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THE SULPHIDO-, SELENO- AND TELLURO-HALIDES OF THE TRANSITION ELEMENTS

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CONTENTS

A. INTRODUCTION

The oxo-halides of the transition elements, especially those of the early transition elements (Groups IVa—VIIa) have been extensively studied and reviewed [1,2]. In direct contrast the sulphido-, seleno- and telluro- halides have received scant attention. Although some sulphido-halides were prepared in the nineteenth century, namely $Mo_5Cl_9S_8$ and $W_2Cl_4S_3$ [3], not until the late 1960's did interest revive in their characterisation and synthesis. Even today, for certain of the transition elements little or no information is available on their ability or otherwise to form sulphido-halides. The extent of knowledge available on these halides is insufficient for general considerations relating to the whole periodic table to be highlighted. Accordingly the material is arranged into a series of descriptive sections based upon the groups in the Periodic Table.

B. GROUP IVa — TITANIUM, ZIRCONIUM AND HAFNIUM

Little is known about the chalcogenide halides of Group IVa. Only compounds for titanium have been isolated [4,5,6], while attempts to prepare zirconium species by allowing zirconium(VI) chloride to react with Sb_2S_3 in CS_2 solutions were unsuccessful [7].

The titanium sulphido-halide $TiCl_2S$ was prepared from the reaction of titanium(IV) chloride with H_2S at 65°C in CS_2 solution [4]. Initially an adduct $TiCl_4.H_2S$ is formed and if the reaction temperature is increased the product is TiS_2. The preparative route has been criticised as only a low yield of $TiCl_2S$ is obtained [6]. Attempts to improve the yield by substituting antimony, arsenic and molybdenum sulphides instead of H_2S were ineffective [6]. No conclusive structural data on $TiCl_2S$ are available although its IR spectrum has been recorded [6].

In a Dutch patent the reaction of alpha titanium(III) chloride with sulphur in benzene at 120°C is reported to give a product consisting of 25% TiClS and 75% $TiCl_2S$ [5]. When activated with aluminium alkyls the sulphido-halides act as a polymerisation catalyst.

C. GROUP Va — VANADIUM, NIOBIUM AND TANTALUM

While no successful reports of vanadium sulphido- or seleno-halides have been made a number of niobium and tantalum compounds are known. The similarity between the niobium and tantalum species is so close that they can best be divided into two classes on the basis of those that contain Y—Y linkages (Y = S or Se) and those that do not. A list of the compounds, together with an outline of the preparative procedures for both groups of compounds, is given in Table 1.

(i) Compounds containing Y—Y linkage (Y = S or Se)

The niobium species with the general formula NbX_2Y_2 (X = Cl, Br or I; Y = S or Se) were all prepared by heating the reactants in an evacuated sealed tube [8,9]. For the chloride $NbCl_2S_2$, two sets of reactants were used, the first being niobium powder and S_2Cl_2 (molar ratio 1 : 1) and the second set

TABLE 1

Niobium and Tantalum sulphido- and seleno-halides

Species	Preparative route	Refs.
$NbClS_2$	$NbCl_5 + S$ (1 : 8 molar ratio) in benzene solution	10
$NbCl_2S$	$NbCl_4 + Sb_2S_3$ or As_2S_3 at 200°C in an inert atmosphere	25
$NbCl_2S_2$	$Nb + S_2Cl_2$ $Nb + S + NbCl_5$	8, 9 8, 9, 11 see Fig. 1.
$NbCl_2Se_2$	$Nb + Se + NbCl_5$	8, 9
$NbBr_2Y_2$ (Y = S or Se)	$Nb + Y + Br_2$	8
NbI_2Y_2 (Y = S or Se)	$Nb + Y + I_2$	8
$TaCl_2S_2$	$TaCl_5 + S$ (molar ratio 1 : 8) in benzene solution	10
$Nb_3S_3Cl_{11}{}^{4-}$	$NbCl_5 + F_2PS_2H \rightarrow NbCl_3(S_2PF_2)_2 \xrightarrow{py} [pyH]_4[Nb_3Cl_{11}S_3]$	26
NbX_3Y (Y = S or Se; X = Cl or Br)	$NbX_5 + Sb_2Y_3$ in CS_2 at room temp. As a decomposition product of NbX_2Y_2 in a mass spectrometer	15 8
$TaCl_3S$	$TaCl_5 + Sb_2S_3$ in CS_2 at room temp. $TaCl_5 + PhNCS \rightarrow TaCl_5 \cdot PhNCS \rightarrow TaCl_3S$	15 27
$TaBr_3Y$ (Y = S or Se)	$TaBr_5 + Sb_2Y_3$ in CS_2; at 20°C Y = S, at 40°C Y = Se	15
$NbCl_9S$	$NbCl_5 + S_2Cl_5$ (at 100°C)	24
$TaCl_9S$	$TaCl_5 + S_2Cl_2$ (at 100°C)	24

being niobium, sulphur and niobium (V) chloride (atomic ratio 1 : 1.8 : 2.3). The selenide $NbCl_2Se_2$ was prepared from the metal, selenium and niobium(V) chloride, while for the remaining compounds NbX_2Y_2 (X = Br or I; Y = S or Se) the reactants were the metal, chalcogen and the halogen. Various atomic ratios were employed and it appears to be an advantage to have a slight excess of the halogen above that required for NbX_2Y_2. Thus samples of the bromide $NbBr_2S_2$ were obtained with the three Nb : S : X_2 atomic ratios 1 : 1.2 : 2.5, 1 : 2 : 1 and 1 : 2 : 3; but with the ratio 1 : 2 : 1 in addition to $NbBr_2S_2$ a niobium—sulphur phase was formed.

Similar reactions to those that led to the successful isolation of $NbCl_2S_2$ from the reaction of the metal with S_2Cl_2, were attempted with vanadium and tantalum. No sulphido-chlorides were obtained, the products being vanadium(III) chloride and a sample of impure tantalum sulphide (TaS_3) containing a small amount of chloride. A species with the curious formula $TaBr_{1.93}S_{2.77}$ was also synthesised by allowing the three elements to react. Recently the grey—green $TaCl_2S_2$ has been isolated from the reaction of tantalum(V) chloride and sulphur [10].

The X-ray crystal structure of $NbCl_2S_2$ has been published [11] (Fig. 1). The structure consists of pairs of niobium atoms (Nb—Nb 2.90 Å) that are bridged by two S_2 units. Each niobium atom is also bonded to 4 chlorine atoms which form chlorine bridges to other niobium atoms; the niobium—niobium distance via a chlorine bridge being 4.12 Å. The co-ordination sphere around each niobium atom consists of 4 chlorine atoms (two at 2.60 Å and two at 2.62 Å) 4 sulphur atoms (two at 2.49 Å and two at 2.51 Å) and a niobium atom (2.90 Å). Thus each niobium atom can be considered to be nine co-ordinate. The short niobium—niobium distance implies considerable metal—metal bonding, and this is supported by magnetic measurements that show all the species of general formula NbX_2Y_2 to be diamagnetic [8].

The IR and Raman spectra of NbX_2S_2 (X = Cl, Br or I) have been extensively studied [12,13] and a normal co-ordinate analysis of the spectra of the chloride has been published [14].

By a direct comparison of the spectra of three species, namely $NbCl_2S_2$, $NbBr_2S_2$ and NbI_2S_2 it is possible to assign the vibrational modes to one of three groups. These groups are vibrations of the S_2 groups, vibration of the $Nb(S_2)Nb$ cage (Table 2) and vibrations of the niobium—halogen bonds. The position of the band associated with the S_2 group falls as expected on going from $NbCl_2S_2$ to NbI_2S_2 thus presenting evidence for a degree of coupling to the metal—halogen modes. The position of the mode involving the S_2 groups is considerably higher than in a number of the polysulphides; however, the normal co-ordinate analysis substantiates the assignment [14].

(ii) Compounds containing M = Y (M = Nb or Ta; Y = S or Se)

When the species NbX_2Y_2 (X = Cl or Br; Y = S or Se) were heated in a mass spectrometer, evidence was obtained for the compounds NbX_3Y (X = Br or Cl; Y = S or Se) [8], but from identical experiments with the iodides NbI_2Y_2 (Y = S or Se) the only volatile product was iodine [8].

Although initial attempts to prepare $TaCl_2S_2$ and $TaBr_2S_2$ failed, the products

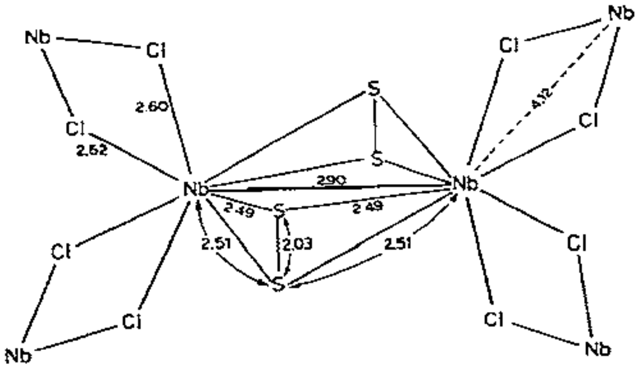


Fig. 1. $NbCl_2S_2$ redrawn from ref. 11.

TABLE 2

IR and Raman absorptions (cm^{-1}) associated with the sulphur atoms in NbX_2S_2 (X = Cl, Br or I); $Mo_2X_3S_5$ (X = Cl or Br); NbX_3S and TaX_3S (X = Cl or Br)

Species	S—S		Nb—S		M=S (M=Nb or Ta)	Ref.
	IR	Raman	IR	Raman	IR	
$NbCl_2S_2$	588 s 582 sh	592 vs	377 m 362 vs 323 vs 166 s	336 s 317 m 252 m 188 m	—	12, 13
$NbBr_2S_2$	585 s 580 sh	585 vs	370 m 358 s 320 s 174 s	328 s 310 m 243 s 183 s	—	12, 13
NbI_2S_2	575 s 570 sh		358 m 348 s 340 sh 315 s	—	—	12, 13
$Mo_2Cl_3S_5$	560	570	—	—	—	12
$Mo_2Br_3S_5$	555	565	—	—	—	12
$NbCl_3S$					552	15
$NbBr_3S$					542	15
$NbCl_3S.SPPh_3$					539	21
$TaCl_3S$					463	15
$TaBr_3S$					448 437	15
$TaCl_3S$. 2 tht					505	21
$TaBr_3S$. 2 tht					505	21

being TaS_3 (containing a trace of chloride) and $TaBr_{1.93}S_{2.77}$, when these products were examined mass spectrometrically, peaks assignable to TaX_3S (X = Cl or Br) were observed [8].

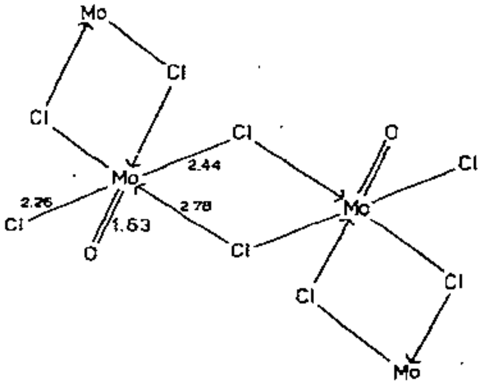
Attempts to prepare $NbCl_3S$ from the reaction of $NbCl_5$ and Sb_2S_3 in a sealed sublimation tube led to products that showed a considerable variation in colour. If the reaction was allowed to proceed for a considerable time a non-stoichiometric product was obtained [15]. However, by allowing $NbCl_5$ to react with the black form of Sb_2S_3 (molar ratio 3 : 1) in CS_2 solution at room temperature, $NbCl_3S$ was isolated.

With the same technique all the sulphido- and seleno-chlorides and bromides of niobium and tantalum, of general formula MX_3Y with the exception of $TaCl_3Se$, have been isolated (see Table 1).

None of these species of the formulation MX_3Y (M = Nb, Ta; X = Cl or Br; Y = S or Se) have been the subject of single crystal X-ray crystallography. The two most likely structures are one with a terminal metal—sulphur that is like the $MoCl_3O$ structure [16,17] (Fig. 2), or alternatively, one with a bridging metal—sulphur—metal moiety that is like the $MoBr_3O$ [18] and $NbCl_3O$ structures [19] (Fig. 3). Although the difference between the terminal Mo=O in $MoCl_3O$ (1.63 Å) and the shortest Mo=O bond in $MoBr_3O$ is small (1.65 Å) the effect of the long Mo—O bond in $MoBr_3O$ (2.31 Å) is to reduce the Mo—O stretching mode in the IR spectra of $MoBr_3O$ from some 1000 cm^{-1} (as seen in $MoCl_3O$) to some 750 cm^{-1}.

On the basis of evidence from IR spectra it is suggested that NbX_3S (X = Cl or Br) has the $MoCl_3O$ structure [16,17] and TaX_3S (X = Cl or Br) the $MoBr_3O$ structure [18]. In Table 2 are given the positions of the M=S stretching modes for the sulphido-halides and a number of their adducts. In the IR spectrum of $NbCl_3S.SPPh_3$ (a species whose structure has been determined and that was shown to contain terminal Nb=S, Figs. 4 and 5 [20]), there is a Nb=S stretching mode at 539 cm^{-1} and that is close to the position observed for ν(Nb=S) in $NbCl_3S$ (552 cm^{-1}) [15]. Thus it is suggested a terminal Nb=S bond is present in $NbCl_3S$. By contrast the position of ν(Ta=S) changes markedly on going from the parent sulphido-halide to an adduct. For example ν(Ta=S) in $TaBr_3S$ is at 448 and 437 cm^{-1} [15] while in $TaBr_3S.2tht$ (tht = tetrahydrothiophene) (a species shown by a structure determination to contain a terminal Ta=S bond) [21] it is at 505 cm^{-1} indicating the presence of a bridging Ta=S· · ·Ta system in $TaBr_3S$.

The two adducts whose structures have been the subject of X-ray crystallography are depicted in Figs. 4, 5 and 6. The niobium compound is interesting in that the unit cell contains two identical monomers of $[NbCl_3S.SPPh_3]$ (Fig. 4) and a centrosymmetric chlorine bridged dimer $[NbCl_3S.SPPh_3]_2$ (Fig. 5) [20]. A small energy difference must exist between the monomer and dimers of species containing M=Y bonds (Y = O or S) and thus packing forces deter-



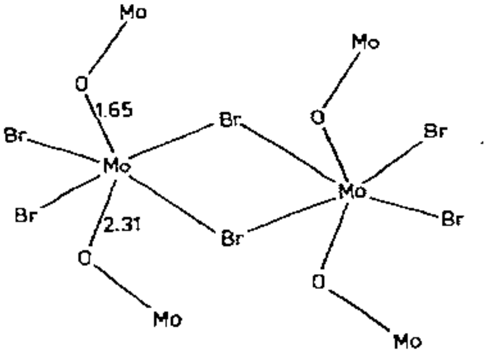


Fig. 2. $MoCl_3O$ redrawn from ref. 16.

Fig. 3. $MoBr_3O$ redrawn from ref. 18.

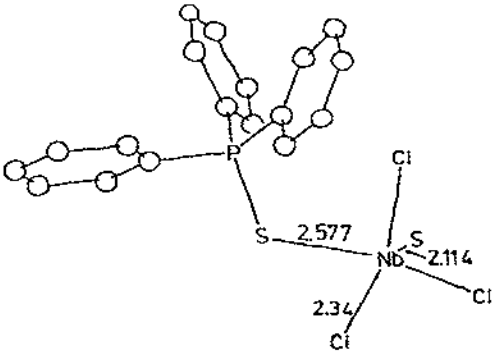


Fig. 4. The five co-ordinate species [$NbCl_3S.SPPh_3$] redrawn from ref. 20.

mine if monomeric (as seen in $MoCl_3O.SPPh_3$) [22], dimeric, or a mixture of both species (as seen in $NbCl_3S.SPPh_3$) are observed.

Both species containing terminal Nb—S bonds (5 co-ordinate Nb—S 2.114(4) Å, 6 co-ordinate 2.129(4) Å) have the metal atom away from the plane formed by the three chlorine atoms (ignoring the bridging atom in the dimer) and the sulphur atom of Ph_3PS (distances from the plane are 5 co-ordinate 0.55 Å, 6 co-ordinate 0.40 Å).

Depicted in Fig. 6 is the structure of $TaBr_3S$. 2 tht. Unfortunately the atoms *trans* to the co-ordinated sulphur atoms of the tetrahydrothiophene molecules are disordered, each site being 50% occupied by sulphur and bromine; however, there is no doubt that the compound contains a terminal tantalum—sulphur bond.

(iii) Compounds whose structures are unknown

The oxo-halide $TaCl_3O$ readily disproportionates at 300°C according to the equation

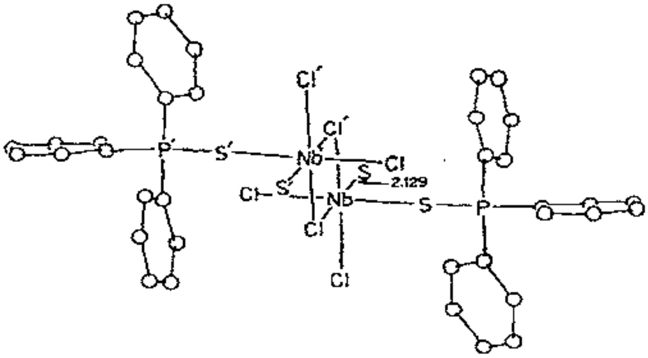
$$2\ TaCl_3O = TaCl_5 + TaClO_2$$

Careful control of the conditions is necessary as at higher temperatures $TaCl_5$ and Ta_2O_5 are formed [23].

Heating $TaCl_3S$ in a vacuum follows a similar pattern; at approximately 200°C $TaClS_2$ is formed, but on raising the temperature to 300°C the involatile product is TaS_3 containing a trace of chlorine [21]. Preliminary experiments indicate that the thermal decomposition of $NbCl_3S$ follows a different route and that at 220°C the products are $NbCl_2S$, $NbCl_5$ and sulphur.

The niobium analogue of $TaClS_2$ has been reported to be formed in the reaction of niobium(V) chloride with sulphur in benzene solution but no characterisation of the compound has been made [10].

Two compounds with unusual formulae are $TaCl_9S$ and $NbCl_9S$. Their struc-



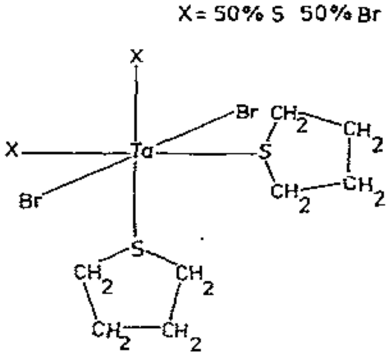


Fig. 5. The six co-ordinate species $[NbCl_3S.SPPh_3]_2$ redrawn from ref. 20

Fig. 6. $TaBr_3S.2tht$ redrawn from ref. 21.

ture and properties are unknown; both are formed by the reaction of the pentachloride with S_2Cl_2 [24].

D. GROUP VIa — CHROMIUM, MOLYBDENUM AND TUNGSTEN

Collectively the sulphido- and seleno-halides of this group have received more attention than those of any other transition metal group, but as with the other groups of early transition metals, studies have been largely confined to the lower two members of the group. Unlike niobium and tantalum which form closely related sulphido- and seleno-halides there are great differences between the species formed by molybdenum and tungsten so the compounds of these later elements are discussed separately.

(i) Chromium

A number of copper and chromium containing spinels such as $CuCr_2S_3X$ (X = Cl or Br), $CuCr_2Se_3Cl$ and $CuCr_2Te_3Cl$ have been reported [28—30] but there appears to be only one report of simple chromium sulphido- or seleno-halides [31]. By heating Cr_2S_3 and $CrBr_3$ to 870°C CrBrS was obtained. Similarly the heating of iodine with CrS, CrSe and CrTe leads to the formation of $CrI_{0.83}S$, CrISe and $CrITe_{0.73}$. All four compounds are black and readily hydrolysed in moist air.

(ii) Molybdenum sulphido-, seleno- and telluro-halides

The preparation of the molybdenum sulphido-, seleno- and telluro-halides can be conveniently sub-divided into three classes according to whether pure molybdenum, a molybdenum chalcogenide or a molybdenum halide was the source of the metal. All the species isolated are listed, together with an outline of the preparation, in Table 3.

TABLE 3

Molybdenum sulphido-, seleno- and telluro-halides

Species	Preparative route	Ref.
$MoXS$ (X = Cl, Br or I)	$[Mo_6X_8]X_4 + Mo + S$ at 1000°C for 24 h (X = Cl, Br or I)	42, 43 see Fig. 7
$MoCl_2S$	$MoS_2 + Cl_2$ at 400°C $3\ MoCl_4 + 2\ Sb_2S_3$ at 140°C for 7 d Disproportionation of $MoCl_3S$ at 260°C for 5 d	35 33 33
$MoCl_2Se$	$3\ MoCl_4 + 2\ Sb_2Se_3$ at 120°C for 14 d Disproportionation of $MoCl_3Se$ at 260°C for 2 d	
$MoCl_2S_2$ [a]	$MoCl_4O + H_2S$ $MoCl_4 + H_2S + CS_2$	34 33
$MoCl_2S_2$ [a]	$Mo + S_2Cl_2$ in a 1 : 1 molar ratio at 500°C for 2 d	32
$MoBr_2S_2$	$Mo + S_2Br_2$ in a 1 : 1 molar ratio at 500°C for 4 d	32
$MoCl_3S$	$MoCl_5 + Sb_2S_3$ at 140°C for 7 d $MoCl_5 + Sb_2S_3$ in CS_2 at room temp. for 2 d $MoCl_5 + Me_3SiSBu^t$	33 15 52
$MoCl_3Se$	$MoCl_5 + Sb_2Se_3$ at 140°C for 14 d	33
$MoCl_3S_2$	$MoCl_5 + S_2Cl_2$ in a 1 : 10 molar ratio at 250°C for 6 h (SCl_2 one of the products) $MoCl_3 + S$ in a 1 : 10 molar ratio in S_2Cl_2 for 6 d with a temp. gradient along the sealed reaction tube of 435 to 450°C	51 45 see Fig. 8
$MoBr_8Te_2$	$MoBr_{10}Te_2$ on gentle heating yields $MoBr_8Te_2$	37
$MoBr_{10}Te_2$	$MoTe_2 + Br_2$ as solvent at room temp.	37
$Mo_2Cl_3S_5$	MoS_3 held at 420 to 480°C in contact with S_2Cl_2 vapour $[Mo_6X_8]X_4 + S$ at 350 to 400°C for several hours	32 12, 13
$Mo_2Br_3S_5$	MoS_3 held at 420°C in contact with S_2Br_2 vapour $[Mo_6Br_8]Br_4 + S$ at 350 to 400°C for several hours	32 12, 13
$Mo_2I_3S_5$	$[Mo_6I_8]I_4$ and excess S at 300°C for 7 d	13
$Mo_2Cl_5S_4$	MoS_3 held at 350 to 400°C in contact with S_2Cl_2 vapour	32
$Mo_3Cl_4S_7$	$MoCl_3 + S$ (molar ratio 1 : 10) at 450°C for 1 d $MoCl_3 + S$ (molar ratio 1 : 10) with S_2Cl_2 as solvent at 450°C for 6 d	46 45 see Fig. 9
$Mo_3Cl_4Se_7$	$MoCl_3 + Se$ (molar ratio 1 : 10) at 400°C for 1 d	46
$Mo_3Br_4S_7$	$[Mo_6Br_8]Br_4 + S$ (molar ratio 1 : 5) at 420°C for 10 h $MoBr_3 + S$ (molar ratio 1 : 5) at 360°C for 5 h	47 47
$Mo_3Br_4Se_7$	$[Mo_6Br_8]Br_4 + Se$ (molar ratio 1 : 5) at 400°C for 10 h $MoBr_3 + Se$ (molar ratio 1 : 5) at 340°C for 10 h	47 47
$Mo_6X_2S_6$ (X = Br or I)	$Mo_6X_{12} + Mo + S$ (appropriate molar ratio) at 1050°C for 48 h	102

TABLE 3 (continued)

Species	Preparative route	Ref.
$Mo_6X_{10}Y$ (X = Br; Y = S, Se or Te) (X = I; Y = Se or Te)	$[Mo_6Br_8]Br_4$ + Y at 800 to 1150°C for 24 h	40
$Mo_6X_xY_{8-x}$ (X = Br or I; Y = Se or Te)	$[Mo_6X_8]X_4$ + Y as above	40
$Mo_6I_8Y_{14}$ (Y = S or Se)	Mo(II) and (III) iodide + Y	39
$Mo_6X_8Y_{14}$ (X = Cl, Br or I) (Y = S or Se)	$[Mo_6X_8]X_4$ + Y	38

[a] Probably two different species with identical molecular formulae.

(a) Reactions involving molybdenum metal

The reactions involving the metal with S_2X_2 (X = Cl or Br) have been investigated, and in 1894 Smith and Oberholtzer [3] reported that when X = Cl the reaction leads to the formation of $Mo_5Cl_9S_8$, while more recently it has been claimed that the moisture sensitive compounds MoX_2S_2 (X = Cl or Br) are formed [32]. The oxidation state of the metal in MoX_2S_2 was not determined [32] but it was thought likely that the species was directly analogous to $NbCl_2S_2$ [8,11], and thus it probably contains S_2 units. The compound $MoCl_2S_2$ is also formed by the reaction of molybdenum(IV) chloride with H_2S in CS_2 solution [33]. A compound with the same molecular formula is obtained from the reaction of $MoCl_4O$ with H_2S [34]; however this latter species is probably more closely related to WCl_2S_2 [15] than $NbCl_2S_2$ and it is likely that it contains molybdenum(VI).

(b) Reactions involving molybdenum chalcogenides

Halogenation of chalcogenides has been more extensively studied as a route to chalcogenide halides than reactions involving the pure metal. Initially the impetus was towards extraction of the metal directly from molybdenite (MoS_2) via chlorination [35]. At 400°C $MoCl_2S$ is formed when chlorine is passed over heated MoS_2, but use of an excess of chlorine leads to molybdenum(V) chloride [35]. The same compound is also formed by the reaction of $MoCl_4$ with Sb_2S_3 (either in CS_2 suspension [7] or in a sealed tube [33]) and by the thermal decomposition of $MoCl_3S$ [33]. The exact nature of this sulphido-halide and the related selenide is uncertain. The IR spectrum of the sulphide has no bands above 400 cm^{-1} thus indicating the absence of a terminal Mo=S bond, and of unsymmetrically co-ordinated S_2 groups [13]. Probably the sulphido- and seleno-halides have a highly polymeric structure like that of $MoCl_2O$ [36] although neither are isomorphous with the oxo-halide [33]. The only other reactions involving a molybdenum sulphide are those of MoS_3 (a species whose exact nature is uncertain, but which probably does not contain molybdenum(VI)) and S_2X_2 ($X = Cl$ or Br). The reaction yielded $Mo_2X_3S_5$ [12,32] above 420°C and below 400°C $Mo_2Cl_5S_4$ was formed [32]. A more convenient route to $Mo_2X_3S_5$ ($X = Br$, Cl or I) is from the reaction of $[Mo_6X_8]X_4$ with an excess of sulphur [12,13]. The structures of the air stable species $Mo_2X_3S_5$ ($X = Br$, Cl or I) have not been determined. They are believed to contain S_2 units as the IR and Raman spectra of all three have a band at 560 (±10) cm^{-1} which by comparison with the spectrum of $NbCl_2S_2$ is assigned to the S—S stretch of S_2 groups [12,13] (Table 2).

The above survey illustrates that with the exception of $Mo_2Cl_5S_4$ [32] all the sulphido-halides obtained by the use of molybdenum sulphides can be more conveniently synthesised from the molybdenum halides. A unique reaction employing a molybdenum chalcogenide is that of $MoTe_2$ with liquid bromine. At room temperature an exothermic reaction occurs leading to the formation of $MoBr_{10}Te_2$ which on gentle warming loses bromine to give $MoBr_8Te_2$ [37]. The latter compound is green, diamagnetic, sublimable, and soluble only in polar solvents such as ether, ethanol and acetone, giving solutions that are non-conducting. Its IR spectrum has a band at 825 cm^{-1} which suggests the presence of contamination with an Mo—O—Mo containing moiety. This system merits further attention.

(c) Reactions involving the molybdenum halides

Molybdenum(II) halides. Of all the halides the dihalides have been most frequently used to prepare sulphido- and seleno-halides (see also section (a)). The simplest reaction undergone by the dihalides is the replacement of the four halides that are associated with the $[Mo_6X_8]^{4+}$ cluster by sulphur or selenium groups carrying the appropriate charge. From the direct reaction of $[Mo_6X_8]X_4$ ($X = Br$, Cl or I) with sulphur or selenium, $[Mo_6X_8]Y_{14}$ ($Y = S$ or Se) was obtained where it is suggested the $Mo_6X_8{}^{4+}$ cluster remains intact [38]. The analogous iodides have also been made from the reaction of molybdenum (II) and (III), iodides and sulphur of selenium [39]. Partial substitution of the halogen ion outside the cluster to yield $[Mo_6X_8]X_2Y$ ($X = Br$ or I; $Y = Se$ or Te) and $[Mo_6Cl_8]Cl_2S$ occurs when the dihalide is allowed to react with the chalcogen and molybdenum in the appropriate molar ratios [40]. The X-ray powder photograph shows the bromide compounds to be isomorphous with Nb_6I_{11} [41]. It is suggested that in these sulphido-bromides the two bromine and sulphur atoms bridge between two clusters, thus more correctly the formula should be $[Mo_6Br_8]Br_{4/2}Y_{2/2}$.

From the reaction of $[Mo_6X_8]X_4$ ($X = Br$, Cl or I) with sulphur and molybdenum in the molar ratio 1 : 8 : 12 at 1000°C for 24 hours, MoXS ($X = Br$, Cl or I) was obtained [42, 43]. These molybdenum(III) compounds are black, air stable and diamagnetic. A single crystal X-ray study of MoBrS has been reported [43]. The cubic crystals contain Mo_4S_4 units (Fig. 7), the angles on the face of the Mo_4S_4 unit being 73.3° (Mo—S—Mo) and 104.45° (S—Mo—S).

A full list of the angles subtended at the molybdenum are given in Table 4. These were not given in the original publication but were calculated from the data contained in it [44]. From these angles and the fact that the molybdenum has three Mo—Mo distances of 2.79(8) Å, three Mo—S distances of 2.34(3) Å and three Mo—Br distances of 2.75(3) Å, the molybdenum can be considered 9 co-ordinate (Fig. 7).

Recently two superconducting compounds $Mo_6Br_2S_6$ and $Mo_6I_2S_6$ have been isolated from the reaction of Mo_6X_{12}, molybdenum and sulphur at 1050°C [102].

Molybdenum(III) halides. From the reaction of molybdenum(III) chloride and sulphur in S_2Cl_2 at 430—450°C two species were obtained, namely $MoCl_3S_2$ and $Mo_3Cl_4S_7$ [45]. The analogous selenide to $Mo_3Cl_4S_7$ has been reported [46], as have the bromides $Mo_3Br_4Y_7$ (Y = S or Se) [47].

The X-ray crystal structure of $MoCl_3S_2$ has been determined [45]. It shows that the molybdenum atoms occur in metal—metal bonded pairs (Mo—Mo distance 2.833(2) Å) and that at approximately right angles to that bond are two bridging S_2 units (S—S 1.980(3) Å, Fig. 8). Each molybdenum atom is attached to four chlorine atoms, two of which bridge to another molybdenum atom (Mo—Mo 3.990(2) Å). The co-ordination number of the molybdenum is nine (as in MoBrS) and the overall structure is similar to that of $NbCl_2S_2$ [11] (Fig. 1).

The species with the formula $Mo_3X_4Y_7$ (X = Br or Cl; Y = S or Se) [45—47] presumably all have the same structure as $Mo_3Cl_4S_7$ (Fig. 9) [45]. The structure is unusual in that it contains an almost equilateral triangle of molybdenum atoms (Mo—Mo distances range from 2.741(3) to 2.748(3) Å). At 1.746(7) Å above the centre of the triangle is a unique sulphur atom that can be considered bonded to the three molybdenum atoms (three Mo—S distances range from 2.35 to 2.37 Å). Situated on or just above the plane of the molybdenum atoms are three sulphur atoms (distances above the plane are S(1)

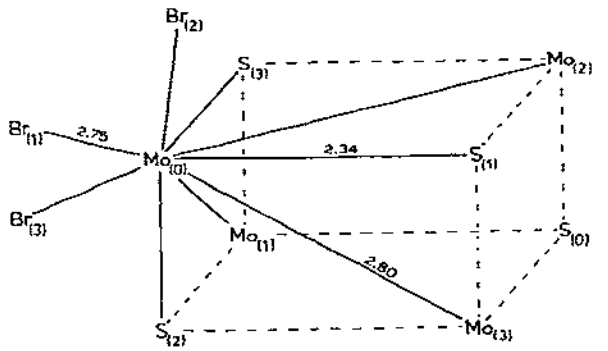


Fig. 7. Co-ordination sphere of Mo in MoBrS, see ref. 43.

TABLE 4

Angles and bond distances relating to Mo(0) in MoBrS [a]

Angles		Distances (Å)	
Mo—Mo—Mo	60.0°		
S—Mo—S	104.45°	Mo(0)—S(1,2 or 3)	2.34
Br—Mo—Br	77.87°		
		Mo(0)—Br(1,2 or 3)	2.75
Mo(1)—Mo(0)—Br(2 or 3)			
Mo(2)—Mo(0)—Br(1 or 3)	140.47°	Mo(0)—Mo(1,2 or 3)	2.80
Mo(3)—Mo(0)—Br(1 or 2)			
		Mo(0)—S(0)	3.98
Mo(1)—Mo(0)—Br(1)			
Mo(2)—Mo(0)—Br(2)	98.22°		
Mo(3)—Mo(0)—Br(3)			
Mo(1)—Mo(0)—S(1)			
Mo(2)—Mo(0)—S(2)	101.15°		
Mo(3)—Mo(0)—S(3)			
Mo(1)—Mo(0)—S(2 or 3)			
Mo(2)—Mo(0)—S(1 or 3)	53.34°		
Mo(3)—Mo(0)—S(1 or 2)			
S(1)—Mo(0)—Br(1)			
S(2)—Mo(0)—Br(2)	160.63°		
S(3)—Mo(0)—Br(3)			
S(1)—Mo(0)—Br(2 or 3)			
S(2)—Mo(0)—Br(1 or 3)	87.13°		
S(3)—Mo(0)—Br(1 or 2)			

[a] Atomic numbering scheme as per Fig. 7. No angles given for S(0)

0.08 Å; S(3) 0.23 Å; S(5) 0.06 Å) and each of them is bound to a further sulphur atom to form an S_2 unit (S(1) to S(2) 2.05 Å; S(3) to S(4) 2.03 Å; and S(5) to S(6) 2.01 Å). These last three sulphur atoms are below the plane of the three molybdenum atoms [distances below the plane: S(2) 1.68 Å; S(4) 1.59 Å; S(6) 1.65 Å]. Each S_2 unit is unsymmetrically bound to two molybdenum atoms. For a given S_2 unit the sulphur atom that is closest to the plane of the

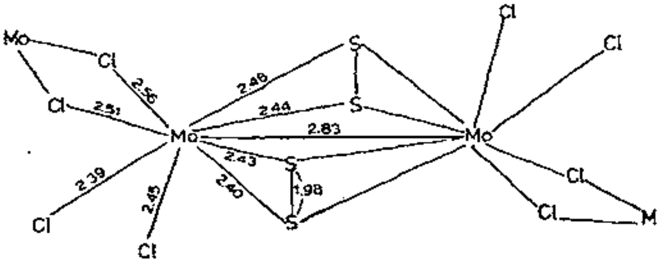
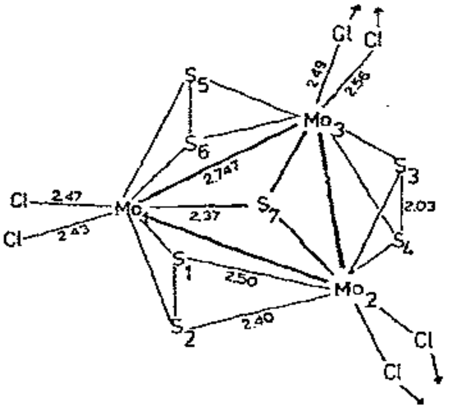


Fig. 8. $MoCl_3S_2$ redrawn from ref. 45.



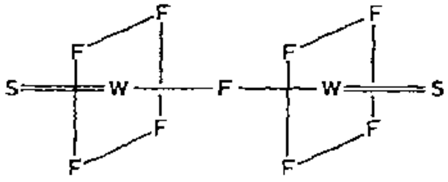


Fig. 9. $Mo_3Cl_4S_7$ redrawn from ref. 45.

Fig. 10 $W_2F_9S_2^-$.

molybdenum atoms has longer Mo—S distances than its partner that is below the plane (for the S_2 unit S(1)—S(2), Mo(1)—S(1) = 2.51 Å and Mo(1)—S(2) = 2.40 Å); thus the S_2 units are not perpendicular to the plane of the molybdenum atoms.

Besides being bonded to four sulphur atoms each molybdenum atom has two chlorine atoms in its co-ordination sphere. Those attached to Mo(1) are terminally bonded, the others being bridging atoms. Thus the structure consists of a zigzag chain with $Mo_3Cl_4S_7$ as the repeat unit.

Molybdenum(V) chloride. The reactions of molybdenum(IV) halides to give sulphido- and seleno-halides were discussed in section (a). The remaining halide that has been investigated is molybdenum(V) chloride. The reaction of molybdenum(V) chloride with Sb_2S_3 carried out in a sealed tube yields $MoCl_3S$ and $SbCl_3$, the products being separated by vacuum sublimation at 140°C [33]. An analogous reaction with Sb_2Se_3 gives $MoCl_3Se$. The sulphido-halide is fairly unreactive towards Lewis bases although a number of adducts have been isolated [48]. A more reactive form of $MoCl_3S$ can be prepared by allowing $MoCl_5$ and Sb_2S_3 to react in CS_2 solution at room temperature [15]. The product from the room temperature reaction is more reactive towards Lewis bases than the product that was heated during its preparation to 140°C and the two products also have different X-ray powder patterns. A re-examination of the IR spectra of the adducts formed by $MoCl_3S$ indicates that the band reported as molybdenum—sulphur terminal stretch is the asymmetric mode of a Mo—S—Mo bridging system [49]. The evidence which supports this suggestion is the occurrence of the Nb=S terminal stretch at 552 cm^{-1} [15] and IR studies on $[Mo_2O_3S(S_2CNEt_2)_2]$ where the asymmetric Mo—S—Mo mode is said to occur at 462 cm^{-1} and the symmetric stretch at 350 cm^{-1} [50].

(iii) Tungsten

The majority of the reported tungsten sulphido- and seleno-halides concern tungsten in the oxidation states (V) and (VI) which is in contrast to the large number of molybdenum sulphido- and seleno-halides prepared from molybdenum(II) and (III) halides.

The known species are listed (together with an outline of their preparative methods) in Table 5. Noticeably all the successful preparations except one mass spectrometric study [53] involve the use of tungsten halides.

The chemistry of WF_4S has been extensively studied by Russian workers by the use of ^{19}F NMR spectroscopy [54]. By allowing WCl_4S to react initially in methyl cyanide with an excess of HF, NMR evidence for $[WCl_4FS]^-$, $[WCl_3F_2S]^-$, $[WCl_2F_3S]^-$, $[WClF_4S]^-$ and $[W_2F_9S_2]^-$ (Fig. 10) was obtained. From the NMR spectra it was deduced that in the mixed chlorine—fluorine species the fluorine preferentially goes into the equatorial positions.

Comparison of the chemical shifts for the fluorine atoms *trans* to the multiple bond show an upfield shift of 12 to 16 ppm on going from $[W_2F_9O_2]^-$ [82] to $[W_2F_9S_2]^-$ while the equatorial fluorine atoms have a 23 ± 3 ppm downfield shift. Thus the *trans* effect of the sulphur atom in W=S is said to be greater than that of oxygen in W=O [54].

The two anions $[WF_5S]^-$ and $[W_2F_9S_2]^-$ are also formed together with

TABLE 5

Tungsten sulphido- and seleno-halides

Species	Preparative route	Ref.
WF_2S	SF_6 + W in a mass spectrometer	53
WX_2Y (X = Br or Cl; Y = S or Se)	Disproportionation of WX_3Y	33
WF_3S	SF_6 + W in a mass spectrometer	53
WCl_3Y (Y = S or Se)	$WCl_5 + Sb_2Y_3$ at 120°C for 7 d	33
WBr_3Se	$WBr_5 + Sb_2Se_3$ at 120°C for 14 d	33
WF_4S	$WF_6 + Sb_2S_3$ at 300°C for 3 h	57
	WCl_4S + HF in CH_3CN	54
	$WF_6 + H_2S$ in CH_3CN	56
WCl_4S	WCl_6 + S at 170°C for 8 h	61 (see Fig. 11)
	$WCl_6 + Sb_2S_3$ at 140°C for 3 d	33 62
	$WCl_6 + Me_3SiSBu^t$ in CS_2 or CCl_4	52
WBr_4S	$WBr_6 + Sb_2S_3$ at 140°C for 7 d	33
WBr_4Se	$WBr_6 + Sb_2Se_3$ at 120°C for 14 d	33
WF_2S_2	WSF_4. MeCN + H_2S	56
WF_2OS	SF_6 + W in mass spectrometer	53
WCl_2S_2	$WCl_4O + H_2S$ in C_6H_6 or CS_2	33, 34
	$WCl_4S + Sb_2S_3$ in CS_2	15
WCl_2SSe	$WCl_4Se + Sb_2S_3$ in CS_2	15
WCl_2OS	$WCl_4S + Sb_2O_3$ in CS_2	15
$W_2Cl_6S_3$	$W + S_2Cl_2$	3
$[W_2Cl_7S]^{3-}$	$K_2W_2Cl_9 + F_2PS_2H$	81

$WF_4S.MeCN$ when WF_6 in methyl cyanide solution is allowed to react with sodium or potassium sulphides [55]. The formation of the sulphido-fluorides is much slower with organic sulphides such as Bu_2S while with the disulphide Me_2S_2, WF_5SMe and $WF_4(SMe)_2$ are formed. The most rapid formation of WF_4S and WF_2S_2 is achieved by passing H_2S into methyl cyanide solutions of WF_6 [55,56].

The pure sulphido-fluoride WF_4S has been synthesised by allowing WF_6 to react with Sb_2S_3 in a nickel reactor at 300°C [57]. By examination of the IR spectrum of WF_4S [57] it was suggested that WF_4S has a tetrameric structure (like WF_4O) [58] containing bridging and terminal tungsten—fluorine bonds and a terminal tungsten—sulphur bond.

Certain sulphido-fluorides have also been synthesised by allowing tungsten and SF_6 to react in a mass spectrometer (Table 5) [53]. From the same study, heats of formation for WF_2S, WF_3S and WF_2S_2 and a number of bond dissociation enthalpies were obtained (Table 6). Noticeably the bond dissociation energies of the W—S bond increases as the valence state of the tungsten decreases.

The observation of ^{19}F shifts have been utilised to rationalise the difference in reactivity of WF_4S and WF_4O towards alcohols [59,60]. Initially the reaction of alcohols with WF_4S leads to the formation of a co-ordination compound with the oxygen atom of the alcohol *trans* to W=S. On the addition of nitrogen bases the formation of tungsten alkoxides occurs with movement of the oxygen into one of the positions occupied by a fluorine atom of the WF_4 moiety. Similar reactions occur with WF_4O but weaker nitrogen bases are effective in causing alcoholysis. The variation in base strength needed to cause alcoholysis is said to reflect the smaller d_π—p_π interaction in the bond of the acido ligand to the central atom in the non-linear fragment S—W—L *cis* compared to O—W—L *cis* [59,60]. The evidence for such a change in d_π—p_π comes from the ^{19}F studies discussed above [54].

The best preparative route for WCl_4S of those published is the reaction of WCl_6 with sulphur in an evacuated sealed tube at 170°C [33,61]. A similar reaction with WBr_6 led to non-stoichiometric products, so WBr_4S is best prepared by allowing WBr_6 to react at 140°C with Sb_2S_3 [33]. The X-ray crystal

TABLE 6

Heats of formation and some bond dissociation energies for a number of tungsten sulphido-fluorides (data taken from Ref. 53)

Gaseous species	$\Delta Hf_{(298)}$ (kJ mol^{-1})	Bond dissociation energies (kJ mol^{-1})	
		SF_2W—F	W—S
WF_2S_2	−496.8 (±17.6)	—	440
WF_3S	−712.5 (±13.4)	456	481
WF_2S	−335.3 (±16.3)	—	527

structures of WCl_4S and WBr_4S have been determined [62] and they both consist of weakly halogen bridged $(WX_4S)_2$ dimers (Fig. 11). The presence of the terminal tungsten—sulphur bond in WCl_4S is in contrast to the compound WCl_4O which is oxygen bridged [63]. The presence of W = S shows up in the IR spectra, $\nu_{W=S}$ being reported at 569 and 555 cm^{-1} in WCl_4S and WBr_4S respectively [33]. The related seleno- compounds WX_4Se (X = Cl or Br) are isomorphous with their sulphur analogues and $\nu_{W=Se}$ was reported at 396 cm^{-1} for WCl_4Se but the stretch curiously was not observed in the IR spectrum of WBr_4Se [33].

All the sulphido- and seleno-halides of the general formula WX_4Y (X = Cl or Br; Y = S or Se) are soluble in CS_2 and $CHCl_3$. They readily form simple adducts with a large range of Lewis bases in which the metal is six co-ordinate and the ligand is *trans* to the W=Y (Y = S or Se) bonds [64]. With some of the pyridine bases more complex reactions can occur, for example the reaction of WCl_4S with bipyridyl yields WCl_3S.bipy and with pyridine WCl_4S forms a compound WCl_4S.3py whose exact nature is uncertain.

Also complicated are the reactions of WX_4Y (X = Cl or Br; Y = S or Se) with ligands of the type $[RYCH_2]_2$ (R = alkyl group; Y = O or S). Under carefully controlled conditions 2 $WCl_4S.[CH_3SCH_2]_2$ was isolated from the reaction of WCl_4S with $[CH_3SCH_2]_2$. Its X-ray crystal structure has been determined [65]. The molecule is approximately centrosymmetric with the ligand bridging two WCl_4S units with the donor atoms *trans* to the tungsten—sulphur double bonds (Fig. 12).

Attempts to isolate pure samples of 2 $WCl_4S.[CH_3OCH_2]_2$ have failed although NMR evidence for its existence in solution has been obtained [66]. From the reaction of WCl_4S with $[CH_3OCH_2]_2$ a molecular species, namely $WCl_4S.WCl_2OS.[CH_3OCH_2]_2$, containing the WCl_2OS moiety was isolated [67]. A study of its X-ray crystal structure revealed that the ligand $[CH_3OCH_2]_2$ chelates to WCl_2OS, the donor atoms being *trans* to W=S and W=O (Fig. 13). The oxygen atom of the WCl_2OS group (formally designated W=O) bridges to the WCl_4S molecule. The formation of a W=O—W bridge rather than W=S—W bridge between WCl_4S and WCl_2OS is directly comparable to the difference in structure between WCl_4O (oxygen bridged polymer) [63] and WCl_4S (weakly chlorine bridged dimer) [62]. A similar reaction between

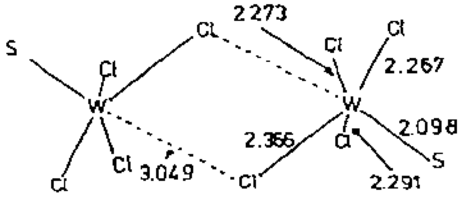


Fig. 11. WCl_4S redrawn from ref. 62.

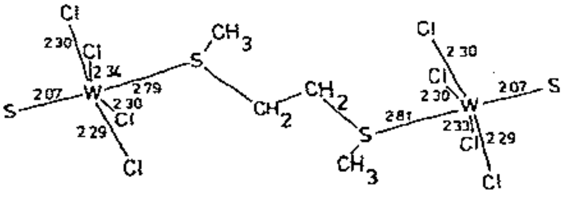
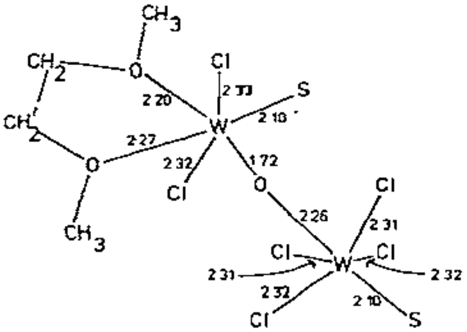


Fig. 12. 2 WCl_4S. $[CH_3SCH_2]_2$ redrawn from ref. 65.



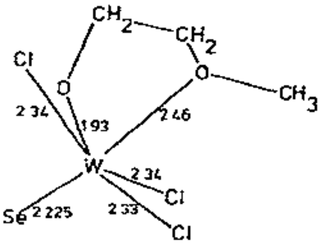


Fig. 13. $WCl_4S.WCl_2OS.[CH_3OCH_2]_2$ redrawn from ref. 67.

Fig. 14. $WCl_3SeOCH_2CH_2OCH_3$ redrawn from ref. 68.

WCl_4Se and $[CH_3OCH_2]_2$ gave the alkoxide $WCl_3SeOCH_2CH_2OCH_3$ whose X-ray structure has also been determined [68] (Fig. 14). The ligand chelates with the donor atom again *trans* to the tungsten selenium double bond. Examination of the tungsten—oxygen bond lengths for the donor oxygen atoms in the three situations *trans* W=Se [68], *trans* W=S [67] and *trans* W=O [67] (this W=O weakly bridges to another tungsten atom) shows the bond lengths to be 2.46 Å (*trans* W=Se), 2.27 Å (*trans* W=S) and 2.20 Å (*trans* to W=O) thus substantiating the suggestion that the *trans* effect series is W=S > W=O [54].

Reinvestigation by ^1H NMR spectroscopy of the reaction of WCl_4Y (Y = O, S, Se, NC_2Cl_5) with $[ROCH_2]_2$ (R = alkyl group) shows that initially 2 $WCl_4Y.(CH_3OCH_2)_2$ is formed [66]. This is followed by the formation of a species in which the ligand chelates. Finally, cleavage of one of the alkyl—oxygen bonds occurs and $WCl_3YOCH_2CH_2OR$ and the alkyl chloride are formed, thus showing the isolation of $WCl_3SeOCH_2CH_2OCH_3$ [68] was just one example of a general reaction. Preliminary results obtained by repeating the reactions with the sulphur ligand $[CH_3SCH_2]_2$ indicate that the cleavage reactions are much slower when a C—S bond has to be broken. No free alkyl chloride was detected and it is thought sulphonium salts of the type $R_2S^+CH_2CH_2SW^-Cl_4$ (or $[R_2SCH_2CH_2SWCl_3]^+Cl^-$) were formed.

The other tungsten(VI) sulphido- and seleno-halides that have been reported are of the type WCl_2YY' (Y = O, S or Se; Y' = S or Se) [15,34,67,69]. The most convenient synthesis is from the reaction of WCl_4Y' (Y' = S or Se) with Sb_2Y_3 (Y = O, S or Se) in CS_2 solution at room temperature [15]. The products that were prepared at room temperature were quite reactive towards Lewis bases, and have been observed in a mass spectrometer [69].

The tungsten(V) sulphido- and seleno-halides WCl_3Y (Y = S or Se) and WBr_3Se are formed by the reaction of WX_5 (X = Cl or Br) with Sb_2Y_3 (Y = S or Se) [33]. They are believed to have a sulphur or selenium bridged structure similar to that of $NbCl_3O$ which is an oxygen and chlorine bridged polymer [19]. The evidence for the structure is their lack of reactivity with Lewis bases and their low magnetic moments [33]. Further evidence is given by a comparison of IR spectra of WCl_3S. bipy [64] (which has a $\nu_{W=S}$ mode at 531 cm^{-1}) and WCl_3S which has no IR absorption above 470 cm^{-1}.

The sulphido- seleno- halides in which the tungsten atom has an oxidation state below (V) are listed in Table 5. Except for the thermochemical data determined for WF_2S [53] only the preparation of the species has been reported. The lack of parallel studies to that carried out with molybdenum(II) and molybdenum(III) halides [12,13,32,40,42,43] is a large gap in the chemistry of the sulphido-halides of tungsten.

E. GROUP VIIa — MANGANESE AND RHENIUM

(i) Manganese

Three manganese sulphido-halides have been reported [70]. By allowing the halogens to react with the rose-coloured form of MnS, $MnCl_2S$, MnBrS and MnIS were obtained. These three compounds were shown by comparison of their X-ray powder photographs not to be mixtures of MnS and manganese(II) halides.

(ii) Rhenium

At least twelve sulphido-, seleno- and telluro-halides of rhenium have been reported (Table 7) but definitive structural evidence does not exist for any of them. Speculation on the basis of analysis would be ill-advised for although adducts of $ReCl_3O$ have been well-characterised [1] the species reported to be one form of $ReCl_3O$ [71] was shown by X-ray crystallography to be $Re_2O_3Cl_6$. 2 ReO_3Cl [72].

By allowing $ReCl_5$ and sulphur (in a 1 : 2 molar ratio) to react at 125°C for 2—3 hours $ReCl_4S$ was formed [73] the other product being S_2Cl_2. Careful control of the reaction conditions was necessary and so the process was monitored by differential thermal analysis. If the same stoichiometries were used, but the reaction was carried out at 160°C, $Re_2Cl_5S_3$ was the product; further increase of temperature to 270°C led to the formation of $ReCl_2S$ and above this Re_2S_7 was obtained. By studying the fusion diagrams of Re_3Cl_9 and S_2Cl_2 it was shown that $ReCl_4S$ melts incongruently at 80 ± 2°C and that it probably undergoes a phase change at −63°C. The IR spectra of $ReCl_4S$ is reported to contain a band at 913 cm^{-1} which was assigned to a rhenium—sulphur stretching mode. The assignment is unlikely; probably the sample was allowed to come into contact with oxygen as the Re—O stretching modes in $ReCl_4O$ are centered at 1040 cm^{-1} and those in ReO_3Cl at 970 cm^{-1} [74]. By comparison with the terminal W=O and W=S stretching modes, the Re=S mode would be expected in the region of 560 cm^{-1}. The same authors also report $ReClS_3$ as having an IR band at 913 cm^{-1} with a shoulder at 890 cm^{-1}. However, the reported analytical figures for this compound add up to 113% so the isolation of $ReClS_3$ must be open to question although from a fusion

TABLE 7

Rhenium sulphido-, seleno- and telluro-halides

Species	Preparative route	Ref.
$ReCl_2S$	$ReS_2 + Cl_2$	76
	$Re_2Cl_4S_3 + Cl_2$ at 400—450°C for 0.5 to 1 h	79
	$2\ ReCl_5 + 4S$ at 160—270°C	73
	$Re_3Cl_9 + S$	75
$ReBr_2S$	$Re_3Br_9 + S$	75
$ReCl_2Se$	$ReSe_2 + Cl_2$ at 480 to 500°C (ICl_3 heated to give Cl_2)	77
	$Re_3Cl_9 + Se$	75
$ReBr_2Se$	$Re_3Br_9 + Se$	75
$ReBrS_2$	$Re_3Br_9 + S$	75
$ReClS_3$	$2\ ReCl_5 + 8\ S$ up to 200°C (product obtained mixed with S_2Cl_2, and reported analysis is not good)	73
$ReCl_3S$	$ReCl_5 + Sb_2S_3$ in CS_2 at room temp.	15
$ReCl_4S$	$2\ ReCl_5 + 4S$ at 125°C	73
$Re_2Cl_4S_3$	$Re_2S_7 + Cl_2/CO_2$ (1 : 5) at 120°C	79
	$2\ ReCl_5 + 4\ S$ at 125 to 160°C	73
$Re_3Cl_5Se_2$	$3\ ReSe_2 + 2\ Re_3Cl_9$ at 700—750°C for 10—15 h (volatile fraction removed at 250°C)	77
$Re_3Br_5Se_2$	$ReSe_2 + Br_2$ at 580°C	78
	$3\ ReSe_2 + 2\ Re_3Br_9$ at 700—750°C for 10—15 h (volatile fraction removed at 250°C)	77
$Re_3Br_5Te_2$	$Re_2Te_5 + Br_2$ at 155 to 160°C yields a mixture from which $TeBr_4$ was sublimed at 290°C leaving $Re_3Te_2Br_5$	77

diagram of ReS_2 and S_2Cl_2 the compound is reported to melt incongruently at 63 ± 2°C.

Four compounds of the general formula ReX_2Y ($X = Cl$ or Br; $Y = S$ or Se) have been reported. The common method for the preparation of all four is the interaction of the cluster halide Re_3X_9 ($X = Cl$ or Br) with sulphur or selenium [75]. Chlorination of ReY_2 ($Y = S$ or Se) also yields $ReCl_2Y$ [76,77]. No physical properties of these species have been reported except that $ReCl_2Se$ is air stable. X-ray powder photographs for a number of them have been obtained [77].

The reaction of $ReSe_2$ with Re_3X_9 ($X = Cl$ or Br) leads to the formation of the isomorphous species $Re_3X_5Se_2$ ($X = Cl$ or Br) [77]. The bromide was first prepared by the bromination of $ReSe_2$ [78] and the analogous telluro-bromide by the bromination of $ReTe_2$ [77]. These compounds are said to be air stable and insoluble in water, hydrochloric acid, alcohol or acetone.

Chlorination of Re_2S_7 goes through a number of steps involving the formation of sulphido-chlorides, the most stable being $Re_2Cl_4S_3$ and $ReCl_2S$ [79].

The action of hydrogen on these sulphido-chlorides gives Re_2S_3 (from $Re_2Cl_4S_3$) and ReS (from $ReCl_2S$) [80].

F. GROUP VIII

Apparently the only report of Group VIII sulphido- or seleno-halides concerns the formation of some platinum sulphido compounds obtained by heating PtX_2 (X = Cl or Br) with sulphur [83]. The products have the general formula PtX_mS_n and are of the polysulphide type, the values of m and n being dependent upon the reaction temperature.

G. GROUP Ib — COPPER, SILVER AND GOLD

(i) Introduction

The sulphido-, seleno- and telluro-halides of the Group Ib elements have been quite extensively studied. Curiously only sulphido-halides appear to have been prepared for silver while for the other members of the group a range of seleno- and telluro- compounds are known but no sulphur containing species.

Similar preparative routes have been developed for all the Group Ib chalcogenide halides. Accordingly the preparations of the compounds are discussed collectively and a separate section is devoted to the structures and properties of the species formed by each element.

(ii) Preparation of the sulphido-, seleno- and telluro-halides of copper, silver and gold

An extensive range of seleno- and telluro- halides of copper and gold have been prepared by Rabenau and his co-workers [84—91]. A number of the copper compounds were prepared by heating stoichiometric amounts of the copper(I) halide and the chalcogen (either selenium or tellurium [86—87]) but the most satisfactory synthetic route to these gold and copper compounds is by use of a hydrothermal process [84,85,87—91].

Full practical details have been published of the hydrothermal process, which is particularly useful for the production of single crystals [91]. The reactants (for the copper compounds, the copper(I) halide, the chalcogen and halogen acid, and for gold, elemental gold, the chalcogen, the halogen and the halogen acid) are sealed into a silica ampoule. The silica ampoule is loaded into an autoclave together with a quantity of solid carbon dioxide sufficient to generate a pressure equal to that inside the ampoule when the autoclave is heated. The autoclave is then placed in a furnace so designed that the autoclave has a temperature gradient. The furnace is then heated and allowed to cool slowly over a period of days. Details of temperatures, cooling times and the compounds of copper and gold that have been prepared are given in Table 8. No systematic study has been carried out and it is thought probable

TABLE 8

Sulphido-, seleno- and telluro-halides of Group 1b

Compound	Preparative procedure	Ref.
$CuXTe_2$ (X = Cl, Br or I)	An excess of CuX (15 g) was allowed to react with Te(5 g) (or 1 g for X=I) in the presence of aqueous HX. The mixture was heated to 440—350°C and allowed to cool to 150°C over a 10 day period	85, 87, 91 98 see Figs. 17 and 18
CuXTe (X = Cl, Br or I)	CuX (X = Cl or Br) (20 g) + Te(1 g) in the presence of HX · X=I: Cu_4Te_3 (10 g) + 10 M HI. Mixture heated to 500—350°C and cooled to 200—150°C over a 10 day period	85, 87, 91 95, 96 See Figs. 15 and 16
$CuClSe_2$	CuCl (15 g) + Se (5 g) in presence of HCl. Heated to 350°C and allowed to cool to 150°C over 10 day period	85, 87, 91
$CuBrSe_3$	CuBr (15 g) + Se (5 g) in presence of HBr. Heated to 340°C and allowed to cool to 150°C	85, 87, 91.
$CuISe_3$	CuI (10 g) + Se (5 g) in the presence of HI. Heated to 390°C and allowed to cool to 200°C	85, 87, 91
Ag_3BrS	Ag_2S + AgBr at 280°C	92
Ag_3IS	Ag_2S + AgI at 235°C for 100 h. Ag_2S + AgI + S at 550°C. Sufficient sulphur is added to give pressure of 1 atm at 550°C in the sealed tube	92, 93, 94
AuBrSe	Au (5.9 g) + Se (2.4 g) + Br_2 (2.4 g) in HBr[a] at 230°C for 9 days	89
AuClSe	Au (5.9 g) + Se (2.4 g) + Cl_2 (12.0 g) in HCl[a] at 200—180°C for 12 days	89, 101 see Fig. 23
AuITe	Au (6.2 g) + Te (4 g) + I_2 (8 g) in HI. Heated to 450°C, allowed to cool to 150°C over 10 days	90, 91
$AuITe_2$	As per AuITe with omission of the I_2	90, 91, 100 see Figs. 19 and 20
$AuClTe_2$	Au (5.9 g) + Te (1.9 g) + Cl_2 (1.0 g) in HCl.[a] Heated to 400°C, allowed to cool to 100°C over 10 days	90, 91, 100 see Figs. 21 and 22
$AuBrTe_2$	Au (13.9 g) + Te (5.1 g) + Br_2 (5.7 g) in HBr. Heated to 350°C, allowed to cool to 150°C over 10 days	90, 91

[a] Anhydrous HCl or HBr.

that a number of other copper and gold seleno- and telluro-halides could be synthesised [91].

Although no sulphido-halides of copper and gold are known, two silver compounds Ag_3BrS and Ag_3IS have been prepared by heating equimolar mixtures of silver halide and Ag_2S [92—94]. The problem in the syntheses involving

Ag_2S is to achieve a temperature such that the reaction proceeds at a reasonable rate, and yet the sulphide does not decompose. The problem of the decomposition has been reduced by carrying out the reaction in the presence of sufficient sulphur to generate a partial pressure of sulphur of one atmosphere pressure at the reaction temperature [93,94].

(iii) Copper

The nine ternary chalcogenides of copper listed in Table 8 are all thought to contain copper(I) and can therefore be considered as pseudo-binary systems formed between copper(I) halides and either selenium or tellurium. All the compounds are diamagnetic and the tellurides exist as two series, namely CuXTe (X = Cl, Br or I) and $CuXTe_2$ (X = Cl, Br or I). Within a series the members are isomorphous, but the two selenides, $CuISe_3$ and $CuBrSe_3$ are not isomorphous [87].

The structures of two members of the isomorphous CuXTe series have been determined, namely CuITe [95] and CuBrTe [96]. The structures consist of infinite spirals of tellurium atoms parallel to the c direction (Figs. 15, 16) similar to those in elemental tellurium [97] except that in these telluro-halides the spirals are alternately left and right-handed while in the element they all have the same handedness. Between the spirals are tetrahedra of halogen atoms and for each unit cell there are four such tetrahedra. In the unit cell are 64 possible sites for the sixteen copper atoms. These sites fall equally into two basic sets. In half of the sites, the copper is co-ordinated to two tellurium and two halogen atoms and in the other half four halogen atoms. The copper atoms are statistically distributed between these two basic groups of sites.

The shortest published copper—tellurium distances differ markedly, that in

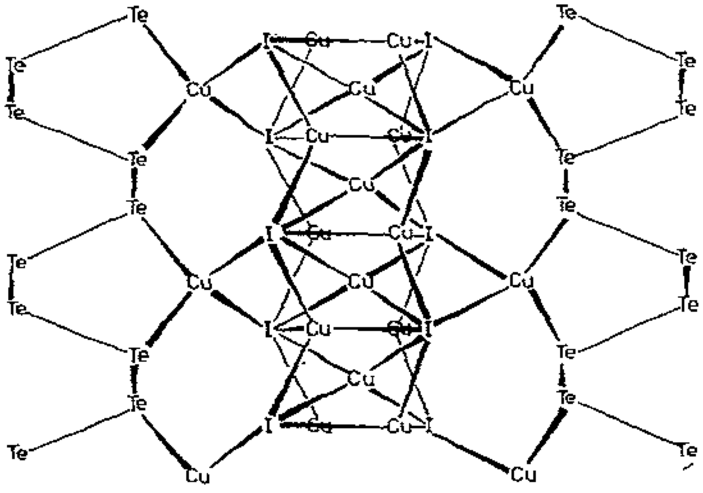
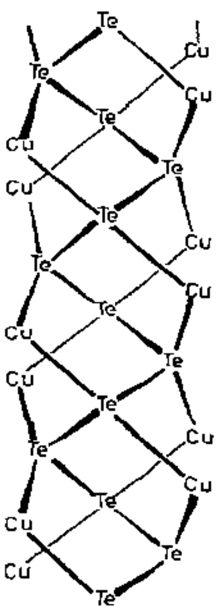


Fig. 15. CuITe showing the various Cu sites redrawn from ref. 95.



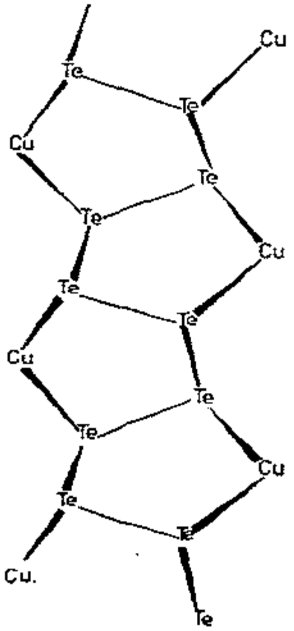


Fig. 16. The screw of Te atoms in CuITe redrawn from ref. 95.

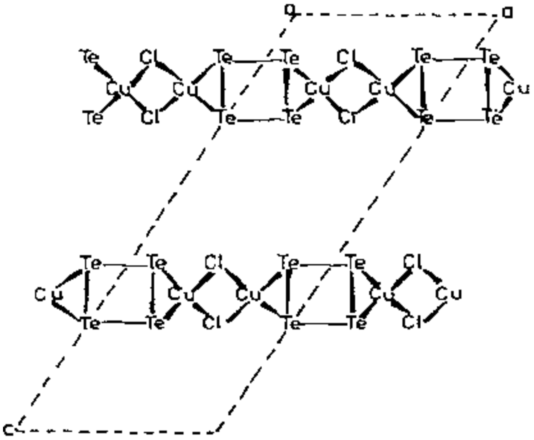
Fig. 17. The pseudo-fourfold screws of Te atoms in $CuClTe_2$ redrawn from ref. 98.

CuITe being 2.648(2) Å and in CuBrTe 3.574(4) Å. In CuBrTe the copper atoms bonded to two tellurium and two bromine atoms can occupy one of two very close sites, so recalculation of the copper—tellurium distance for copper atoms in these sites [44] from the published data yielded Cu—Te distances of 2.54 and 2.66 Å, which are in close agreement with those seen in CuITe [95] and those in $CuClTe_2$ (2.595(5) and 2.586(7) Å) [98].

Screws of tellurium atoms are also found in $CuClTe_2$ [98] which is one compound in the isomorphous series $CuXTe_2$ (X = Cl, Br or I). These screws are parallel to the *b* axis (Fig. 17) and two adjacent screws are linked via Cu—Cl—Cu bridges to give layers parallel to the *ab* plane (Fig. 18). Thus the copper atoms are co-ordinated to two tellurium atoms (2.595(5) and 2.586(7) Å), and two chlorine atoms (2.343(8) and 2.348(13) Å).

The existence of tellurium screws in both CuXTe (X = Cl, Br or I) and $CuXTe_2$ (X = Cl, Br or I) together with the diamagnetic nature of the materials supports the suggestion that they are copper(I) species, and the difference in the mode of co-ordination of the copper atoms to the tellurium screws in CuITe [95] and $CuClTe_2$ [98] is shown in Figs. 16 and 17.

Certain optical properties of the copper telluro-halides have been measured [86] and the band gap is independent of the nature of the halogen. The band gaps are approximately 1.6 ev for CuXTe (X = Cl, Br or I) and 1.2 ev for $CuXTe_2$ (X = Cl, Br or I).



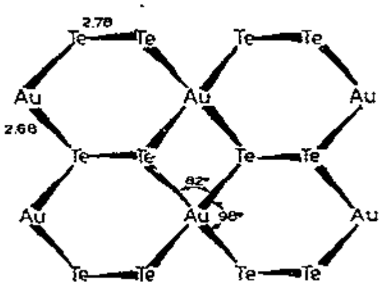


Fig. 18. The $CuClTe_2$ layers projected down the *b*-axis, redrawn from ref. 98.

Fig. 19. $AuTe_2$ nets in $AuITe_2$, redrawn from ref. 100.

(iv) Silver

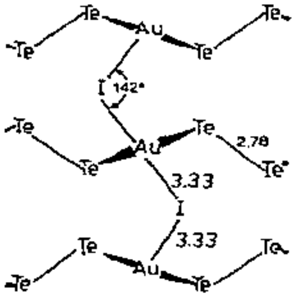
The silver compounds Ag_3BrS and the β form of Ag_3IS have a simple cubic lattice. Their structure is derived from the ideal antiperovskite structure by displacement of the silver ions from the centre of the faces towards the edges of the cell [99].

The iodide has been studied because it is a highly conducting solid electrolyte and such compounds are potentially of interest as current sources and electrochemical information convertors [94].

(v) Gold

The three telluro species $AuXTe_2$ (X = Cl, Br or I) are all metallic conductors while the remaining gold telluro-halide AuITe has a band gap of 0.9 ev. Three of the compounds $AuITe_2$, $AuBrTe_2$ and AuITe exhibit temperature independent diamagnetism [90]. The copper compounds analogous to the $AuXTe_2$ (X = Cl, Br or I) series are diamagnetic, and also differ from the gold species in being semi-conductors [86]. Structural studies on $AuClTe_2$ (which is isomorphous with $AuBrTe_2$ [90]) and $AuITe_2$ show that they have totally different structures from $CuClTe_2$ [98].

The structures of $AuClTe_2$ and $AuITe_2$ are remarkably similar [100] (Figs. 19 to 22). The tellurium atoms occur as Te_2 units in a two-dimensional net of gold and tellurium atoms. This is unlike the situation in CuXTe (X = Cl or I) [95,96] and $CuClTe_2$ [98] where continuous tellurium screws were observed. Each gold atom is bonded to four tellurium atoms and each tellurium atom to two gold atoms. Thus two adjacent gold atoms are bridged by a Te—Te



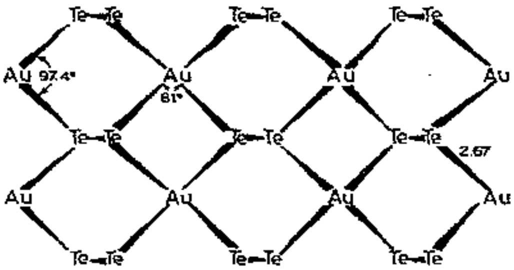
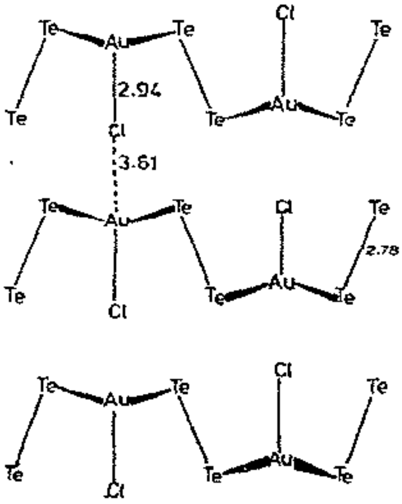


Fig. 20. The halogen bridging in $AuITe_2$, redrawn from ref. 100.

Fig. 21. $AuTe_2$ nets in $AuClTe_2$, redrawn from ref. 100.

unit. The iodine atoms in $AuITe_2$ are equidistant from two gold atoms (3.3300(6) Å) while the chlorine atoms in $AuClTe_2$ form one long (3.61 Å) and one short (2.9369(22) Å) gold—chlorine bond. Another interesting difference between the two structures is in the disposition of the Te—Te units. In the chloride they are alternately up and down while in the iodide all the Te—Te units are parallel. (Compare Fig. 19 with Fig. 21, and Fig. 20 with Fig. 22.) Examination of the structures reveals no apparent reason for the metallic conductivity as the gold—gold distances are approximately 4 Å [90].

The two gold chalcogenide halides which have proved most difficult to prepare in a pure state are AuClSe and AuBrSe [89]. The structure of the bro-



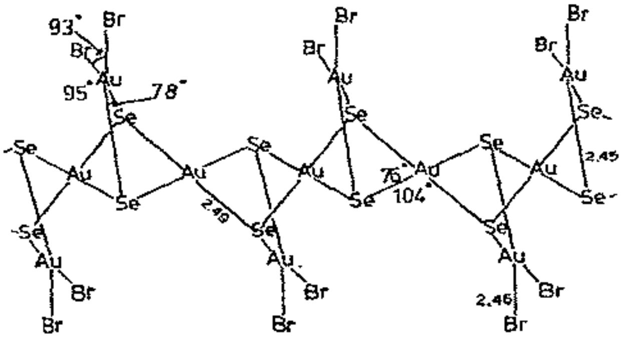


Fig. 22. The unsymmetrical halogen bridge in $AuClTe_2$, redrawn from ref. 100.

Fig. 23. The two gold environments in AuBrSe, redrawn from ref. 101.

mide AuBrSe has been determined (see Fig. 23) and it consists of a ribbon of selenium and gold atoms. Within the ribbon each gold atom is bonded to four selenium atoms with which it is co-planar.

A second type of gold atom is off the spine of the ribbon. These gold atoms are bound to two selenium atoms and terminally to two bromine atoms. Thus all the gold atoms are four co-ordinate and the selenium atoms three co-ordinate.

The structural studies of the three gold compounds $AuClTe_2$ [100], $AuITe_2$ [100] and AuBrSe [101] indicate that the metal is in the Au(III) oxidation state in all of them, in contrast to the analogous copper species where the nature of the tellurium spirals suggests the presence of Te(0) and Cu(I).

H. CONCLUSION

The author thanks past and present co-workers at the University of Reading who have investigated the sulphido- and seleno-halides of the early transition metals. An attempt has been made to be comprehensive in this review; the author apologises for any unintentional omission.

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