $Ph_3PH[ReOCl_4Ph_3P]$[57]. Alternatively either reduction of perrhenate with zinc in conc. sulphuric acid[209,218] or aerial oxidation of rhenium(III) bromide in hydrobromic acid can be used[115]. Some of the known compounds are listed in Table 14. The complexes are reactive[209] and undergo a variety of reactions which are listed in Fig. 6. The compounds are diamagnetic[209,218] and are 1 : 1 electrolytes though some further electrolytic dissociation occurs for certain compounds[209].

TABLE 14

RHENIUM(V) $(ReOX_4)^-$ COMPLEXES

Compound	*Colour*	*ν(Re–O) (cm^{-1})*	*Other data*	*Ref.*
$Ph_3PH[ReOCl_4Ph_3P]$	green	979	ν(P–H) 2405 cm^{-1}	57
$Ph_4As[ReOCl_4]$	cream	1000	1 : 1 electrolyte	209, 218
$Cs[ReOBr_4]$	red-orange	955		114, 209, 218
$Et_4N[ReOBr_4 \cdot \frac{1}{2} H_2O]$	red-orange	1004	slightly high 1 : 1 electrolyte	209
$Et_4N[ReOBr_4 \cdot H_2O]$		1005		114, 218
$n\text{-}Bu_4N[ReOBr_4]$	coral-red	1010	1 : 1 electrolyte	209
$Ph_4As[ReOBr_4CH_3CN]$	coral-red			209, 218, 219
$Ph_4As[ReOBr_4]$	coral-red	1000	slightly high 1 : 1 electrolyte	209, 218
$pyH[ReOBr_4]$	golden-brown	1000		209
$n\text{-}Bu_4N[ReOI_4]$	purple-back			209



$R = p\text{-}CH_3C_6H_4$, C_6H_5 or $C_6H_5CH_2$

Fig. 6. Reactions of $(ReOX_4)^-$ ions[209].

The infrared spectra of the compounds are interesting in that the ν(Re–O) stretching mode is at a high energy of 1000 cm^{-1} (955 cm^{-1} for Cs(ReOBr$_4$)) suggesting a strong Re–O bond[209, 218]. The value is higher than assigned for the complexes $ReOX_3L_2$ (958–985 cm^{-1}) where a similar mono-oxo-ligand occurs. The Re–O bond length in the complex $ReOCl_3(Et_2PhP)_2$ is however, shorter than in the $(ReOBr_4L)^-$ anion (see Table 15) which is not consistent with the lower stretching frequency. The accumulated infrared data available for both types of complexes strongly suggest that the assignments are correct. The situation needs investigating further as there may be other reasons for the different Re–O bond lengths. The low value of the ν(Re–O) stretch for $CsReOBr_4$ has been attributed to some Cs–O interaction[209, 218].

Two salts have been investigated by X-ray diffraction techniques, viz.[219], $Ph_4As[ReOBr_4CH_3CN]$ and[125] $Et_4N[ReOBr_4H_2O]$. The $ReOX_4$ unit is square

TABLE 15

STRUCTURAL DATA ON $[ReOBr_4L]^-$

	$Ph_4As[ReOBr_4CH_3CN]$[219]	$Et_4N[ReOBr_4 \cdot H_2O]$[125]
Re–Br	2.43–2.51	2.51
Re–O	1.73	1.71
Re–L	2.31 (CH_3CN)	2.32 (H_2O)
Br–Re=O	92–104°	~98°

pyramidal (C_{4v} symmetry) with the oxygen atom at the apex. The sixth ligand CH_3CN or H_2O is weakly bonded (~0.3 Å greater than expected for a normal bond) *trans* to the oxo-ligand. The structural data are listed in Table 15. The Re–Br distance, comparable to that found in other compounds of rhenium, is independent of the oxidation state of the metal. The Re–O bond is very short, indicative of a triple bond (Re–O calc., 2.04 Å; Re=O in $(Re_2OCl_{10})^{4-}$, 1.86 Å). The bonding can be described in terms of a molecular-orbital theory similar to that used for the complexes $ReOX_3L_2$.

(ii) Di-oxo complexes

A number of dioxo-complexes have been prepared and these are listed in Table 16. The best-known and well-defined compounds are those containing the ionic species $[ReO_2(CN)_4]^{3-}$, $[ReO_2(en)_2]^+$, and $[ReO_2(py)_4]^+$.

The cyanide complex can be prepared either by treating rhenium(IV) oxide with hydrogen peroxide in the presence of cyanide or by the reduction of the perrhenate ion with hydrazine hydrate[237–239].

The addition of excess ethylenediamine to potassium rhenium(IV) chloride produces the ethylenediamine complex. The preparation of the pyridine complex is very similar. Pyridine reacts with a number of rhenium compounds such as $ReOX_3L_2$[57], $(ReOX_4)^-$ [209], $(ReOCl_5)^{2-}$ [240], $(ReCl_6)^{2-}$ [214], $(ReO_4)^-$ [210], or $ReBr_3$[211], to give the pentavalent compound.

The three dioxo-species, $[ReO_2(CN)_4]^{3-}$, $[ReO_2(en)_2]^+$, and $[ReO_2(py)_4]^+$, have strong bands in the infrared in the range 780–825 cm^{-1} which have been assigned to the ν(Re–O) stretching frequency[57,214,239]. The low value of this mode of vibration has been attributed to the *trans* effect of the oxo-groups upon each other. The removal of the *trans* effect in the protonated complex, $[ReO(OH)(en)_2]^{2+}$, is reflected in an increase of the ν(Re–O) stretching frequency to[57] 981 cm^{-1}. The cyanide $K_3ReO_2(CN)_4$ has one $\nu(C{\equiv}N)$ stretching frequency[239] at 2110 cm^{-1}.

Compounds containing the dioxo-species are diamagnetic[13,217,233] a fact which can be readily explained in terms of multiple bonding between the rhenium and oxo-ligands[242]. The four donor ligands other than the oxo-ligands can bond using dsp^2 hybrids of the rhenium atom and the oxo-groups form σ-bonds with rhenium dp hybrids. The empty d_{yz} and d_{zx} orbitals can overlap with filled p orbitals of each oxygen giving effectively one π-bond per Re–O group. This leaves the d_{xy} orbital free for accommodating the two d-electrons. A Re–O bond order of two is confirmed by the results of the structure determination carried out on[243] $K_3ReO_2(CN)_4$. The oxo-ligands are shown to be *trans* and the Re–O bond length 1.87 Å. The bond length is comparable to that found in $K_4[Re_2OCl_{10}]$ where Re–O double bonding is also proposed. The bond lengths Re–C, 1.91 Å and C–N, 1.5 Å, have also been reported.

Protonation reactions of the ethylenediamine and pyridine complexes have been widely studied. In the case of the ethylenediamine-complex anion the reaction scheme is reported to be

$$\underset{\text{yellow}}{[ReO_2(en)_2]^+} \xrightarrow{H^+} \underset{\text{red-violet}}{[ReO(OH)\,(en)_2]^{2+}} \xrightarrow{H^+} \underset{\text{blue}}{[Re(OH)_2(en)_2]^{3+}}$$

in the initial stages[217, 233]. Further acidification leads to replacement of an ethylenediamine ligand according to the reactions[217]:

$$[Re(en)_2O(OH)]^{2+} \xrightarrow{2\,M\ HCl} \underset{\text{dark green}}{[Re(en)Cl_2O(OH)]},$$

and

$$[Re(en)_2(CH)_2]^{3+} \xrightarrow{\text{conc. HCl}} \underset{\text{green}}{[Re(en)Cl_2(OH)_2]^+}.$$

Ultimately all the amine can be replaced and products formulated as $Cs[ReCl_4(OH)_2]$ and $Ph_4As[ReCl_4(OH)_2]$ have been isolated. A band in the infrared at 960–1010 cm^{-1} used in evidence for the presence of ν(Re–OH) stretch[217], in the latter compounds is more probably due to a $\nu(Re{=}O)$ stretching frequency, and the compounds should be reformulated as[209] $Cs[ReCl_4O(H_2O)]$ and $Ph_4As[ReCl_4O(H_2O)]$. It is very likely that the dihydroxy-compounds mentioned in the first and third equations above are also mono-oxo-complexes $[ReO(H_2O)\,(en)_2]^{3+}$ and $Re[O(H_2O)Cl_2(en)]^+$, respectively[287].

The protonation reactions of the ethylenediamine-complex anion have been interpreted on an entirely different basis[244]. The yellow starting material is formulated as $[Re(OH)_2(en^-)_2]^+$ and protonation is said to occur on the en^- anion. The main line of evidence for this scheme is the presence of a broad band in the infrared spectra of the compounds at approximately 3500 cm^{-1} attributed to the ν(O–H) stretching frequency. This evidence is inconclusive and at present there seems no reason why this proposal should supersede the first one described above. The ultimate product proposed in the latter work is the anion $(ReOCl_5)^{2-}$.

Confusion over the nature of the protonation reactions of the pyridine complex have existed for some time[203, 240, 241]. However, the reaction appears to go in a very similar way to that of the ethylenediamine complex but at a slower rate[217]. It has been suggested recently that similar protonation reactions occur when the dioxocyanide complex is treated with acid[245, 246].

The other dioxo-complexes listed in Table 16 will not be discussed further as in most cases little information is available.

Pyridine forms further compounds with rhenium(V)[241, 247, 248], the most interesting of which is the dimeric oxybridged compound $Re_2O_3Cl_4(py)_4$[248]. It is

TABLE 16

RHENIUM(V)–DIOXO COMPLEXES

Compound	*Comments*	*Ref.*
$[ReO_2(CNS)_4]^{3-}$	evidence for solid compound doubtful	220–229
$[ReO_2(CN)_4]^{3-}$	$\nu(Re{=}O)$ 780 cm^{-1} Re=O = 1.87 Å	see text
$[ReO_2(en)_2]^+$	$\nu(Re{=}O)$ 820 cm^{-1}	see text
$[ReO_2(amine)_4]^+$	monodentate, CH_3NH_2, $C_2H_5NH_2$	217, 230
$[ReO_2(amine)_2]^+$	bidentate 1,2- and 1,3-propyldiamine, biguanide	231–234
$[ReO_2(py)_4]^+$	$\nu(Re{=}O)$ 825 cm^{-1}	57, 211, see text
$[ReO_2(diphos)_2]^+$	$\nu(Re{=}O)$ 789 cm^{-1}	50
$[ReO_2Br_2]^+$	$\nu(Re{=}O)$ 935, 875 cm^{-1}	114
$[ReO_2(thiourea)_4]^+$		224, 235, 236

obtained as green needles from the reaction of rhenium(V) chloride and pyridine in the presence of water. In Fig. 7 a possible reaction scheme is suggested. It appears from more recent work that "aged" rhenium(V) chloride is necessary[74]. The compound is diamagnetic and a non-electrolyte. A bipyridyl product, $Re_2O_3Cl_4(bipy)_2$, can also be obtained; this must have a *cis* configuration. The dimeric pyridine complex has also been obtained by oxidation of the dimeric rhenium(IV) chloride in the presence of pyridine (Fig. 4)[73]. A band in the infrared at 970 cm^{-1} has been assigned to the $\nu(Re{=}O)$ stretching frequency[248], and a band at 710–625 cm^{-1} to the $\nu(Re{-}O{-}Re)$ stretching mode. The latter band is probably at low energy due to the bridging bonds being weakened by the *trans* oxo-ligands[73].

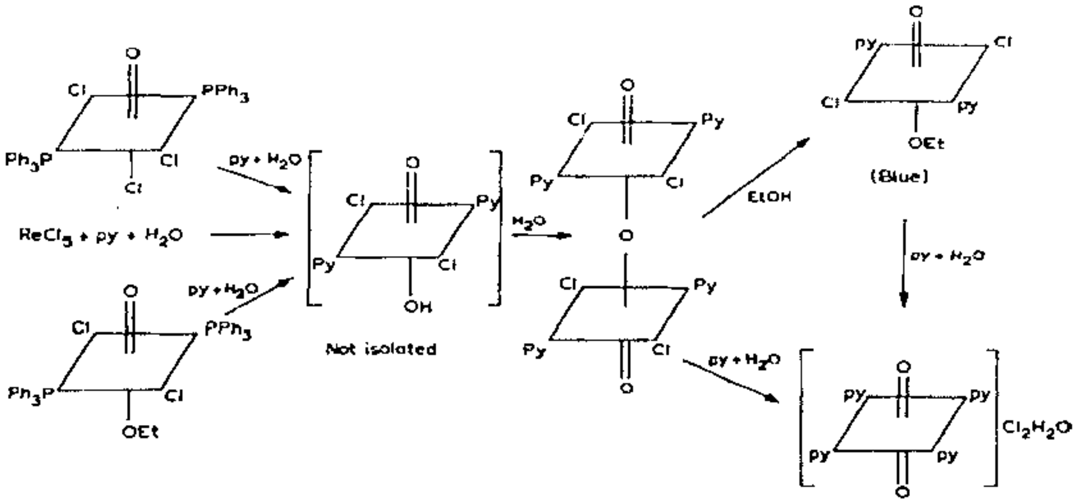


Fig. 7. Reactions of rhenium(V)–pyridine complexes[211].

(iii) Nitrido and imido complexes

A complex reported as[17] $ReCl_2(Ph_3P)_2$ was obtained by reducing rhenium(VII) with hydrazine hydrochloride in the presence of triphenylphosphine and water[17,18,249]. However, the compound contains the nitrido ligand, N^{3-} and is therefore a complex of rhenium(V). The nitrido-compounds known at present, $ReNX_2L_{2\text{ or }3}$ (Table 17), are monomeric and in the case when $L = Ph_3P$ are apparently five-coordinate compounds. The complexes which are stable and not hydrolysed are non-electrolytes and diamagnetic. The ν(Re–N) stretching frequency in the infrared is masked by overlapping phosphine bands. However, a band at 1052–1053 cm^{-1} has been assigned to it. There is no N–H resonance in the NMR spectra of the compounds ruling out the possibility that they are rhenium(IV)-imido complexes[18,249].

TABLE 17

RHENIUM(V)-NITRIDO AND -IMIDO COMPLEXES

Compound	*Colour*	*Meling point (decomp)*	*Dipole moment*	*Ref.*
Nitrido-complexes				
$ReNCl_2(Ph_3P)_2$	brick red	219–221	1.6	18, 249
$ReNBr_2(Ph_3P)_2$	orange-red	213–216	1.5	18, 249
$ReNI_2(Ph_3P)_2$	red-brown	178–180	0.75	18, 249
$ReNCl_2(Et_2PhP)_3$	yellow	151–154	6.4	18, 249
$ReNBr_2(Et_2PhP)_3$	yellow	151–155	5.8	18
$ReNI_2(Et_2PhP)_3$	yellow	115–118	6.5	18
$ReNCl_2(Et_3P)_3$	yellow	90–96	6.2	18
$ReNCl_2(n\text{-}Pr_3P)_3$	yellow	114–120	6.1	18
$K_2[ReN(CN)_4H_2O]^a$	pink			239
Arylimido-complexes				
$ReCl_3(NR)(Et_2PhP)_2$				18
R = Ph	green	201–205	5.9	
R = p-C_6H_4Br	green	216–220	5.2	
R = p-C_6H_4Cl	green	207–210	5.0	
R = p-C_6H_4F	green	177–181	4.6	
R = p-C_6H_4Me	green	182–184	6.5	
R = p-C_6H_4OMe	green	168–170	7.2	
R = p-C_6H_4COMe	dark green	146–148	4.5	
R = p-C_6H_4I, p-C_6H_4CN, p-$C_6H_4NMe_2$, p-$C_6H_4NH_2$, p,p-$C_6H_4C_6H_4NH_2$, and α-$C_{10}H_7$.				
$ReCl_3(NPh)(Et_3P)_2$	brown-green	132–133		18
$ReI_2(NPh)(Et_2PhP)_2$	golden-yellow	191–193		18
$ReCl_3(NPh)[(Et_2P)_2C_2H_4]$	pale green	245–280		18
$ReCl_3(NPh)[(Ph_2P)_2C_2H_4]$	blue green			50
Alkylimido-complexes				
$[Re(CH_3NH_2)_4(CH_3N)X]$				
X = Cl, OH^b	blue			230

[a] $\nu(Re\equiv N)$, 997, 974 cm^{-1}. [b] diamagnetic

Substituted anilines form similar compounds Re(NR)Cl_3L_2 (Table 17) by treating the complexes $ReOCl_3L_2$ or ReO(OEt)X_2L_2 with the aniline[18,50]. The compounds are diamagnetic, non-electrolytes and it is known that the phenylimido compound is monomeric. The ν(Re–N–R) stretching mode has been assigned to a band around 780 cm^{-1}. Monomethylamine reacts at room temperature with rhenium(IV) chloride to give imido complexes, $[Re(CH_3NH_2)_4(CH_3N)X]^{2+}$ (X = Cl, OH)[230], in the presence of gaseous oxygen. NMR studies have demonstrated that the compound has a symmetrical structure confirming that only one amine has lost the protons.

A nitrido–cyanide complex, $K_2[ReN(CN)_4H_2O]$, has recently been obtained by reducing potassium perrhenate with hydrazine hydrate[239]. The reaction is reported to give $K_3ReO_2(CN)_4$ but the nitrido complex forms as well. Strong bands in the infrared at 997 and 974 cm^{-1} are assigned to the ν(Re–N) stretching frequency.

(iv) Eight-coordinate complexes

A small number of *d*-electrons in a metal ion allow for high coordination numbers and rhenium(V)-cyanide and -diarsine complexes can be formed with a coordination number of eight. The compounds are diamagnetic[55] or have a small temperature-independent paramagnetism[79,208]. The stereochemistry is probably dodecahedral.

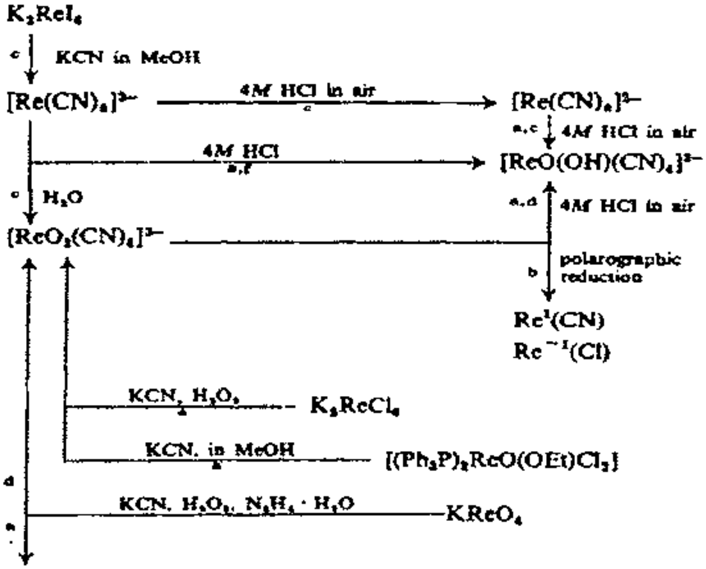


Fig. 8. Reaction of the rhenium(V) octacyanide. [a] ref. 239, [b] ref. 285, [c] ref. 55, [d] ref. 238, [e] ref. 237, [f] ref. 245.

The cyanide complex $K_3Re(CN)_8$ has one $\nu(C{\equiv}N)$ stretching frequency in the infrared at 2100 cm^{-1} in aqueous solution[55] but this is split into three bands, 2140, 2100, and 2050 cm^{-1} in the solid presumably due to crystal-lattice interactions[55,207,239]. However, the compound cannot be obtained[239] completely free from $K_3ReO_2(CN)_4$. This is probably formed due to hydrolysis during the preparation which involves treating potassium rhenium(IV) iodide with cyanide in methanol[55,207,239]. Some reactions of the rhenium(IV) cyanides are illustrated in Fig. 8, these include the formation of the rhenium(VI)-octacyanide ion[55] $(Re(CN)_8)^{2-}$.

Oxidation of the tervalent-rhenium complexes of *o*-phenylenebisdimethylarsine with chlorine, bromine, or ceric ions gives the eight-coordinate complexes $[Re(diarsine)_2X_4]^+$ (X = Cl, Br)[208]. An oxy-bridged complex anion, $(Re(diarsine)_2Cl_2O]^{4+}$, is obtained if nitric acid is used as the oxidising agent. This appears to contain seven-coordinate rhenium(V). The magnetic moment of 2.0 BM per rhenium is unexpected. When the complex is treated with hydrochloric acid it gives the eight-coordinate product, $[Re(diarsine)_2Cl_4]^+$, described above[79].

(v) Rhenium(V) and -(VI) fluorides

The only halogeno-anions of rhenium(V) which are free of the oxo-ligand are the very reactive fluorides ReF_6^-. These are isolated with alkali-metal cations by treating rhenium (VI) fluoride with the alkali-metal iodide in sulphur dioxide[250,251]. Nitric oxide reacts spontaneously with rhenium hexafluoride to give[252] the salt $NO^+ReF_6^-$. The compounds are paramagnetic with magnetic moments as follows[286]:

	θ (°K)	μ_{300} (B.M.)
$NaReF_6$	100	1.57
$KReF_6$	58	2.05
$RbReF_6$	50	1.56
$CsReF_6$	35	1.53

There is a possibility of some antiferromagnetic interaction in the solid compounds.

It is convenient at this point to mention the eight-coordinate fluoro-anion $(ReF_8)^{2-}$ of rhenium(VI) formed with the cations Na^+, K^+, Rb^+ and Cs^+. They are prepared by treating rhenium hexafluoride with the alkali fluoride[253,254]. The pink compounds undergo hydrolysis to the blue oxyfluoride $MReOF_5$[253,255] and they react further with rhenium(VI) fluoride to give the yellow salts $MReF_7$ (M = K, Rb, Cs)[254]. The salts M_2ReF_8 have magnetic moments in the range 1.6–1.71 BM while the salts $MReF_7$ are only weakly paramagnetic, μ = 0.6–0.7 BM[254]. This latter fact must indicate some spin coupling.

The structure of the potassium salt K_2ReF_8, is that of a square antiprism and the Re–F distance is 1.87–1.93 Å[256,257].

F. RHENIUM–HYDRIDO COMPLEXES

Rhenium and technetium form a number of hydrido-complexes, the most unusual of which are K_2ReH_9 and K_2TcH_9.

Polarographic and zinc-amalgam reduction of the perrhenate ion gave indications for the existence of a rhenide (Re^{-1}) state in solution[258–260]. This oxidation state of rhenium is, in fact, considered unstable primarily due to the high sublimation energy of rhenium metal[261].

In order to isolate a solid rhenide the technique used was to reduce potassium perrhenate with potassium metal in an ethylenediamine–water medium[262]. The product obtained, which was invariably contaminated with KOH, $KReO_4$ and K_2CO_3, was postulated as $KRe \cdot 4\,H_2O$.

Almost simultaneously a number of workers[263–265] showed from chemical and NMR studies that the compounds isolated were metal–hydrido complexes which infers the rhenium oxidation state is positive. The first proposals as to the composition were $KReH_4 \cdot x\,H_2O$ ($x = 2$ to 4)[264] and[265] $K_6Re_2H_{14} \cdot 6\,H_2O$. The compound was found to have a strong infrared band at 1850 cm^{-1} probably due to the ν(Re–H) stretching frequency. An independent study suggested the composition was K_2ReH_8[266, 267] and bands in the infrared at 1846 and 735 cm^{-1} were assigned to the vibration modes of the Re–H bond. However, the compound appeared to be diamagnetic which may be possible for a rhenium(III) compound ($KReH_4$) but not rhenium(VI) (K_2ReH_8), especially as a preliminary X-ray structural analysis[268, 269] demonstrated that the rhenium atoms were 5.5 Å apart ruling out possible spin coupling.

The situation was resolved by a neutron-diffraction study[270, 271] which indicated a rhenium(VII) compound K_2ReH_9. The compound has D_{3h} symmetry and consists of a rhenium atom surrounded by six hydrogens at the corners of a trigonal prism while the remaining three hydrogen atoms protrude from the centres of the three prism faces. The hydrogen atoms appear to be equivalent from NMR studies[270]. The Re–H bond is determined at 1.72 Å (3 bonds) and 1.67 Å (6 bonds) and the $\widehat{HReH}$ bond angle is approximately 90°.

A molecular-orbital description[270] of the bonding indicates how it is possible to accommodate the eighteen bonding electrons, in suitable bonding orbitals, $(e'^{(2)})^4(a''_2)^2(a'^{(2)}_1)^2(e'')^4(e'^{(1)})^4(a'^{(1)}_1)^2$. The single electronic spectral band at 46,080 cm^{-1} is assigned to the lowest energy symmetry-allowed transition $(e'^{(1)}) \rightarrow (a'^{(1)}_1)^*$.

The existence of the hydride complex without the usual stabilisation necessary by means of π-bonding ligands is of interest and could mean a reassessment of the place of hydrogen as a ligand in transition-metal complexes.

It has been suggested that the product obtained by treatment of the perrhenate ion with lithium is the same compound[264]. Preliminary evidence suggests that the species formed by polarographic or zinc-amalgam treatment of the perrhenate ion is a hydride of different composition to that discussed above[272]. Treatment of rhenium(IV)–hexahalogeno anions with potassium in liquid ammonia probably gives a hydride complex also[273].

Rhenium–hydrido complexes have also been obtained in conjunction with phosphine ligands. There is some disagreement over the number of hydrido-ligands in some of the complexes. Table 18 lists the compounds reported and possible reinterpretations.

The complexes are obtained in admixture by treating the rhenium(V) compounds $ReOCl_3(R_3P)_2$ and $ReO(OR')Cl_2(PR_3)_2$ or the rhenium(IV) complex, $ReCl_4(R_3P)_2$, with either sodium borohydride[197–199, 275] or lithium aluminium hydride[274]. The compounds are non-electrolytes and are diamagnetic. The presence of the protons is confirmed by analysis, infrared, and NMR studies. Only one NMR signal is found which must indicate that the hydrogen atoms are equivalent by rapid exchange[199, 274]. It is possible that the dimeric compound $[ReH_x(PEt_2Ph)_2]_2$ contains a Re–Re bond[274]. The compounds $ReH_7(R_3P)_2$ can be considered as derivatives of the $(ReH_9)^{2-}$ anion[274].

TABLE 18

RHENIUM–HYDRIDO–PHOSPHINE COMPLEXES

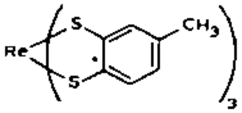
Compound	*ν(Re–H) (cm⁻¹)*	*Comments*	*Ref.*
$ReH_3(Ph_3P)_2$	2000	reinterpreted as $[ReH_x(Ph_3P)_2]_n$	197–199, 274
$ReH_3(Ph_3P)_4$	2050		197–199
$ReH_5(Ph_3P)_2$	1875	reinterpreted as $ReH_7(Ph_3P)_2$	274, 275
$ReH_5(R_3P)_3$	1900, 1970	R_3 = $EtPh_2$, Ph_3	274, 275
$ReH_5(Ph_3P)(Ph_3As)$	in region 1800–2000		274
$ReH_7(R_3P)_2$		R_3 = Et_2Ph, $EtPh_2$, Ph_3; $(R_3)_2$ = $Ph_2PC_2H_4PPh_2$	274
$[ReH_x(R_3P)_2]_n$		R_3 = Et_2Ph, $n = 2$; R_3 = Ph_3, n unknown, $x \sim 4$.	274

Certain of the hydrido-complexes can be converted to the paramagnetic rhenium(IV) complexes $ReX_4(Ph_3P)_2$ (X = Cl and Br) under halogenating conditions[197–199]. Treatment with hydrogen chloride or bromide is said to give the rhenium(IV) salt, $[Re(Ph_3P)H_5]^-Ph_3PH^+$, which is a 1:1 electrolyte and has a magnetic moment of 3.6 BM[276]. With nitric acid, a nitrosyl compound is obtained, $Re(NO)_2(Ph_3P)_2(NO_3)_2$, which is said to be a non-electrolyte and paramagnetic. The nitrate can be replaced by the halogens Cl, Br, and I, and in the latter case the compound is reported as diamagnetic[277].

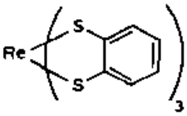
G. TRIS(1,2-DITHIOLATO)RHENIUM COMPLEXES

The rhenium complex formed with the ligand *cis*-1,2-diphenylethene-1,2-dithiol is of particular interest in that the stereochemistry around the rhenium is trigonal prismatic. The stereochemistry is not unique to rhenium but it is the rhenium compound $Re(S_2C_2Ph_2)_3$, whose structure has been determined. Complexes formed by other metal atoms are isomorphous with the rhenium complex.

The compound is readily made by reacting rhenium(V) chloride in ethanol with benzoin and P_4S_{10} in xylene[278, 279]. Other complexes, such as



and



are obtained by mixing rhenium(V) chloride and the ligand in carbon tetrachloride[279]. The compounds are isolated as green crystals with a paramagnetism indicating one unpaired electron[278–280]. The related dithioglyoxal complex $Re(C_2H_2S_2)_3$[281] has also been prepared and is presumably similar to those above.

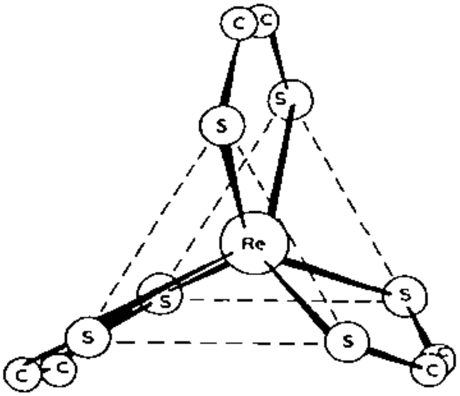
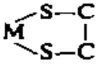


Fig. 9. Structural unit of tris(1,2-dithiolato)-rhenium complexes.

The structure of $Re(S_2C_2Ph_2)_3$ is a near-perfect trigonal prism (Fig. 9) with the following structural parameters: $Re\text{–}S_{av} = 2.325$ Å, $\widehat{SReS} = 81.4°$. The sides of the prism are nearly perfect squares of side length 3.043 Å[282, 283].

From a study of the electronic absorption spectra and ESR measurements, in solution, of the compounds $Re(S_2C_2Ph_2)_3$ and $Re(S_2C_6H_3CH_3)_3$ it is clear that the structure persists in solution. It is concluded that the stereochemistry in the solid state is not a consequence of crystal packing[280]. The ReS_6 group appears to be the main contributor to the electronic spectra and structure. Variation in the organic part of the ligand does not appear to affect the bonding of the ligand to the metal atom[280]. There is some evidence[284] for aromatic character in the ring



Two independent molecular-orbital treatments of the bonding, which agree in broad outline, have been proposed[279,281,284]. It is clear that the compounds are predicted to have one unpaired electron. An analysis of the electronic spectra has been carried out, and the bands have been assigned on the basis of the molecular-orbital treatment[279]. The two main spectral bands occur in the ranges 14050–14450 cm^{-1} and 23450–24930 cm^{-1}.

Certain complexes have been polarographically reduced from $n = +1$ to $n = -3$. The single electron is lost relatively easily[279].

The ν(Re–S) stretching frequency has been assigned to the infrared bands as listed below[284]:

$Re(S_2C_2Ph_2)_3$	373cm^{-1}	359cm^{-1}
$[N(C_2H_5)_4]^+[Re(S_2C_2Ph_2)_3]^-$	361	350
$Re(S_2C_2H_2)_3$	338	333
$[Ph_4As]^+[Re(S_2C_2H_2)_3]^-$	361	333

H. CONCLUSION

The chemistry of rhenium is a good example of how an understanding of the chemistry of an element can change rapidly over a few years. The detection of mononuclear oxo-, nitrido-, and hydrido-ligands and the discovery of the metal–halogen clusters, point the way to future investigations. It is apparent that the divalent and quadrivalent oxidation states of rhenium need further attention. With the correct ligand and under the right conditions the chemistry of these oxidation states could be developed. For example, whereas oxidation of the tervalent complex anion $[Re(diarsine)_2Cl_2]^+$ gave a rhenium(V) complex with no evidence for an intermediate quadrivalent compound[208] the oxidation of $Re(CO)_3$(diarsine)Cl did give[58] a quadrivalent complex Re(diarsine)Cl_4. Finally rhenium (and technetium) is somewhat unique in its central position in the transition-metal series. Its chemistry is related to the metals on the left in the formation of metal–metal bonded halide structures and stable oxo-complexes, and also to the platinum metals on the right in the formation of varied arsine and phosphine complexes. The resulting variety in the chemistry of rhenium, by virtue of its central position, will ensure a fruitful chemistry for the future.

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