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THE CHEMISTRY OF COORDINATED PERRHENATE (ReO_4^-)

M.C. CHAKRAVORTI

Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302 (India)

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CONTENTS

A. INTRODUCTION

Rhenium was the last of the non-radioactive elements to be discovered and is among the least-abundant elements. Its chemistry has been explored with great interest since the early 1960s and found to be one of the most complex. Several reviews, books and monographs have appeared on the chemistry of the element and its coordination compounds [1–8]. The most stable oxidation number of rhenium is +7 and the most readily accessible compounds of the element are the perrhenates (ReO_4^-). Perrhenates are almost completely different in properties from permanganates and perchlorates which are of exceptional stability. The alkali metal perrhenates melt and boil without decomposition and are reducible only by very powerful reducing agents, preferably in the presence of coordinating agents. Perrhenate ion is a stronger base than $[ClO_4]^-$ and should coordinate to metal ions more readily than the latter. The coordination chemistry of

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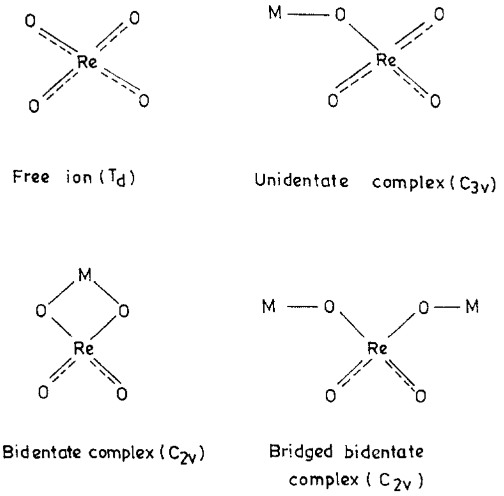
perchlorate ion which was at one time regarded as non-coordinating, has been studied in considerable detail and recently a good review on this has appeared [9]. On the contrary, there has been only scant work on the coordination chemistry of $[ReO_4]^-$, the first report [10] appearing only in 1968. However, some interesting work on perrhenato complexes has been made in recent years, justifying a comprehensive review. The object of this article is to present a fairly complete account of the chemistry of coordinated perrhenate giving both preparative and structural aspects. A few recent works on the coordination chemistry of analogous thioperrhenate (ReS_4^-) have also been included.

B. PHYSICAL PROBES USED FOR THE DETECTION OF COORDINATED PERRHENATE

(i) *Vibrational spectra*

The perrhenate ion is strictly tetrahedral in solution, but may have a lower symmetry in crystalline salts [11, 12]. It should thus show four Raman-active and two (υ_3 and υ_4) infra-red (IR) active fundamentals. Only three fundamentals have been observed for $[ReO_4]^-$ (aq). These appear [13] at 971 (υ_1), 332 (υ_4) and 916 (υ_3) cm^{-1}. The absence of υ_2 in the spectrum is attributed [11] to the accidental coincidence of $\upsilon_2(E)$ and $\upsilon_4(F_2)$. Another explanation suggested is that $\upsilon_2(E)$ is too weak and broad to be detected [13, 14]. Like sulphate or perchlorate, perrhenate ion may coordinate to a metal ion in various ways, as shown in Fig. 1. The symmetry of $[ReO_4]^-$ is lowered by complex formation, the degenerate vibrations split



Free ion (T_d)

Unidentate complex (C_{3v})

Bidentate complex (C_{2v})

Bridged bidentate complex (C_{2v})

Fig. 1. Mode of coordination of $[ReO_4]^-$.

and Raman-active modes appear in the IR spectrum. For unidentate coordination of $[ReO_4]^-$ both υ_3 and υ_4 should split into two bands, while υ_1 and υ_2 become IR active. For a bidentate or bridging perrhenate, υ_3 and υ_4 should split into three bands.

The assignment of υ_2 and υ_4 in perrhenate complexes is difficult due to the reasons cited above. The assignment is more difficult in complexes containing both perrhenate and amines, phosphines, amides, amine oxides, phosphine oxides, etc. (which are some common ligands usually associated with $[ReO_4]^-$ in many of the complexes reported), since other vibrations, e.g. υ(M–N), υ(M–O), δ(NMN), δ(NMO) or ligand vibrations may also appear in the same region. The spectra of the few perrhenato complexes which have been reported hitherto indicate that the splitting of υ_3 is very small (Table 1) compared with the analogous sulphato or perchlorato complexes. The only perrhenato complex which has been reported to have a very large splitting (about 100 cm^{-1}) of the υ_3 band is $[Co(NH_3)_5(ReO_4)]Cl_2$. It appears, however, that the authors [10] have incorrectly assigned the lower energy band at about 835 cm^{-1} to a coordinated perrhenate group vibration. The vibration is probably due to a rocking mode of coordinated ammonia which occurs [15] at 831 cm^{-1} in $[Co(NH_3)_6]Cl_3$. The inference of perrhenate coordination (or the nature of the coordination) from weak splitting of the bands must be treated with caution, since weak splitting of IR spectral bands may arise for various other reasons, e.g. lattice effects. In fact, the broad and strong band due to υ_3 which appears for ionic perrhenates, e.g., $KReO_4$, is often split by about 10 cm^{-1}. Despite these limitations, IR spectroscopy remains the commonest tool for the identification of coordinated perrhenate.

(ii) *Electronic spectra*

Since the nature of the ligand field around the metal ion is often reflected in the spectral features, perrhenate coordination in a transition metal complex may be revealed by the analysis of the electronic spectra of the complex. Quite a few perrhenato complexes of Ni(II), Co(II) and Cu(II) have been prepared, the study of the electronic spectra of which has resulted in establishing the geometry of the complexes, thus helping in concluding the presence of coordinated perrhenate. The electronic spectra of $[Nipy_4(ReO_4)_2]$, $[Ni(4\text{-mepy})_4(ReO_4)_2]$, $[Ni(NH_3)_4(ReO_4)_2]$ and $[Ni(NH_3)_2(ReO_4)_2]$ indicate [16, 17] that these are tetragonally distorted octahedral complexes. While there have been quite a number of attempts to fix the position of perchlorate ion in the spectrochemical series, only one or two reports [16] are available that compare the strength of perrhenate coordination with $[ClO_4]^-$, BF_4^-, Br^- and I^- in the Ni(II) complexes of the type $[NiL_4(ReO_4)_2]$ where L = pyridine or 4-methylpyridine.

TABLE 1

Infrared and Raman spectral data of some perrhenato complexes (υ, cm^{-1})

Compound	υ_1	υ_2	υ_3	υ_4	Ref.
$[Mn(py)_4(ReO_4)_2]$	940	336, 342	898, 928	310, 317, 321, 325	16
$[Co(py)_4(ReO_4)_2]$	936	338, 342	905, 923	311, 319, 322	16
$[Ni(py)_4(ReO_4)_2]$	935	343	903, 921	314, 321, 326, 329	16
	985		870, 910, 930		17
	R 974		R 925, 912		17
$[Cu(py)_4(ReO_4)_2]$	928	339	900, 907, 918	310, 320, 325	16
	955, 965		880, 915, 925		20
$[Zn(py)_4(ReO_4)_2]$	935	338, 342	900, 922	311, 319, 322, 325	16
	960		900, 925, 935		19
$[Cd(py)_4(ReO_4)_2]$	960		900, 925, 935, 945		19
$[Ni(4\text{-}mepy)_4(ReO_4)_2]$	928	338	903, 928	320, 326, 329	16
$[Ni(NH_3)_4(ReO_4)_2]$	980	360, 380	870, 900, 930	305, 315	17
$[Cu(NH_3)_4(ReO_4)_2]$	965		890, 900		20
$[Ni(py)_2(ReO_4)_2]$	965	340, 350, 360	870, 900, 930	305, 315	17
$[Cu(py)_2(ReO_4)_2]$	960		905, 920, 930, 940		20
$[Zn(py)_2(ReO_4)_2]$	960, 975		875, 900, 930, 945		19
$[Cd(py)_2(ReO_4)_2]$	960, 980		895, 925, 940		19
$[Ni(NH_3)_2(ReO_4)_2]$	980	360, 380	875, 910, 925	300, 310	17
	R 969	R 338, 344	R 895, 918		17
$[Cu(NH_3)_2(ReO_4)_2]$	965		890, 910		20
$[Zn(NH_3)_2(ReO_4)_2]$	985		890, 915		19
	R 969, 982	R 338, 345	R 895, 918		19
$[Cd(NH_3)_2(ReO_4)_2]$	970		890, 910		19
	R 969, 974	R 339, 345	R 895, 917		19
$[Ni(Ph_3PO)_4(ReO_4)]ReO_4$			906, 921, 931		23
$[Co(Ph_3PO)_4(ReO_4)]ReO_4$			897, 908, 921, 931		23
$[Cu(Ph_3PO)_4(ReO_4)]ReO_4$			888, 910, 922, 927		23
$[Ni(Ph_3AsO)_4(ReO_4)]ReO_4$			908, 916, 931		23
$[Co(Ph_3AsO)_4(ReO_4)]ReO_4$			907, 916, 929		23
$[Cu(Ph_3AsO)_4(ReO_4)]ReO_4$			906, 916, 921		23

(iii) *Magnetic susceptibility*

The coordination of perrhenate will affect the coordination number of the metal ion and the stereochemistry of the complex which will influence its magnetism. Thus, magnetic susceptibility measurements may be of diagnostic value in determining the presence of a metal–perrhenate linkage. Studies on the variation in magnetic susceptibility with temperature may give still more useful information. The magnetic moment of both $[Ni(NH_3)_4(ReO_4)_2]$ and $[Ni(NH_3)_2(ReO_4)_2]$ is 3.08 BM and practically independent of temperature over 300–100 K indicating the presence of six-coordinate Ni(II) in these complexes [17].

No report on the study of a perrhenato complex by electron spin resonance (ESR) spectroscopy is available.

(iv) *X-ray structure determination*

Full X-ray structure analysis of a few perrhenato complexes has unequivocally established the coordination of perrhenate in a number of complexes; these are included in subsequent sections. The magnitude of the Re–O bond length should give an idea of metal–oxygen bond strength. The Re–O bond length of coordinated $[ReO_4]^-$ is generally somewhat longer than that of uncoordinated $[ReO_4]^-$. Unidentate and bridging modes of the coordination of perrhenate have been established by X-ray crystal structure analysis. Interestingly, in some of the compounds studied, perrhenate is bonded to another rhenium atom in +3, +5 or +7 oxidation states.

C. COMPLEX COMPOUNDS CONTAINING COORDINATED PERRHENATE AND AMMONIA, AMINES, PYRIDINE, SUBSTITUTED PYRIDINE, PHOSPHINE OXIDES, ARSINE OXIDES, ETC.

The first account of perrhenate coordination to metal ions was reported by Lenz and Murmann [10] in 1968. These authors isolated a well-defined compound containing both coordinated and ionic perrhenate, viz. $[Co(NH_3)_5(ReO_4)](ReO_4)_2$, by the dehydration of $[Co(NH_3)_5(H_2O)](ReO_4)_3 \cdot 2H_2O$ in vacuum at 95–130°C. Other salts of the ion, e.g. $[Co(NH_3)_5(ReO_4)]X_2$ (where $X = Cl^-$, NO_3^- or ClO_4^-) were prepared by ion exchange. As indicated above, the IR spectra have not been properly assigned. The broad band centred around 930 cm^{-1} observed in this study is believed to be the unresolved band due to coordinated perrhenate. In aqueous solution, $[Co(NH_3)_5(ReO_4)]X_2$ aquates at a measurable rate and follows the rate law:

$$\text{rate} = k_O + k_H[H^+] + k_{OH}[OH^-][Co(NH_3)_5(ReO_4)^{+2}]$$

Using O^{18} as a tracer, the formation in the solid state was found to occur by fission of the Co–O bond, while hydrolysis in dilute H^+ or OH^- occurred by Re–O bond breaking. In the pH range 4–7 more complex oxygen transfer behaviour was observed. Hydrolysis was strongly catalysed by acetic acid, acetate and $H(phthalate)^-$. Although no X-ray structure determination has been made, judging by the method of formation and the kinetic studies it appears that this first claim of perrhenate coordination is authentic. The synthesis has found a place in *Inorganic Syntheses* [18].

Mayfield and Bull [16] reported a series of complexes of the general formula $[ML_4(ReO_4)_2]$, where M = Co(II), Cu(II), Mn(II), Ni(II) or Zn and L = pyridine or 4-methylpyridine. The copper complex was prepared by treating an aqueous solution of Cu(II) perrhenate with pyridine. The other complexes were obtained in a similar manner in nonaqueous medium. The magnetic moments of the Co(II), Ni(II) and Mn(II) compounds with pyridine are 5.19, 3.25 and 6.02 BM, respectively (at $23 \pm 2°C$), which are representative of high-spin octahedral complexes and not typical of tetrahedral structures. The IR spectra show splitting of the υ_3 mode of perrhenate (Table 1). The authors have probably incorrectly assigned a strong band at about 935 cm^{-1} as the υ_1 mode of perrhenate. This band is more likely to be a component of υ_3. Metal–ligand vibrations were assigned from the far-IR spectral data at 210–260 cm^{-1}. The low-temperature electronic spectra of the Ni(II) complexes (Fig. 2) are strongly suggestive of a tetragonally distorted octahedral complex. The band positions along with the tentative assignment are given in Table 2. The ligand-field parameters of the Ni(II) complexes were calculated. A comparison of the *Dt* values indicated that the

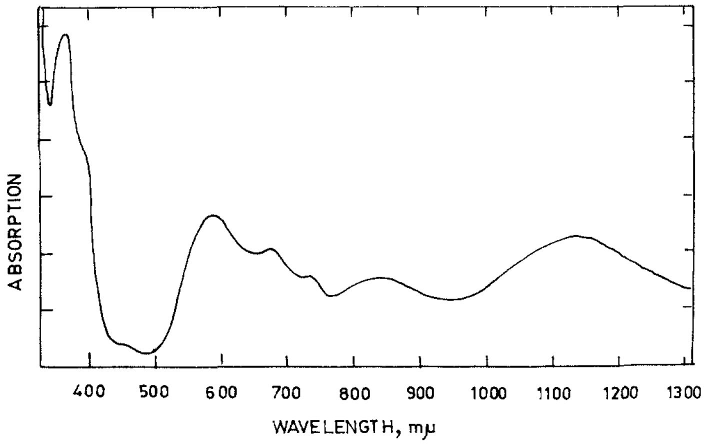


Fig. 2. Low-temperature electronic spectrum of $[Ni(4\text{-mepy})_4(ReO_4)_2]$. (Redrawn with permission from ref. 16.)

TABLE 2
Visible and near IR spectral data (cm^{-1})

$[Ni(py)_4(ReO_4)_2]$	$[Ni(4\text{-}mepy)_4(ReO_4)_2]$	Assignment
8780 s	8840 s	${}^3B_{1g}\rightarrow{}^3E_g$
12 000 s	11 800 m	${}^3B_{1g}\rightarrow{}^3B_{2g}$
13 300 w	13 500 w	${}^3B_{1g}\rightarrow{}^1A_{1g}, B_{1g}({}^1D)$
15 000 m	14 400 w	${}^3B_{1g}\rightarrow{}^3A_{2g}$
17 700 s	17 100 m	${}^3B_{1g}\rightarrow{}^3E_g$
21 700 vw	21 400 vw	${}^3B_{1g}\rightarrow{}^1A_{1g}({}^1G), {}^1E_g({}^1D)$
25 600 sh	24 800 sh	${}^3B_{1g}\rightarrow{}^3A_{2g}({}^3P)$
27 500 vs	27 200 vs	${}^3B_{1g}\rightarrow{}^3E_g({}^3P)$

perrhenate ion coordinates more strongly than the ClO_4^- and BF_4^- ions, but less strongly than the Br^- and Cl^- ions.

Chakravorti and co-workers [17, 19, 20] have prepared a number of perrhenato complexes containing ammonia or pyridine. The complexes $[M(NH_3)_4(ReO_4)_2]$ and $[M'py_4(ReO_4)_2]$, (where M = Ni or Cu and M' = Ni, Cu, Zn or Cd) were obtained by adding ammonia solution or pyridine to aqueous solutions of metal perrhenates. The pyridine compounds were also obtained by reacting the metal chlorides with aqueous pyridine in the presence of perrhenic acid. Pyrolysis of the compounds at around 140°C gave $M(NH_3)_2(ReO_4)_2$ and $M'py_2(ReO_4)_2$. The IR spectra of all these compounds show the presence of the υ_1 mode of perrhenates and the splitting of the υ_3, υ_2 and υ_4 vibrations (Table 1). The electronic spectra of the Ni(II) complexes are consistent with tetragonally distorted octahedral complexes (Table 3). The magnetic moments of the Ni(II) complexes are about 3.1 BM at room temperature. The fact that the magnetic moments of $[Ni(NH_3)_4(ReO_4)_2]$ and $[Ni(NH_3)_2(ReO_4)_2]$ are independent of temperature supports the presence of six-coordinate Ni(II). The X-ray powder pattern of $[Ni(NH_3)_4(ReO_4)_2]$ shows that it is not isostructural with $[Co(NH_3)_4](ReO_4)_2$ and $[Zn(NH_3)_4](ReO_4)_2$. The latter two complexes were earlier shown [21, 22] to be four-coordinate containing ionic perrhenate. No conclusion about the mode of bonding of ReO_4^- (viz. bidentate or bridging) in the $ML_2(ReO_4)_2$ complexes was made.

A series of isomorphous five-coordinate complexes, viz. $[ML_4(ReO_4)]ReO_4$ (where M = Co(II), Ni(II) or Cu(II) and L = triphenylphosphine oxide and triphenylarsine oxide) have been characterized by Hunter et al. [23] from electronic and IR spectra. All the complexes give three to four υ(Re–O) absorption bands within the 930–890 cm^{-1} region (Table 1) indicating the presence of both ionic and coordinated ReO_4^-. Diphenyl-

TABLE 3

Electronic spectral data

Compound	Band maximum (kK)	Ref.
$[Ni(NH_3)_4(ReO_4)_2]$	10.6, 16.1, 21.3, 27.0, 25.6	17
$[Ni(py)_4(ReO_4)_2]$	8.78, 12.0, 13.3, 15.0, 17.7, 21.7, 25.6, 27.5	16
	11.9, 13.5, 15.2, 17.4, 21.7, 26.3, 30.3	17
$[Ni(NH_3)_2(ReO_4)_2]$	10.8, 12.8, 14.3, 16.7, 19.6, 25.6, 31.3	17
$[Ni(py)_2(ReO_4)_2]$	11.1, 12.5, 15.2, 17.2, 24.4	17
$[Cu(py)_2(ReO_4)_2]$	14.0	20
$[Ni(Ph_3PO)_4(ReO_4)]ReO_4$	7.4, 11.0, 14.1, 17.0, 19.2, 22.4	23
$[Co(Ph_3PO)_4(ReO_4)]ReO_4$	6.5, 10.9, 16.6, 19.2, 20.1, 21.2	23
$[Cu(Ph_3PO)_4(ReO_4)]ReO_4$	12.0	23
$[Ni(Ph_3AsO)_4(ReO_4)]ReO_4$	8.1, 11.5, 13.8, 16.3, 18.8, 22.8	23
$[Co(Ph_3AsO)_4(ReO_4)]ReO_4$	6.9, 11.4, 16.5, 18.3, 21.4	23
$[Cu(Ph_3AsO)_4(ReO_4)]ReO_4$	13.4	23
$[Ni(Ph_2MeAsO)_4(ClO_4)]ClO_4$	7.4 br, 11.7, 13.8, 16.5, 18.7, 23.0	23
$[Co(Ph_2MeAsO)_4(ClO_4)]ClO_4$	6.6 br, 11.3, 16.8, 22.2	23
$[Cu(Ph_2MeAsO)_4(ClO_4)]ClO_4$	14.2 br, 16.4 sh	23

methylarsine oxide was earlier [24, 25] shown to form isomorphous five-coordinate square-pyramidal complexes $[M(Ph_2MeAsO)_4(ClO_4)]ClO_4$ for M = Mn, Fe, Co, Ni, Cu or Zn. The details of the molecular structure of the cobalt complex were studied by X-ray analysis [25]. A close similarity (Table 3) of the electronic spectra of $[CoL_4(ReO_4)]ReO_4$, $[NiL_4(ReO_4)]$-ReO_4 and $[CuL_4(ReO_4)]ReO_4$ (where L = triphenylphosphine oxide) and of the corresponding complexes of cobalt, nickel and copper with perchlorate and diphenylmethylarsine oxide or diphenylmethylphosphine oxide suggest that the perrhenato complexes also adopt square-pyramidal structure.

Russian workers [26] have recently reported a nitroso ruthenium ammine containing coordinated perrhenate. Boiling $[Ru(NH_3)_4(NO)(H_2O)](ReO_4)_3 \cdot 2H_2O$ with excess concentrated perrhenic acid gave $[Ru(NH_3)_4(NO)(ReO_4)](ReO_4)_2$. The latter reacted with $H_2[PtCl_6]$ giving $[Ru(NH_3)_4(NO)(ReO_4)]$-$PtCl_6$. The main evidence in favour of coordinated perrhenate comes from IR spectra.

X-ray structural studies on a perrhenato complex were made by Liss and Schlemper [27]. The complex, perrhenato-2,2′-(1,3-diaminopropane)bis(2-methyl-3-butanone oximato)copper(II), $[Cu(PnAO{-}H)(ReO_4)]$, was made by evaporation of a solution containing $[Cu(PnAO{-}H)]^+$ and $NaReO_4$. The neutral five-coordinate square-pyramidal complex gave IR bands at 922 and 898 cm^{-1}. The structure is shown in Fig. 3. The tetradentate α-amine

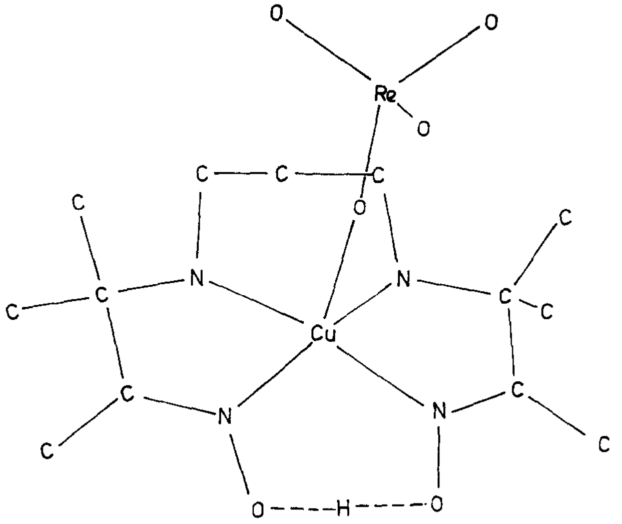


Fig. 3. Structure of perrhenato-2,2′-(1,3-diaminopropane)bis-(2-methyl-3-butanone oximato)copper(II). (Redrawn with permission from ref. 27.)

oxime ligand is bonded in a square plane about the copper atom with Cu–N(amine) = 1.99(1) Å and Cu–N(oxime) = 1.96(1) Å. The copper atom is displaced approximately 0.24 Å out of the best plane through the four nitrogen atoms towards the coordinated $[ReO_4]^-$. The perrhenate oxygen to copper bond is not quite perpendicular to the nitrogen plane as evidenced by the O–Cu–N(amine) angle (99.0°) and the O–Cu–N(oxime) angle (95.0°). A similar distortion was also observed [28] in the square-pyramidal $[Cu(NH_3)_4(H_2O)]^{2+}$ ion in $[Cu(NH_3)_4(H_2O)]SO_4$. The Cu–O(ReO_3) distance is long, 2.40(1) Å. Within the perrhenate an average Re–O distance of 1.70(3) Å was observed, which is lower than the Re–O distance of 1.77(3) Å in $KReO_4$ [29]. The Re–O coordinated to copper is reported to have a bond length of 1.72 Å, while two other non-coordinated Re–O bonds have distances of 1.64 and 1.72 Å. The reported bond lengths appear to be somewhat approximate and the authors suggest that a careful study is required to establish the difference between the coordinated and uncoordinated Re–O distances. The short intra-molecular hydrogen bond involves a separation of the oxime oxygens of 2.46(2) Å.

D. ADDUCTS WITH AMIDES, SULPHOXIDES, AMINE OXIDES, ETC.

A large number of adducts of lanthanide perrhenates with amides, sulphoxides, amine oxides, etc., have been prepared by reacting the hydrated perrhenates with these ligands. None of these complexes have been adequately characterised. The composition of the complexes varies widely, e.g. $Ln(ReO_4)_3{\cdot}4DMA$ [30], $Ln(ReO_4)_3{\cdot}5TMU$, $Ln(ReO_4)_3{\cdot}6TMU$ [31], $Ln(ReO_4)_3{\cdot}2DDPA$, $Ln(ReO_4)_3{\cdot}3DDPA$ [32], $Ln(ReO_4)_3{\cdot}4TSO$,$Ln(ReO_4)_3{\cdot}7.5TMSO$ [33, 34], $Ln(ReO_4)_3{\cdot}8DMSO$ [35], $Ln(ReO_4)_3{\cdot}npicO$ [36], $Ln(ReO_4)_3{\cdot}bipyOO$ [37], $Ln(ReO_4)_3{\cdot}nTDTD{\cdot}xH_2O$ [38, 39], $[Ln(HMPA)_n(ReO_4)_2]ReO_4$ [40], etc.* The main evidence put forward in support of perrhenate coordination in these complexes is the splitting of the υ_3 mode of $[ReO_4]^-$ and the conductivity of their solutions. However, while some of these, e.g. $Ln(ReO_4)_3{\cdot}5TMU$, show two or more υ_3 modes, others, e.g. $Ln(ReO_4)_3{\cdot}6TMU$, do not show any splitting. The IR spectra have been variously interpreted as containing coordinated $[ReO_4]^-$ or both ionic and coordinated $[ReO_4]^-$. The conductivity data in various solvents are also confusing. $Ln(ReO_4)_3{\cdot}2DDPA$ and $Ln(ReO_4)_3{\cdot}3DDPA$ are stated to behave as 1:1 electrolytes in acetone and 1:2 electrolytes in methanol. The lanthanide complexes with *trans*-1,4-dithiane-1,4-dioxide are probably polymeric, e.g. the praseodymium, neodymium and the europium complexes are represented as $[Ln(H_2O)_4(TDTD)_2(ReO_4)(\mu\text{-}TDTD)]_n(ReO_4)_{2n}{\cdot}nTDTD$. Thermal studies of the TDTD complexes have been made [41].

A uranyl complex with tributylphosphine oxide, viz. $UO_2(Bu_3PO)_2(ReO_4)_2$, has been prepared [42] by dissolving UO_3 in 5M $HReO_4$ followed by the addition of n-Bu_3PO. It is non-conducting in benzene, but dissociates in methanol; the molecular weight corresponds to a trimer.

E. METAL PERRHENATES AND DOUBLE METAL PERRHENATES

In solid $M(ReO_4)_3{\cdot}nH_2O$, the perrhenate ion is likely to be weakly coordinated to M(III), and a crystal-structure determination on some of these compounds would be interesting. The structures of the compounds $M(ReO_4)_4{\cdot}nH_2O$ ($M = Th$ or Np, $n = 0$ or 4; $M = Zr$ or Hf, $n = 6$) and $M_2O(ReO_4)_6{\cdot}nH_2O$ ($M = Zr$ or Hf, $n = 0$ or 9) have been interpreted to contain M(IV)–O–Re(VII) bridges [43–45].

DTA and X-ray phase analysis for the reaction of $KReO_4$ with $Y(ReO_4)_3$ showed the formation of double perrhenates $KY(ReO_4)_4$ and $KY_2(ReO_4)_7$. Infra-red spectra, however, indicate that both these complexes contain tetrahedral perrhenate groups [46]. A number of lanthanon–sodium perrhenates of the type $LnNa(ReO_4)_4{\cdot}nH_2O$ ($n = 0$ or 4) have also been reported [47].

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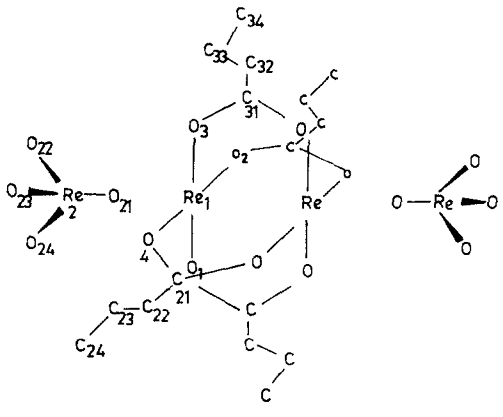
*Abbreviations: DMA, *N*,*N*-dimethylacetamide; TMU, tetramethylurea; DDPA, *N*,*N*-dimethyldiphenylphosphinnamide; TSO, thioxane oxide; TMSO, tetramethylene sulphoxide; DMSO, dimethylsulphoxide; picO, 2,picoline-*N*-oxide; bipyOO, 2,2′-bipyridine-*N*,*N*′-dioxide; TDTD, 1,4-dithiane-1,4-dioxide; HMPA, hexamethylphosphoramide.

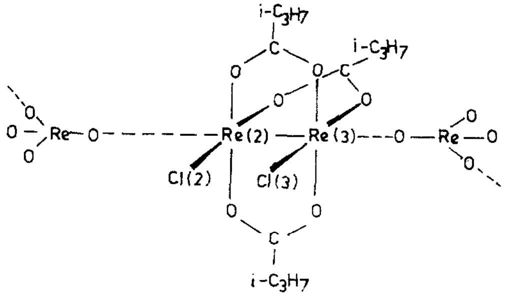
F. COMPOUNDS CONTAINING PERRHENATE COORDINATED TO ANOTHER RHENIUM ATOM

A few compounds have been characterised by X-ray structure determination in which perrhenate is bonded to another rhenium atom in +3, +5 or +7 oxidation state. By reacting rhenium(III) chloride with *n*-butyric acid and isobutyric acid in a stream of oxygen, two compounds have been isolated and formulated as $Re_2(n\text{-}C_4H_7O_2)_4(ReO_4)_2$ (**I**) and Re_2 (iso-$C_4H_7O_2)_3Cl_2(ReO_4)$ (**II**) [48, 49]. The structures of these complexes are related to those of the carboxylate bridged Re(III) dimers, e.g. $Re_2Cl_2(RCOO)_4$ [50–52]. Each dimeric unit has four bridging carboxylate groups in **I** and three carboxylate groups with two chlorine atoms, one for each rhenium atom, in **II**. In compound **II** the two oxygen atoms of two different perrhenate groups coordinate to the dimeric unit and form a chain of alternate Re_2 dimer and $[ReO_4]^-$ units running parallel forming a continuous chain. In compound **I** the dimeric unit $Re_2(n\text{-}C_3H_7COO)_4$ is weakly coordinated to two $[ReO_4]^-$ groups, one at each end of the dimer unit. The structure results from packing of short chains consisting of the dimer unit and the two perrhenate groups (Fig. 4). Within the dimer unit the two rhenium atoms are separated by a distance of 2.251(2) and 2.259(3) Å in **I** and **II**, respectively, distances which are very similar to those observed in other dimeric Re(III) compounds [53–57]. The two Re–Cl distances, which are 2.29(1) and 2.22(2) Å, respectively, are within the range of distances observed in $[Re_2Cl_8]^{2-}$, $[Re_2Cl_6(PEt_3)]$, etc. [53–55]. Within the carboxylates, the bond lengths and angles are similar to those found in rhenium carboxylates [57]. The four atoms O, Re, Re and O in the grouping $O_3ReO\text{–}Re\text{–}Re\text{–}ORe_3$ are almost linear. Although there are large errors in the Re–O distances, the Re(dimer)–O(perrhenate) distances are larger than the mean Re–O(carboxylate) distance. Within the perrhenate mean Re–O bond lengths of 1.75 and 1.74 Å for **I** and **II**, respectively, are observed. The bonded Re–O distance is somewhat longer (1.81 Å) than the non-bonded Re–O distances (1.82, 1.69 and 1.70 Å) in compound **I**.

A novel organoimido complex of Re(VII) containing coordinated bridging perrhenate has been characterised by Nugent and Harlow [58]. Reaction of trimethylsilyl perrhenate, $Me_3SiOReO_3$, with an insufficient amount of *tert*-butyltrimethylsilyl amine, *t*-$BuNHSiMe_3$, gave a yellow low-melting solid analysed as $Re_3(N\text{-}t\text{-}Bu)_4O_5(OSiMe_3)_3$, the structure of which is shown in Fig. 5. One of the perrhenate oxygen atoms bridges two other rhenium atoms in a manner similar to an alkoxide group. As expected, within the perrhenate the Re–O bond involving the bridging oxygen is somewhat longer, 1.80(1) Å, than the Re–O bond length in ionic $[ReO_4]^-$ (1.77 Å), and is also longer than the other Re–O bonds, 1.68(1), 1.74(1) and 1.70(1) Å.



(I)



(II)

Fig. 4. Structures of $[Re_2Cl_2(iso\text{-}C_3H_7COO)_3](ReO_4)$ and $[Re_2(n\text{-}C_3H_7COO)_4](ReO_4)_2$. (Redrawn with permission from refs. 48 and 49.)

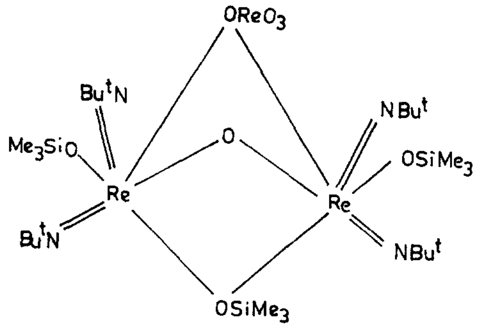
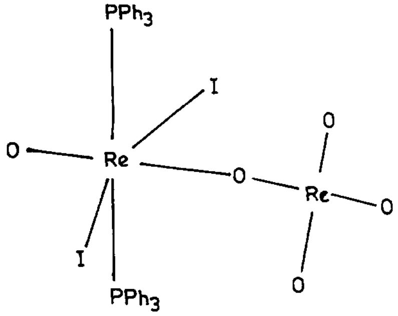


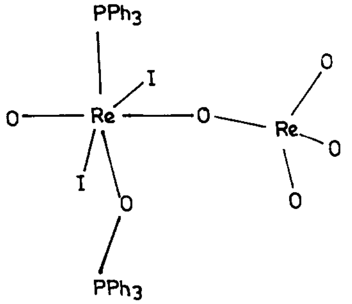
Fig. 5. Structure of $Re_3(N\text{-}t\text{-}Bu)_4O_5(OSiMe_3)_3$. (Redrawn with permission from ref. 58.)

The two Re–OReO$_3$ bonds are also longer, 2.46(1) and 2.47(1) Å. The average Re–N bond length of 1.70 Å is close to the average Re–N distance (1.69 Å) found in other organoimido complexes of rhenium [59, 60]. The distance between the two rhenium atoms connected by [ReO$_4$], O^{2-} and OSiMe$_3^-$ groups is large, 3.165(1) Å. All the *t*-butyl groups are apparently equivalent at 25°C on the NMR time-scale.

Two complexes of rhenium(V) containing unidentate perrhenate have been obtained [61] by the oxygenation reaction of the five-coordinate species, ReO$_2$I(PPh$_3$)$_2$ [62]. Both complexes have been characterised by X-ray diffraction analysis. The structures of the two compounds, viz. ReOI$_2$(PPh$_3$)$_2$(ReO$_4$) (I), which is the major product, and ReOI$_2$(PPh$_3$) (OPPh$_3$) (ReO$_4$)·0.5C$_6$H$_6$ (II) are shown in Fig. 6. Both complexes show a distorted



(I)



(II)

Fig. 6. Structure of ReOI$_2$(PPh$_3$)$_2$(ReO$_4$) (I) and ReOI$_2$(PPh$_3$)(OPPh$_3$)(ReO$_4$)·0.5C$_6$H$_6$ (II). (Redrawn with permission from ref. 61.)

octahedral geometry and the ligand stereochemistry is related to that of *trans*-[$ReOI_2(OR)(PPh_3)_2$] [62], the perrhenate group substituting the alkoxo ligand. Furthermore, in compound **II** a phosphine oxide group occupies the position of one of the two phosphines. Within the perrhenate the Re–O bond involving the bridging oxygen atom is slightly longer than the other Re–O bonds, 1.797(6) Å vs. a mean value of 1.73 Å in compound **I** and 1.78(1) Å vs. 1.69 Å (mean) in compound **II**. The Re–O bonds (Re attached to $OPPh_3$ or $OReO_3$) are, as expected, much longer and may be considered as metal–oxygen single bonds. For example, the Re–$OReO_3$ bonds are 2.031(6) and 2.079(9) Å in compounds **I** and **II**, respectively. The Re–O bonds in the Re–oxo group are very short, 1.670(7) and 1.639(9) Å in compounds **I** and **II**, respectively, and are essentially triple bonds [63, 64]. These bonds are even shorter than those found in the $ReOI_2(OR)(PPh_3)_2$ species, 1.698(5) and 1.715(9) Å with R = Me and Et, respectively [61]. This shortening has been ascribed to weaker Re–O interaction with the $[ReO_4]^-$ ligand in the *trans* position, vs. alkoxides. The Re–P bond lengths in compound **I** are comparable with the corresponding bonds in $ReOI_2(OR)(PPh_3)_2$ [mean values 2.518 and 2.523 Å in the alkoxides with R = Me and Et, respectively; and 2.513 Å in compound **I**]. In compound **II** the Re–P bond is slightly shorter, 2.453(4) Å, probably because of a higher Re to P π-back-donation, due to the presence of the electron-donating oxygen atom of the $OPPh_3$ ligand in *trans* position. The Re–I bonds [mean values 2.730 and 2.727 Å in **I** and **II**, respectively] are intermediate between the corresponding mean values in $ReOI_2(OR)(PPh_3)_2$ [2.782 Å (R = Me), 2.789 Å (R = Et)] and in $ReO_2I(PPh_3)_2$ (2.664(2) Å)]. As in $ReOI_2(OR)(PPh_3)_2$, the P–Re–P interaction in compound **I** is almost linear; the I–Re–I interactions are bent away from the oxide ligand, with values of 166.89°, 169.8° and 160.43° in $ReOI_2(OMe)(PPh_3)_2$, $ReOI_2(OEt)(PPh_3)_2$ and $ReOI_2(ReO_4)(PPh_3)_2$, respectively. The larger bending in the perrhenate complex can be related to the Re–$OReO_3$ bond being weaker than the Re–OR ones. Both the compounds **I** and **II** are, as expected, diamagnetic and non-ionic and give 3–5 IR bands in the region 950–825 cm^{-1}.

In the compound $Re_2O(\mu\text{-}O)_2(\eta^5\text{-}C_5Me_5)_2(ReO_4)_2$, two perrhenato ligands are bound unsymmetrically to one of the two Re(V) nuclei (Fig. 7). This diamagnetic, air-stable complex was obtained by reacting $(C_5Me_5)ReO_3$ with traces of atmospheric oxygen in the presence of triphenylphosphine [65, 66]. Within the perrhenate the Re–O (bonded to the rhenium centre) bond distance is 1.77(1) Å, while the other three non-bonded Re–O distances are 1.71(1) Å. The Re–O (terminal) bond length is 1.72(1) Å, typical of that found in Re(V) oxo complexes [67]. The bridging Re–O bond lengths are longer, 1.89(1) and 1.99(1) Å, and are comparable with those found in, e.g. $[Pt(NH_3)_4]_2[Re_2O_3(CN)_8]$, $Re_2O_3(Et_2dtc)_4$ and

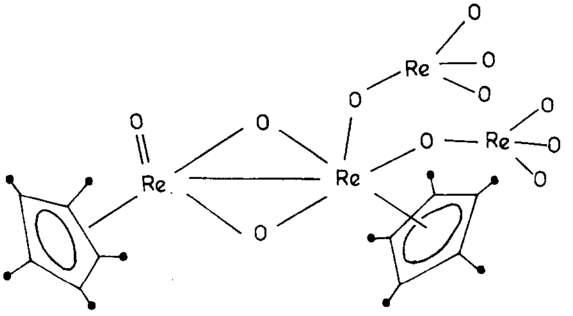


Fig. 7. Structure of $Re_2O(\mu\text{-}O)_2(\eta^5\text{-}C_5Me_5)_2(ReO_4)_2$. (Redrawn with permission from ref. 65.)

$Re_2O_3Cl_4(en)_2$ (1.9149(4), 1.910 and 1.912(5) Å, respectively) [68–71]. The Re–Re distance is comparatively short, 2.651(1) Å. The Re–$OReO_3$ bond length (2.096(9) Å) is very close to the values for normal single metal–oxygen bonds and is comparable with the corresponding interactions in $ReOI_2(PPh_3)_2(ReO_4)$ (2.031(6) Å) and $ReOI_2(OPPh_3)_2(ReO_4)\cdot0.5C_6H_6$ (2.079(9) Å). The IR spectra give bands due to Re–O (terminal), coordinated $[ReO_4]^-$ and δ(Re–O–Re) at 973, 934, 899, 855, 827, 729, 700 and 688 cm^{-1}.

A compound in which perrhenate is coordinated to rhenium(I) along with CO has recently been reported [72]. Pentacarbonyl-(perrhenato)rhenium(I), $Re(CO)_5(ReO_4)$, has been prepared by reacting $Re(CO)_5Br$ with $AgReO_4$ in dichloromethane at room temperature. A number of analogous compounds of composition $ML_n(ReO_4)$, where $ML_n = Rh(PPh_3)_2(CO)$, $Ir(PPh_3)_2(CO)$, $Pt(PPh_3)_2H$, $Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2$, $Os(PPh_3)_3)(CO)H$ or $Ir(PPh_3)_2(CO)(H)(Cl)$, have also been isolated by a similar method [72, 73]. The IR spectra of these compounds show two to three bands (two of the compounds, however, show only one band) in the region 930–860 cm^{-1}. Following Mayfield and Bull [16], the authors assigned the bands around 920 cm^{-1} to the υ_1 mode of $[ReO_4]^-$, which, as stated earlier, may better be assigned as a component of υ_3. The authors also assigned certain bands around 320 and 300 cm^{-1} to the υ_2 and υ_4 modes of perrhenate. The IR spectral data as a whole do not appear to support firmly the coordination of $[ReO_4]^-$. The authors were able to prepare $Ir(PPh_3)_2(CO)(Cl)(H)(ReO_4)$ by substituting BF_4^- in $Ir(PPh_3)_2(CO)(Cl)(H)(BF_4)$ with sodium perrhenate which indicates that $[ReO_4]^-$ is a stronger ligand than BF_4^-. Comparison of υ(Ir–H) and δ(M–^{1}H) in the IR and NMR spectra of the complexes $Ir(PPh_3)_2(CO)ClHX$ and of $Pt(PPh_3)_2HX$, where $X = [ReO_4]^-$, Cl^- or ClO_4^-, also indicates that $[ReO_4]^-$ is a stronger ligand than ClO_4^- and BF_4^-. The electronic spectra of the complexes $[Rh(X)(CO)(PPh_3)_2]$ and $[Ir(X)(CO)(PPh_3)_2]$, where $X = ReO_4$, ClO_4, OH, F, Cl, Br, I, NCS, NCO, NO_2, CN, etc., have been measured [73]. The spectrochemical order for the ligands (in decreasing energy of the longest-wavelength spectral band) in the two metal complexes is: $ClO_4 > ReO_4 > OH > F > Cl > Br > I > NCO > NO_2$, $I > NCS > CN$ for the rhodium complex and $OH > F > Cl > ReO_4 > ClO_4 > NCO > Br > NCS$, NO_2, $I > CN$ for the iridium complex. However, the spectral differences in most cases (including the complexes with perchlorate and perrhenate) are relatively too small to make any meaningful correlation.

G. OTHER COMPOUNDS

Very recently a complex in which $[ReO_4]^-$ is coordinated to a Rh(COD) centre (COD = 1,5-C_8H_{12}) has been characterised [74]. The orange crystalline complex $[(COD)Rh(\mu\text{-}\eta^2\text{-}ReO_4)]_n$ was obtained by the reaction of $[(COD)Rh(\mu\text{-}Cl)]_2$ with $AgReO_4$ in dry tetrahydrofuran. The moisture-sensitive complex gives a good resolution of the $[ReO_4]^-$ bands (943vs, 935sh, 905sh and 899vs). The perrhenate group acts as a bidentate bridging ligand. The structure (Fig. 8) consists of infinite chains in which the metal atoms are connected by oxygen bridges to form a $(-ReO_2-O-Rh(COD)-O-)_n$ polymer. One of the two Re–O–Rh angles in the complex is nearly linear, while the other is significantly bent. This is consistent with a largely σ-bonding interaction of one oxygen atom with the Rh(1) centre and a largely π-bonding interaction with the other. However, the two Rh–O distances differ only slightly, Rh–O(4) and Rh–O(3) being 2.07(2) and 2.09(2) Å, respectively. The Re–O(bridge) and Re–O(terminal) distances are likewise only marginally different, Re–O(4), Re–O(1), Re–O(2) and Re–O(3) being 1.74(2), 1.70(2), 1.69(2) and 1.72(2) Å, respectively.

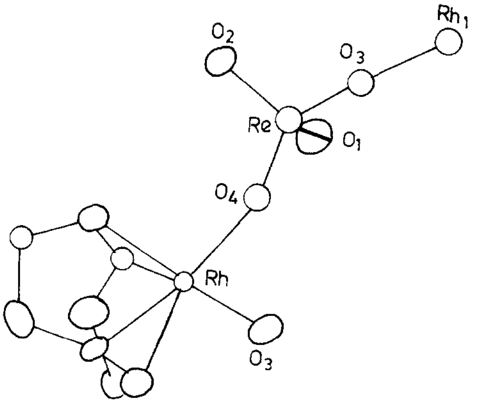


Fig. 8. Structure of $[(COD)Rh(\mu\text{-}\eta^2\text{-}ReO_4)]_n$. (Redrawn with permission from ref. 74.)

H. STUDIES IN SOLUTION

Virtually no significant work has been done on perrhenate complex formation in solution. However, it appears that weak perrhenate coordination may take place even in aqueous solution. Certain bands in the electronic spectra of the lanthanide ions shift by about 1 nm in fairly concentrated aqueous perrhenic acid (>3 M), and this has been attributed to the formation of 1:1 and 1:2 complexes of perrhenate [75]. However, the shift does not occur in $NaReO_4$ and it might have been caused by H_3O^+, rather than $[ReO_4]^-$. The spectrophotometric study of lanthanides with 0.1–12 M $HReO_4$ indicated the formation of $MReO_4^{2+}$ at >3 M and $M(ReO_4)_2^+$ at >7 M $HReO_4$. Formation constants were also calculated [76].

I. THIOPERRHENATE ION (ReS_4^-) AS A LIGAND

Very recently a few complexes with thioperrhenate (ReS_4^-) as ligand have been prepared by Müller and co-workers who had earlier isolated many complexes containing the analogous WS_4^{2-} and MoS_4^{2-} ions [77, 78]. The crystalline Ph_4P^+ salt of the discrete complex ion $[Cl_2Fe(ReS_4)FeCl_2]^{2-}$ has been obtained by reacting $(Et_4N)[ReS_4]$ with $FeCl_2$ in the presence of Ph_4PCl in dichloromethane [79]. The structure of the complex (Fig. 9) can be described as an array of three edge-connected tetrahedra, with the central tetrahedral (S_2ReS_2) unit bridging the two terminal $FeCl_2$ groups. The Fe···Re···Fe moiety is almost linear with Fe···Re distances of 2.740(2) and 2.747(2) Å. As expected, the average Re–S bond length (2.200 Å) is longer than that reported for $(Et_4N)[ReS_4]$ (2.125 Å), mainly due to an increase in electron density within the ReS_4 unit. The Fe···Re distance is rather short, while the isomeric shift in the Mössbauer spectra is small ($\delta = 0.46$). There is no clear overtone progression of $\upsilon_s(ReS)$ in the resonance-Raman spectrum and the band maxima and their extinction coefficients in the electronic spectrum do not correspond to those which would be expected for discrete (ReS_4) and $FeCl_2S_2$ chromophores. All these facts coupled with the results

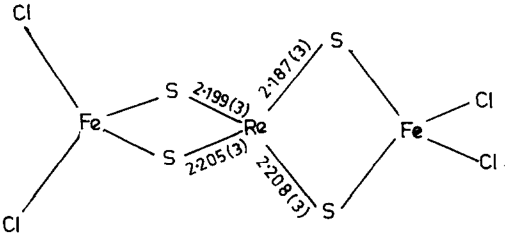


Fig. 9. Structure of $(Ph_4P)_2[Cl_2Fe(ReS_4)FeCl_2]$. (Redrawn with permission from ref. 79.)

of EH–SCCC–MO calculations indicate strong metal–metal and metal (Fe)–σ-acceptor-ligand (ReS_4^-) interactions. ReS_4^- is a strongly electron-withdrawing (σ-acceptor) ligand leading to an extreme electron delocalisation over the whole system. The same authors also isolated [80] the mixed crystal compounds, $(PPh_4)_2[Cl_2Fe(MoS_4)FeCl_2]_x[Cl_2Fe(ReS_4)FeCl_2]_{1-x}$ ($x = 0.3$ or 0.5) and compared their structures with that of $(PPh_4)_2[Cl_2Fe(ReS_4)FeCl_2]$.

The complex, $[Ph_4P]_2[NEt_4][Cl_7Cu_5(ReS_4)]$ is obtained by reacting $[NEt_4][ReS_4]$, anhydrous CuCl and Ph_4PCl in dichloromethane [81]. The structure (Fig. 10) has been determined by X-ray diffraction. The six metal atoms form approximately a basal-plane-centred "rectangle pyramid". The Re–Cu distances are very short (2.637(2)–2.668(4) Å), while the Re–S distances are larger (bond lengths are given in Fig. 10). Two S^{2-} groups have a coordination number of 4, with formation of the "double-cubane"-like structure. The diamagnetic complex gives υ(Re–S) at 451 and 442 cm^{-1} in the IR spectrum, while the solid-state reflectance spectrum gives a Cu(I)–Re(VII) charge transfer band at 700 nm and $S^{2-} \rightarrow$ Re(VII) charge transfer bands at 480 and 350 nm. A bromo complex analogous to the above was obtained by using CuBr and Ph_4PBr in place of CuCl and Ph_4PCl, while using CuI and Ph_4PI, the compound $(PPh_4)_2[Cu_3I_4(ReS_4)]$ was obtained [82]. It thus appears that the ReS_4^- ion may offer a still more varied and interesting coordination chemistry than $[ReO_4]^-$.

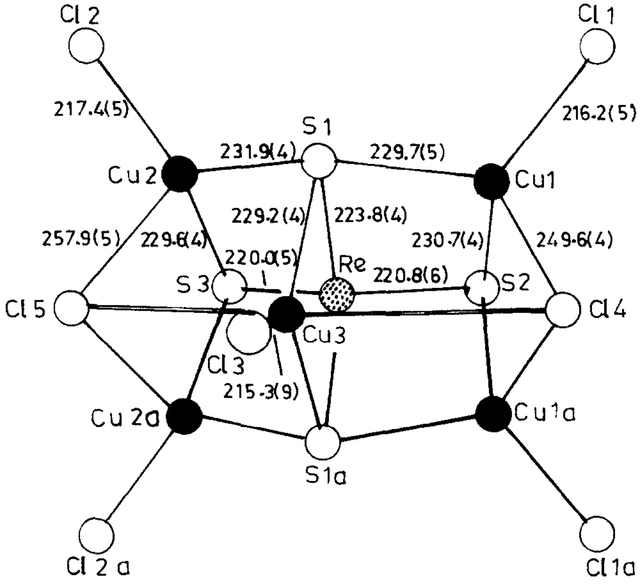


Fig. 10. Structure of $[PPh_4]_2[NEt_4][Cl_7Cu_5(ReS_4)]$. (Redrawn with permission from ref. 81.)

J. CONCLUSION

It is evident from the foregoing account that the chemistry of coordinated perrhenate, although not yet explored in detail, is even more interesting than the chemistry of coordinated perchlorate. Perrhenato complexes with a large number of metals (including rhenium itself in different oxidation states) have been prepared by reaction in the solid state, from both non-aqueous media and from aqueous solutions. Perrhenate appears to be a more powerful complexing agent than perchlorate. The ligand may be bonded to a metal ion in a varied manner which has been amply demonstrated by X-ray structural analysis of a fairly large number of compounds. The Re–O bond of the M–O–Re unit is generally longer than uncoordinated $[ReO_4]^-$, although there are some uncertainties in the measured bond lengths. The splittings of the $[ReO_4]^-$ frequencies in the vibrational spectra are small, rendering the diagnosis of perrhenate coordination difficult from vibrational spectra. Unfortunately, there is hardly any authentic report of the position of υ(M–O) which can convey much information about the strength of the metal–oxygen bond. An attempt to evaluate the M–O bond strength in perrhenato complexes is worth undertaking. The chemistry of the ReS_4^- ligand appears to be as interesting as the chemistry of WS_4^{2-}.

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