

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

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### 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  $\text{Mo}_5\text{Cl}_9\text{S}_8$  and  $\text{W}_2\text{Cl}_4\text{S}_3$  [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  $\text{Sb}_2\text{S}_3$  in  $\text{CS}_2$  solutions were unsuccessful [7].

The titanium sulphido-halide  $\text{TiCl}_2\text{S}$  was prepared from the reaction of titanium(IV) chloride with  $\text{H}_2\text{S}$  at  $65^\circ\text{C}$  in  $\text{CS}_2$  solution [4]. Initially an adduct  $\text{TiCl}_4 \cdot \text{H}_2\text{S}$  is formed and if the reaction temperature is increased the product is  $\text{TiS}_2$ . The preparative route has been criticised as only a low yield of  $\text{TiCl}_2\text{S}$  is obtained [6]. Attempts to improve the yield by substituting antimony, arsenic and molybdenum sulphides instead of  $\text{H}_2\text{S}$  were ineffective [6]. No conclusive structural data on  $\text{TiCl}_2\text{S}$  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  $120^\circ\text{C}$  is reported to give a product consisting of 25%  $\text{TiClS}$  and 75%  $\text{TiCl}_2\text{S}$  [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 ( $\text{Y} = \text{S}$  or  $\text{Se}$ ) 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 ( $\text{Y} = \text{S}$ or $\text{Se}$ )

The niobium species with the general formula  $\text{NbX}_2\text{Y}_2$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ;  $\text{Y} = \text{S}$  or  $\text{Se}$ ) were all prepared by heating the reactants in an evacuated sealed tube [8,9]. For the chloride  $\text{NbCl}_2\text{S}_2$ , two sets of reactants were used, the first being niobium powder and  $\text{S}_2\text{Cl}_2$  (molar ratio 1 : 1) and the second set

**TABLE 1**  
**Niobium and Tantalum sulphido- and seleno-halides**

Species	Preparative route	Refs.
NbClS <sub>2</sub>	NbCl <sub>5</sub> + S (1 : 8 molar ratio) in benzene solution	10
NbCl <sub>2</sub> S	NbCl <sub>4</sub> + Sb <sub>2</sub> S <sub>3</sub> or As <sub>2</sub> S <sub>3</sub> at 200°C in an inert atmosphere	25
NbCl <sub>2</sub> S <sub>2</sub>	Nb + S <sub>2</sub> Cl <sub>2</sub>	8, 9
	Nb + S + NbCl <sub>5</sub>	8, 9, 11 see Fig. 1.
NbCl <sub>2</sub> Se <sub>2</sub>	Nb + Se + NbCl <sub>5</sub>	8, 9
NbBr <sub>2</sub> Y <sub>2</sub> (Y = S or Se)	Nb + Y + Br <sub>2</sub>	8
NbI <sub>2</sub> Y <sub>2</sub> (Y = S or Se)	Nb + Y + I <sub>2</sub>	8
TaCl <sub>2</sub> S <sub>2</sub>	TaCl <sub>5</sub> + S (molar ratio 1 : 8) in benzene solution	10
Nb <sub>3</sub> S <sub>3</sub> Cl <sub>11</sub> <sup>4-</sup>	NbCl <sub>5</sub> + F <sub>2</sub> PS <sub>2</sub> H → NbCl <sub>3</sub> (S <sub>2</sub> PF <sub>2</sub> ) <sub>2</sub> $\xrightarrow{PY}$ [pyH] <sub>4</sub> [Nb <sub>3</sub> Cl <sub>11</sub> S <sub>3</sub> ]	26
NbX <sub>3</sub> Y (Y = S or Se; X = Cl or Br)	NbX <sub>5</sub> + Sb <sub>2</sub> Y <sub>3</sub> in CS <sub>2</sub> at room temp.	15
	As a decomposition product of NbX <sub>2</sub> Y <sub>2</sub> in a mass spectrometer	8
TaCl <sub>3</sub> S	TaCl <sub>5</sub> + Sb <sub>2</sub> S <sub>3</sub> in CS <sub>2</sub> at room temp.	15
	TaCl <sub>5</sub> + PhNCS → TaCl <sub>5</sub> · PhNCS → TaCl <sub>3</sub> S	27
TaBr <sub>3</sub> Y (Y = S or Se)	TaBr <sub>5</sub> + Sb <sub>2</sub> Y <sub>3</sub> in CS <sub>2</sub> ; at 20°C Y = S, at 40°C Y = Se	15
NbCl <sub>9</sub> S	NbCl <sub>5</sub> + S <sub>2</sub> Cl <sub>5</sub> (at 100°C)	24
TaCl <sub>9</sub> S	TaCl <sub>5</sub> + S <sub>2</sub> Cl <sub>2</sub> (at 100°C)	24

being niobium, sulphur and niobium (V) chloride (atomic ratio 1 : 1.8 : 2.3). The selenide NbCl<sub>2</sub>Se<sub>2</sub> was prepared from the metal, selenium and niobium(V) chloride, while for the remaining compounds NbX<sub>2</sub>Y<sub>2</sub> (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<sub>2</sub>Y<sub>2</sub>. Thus samples of the bromide NbBr<sub>2</sub>S<sub>2</sub> were obtained with the three Nb : S : X<sub>2</sub> 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<sub>2</sub>S<sub>2</sub> a niobium-sulphur phase was formed.

Similar reactions to those that led to the successful isolation of NbCl<sub>2</sub>S<sub>2</sub> from the reaction of the metal with S<sub>2</sub>Cl<sub>2</sub>, 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<sub>3</sub>) containing a small amount of chloride. A species with the curious formula TaBr<sub>1.93</sub>S<sub>2.77</sub> was also synthesised by allowing the three elements to react. Recently the grey-green TaCl<sub>2</sub>S<sub>2</sub> has been isolated from the reaction of tantalum(V) chloride and sulphur [10].

The X-ray crystal structure of  $\text{NbCl}_2\text{S}_2$  has been published [11] (Fig. 1). The structure consists of pairs of niobium atoms ( $\text{Nb-Nb}$  2.90 Å) that are bridged by two  $\text{S}_2$  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  $\text{NbX}_2\text{Y}_2$  to be diamagnetic [8].

The IR and Raman spectra of  $\text{NbX}_2\text{S}_2$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) 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  $\text{NbCl}_2\text{S}_2$ ,  $\text{NbBr}_2\text{S}_2$  and  $\text{NbI}_2\text{S}_2$  it is possible to assign the vibrational modes to one of three groups. These groups are vibrations of the  $\text{S}_2$  groups, vibration of the  $\text{Nb}(\text{S}_2)\text{Nb}$  cage (Table 2) and vibrations of the niobium—halogen bonds. The position of the band associated with the  $\text{S}_2$  group falls as expected on going from  $\text{NbCl}_2\text{S}_2$  to  $\text{NbI}_2\text{S}_2$ , thus presenting evidence for a degree of coupling to the metal—halogen modes. The position of the mode involving the  $\text{S}_2$  groups is considerably higher than in a number of the polysulphides; however, the normal co-ordinate analysis substantiates the assignment [14].

(ii) *Compounds containing  $M = Y$  ( $M = \text{Nb}$  or  $\text{Ta}$ ;  $Y = \text{S}$  or  $\text{Se}$ )*

When the species  $\text{NbX}_2\text{Y}_2$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ;  $Y = \text{S}$  or  $\text{Se}$ ) were heated in a mass spectrometer, evidence was obtained for the compounds  $\text{NbX}_3\text{Y}$  ( $\text{X} = \text{Br}$  or  $\text{Cl}$ ;  $Y = \text{S}$  or  $\text{Se}$ ) [8], but from identical experiments with the iodides  $\text{NbI}_2\text{Y}_2$  ( $Y = \text{S}$  or  $\text{Se}$ ) the only volatile product was iodine [8].

Although initial attempts to prepare  $\text{TaCl}_2\text{S}_2$  and  $\text{TaBr}_2\text{S}_2$  failed, the products

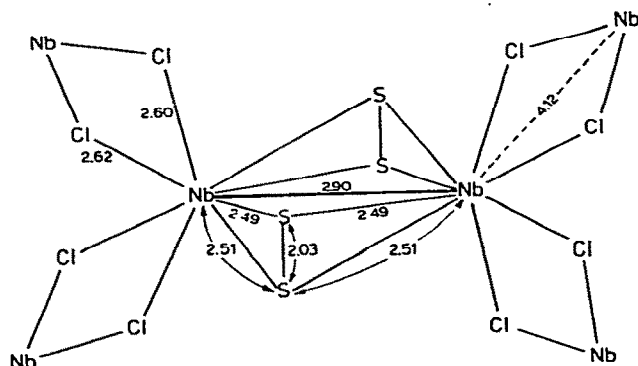


Fig. 1.  $\text{NbCl}_2\text{S}_2$  redrawn from ref. 11.

TABLE 2

IR and Raman absorptions ( $\text{cm}^{-1}$ ) associated with the sulphur atoms in  $\text{NbX}_2\text{S}_2$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$  or  $\text{I}$ );  $\text{Mo}_2\text{X}_3\text{S}_5$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ );  $\text{NbX}_3\text{S}$  and  $\text{TaX}_3\text{S}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ )

Species	S—S		Nb—S		M=S (M=Nb or Ta) IR	Ref.
	IR	Raman	IR	Raman		
$\text{NbCl}_2\text{S}_2$	588 s 582 sh	592 vs	377 m 362 vs 323 vs 166 s	336 s 317 m 252 m 188 m	—	12, 13
$\text{NbBr}_2\text{S}_2$	585 s 580 sh	585 vs	370 m 358 s 320 s 174 s	328 s 310 m 243 s 183 s	—	12, 13
$\text{NbI}_2\text{S}_2$	575 s 570 sh		358 m 348 s 340 sh 315 s	—	—	12, 13
$\text{Mo}_2\text{Cl}_3\text{S}_5$	560	570	—	—	—	12
$\text{Mo}_2\text{Br}_3\text{S}_5$	555	565	—	—	—	12
$\text{NbCl}_3\text{S}$					552	15
$\text{NbBr}_3\text{S}$					542	15
$\text{NbCl}_3\text{S} \cdot \text{SPPH}_3$					539	21
$\text{TaCl}_3\text{S}$					463	15
$\text{TaBr}_3\text{S}$					448 437	15
$\text{TaCl}_3\text{S} \cdot 2 \text{ tht}$					505	21
$\text{TaBr}_3\text{S} \cdot 2 \text{ tht}$					505	21

being  $\text{TaS}_3$  (containing a trace of chloride) and  $\text{TaBr}_{1.93}\text{S}_{2.77}$ , when these products were examined mass spectrometrically, peaks assignable to  $\text{TaX}_3\text{S}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) were observed [8].

Attempts to prepare  $\text{NbCl}_3\text{S}$  from the reaction of  $\text{NbCl}_5$  and  $\text{Sb}_2\text{S}_3$  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  $\text{NbCl}_5$  to react with the black form of  $\text{Sb}_2\text{S}_3$  (molar ratio 3 : 1) in  $\text{CS}_2$  solution at room temperature,  $\text{NbCl}_3\text{S}$  was isolated.

With the same technique all the sulphido- and seleno-chlorides and bromides of niobium and tantalum, of general formula  $\text{MX}_3\text{Y}$  with the exception of  $\text{TaCl}_3\text{Se}$ , have been isolated (see Table 1).

None of these species of the formulation  $\text{MX}_3\text{Y}$  ( $\text{M} = \text{Nb}$ ,  $\text{Ta}$ ;  $\text{X} = \text{Cl}$  or  $\text{Br}$ ;  $\text{Y} = \text{S}$  or  $\text{Se}$ ) 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  $\text{MoCl}_3\text{O}$  structure [16,17] (Fig. 2), or alternatively, one with a bridging metal—sulphur—metal moiety that is like the  $\text{MoBr}_3\text{O}$  [18] and  $\text{NbCl}_3\text{O}$  structures [19] (Fig. 3). Although the difference between the terminal  $\text{Mo}=\text{O}$  in  $\text{MoCl}_3\text{O}$  (1.63 Å) and the shortest  $\text{Mo}=\text{O}$  bond in  $\text{MoBr}_3\text{O}$  is small (1.65 Å) the effect of the long  $\text{Mo}-\text{O}$  bond in  $\text{MoBr}_3\text{O}$  (2.31 Å) is to reduce the  $\text{Mo}-\text{O}$  stretching mode in the IR spectra of  $\text{MoBr}_3\text{O}$  from some  $1000\text{ cm}^{-1}$  (as seen in  $\text{MoCl}_3\text{O}$ ) to some  $750\text{ cm}^{-1}$ .

On the basis of evidence from IR spectra it is suggested that  $\text{NbX}_3\text{S}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) has the  $\text{MoCl}_3\text{O}$  structure [16,17] and  $\text{TaX}_3\text{S}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) the  $\text{MoBr}_3\text{O}$  structure [18]. In Table 2 are given the positions of the  $\text{M}=\text{S}$  stretching modes for the sulphido-halides and a number of their adducts. In the IR spectrum of  $\text{NbCl}_3\text{S} \cdot \text{SPPH}_3$  (a species whose structure has been determined and that was shown to contain terminal  $\text{Nb}=\text{S}$ , Figs. 4 and 5 [20]), there is a  $\text{Nb}=\text{S}$  stretching mode at  $539\text{ cm}^{-1}$  and that is close to the position observed for  $\nu(\text{Nb}=\text{S})$  in  $\text{NbCl}_3\text{S}$  ( $552\text{ cm}^{-1}$ ) [15]. Thus it is suggested a terminal  $\text{Nb}=\text{S}$  bond is present in  $\text{NbCl}_3\text{S}$ . By contrast the position of  $\nu(\text{Ta}=\text{S})$  changes markedly on going from the parent sulphido-halide to an adduct. For example  $\nu(\text{Ta}=\text{S})$  in  $\text{TaBr}_3\text{S}$  is at 448 and  $437\text{ cm}^{-1}$  [15] while in  $\text{TaBr}_3\text{S} \cdot 2\text{tht}$  (tht = tetrahydrothiophene) (a species shown by a structure determination to contain a terminal  $\text{Ta}=\text{S}$  bond) [21] it is at  $505\text{ cm}^{-1}$  indicating the presence of a bridging  $\text{Ta}=\text{S} \cdots \text{Ta}$  system in  $\text{TaBr}_3\text{S}$ .

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  $[\text{NbCl}_3\text{S} \cdot \text{SPPH}_3]$  (Fig. 4) and a centrosymmetric chlorine bridged dimer  $[\text{NbCl}_3\text{S} \cdot \text{SPPH}_3]_2$  (Fig. 5) [20]. A small energy difference must exist between the monomer and dimers of species containing  $\text{M}=\text{Y}$  bonds ( $\text{Y} = \text{O}$  or  $\text{S}$ ) and thus packing forces deter-

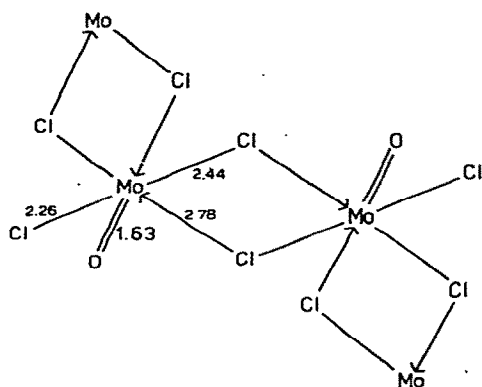


Fig. 2.  $\text{MoCl}_3\text{O}$  redrawn from ref. 16.

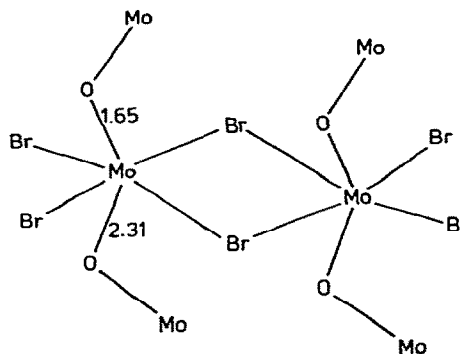


Fig. 3.  $\text{MoBr}_3\text{O}$  redrawn from ref. 18.

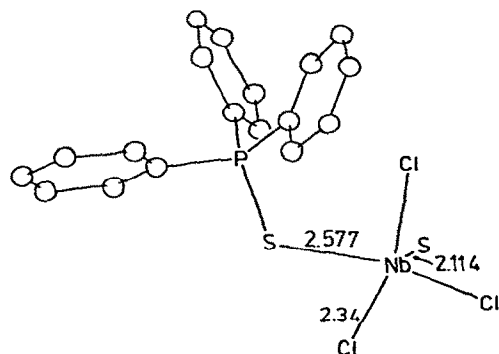


Fig. 4. The five co-ordinate species  $[\text{NbCl}_3\text{S.SPPh}_3]$  redrawn from ref. 20.

mine if monomeric (as seen in  $\text{MoCl}_3\text{O.SPPh}_3$ ) [22], dimeric, or a mixture of both species (as seen in  $\text{NbCl}_3\text{S.SPPh}_3$ ) 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  $\text{Ph}_3\text{PS}$  (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  $\text{TaBr}_3\text{S} \cdot 2 \text{ tht}$ . 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  $\text{TaCl}_3\text{O}$  readily disproportionates at 300°C according to the equation



Careful control of the conditions is necessary as at higher temperatures  $\text{TaCl}_5$  and  $\text{Ta}_2\text{O}_5$  are formed [23].

Heating  $\text{TaCl}_3\text{S}$  in a vacuum follows a similar pattern; at approximately 200°C  $\text{TaClS}_2$  is formed, but on raising the temperature to 300°C the involatile product is  $\text{TaS}_3$  containing a trace of chlorine [21]. Preliminary experiments indicate that the thermal decomposition of  $\text{NbCl}_3\text{S}$  follows a different route and that at 220°C the products are  $\text{NbCl}_2\text{S}$ ,  $\text{NbCl}_5$  and sulphur.

The niobium analogue of  $\text{TaClS}_2$  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  $\text{TaCl}_7\text{S}$  and  $\text{NbCl}_7\text{S}$ . Their struc-

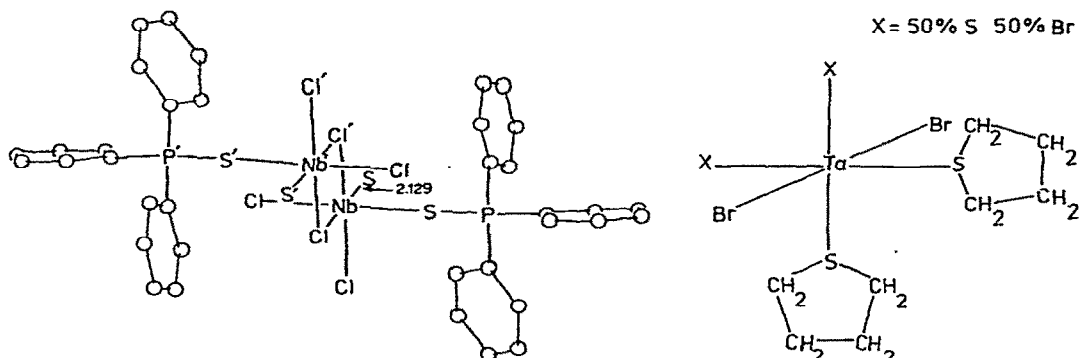


Fig. 5. The six co-ordinate species  $[\text{NbCl}_3\text{S.SPPh}_3]_2$  redrawn from ref. 20

Fig. 6.  $\text{TaBr}_3\text{S.2tht}$  redrawn from ref. 21.

ture and properties are unknown; both are formed by the reaction of the pentachloride with  $\text{S}_2\text{Cl}_2$  [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  $\text{CuCr}_2\text{S}_3\text{X}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ),  $\text{CuCr}_2\text{Se}_3\text{Cl}$  and  $\text{CuCr}_2\text{Te}_3\text{Cl}$  have been reported [28–30] but there appears to be only one report of simple chromium sulphido- or seleno-halides [31]. By heating  $\text{Cr}_2\text{S}_3$  and  $\text{CrBr}_3$  to  $870^\circ\text{C}$   $\text{CrBrS}$  was obtained. Similarly the heating of iodine with  $\text{CrS}$ ,  $\text{CrSe}$  and  $\text{CrTe}$  leads to the formation of  $\text{CrI}_{0.83}\text{S}$ ,  $\text{CrISe}$  and  $\text{CrITe}_{0.73}$ . 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 <sub>6</sub> X <sub>8</sub> ]X <sub>4</sub> + Mo + S at 1000°C for 24 h (X = Cl, Br or I)	42, 43 see Fig. 7
MoCl <sub>2</sub> S	MoS <sub>2</sub> + Cl <sub>2</sub> at 400°C	35
	3 MoCl <sub>4</sub> + 2 Sb <sub>2</sub> S <sub>3</sub> at 140°C for 7 d	33
	Disproportionation of MoCl <sub>3</sub> S at 260°C for 5 d	33
MoCl <sub>2</sub> Se	3 MoCl <sub>4</sub> + 2 Sb <sub>2</sub> Se <sub>3</sub> at 120°C for 14 d	
	Disproportionation of MoCl <sub>3</sub> Se at 260°C for 2 d	
MoCl <sub>2</sub> S <sub>2</sub> <sup>a</sup>	MoCl <sub>4</sub> O + H <sub>2</sub> S	34
	MoCl <sub>4</sub> + H <sub>2</sub> S + CS <sub>2</sub>	33
MoCl <sub>2</sub> S <sub>2</sub> <sup>a</sup>	Mo + S <sub>2</sub> Cl <sub>2</sub> in a 1 : 1 molar ratio at 500°C for 2 d	32
MoBr <sub>2</sub> S <sub>2</sub>	Mo + S <sub>2</sub> Br <sub>2</sub> in a 1 : 1 molar ratio at 500°C for 4 d	32
MoCl <sub>3</sub> S	MoCl <sub>5</sub> + Sb <sub>2</sub> S <sub>3</sub> at 140°C for 7 d	33
	MoCl <sub>5</sub> + Sb <sub>2</sub> S <sub>3</sub> in CS <sub>2</sub> at room temp. for 2 d	15
	MoCl <sub>5</sub> + Me <sub>3</sub> SiSBu <sup>t</sup>	52
MoCl <sub>3</sub> Se	MoCl <sub>5</sub> + Sb <sub>2</sub> Se <sub>3</sub> at 140°C for 14 d	33
MoCl <sub>3</sub> S <sub>2</sub>	MoCl <sub>5</sub> + S <sub>2</sub> Cl <sub>2</sub> in a 1 : 10 molar ratio at 250°C for 6 h (SCL <sub>2</sub> one of the products)	51
	MoCl <sub>3</sub> + S in a 1 : 10 molar ratio in S <sub>2</sub> Cl <sub>2</sub> for 6 d with a temp. gradient along the sealed reaction tube of 435 to 450°C	45 see Fig. 8
MoBr <sub>8</sub> Te <sub>2</sub>	MoBr <sub>10</sub> Te <sub>2</sub> on gentle heating yields MoBr <sub>8</sub> Te <sub>2</sub>	37
MoBr <sub>10</sub> Te <sub>2</sub>	MoTe <sub>2</sub> + Br <sub>2</sub> as solvent at room temp.	37
Mo <sub>2</sub> Cl <sub>3</sub> S <sub>5</sub>	MoS <sub>3</sub> held at 420 to 480°C in contact with S <sub>2</sub> Cl <sub>2</sub> vapour	32
	[Mo <sub>6</sub> X <sub>8</sub> ]X <sub>4</sub> + S at 350 to 400°C for several hours	12, 13
Mo <sub>2</sub> Br <sub>3</sub> S <sub>5</sub>	MoS <sub>3</sub> held at 420°C in contact with S <sub>2</sub> Br <sub>2</sub> vapour	32
	[Mo <sub>6</sub> Br <sub>8</sub> ]Br <sub>4</sub> + S at 350 to 400°C for several hours	12, 13
Mo <sub>2</sub> I <sub>3</sub> S <sub>5</sub>	[Mo <sub>6</sub> I <sub>8</sub> ]I <sub>4</sub> and excess S at 300°C for 7 d	13
Mo <sub>2</sub> Cl <sub>5</sub> S <sub>4</sub>	MoS <sub>3</sub> held at 350 to 400°C in contact with S <sub>2</sub> Cl <sub>2</sub> vapour	32
Mo <sub>3</sub> Cl <sub>4</sub> S <sub>7</sub>	MoCl <sub>3</sub> + S (molar ratio 1 : 10) at 450°C for 1 d	46
	MoCl <sub>3</sub> + S (molar ratio 1 : 10) with S <sub>2</sub> Cl <sub>2</sub> as solvent at 450°C for 6 d	45 see Fig. 9
Mo <sub>3</sub> Cl <sub>4</sub> Se <sub>7</sub>	MoCl <sub>3</sub> + Se (molar ratio 1 : 10) at 400°C for 1 d	46
Mo <sub>3</sub> Br <sub>4</sub> S <sub>7</sub>	[Mo <sub>6</sub> Br <sub>8</sub> ]Br <sub>4</sub> + S (molar ratio 1 : 5) at 420°C for 10 h	47
	MoBr <sub>3</sub> + S (molar ratio 1 : 5) at 360°C for 5 h	47
Mo <sub>3</sub> Br <sub>4</sub> Se <sub>7</sub>	[Mo <sub>6</sub> Br <sub>8</sub> ]Br <sub>4</sub> + Se (molar ratio 1 : 5) at 400°C for 10 h	47
	MoBr <sub>3</sub> + Se (molar ratio 1 : 5) at 340°C for 10 h	47
Mo <sub>6</sub> X <sub>2</sub> S <sub>6</sub> (X = Br or I)	Mo <sub>6</sub> X <sub>12</sub> + Mo + S (appropriate molar ratio) at 1050°C for 48 h	102

TABLE 3 (continued)

Species	Preparative route	Ref.
Mo <sub>6</sub> X <sub>10</sub> Y (X = Br; Y = S, Se or Te) (X = I; Y = Se or Te)	[Mo <sub>6</sub> Br <sub>8</sub> ]Br <sub>4</sub> + Y at 800 to 1150°C for 24 h	40
Mo <sub>6</sub> X <sub>x</sub> Y <sub>8-x</sub> (X = Br or I; Y = Se or Te)	[Mo <sub>6</sub> X <sub>8</sub> ]X <sub>4</sub> + Y as above	40
Mo <sub>6</sub> I <sub>8</sub> Y <sub>14</sub> (Y = S or Se)	Mo(II) and (III) iodide + Y	39
Mo <sub>6</sub> X <sub>8</sub> Y <sub>14</sub> (X = Cl, Br or I) (Y = S or Se)	[Mo <sub>6</sub> X <sub>8</sub> ]X <sub>4</sub> + Y	38

<sup>a</sup> Probably two different species with identical molecular formulae.

*(a) Reactions involving molybdenum metal*

The reactions involving the metal with S<sub>2</sub>X<sub>2</sub> (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<sub>3</sub>Cl<sub>9</sub>S<sub>6</sub>, while more recently it has been claimed that the moisture sensitive compounds MoX<sub>2</sub>S<sub>2</sub> (X = Cl or Br) are formed [32]. The oxidation state of the metal in MoX<sub>2</sub>S<sub>2</sub> was not determined [32] but it was thought likely that the species was directly analogous to NbCl<sub>2</sub>S<sub>2</sub> [8,11], and thus it probably contains S<sub>2</sub> units. The compound MoCl<sub>2</sub>S<sub>2</sub> is also formed by the reaction of molybdenum(IV) chloride with H<sub>2</sub>S in CS<sub>2</sub> solution [33]. A compound with the same molecular formula is obtained from the reaction of MoCl<sub>4</sub>O with H<sub>2</sub>S [34]; however this latter species is probably more closely related to WCl<sub>2</sub>S<sub>2</sub> [15] than NbCl<sub>2</sub>S<sub>2</sub> 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<sub>2</sub>) via chlorination [35]. At 400°C MoCl<sub>2</sub>S is formed when chlorine is passed over heated MoS<sub>2</sub>, but use of an excess of chlorine leads to molybdenum(V) chloride [35]. The same compound is also formed by the reaction of MoCl<sub>4</sub> with Sb<sub>2</sub>S<sub>3</sub> (either in CS<sub>2</sub> suspension [7] or in a sealed tube [33]) and by the thermal decomposition of MoCl<sub>3</sub>S [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<sup>-1</sup> thus indicating the absence of a terminal Mo=S bond, and of unsymmetrically co-ordinated S<sub>2</sub> groups [13]. Prob-

ably the sulphido- and seleno-halides have a highly polymeric structure like that of  $\text{MoCl}_2\text{O}$  [36] although neither are isomorphous with the oxo-halide [33]. The only other reactions involving a molybdenum sulphide are those of  $\text{MoS}_3$  (a species whose exact nature is uncertain, but which probably does not contain molybdenum(VI)) and  $\text{S}_2\text{X}_2$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ). The reaction yielded  $\text{Mo}_2\text{X}_3\text{S}_5$  [12,32] above  $420^\circ\text{C}$  and below  $400^\circ\text{C}$   $\text{Mo}_2\text{Cl}_5\text{S}_4$  was formed [32]. A more convenient route to  $\text{Mo}_2\text{X}_3\text{S}_5$  ( $\text{X} = \text{Br}$ ,  $\text{Cl}$  or  $\text{I}$ ) is from the reaction of  $[\text{Mo}_6\text{X}_8]\text{X}_4$  with an excess of sulphur [12,13]. The structures of the air stable species  $\text{Mo}_2\text{X}_3\text{S}_5$  ( $\text{X} = \text{Br}$ ,  $\text{Cl}$  or  $\text{I}$ ) have not been determined. They are believed to contain  $\text{S}_2$  units as the IR and Raman spectra of all three have a band at  $560 (\pm 10) \text{ cm}^{-1}$  which by comparison with the spectrum of  $\text{NbCl}_3\text{S}_2$  is assigned to the S—S stretch of  $\text{S}_2$  groups [12,13] (Table 2).

The above survey illustrates that with the exception of  $\text{Mo}_2\text{Cl}_5\text{S}_4$  [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  $\text{MoTe}_2$  with liquid bromine. At room temperature an exothermic reaction occurs leading to the formation of  $\text{MoBr}_{10}\text{Te}_2$  which on gentle warming loses bromine to give  $\text{MoBr}_8\text{Te}_2$  [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  $825 \text{ cm}^{-1}$  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  $[\text{Mo}_6\text{X}_8]^{4+}$  cluster by sulphur or selenium groups carrying the appropriate charge. From the direct reaction of  $[\text{Mo}_6\text{X}_8]\text{X}_4$  ( $\text{X} = \text{Br}$ ,  $\text{Cl}$  or  $\text{I}$ ) with sulphur or selenium,  $[\text{Mo}_6\text{X}_8]\text{Y}_{14}$  ( $\text{Y} = \text{S}$  or  $\text{Se}$ ) was obtained where it is suggested the  $\text{Mo}_6\text{X}_8^{4+}$  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  $[\text{Mo}_6\text{X}_8]\text{X}_2\text{Y}$  ( $\text{X} = \text{Br}$  or  $\text{I}$ ;  $\text{Y} = \text{Se}$  or  $\text{Te}$ ) and  $[\text{Mo}_6\text{Cl}_8]\text{Cl}_2\text{S}$  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  $\text{Nb}_6\text{I}_{11}$  [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  $[\text{Mo}_6\text{Br}_8]\text{Br}_{4/2}\text{Y}_{2/2}$ .

From the reaction of  $[\text{Mo}_6\text{X}_8]\text{X}_4$  ( $\text{X} = \text{Br}$ ,  $\text{Cl}$  or  $\text{I}$ ) with sulphur and molybdenum in the molar ratio 1 : 8 : 12 at  $1000^\circ\text{C}$  for 24 hours,  $\text{MoXS}$  ( $\text{X} = \text{Br}$ ,  $\text{Cl}$  or  $\text{I}$ ) was obtained [42, 43]. These molybdenum(III) compounds are black, air stable and diamagnetic. A single crystal X-ray study of  $\text{MoBrS}$  has been

reported [43]. The cubic crystals contain  $\text{Mo}_4\text{S}_4$  units (Fig. 7), the angles on the face of the  $\text{Mo}_4\text{S}_4$  unit being  $73.3^\circ$  (Mo—S—Mo) and  $104.45^\circ$  (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  $\text{Mo}_6\text{Br}_2\text{S}_6$  and  $\text{Mo}_6\text{I}_2\text{S}_6$  have been isolated from the reaction of  $\text{Mo}_6\text{X}_{12}$ , molybdenum and sulphur at  $1050^\circ\text{C}$  [102].

**Molybdenum(III) halides.** From the reaction of molybdenum(III) chloride and sulphur in  $\text{S}_2\text{Cl}_2$  at  $430$ – $450^\circ\text{C}$  two species were obtained, namely  $\text{MoCl}_3\text{S}_2$  and  $\text{Mo}_3\text{Cl}_4\text{S}_7$  [45]. The analogous selenide to  $\text{Mo}_3\text{Cl}_4\text{S}_7$  has been reported [46], as have the bromides  $\text{Mo}_3\text{Br}_4\text{Y}_7$  ( $\text{Y} = \text{S}$  or  $\text{Se}$ ) [47].

The X-ray crystal structure of  $\text{MoCl}_3\text{S}_2$  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  $\text{S}_2$  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  $\text{MoBrS}$ ) and the overall structure is similar to that of  $\text{NbCl}_2\text{S}_2$  [11] (Fig. 1).

The species with the formula  $\text{Mo}_3\text{X}_4\text{Y}_7$  ( $\text{X} = \text{Br}$  or  $\text{Cl}$ ;  $\text{Y} = \text{S}$  or  $\text{Se}$ ) [45–47] presumably all have the same structure as  $\text{Mo}_3\text{Cl}_4\text{S}_7$  (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  $\text{S}(1)$

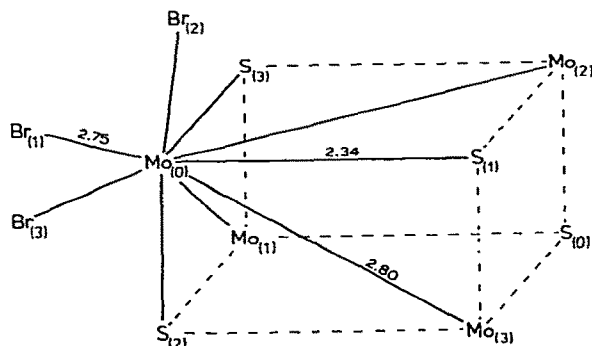


Fig. 7. Co-ordination sphere of Mo in  $\text{MoBrS}$ , see ref. 43.

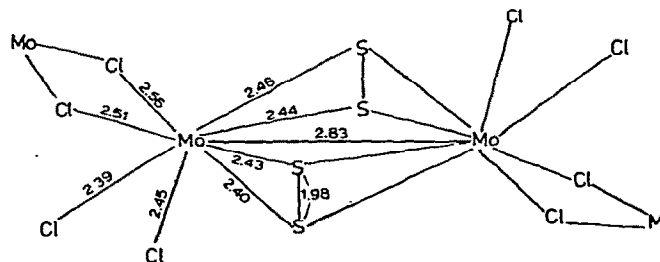
TABLE 4

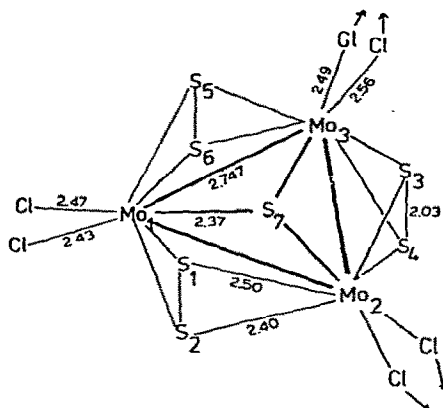
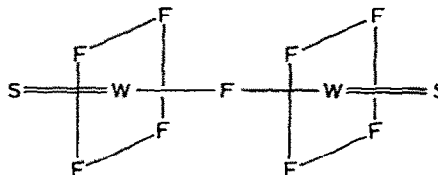
Angles and bond distances relating to Mo(0) in MoBrS<sup>a</sup>

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(0)—Mo(1,2 or 3)	2.80
Mo(2)—Mo(0)—Br(1 or 3)	140.47°		
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)			

<sup>a</sup> 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<sub>2</sub> 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<sub>2</sub> unit is unsymmetrically bound to two molybdenum atoms. For a given S<sub>2</sub> unit the sulphur atom that is closest to the plane of the

Fig. 8. MoCl<sub>3</sub>S<sub>2</sub> redrawn from ref. 45.

Fig. 9.  $\text{Mo}_3\text{Cl}_4\text{S}_7$  redrawn from ref. 45.Fig. 10  $\text{W}_2\text{F}_9\text{S}_2^-$ .

molybdenum atoms has longer Mo—S distances than its partner that is below the plane (for the  $\text{S}_2$  unit  $\text{S}(1)\text{—S}(2)$ ,  $\text{Mo}(1)\text{—S}(1) = 2.51 \text{ \AA}$  and  $\text{Mo}(1)\text{—S}(2) = 2.40 \text{ \AA}$ ); thus the  $\text{S}_2$  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  $\text{Mo}(1)$  are terminally bonded, the others being bridging atoms. Thus the structure consists of a zig-zag chain with  $\text{Mo}_3\text{Cl}_4\text{S}_7$  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  $\text{Sb}_2\text{S}_3$  carried out in a sealed tube yields  $\text{MoCl}_3\text{S}$  and  $\text{SbCl}_3$ , the products being separated by vacuum sublimation at  $140^\circ\text{C}$  [33]. An analogous reaction with  $\text{Sb}_2\text{Se}_3$  gives  $\text{MoCl}_3\text{Se}$ . The sulphido-halide is fairly unreactive towards Lewis bases although a number of adducts have been isolated [48]. A more reactive form of  $\text{MoCl}_3\text{S}$  can be prepared by allowing  $\text{MoCl}_5$  and  $\text{Sb}_2\text{S}_3$  to react in  $\text{CS}_2$  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  $140^\circ\text{C}$  and the two products also have different X-ray powder patterns. A re-examination of the IR spectra of the adducts formed by  $\text{MoCl}_3\text{S}$  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  $552 \text{ cm}^{-1}$  [15] and IR studies on  $[\text{Mo}_2\text{O}_3\text{S}(\text{S}_2\text{CNEt}_2)_2]$  where the asymmetric Mo—S—Mo mode is said to occur at  $462 \text{ cm}^{-1}$  and the symmetric stretch at  $350 \text{ cm}^{-1}$  [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  $\text{WF}_6\text{S}$  has been extensively studied by Russian workers by the use of  $^{19}\text{F}$  NMR spectroscopy [54]. By allowing  $\text{WCl}_6\text{S}$  to react initially in methyl cyanide with an excess of HF, NMR evidence for  $[\text{WCl}_4\text{FS}]^-$ ,  $[\text{WCl}_3\text{F}_2\text{S}]^-$ ,  $[\text{WCl}_2\text{F}_3\text{S}]^-$ ,  $[\text{WClF}_4\text{S}]^-$  and  $[\text{W}_2\text{F}_9\text{S}_2]^-$  (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  $[\text{W}_2\text{F}_9\text{O}_2]^-$  [82] to  $[\text{W}_2\text{F}_9\text{S}_2]^-$  while the equatorial fluorine atoms have a  $23 \pm 3$  ppm downfield shift. Thus the *trans* effect of the sulphur atom in  $\text{W}=\text{S}$  is said to be greater than that of oxygen in  $\text{W}=\text{O}$  [54].

The two anions  $[\text{WF}_5\text{S}]^-$  and  $[\text{W}_2\text{F}_9\text{S}_2]^-$  are also formed together with

TABLE 5

Tungsten sulphido- and seleno-halides

Species	Preparative route	Ref.
$\text{WF}_2\text{S}$	$\text{SF}_6 + \text{W}$ in a mass spectrometer	53
$\text{WX}_2\text{Y}$ (X = Br or Cl; Y = S or Se)	Disproportionation of $\text{WX}_3\text{Y}$	33
$\text{WF}_3\text{S}$	$\text{SF}_6 + \text{W}$ in a mass spectrometer	53
$\text{WCl}_3\text{Y}$ (Y = S or Se)	$\text{WCl}_5 + \text{Sb}_2\text{Y}_3$ at $120^\circ\text{C}$ for 7 d	33
$\text{WBr}_3\text{Se}$	$\text{WBr}_5 + \text{Sb}_2\text{Se}_3$ at $120^\circ\text{C}$ for 14 d	33
$\text{WF}_4\text{S}$	$\text{WF}_6 + \text{Sb}_2\text{S}_3$ at $300^\circ\text{C}$ for 3 h	57
	$\text{WCl}_4\text{S} + \text{HF}$ in $\text{CH}_3\text{CN}$	54
	$\text{WF}_6 + \text{H}_2\text{S}$ in $\text{CH}_3\text{CN}$	56
$\text{WCl}_4\text{S}$	$\text{WCl}_6 + \text{S}$ at $170^\circ\text{C}$ for 8 h	61 (see Fig. 11)
	$\text{WCl}_6 + \text{Sb}_2\text{S}_3$ at $140^\circ\text{C}$ for 3 d	33 62
	$\text{WCl}_6 + \text{Me}_3\text{SiSBut}$ in $\text{CS}_2$ or $\text{CCl}_4$	52
$\text{WBr}_4\text{S}$	$\text{WBr}_6 + \text{Sb}_2\text{S}_3$ at $140^\circ\text{C}$ for 7 d	33
$\text{WBr}_4\text{Se}$	$\text{WBr}_6 + \text{Sb}_2\text{Se}_3$ at $120^\circ\text{C}$ for 14 d	33
$\text{WF}_2\text{S}_2$	$\text{WSF}_4$ , $\text{MeCN} + \text{H}_2\text{S}$	56
$\text{WF}_2\text{OS}$	$\text{SF}_6 + \text{W}$ in mass spectrometer	53
$\text{WCl}_2\text{S}_2$	$\text{WCl}_4\text{O} + \text{H}_2\text{S}$ in $\text{C}_6\text{H}_6$ or $\text{CS}_2$	33, 34
	$\text{WCl}_4\text{S} + \text{Sb}_2\text{S}_3$ in $\text{CS}_2$	15
$\text{WCl}_2\text{SSe}$	$\text{WCl}_4\text{Se} + \text{Sb}_2\text{S}_3$ in $\text{CS}_2$	15
$\text{WCl}_2\text{OS}$	$\text{WCl}_4\text{S} + \text{Sb}_2\text{O}_3$ in $\text{CS}_2$	15
$\text{W}_2\text{Cl}_9\text{S}_3$	$\text{W} + \text{S}_2\text{Cl}_2$	3
$[\text{W}_2\text{Cl}_7\text{S}]^{3-}$	$\text{K}_2\text{W}_2\text{Cl}_9 + \text{F}_2\text{PS}_2\text{H}$	81

$\text{WF}_6 \cdot \text{S} \cdot \text{MeCN}$  when  $\text{WF}_6$  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  $\text{Bu}_2\text{S}$  while with the disulphide  $\text{Me}_2\text{S}_2$ ,  $\text{WF}_6 \cdot \text{SMe}$  and  $\text{WF}_6 \cdot (\text{SMe})_2$  are formed. The most rapid formation of  $\text{WF}_6 \cdot \text{S}$  and  $\text{WF}_6 \cdot \text{S}_2$  is achieved by passing  $\text{H}_2\text{S}$  into methyl cyanide solutions of  $\text{WF}_6$  [55,56].

The pure sulphido-fluoride  $\text{WF}_6 \cdot \text{S}$  has been synthesised by allowing  $\text{WF}_6$  to react with  $\text{Sb}_2\text{S}_3$  in a nickel reactor at  $300^\circ\text{C}$  [57]. By examination of the IR spectrum of  $\text{WF}_6 \cdot \text{S}$  [57] it was suggested that  $\text{WF}_6 \cdot \text{S}$  has a tetrameric structure (like  $\text{WF}_6 \cdot \text{O}$ ) [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  $\text{SF}_6$  to react in a mass spectrometer (Table 5) [53]. From the same study, heats of formation for  $\text{WF}_6 \cdot \text{S}$ ,  $\text{WF}_6 \cdot \text{S}_2$  and  $\text{WF}_6 \cdot \text{S}_3$  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  $^{19}\text{F}$  shifts have been utilised to rationalise the difference in reactivity of  $\text{WF}_6 \cdot \text{S}$  and  $\text{WF}_6 \cdot \text{O}$  towards alcohols [59,60]. Initially the reaction of alcohols with  $\text{WF}_6 \cdot \text{S}$  leads to the formation of a co-ordination compound with the oxygen atom of the alcohol *trans* to  $\text{W}=\text{S}$ . 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  $\text{WF}_6$  moiety. Similar reactions occur with  $\text{WF}_6 \cdot \text{O}$  but weaker nitrogen bases are effective in causing alcoholysis. The variation in base strength needed to cause alcoholysis is said to reflect the smaller  $d_\pi-p_\pi$  interaction in the bond of the acido ligand to the central atom in the non-linear fragment  $\text{S}-\text{W}-\text{L}$  *cis* compared to  $\text{O}-\text{W}-\text{L}$  *cis* [59,60]. The evidence for such a change in  $d_\pi-p_\pi$  comes from the  $^{19}\text{F}$  studies discussed above [54].

The best preparative route for  $\text{WCl}_6 \cdot \text{S}$  of those published is the reaction of  $\text{WCl}_6$  with sulphur in an evacuated sealed tube at  $170^\circ\text{C}$  [33,61]. A similar reaction with  $\text{WBr}_6$  led to non-stoichiometric products, so  $\text{WBr}_6 \cdot \text{S}$  is best prepared by allowing  $\text{WBr}_6$  to react at  $140^\circ\text{C}$  with  $\text{Sb}_2\text{S}_3$  [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	$\Delta H_f(298)$ (kJ mol <sup>-1</sup> )	Bond dissociation energies (kJ mol <sup>-1</sup> )	
		$\text{SF}_2\text{W}-\text{F}$	$\text{W}-\text{S}$
$\text{WF}_6 \cdot \text{S}_2$	-496.8 ( $\pm 17.6$ )	—	440
$\text{WF}_6 \cdot \text{S}$	-712.5 ( $\pm 13.4$ )	456	481
$\text{WF}_6 \cdot \text{S}$	-335.3 ( $\pm 16.3$ )	—	527



structures of  $\text{WCl}_4\text{S}$  and  $\text{WBr}_4\text{S}$  have been determined [62] and they both consist of weakly halogen bridged  $(\text{WX}_4\text{S})_2$  dimers (Fig. 11). The presence of the terminal tungsten-sulphur bond in  $\text{WCl}_4\text{S}$  is in contrast to the compound  $\text{WCl}_4\text{O}$  which is oxygen bridged [63]. The presence of  $\text{W}=\text{S}$  shows up in the IR spectra,  $\nu_{\text{W}=\text{S}}$  being reported at 569 and 555  $\text{cm}^{-1}$  in  $\text{WCl}_4\text{S}$  and  $\text{WBr}_4\text{S}$  respectively [33]. The related seleno-compounds  $\text{WX}_4\text{Se}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) are isomorphous with their sulphur analogues and  $\nu_{\text{W}=\text{Se}}$  was reported at 396  $\text{cm}^{-1}$  for  $\text{WCl}_4\text{Se}$  but the stretch curiously was not observed in the IR spectrum of  $\text{WBr}_4\text{Se}$  [33].

All the sulphido- and seleno-halides of the general formula  $\text{WX}_4\text{Y}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ;  $\text{Y} = \text{S}$  or  $\text{Se}$ ) are soluble in  $\text{CS}_2$  and  $\text{CHCl}_3$ . 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  $\text{W}=\text{Y}$  ( $\text{Y} = \text{S}$  or  $\text{Se}$ ) bonds [64]. With some of the pyridine bases more complex reactions can occur, for example the reaction of  $\text{WCl}_4\text{S}$  with bipyridyl yields  $\text{WCl}_3\text{S} \cdot \text{bipy}$  and with pyridine  $\text{WCl}_4\text{S}$  forms a compound  $\text{WCl}_4\text{S} \cdot 3\text{py}$  whose exact nature is uncertain.

Also complicated are the reactions of  $\text{WX}_4\text{Y}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ;  $\text{Y} = \text{S}$  or  $\text{Se}$ ) with ligands of the type  $[\text{RYCH}_2]_2$  ( $\text{R} = \text{alkyl group}$ ;  $\text{Y} = \text{O}$  or  $\text{S}$ ). Under carefully controlled conditions  $2 \text{WCl}_4\text{S} \cdot [\text{CH}_3\text{SCH}_2]_2$  was isolated from the reaction of  $\text{WCl}_4\text{S}$  with  $[\text{CH}_3\text{SCH}_2]_2$ . Its X-ray crystal structure has been determined [65]. The molecule is approximately centrosymmetric with the ligand bridging two  $\text{WCl}_4\text{S}$  units with the donor atoms *trans* to the tungsten-sulphur double bonds (Fig. 12).

Attempts to isolate pure samples of  $2 \text{WCl}_4\text{S} \cdot [\text{CH}_3\text{OCH}_2]_2$  have failed although NMR evidence for its existence in solution has been obtained [66]. From the reaction of  $\text{WCl}_4\text{S}$  with  $[\text{CH}_3\text{OCH}_2]_2$  a molecular species, namely  $\text{WCl}_4\text{S} \cdot \text{WCl}_2\text{OS} \cdot [\text{CH}_3\text{OCH}_2]_2$ , containing the  $\text{WCl}_2\text{OS}$  moiety was isolated [67]. A study of its X-ray crystal structure revealed that the ligand  $[\text{CH}_3\text{OCH}_2]_2$  chelates to  $\text{WCl}_2\text{OS}$ , the donor atoms being *trans* to  $\text{W}=\text{S}$  and  $\text{W}=\text{O}$  (Fig. 13). The oxygen atom of the  $\text{WCl}_2\text{OS}$  group (formally designated  $\text{W}=\text{O}$ ) bridges to the  $\text{WCl}_4\text{S}$  molecule. The formation of a  $\text{W}=\text{O}-\text{W}$  bridge rather than  $\text{W}=\text{S}-\text{W}$  bridge between  $\text{WCl}_4\text{S}$  and  $\text{WCl}_2\text{OS}$  is directly comparable to the difference in structure between  $\text{WCl}_4\text{O}$  (oxygen bridged polymer) [63] and  $\text{WCl}_4\text{S}$  (weakly chlorine bridged dimer) [62]. A similar reaction between

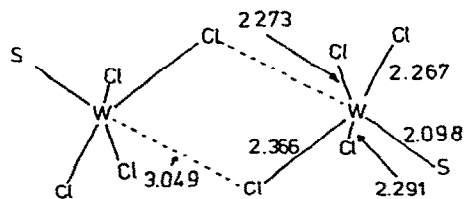


Fig. 11.  $\text{WCl}_4\text{S}$  redrawn from ref. 62.

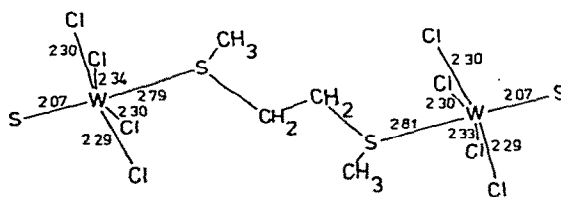
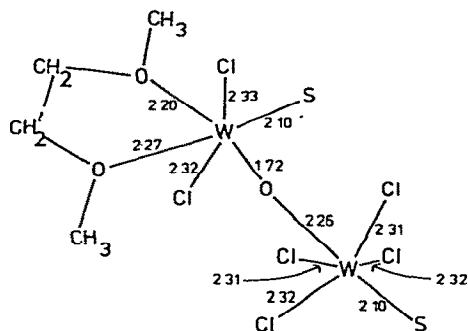
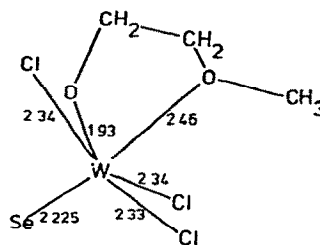


Fig. 12.  $2 \text{WCl}_4\text{S} \cdot [\text{CH}_3\text{SCH}_2]_2$  redrawn from ref. 65.

Fig. 13.  $\text{WCl}_4\text{S} \cdot \text{WCl}_2\text{OS} \cdot [\text{CH}_3\text{OCH}_2]_2$  redrawn from ref. 67.Fig. 14.  $\text{WCl}_3\text{SeOCH}_2\text{CH}_2\text{OCH}_3$  redrawn from ref. 68.

$\text{WCl}_3\text{Se}$  and  $[\text{CH}_3\text{OCH}_2]_2$  gave the alkoxide  $\text{WCl}_3\text{SeOCH}_2\text{CH}_2\text{OCH}_3$  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*  $\text{W}=\text{Se}$  [68], *trans*  $\text{W}=\text{S}$  [67] and *trans*  $\text{W}=\text{O}$  [67] (this  $\text{W}=\text{O}$  weakly bridges to another tungsten atom) shows the bond lengths to be 2.46 Å (*trans*  $\text{W}=\text{Se}$ ), 2.27 Å (*trans*  $\text{W}=\text{S}$ ) and 2.20 Å (*trans* to  $\text{W}=\text{O}$ ) thus substantiating the suggestion that the *trans* effect series is  $\text{W}=\text{S} > \text{W}=\text{O}$  [54].

Reinvestigation by  $^1\text{H}$  NMR spectroscopy of the reaction of  $\text{WCl}_4\text{Y}$  ( $\text{Y} = \text{O}, \text{S}, \text{Se}, \text{NC}_2\text{Cl}_5$ ) with  $[\text{ROCH}_2]_2$  ( $\text{R} = \text{alkyl group}$ ) shows that initially  $2 \text{WCl}_4\text{Y} \cdot (\text{CH}_3\text{OCH}_2)_2$  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  $\text{WCl}_3\text{YOCH}_2\text{CH}_2\text{OR}$  and the alkyl chloride are formed, thus showing the isolation of  $\text{WCl}_3\text{SeOCH}_2\text{CH}_2\text{OCH}_3$  [68] was just one example of a general reaction. Preliminary results obtained by repeating the reactions with the sulphur ligand  $[\text{CH}_3\text{SCH}_2]_2$  indicate that the cleavage reactions are much slower when a  $\text{C}-\text{S}$  bond has to be broken. No free alkyl chloride was detected and it is thought sulphonium salts of the type  $\text{R}_2\text{S}^+\text{CH}_2\text{CH}_2\text{SW}^-\text{Cl}_4$  (or  $[\text{R}_2\text{SCH}_2\text{CH}_2\text{SWCl}_3]^+\text{Cl}^-$ ) were formed.

The other tungsten(VI) sulphido- and seleno-halides that have been reported are of the type  $\text{WCl}_2\text{YY}'$  ( $\text{Y} = \text{O}, \text{S}$  or  $\text{Se}$ ;  $\text{Y}' = \text{S}$  or  $\text{Se}$ ) [15,34,67,69]. The most convenient synthesis is from the reaction of  $\text{WCl}_4\text{Y}'$  ( $\text{Y}' = \text{S}$  or  $\text{Se}$ ) with  $\text{Sb}_2\text{Y}_3$  ( $\text{Y} = \text{O}, \text{S}$  or  $\text{Se}$ ) in  $\text{CS}_2$  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  $\text{WCl}_3\text{Y}$  ( $\text{Y} = \text{S}$  or  $\text{Se}$ ) and  $\text{WBr}_3\text{Se}$  are formed by the reaction of  $\text{WX}_5$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) with  $\text{Sb}_2\text{Y}_3$  ( $\text{Y} = \text{S}$  or  $\text{Se}$ ) [33]. They are believed to have a sulphur or selenium bridged structure similar to that of  $\text{NbCl}_3\text{O}$  which is an oxygen and chlorine bridged poly-

mer [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  $\text{WCl}_3\text{S}$ . bipy [64] (which has a  $\nu_{\text{W}=\text{S}}$  mode at  $531\text{ cm}^{-1}$ ) and  $\text{WCl}_3\text{S}$  which has no IR absorption above  $470\text{ cm}^{-1}$ .

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  $\text{WF}_2\text{S}$  [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  $\text{MnS}$ ,  $\text{MnCl}_2\text{S}$ ,  $\text{MnBrS}$  and  $\text{MnIS}$  were obtained. These three compounds were shown by comparison of their X-ray powder photographs not to be mixtures of  $\text{MnS}$  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  $\text{ReCl}_3\text{O}$  have been well-characterised [1] the species reported to be one form of  $\text{ReCl}_3\text{O}$  [71] was shown by X-ray crystallography to be  $\text{Re}_2\text{O}_3\text{Cl}_6 \cdot 2\text{ReO}_3\text{Cl}$  [72].

By allowing  $\text{ReCl}_5$  and sulphur (in a 1 : 2 molar ratio) to react at  $125^\circ\text{C}$  for 2–3 hours  $\text{ReCl}_4\text{S}$  was formed [73] the other product being  $\text{S}_2\text{Cl}_2$ . 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  $160^\circ\text{C}$ ,  $\text{Re}_2\text{Cl}_4\text{S}_3$  was the product; further increase of temperature to  $270^\circ\text{C}$  led to the formation of  $\text{ReCl}_2\text{S}$  and above this  $\text{Re}_2\text{S}_7$  was obtained. By studying the fusion diagrams of  $\text{Re}_3\text{Cl}_9$  and  $\text{S}_2\text{Cl}_2$  it was shown that  $\text{ReCl}_4\text{S}$  melts incongruently at  $80 \pm 2^\circ\text{C}$  and that it probably undergoes a phase change at  $-63^\circ\text{C}$ . The IR spectra of  $\text{ReCl}_4\text{S}$  is reported to contain a band at  $913\text{ cm}^{-1}$  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  $\text{Re}-\text{O}$  stretching modes in  $\text{ReCl}_4\text{O}$  are centered at  $1040\text{ cm}^{-1}$  and those in  $\text{ReO}_3\text{Cl}$  at  $970\text{ cm}^{-1}$  [74]. By comparison with the terminal  $\text{W}=\text{O}$  and  $\text{W}=\text{S}$  stretching modes, the  $\text{Re}=\text{S}$  mode would be expected in the region of  $560\text{ cm}^{-1}$ . The same authors also report  $\text{ReClS}_3$  as having an IR band at  $913\text{ cm}^{-1}$  with a shoulder at  $890\text{ cm}^{-1}$ . However, the reported analytical figures for this compound add up to 113% so the isolation of  $\text{ReClS}_3$  must be open to question although from a fusion

TABLE 7

Rhenium sulphido-, seleno- and telluro-halides

Species	Preparative route	Ref.
ReCl <sub>2</sub> S	ReS <sub>2</sub> + Cl <sub>2</sub>	76
	Re <sub>2</sub> Cl <sub>4</sub> S <sub>3</sub> + Cl <sub>2</sub> at 400–450°C for 0.5 to 1 h	79
	2 ReCl <sub>5</sub> + 4S at 160–270°C	73
	Re <sub>3</sub> Cl <sub>9</sub> + S	75
ReBr <sub>2</sub> S	Re <sub>3</sub> Br <sub>9</sub> + S	75
ReCl <sub>2</sub> Se	ReSe <sub>2</sub> + Cl <sub>2</sub> at 480 to 500°C (ICl <sub>3</sub> heated to give Cl <sub>2</sub> )	77
	Re <sub>3</sub> Cl <sub>9</sub> + Se	75
ReBr <sub>2</sub> Se	Re <sub>3</sub> Br <sub>9</sub> + Se	75
ReBrS <sub>2</sub>	Re <sub>3</sub> Br <sub>9</sub> + S	75
ReClS <sub>3</sub>	2 ReCl <sub>5</sub> + 8 S up to 200°C (product obtained mixed with S <sub>2</sub> Cl <sub>2</sub> , and reported analysis is not good)	73
ReCl <sub>3</sub> S	ReCl <sub>5</sub> + Sb <sub>2</sub> S <sub>3</sub> in CS <sub>2</sub> at room temp.	15
ReCl <sub>4</sub> S	2 ReCl <sub>5</sub> + 4S at 125°C	73
Re <sub>2</sub> Cl <sub>4</sub> S <sub>3</sub>	Re <sub>2</sub> S <sub>7</sub> + Cl <sub>2</sub> /CO <sub>2</sub> (1 : 5) at 120°C	79
	2 ReCl <sub>5</sub> + 4 S at 125 to 160°C	73
Re <sub>3</sub> Cl <sub>5</sub> Se <sub>2</sub>	3 ReSe <sub>2</sub> + 2 Re <sub>3</sub> Cl <sub>9</sub> at 700–750°C for 10–15 h (volatile fraction removed at 250°C)	77
Re <sub>3</sub> Br <sub>5</sub> Se <sub>2</sub>	ReSe <sub>2</sub> + Br <sub>2</sub> at 580°C	78
	3 ReSe <sub>2</sub> + 2 Re <sub>3</sub> Br <sub>9</sub> at 700–750°C for 10–15 h (volatile fraction removed at 250°C)	77
Re <sub>3</sub> Br <sub>5</sub> Te <sub>2</sub>	Re <sub>2</sub> Te <sub>5</sub> + Br <sub>2</sub> at 155 to 160°C yields a mixture from which TeBr <sub>4</sub> was sublimed at 290°C leaving Re <sub>3</sub> Te <sub>2</sub> Br <sub>5</sub>	77

diagram of ReS<sub>2</sub> and S<sub>2</sub>Cl<sub>2</sub> the compound is reported to melt incongruently at  $63 \pm 2^\circ\text{C}$ .

Four compounds of the general formula ReX<sub>2</sub>Y (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<sub>3</sub>X<sub>9</sub> (X = Cl or Br) with sulphur or selenium [75]. Chlorination of ReY<sub>2</sub> (Y = S or Se) also yields ReCl<sub>2</sub>Y [76,77]. No physical properties of these species have been reported except that ReCl<sub>2</sub>Se is air stable. X-ray powder photographs for a number of them have been obtained [77].

The reaction of ReSe<sub>2</sub> with Re<sub>3</sub>X<sub>9</sub> (X = Cl or Br) leads to the formation of the isomorphous species Re<sub>3</sub>X<sub>5</sub>Se<sub>2</sub> (X = Cl or Br) [77]. The bromide was first prepared by the bromination of ReSe<sub>2</sub> [78] and the analogous telluro-bromide by the bromination of ReTe<sub>2</sub> [77]. These compounds are said to be air stable and insoluble in water, hydrochloric acid, alcohol or acetone.

Chlorination of Re<sub>2</sub>S<sub>7</sub> goes through a number of steps involving the formation of sulphido-chlorides, the most stable being Re<sub>2</sub>Cl<sub>4</sub>S<sub>3</sub> and ReCl<sub>2</sub>S [79].

The action of hydrogen on these sulphido-chlorides gives  $\text{Re}_2\text{S}_3$  (from  $\text{Re}_2\text{Cl}_4\text{S}_3$ ) and  $\text{ReS}$  (from  $\text{ReCl}_2\text{S}$ ) [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  $\text{PtX}_2$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) with sulphur [83]. The products have the general formula  $\text{PtX}_m\text{S}_n$  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.
$\text{CuXTe}_2$ (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
$\text{CuXTe}$ (X = Cl, Br or I)	CuX (X = Cl or Br) (20 g) + Te(1 g) in the presence of HX · X=I: $\text{Cu}_4\text{Te}_3$ (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
$\text{CuClSe}_2$	$\text{CuCl}$ (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
$\text{CuBrSe}_3$	$\text{CuBr}$ (15 g) + Se (5 g) in presence of HBr. Heated to 340°C and allowed to cool to 150°C	85, 87, 91.
$\text{CuISe}_3$	$\text{CuI}$ (10 g) + Se (5 g) in the presence of HI. Heated to 390°C and allowed to cool to 200°C	85, 87, 91
$\text{Ag}_3\text{BrS}$	$\text{Ag}_2\text{S}$ + $\text{AgBr}$ at 280°C	92
$\text{Ag}_3\text{IS}$	$\text{Ag}_2\text{S}$ + $\text{AgI}$ at 235°C for 100 h. $\text{Ag}_2\text{S}$ + $\text{AgI}$ + S at 550°C. Sufficient sulphur is added to give pressure of 1 atm at 550°C in the sealed tube	92, 93, 94
$\text{AuBrSe}$	Au (5.9 g) + Se (2.4 g) + $\text{Br}_2$ (2.4 g) in HBr <sup>a</sup> at 230°C for 9 days	89
$\text{AuClSe}$	Au (5.9 g) + Se (2.4 g) + $\text{Cl}_2$ (12.0 g) in HCl <sup>a</sup> at 200–180°C for 12 days	89, 101 see Fig. 23
$\text{AuITe}$	Au (6.2 g) + Te (4 g) + $\text{I}_2$ (8 g) in HI. Heated to 450°C, allowed to cool to 150°C over 10 days	90, 91
$\text{AuITe}_2$	As per AuITe with omission of the $\text{I}_2$	90, 91, 100 see Figs. 19 and 20
$\text{AuClTe}_2$	Au (5.9 g) + Te (1.9 g) + $\text{Cl}_2$ (1.0 g) in HCl. <sup>a</sup> Heated to 400°C, allowed to cool to 100°C over 10 days	90, 91, 100 see Figs. 21 and 22
$\text{AuBrTe}_2$	Au (13.9 g) + Te (5.1 g) + $\text{Br}_2$ (5.7 g) in HBr. Heated to 350°C, allowed to cool to 150°C over 10 days	90, 91

<sup>a</sup> 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  $\text{Ag}_3\text{BrS}$  and  $\text{Ag}_3\text{IS}$  have been prepared by heating equimolar mixtures of silver halide and  $\text{Ag}_2\text{S}$  [92–94]. The problem in the syntheses involving

$\text{Ag}_2\text{S}$  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  $\text{CuXTe}$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) and  $\text{CuXTe}_2$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ). Within a series the members are isomorphous, but the two selenides,  $\text{CuISe}_3$  and  $\text{CuBrSe}_3$  are not isomorphous [87].

The structures of two members of the isomorphous  $\text{CuXTe}$  series have been determined, namely  $\text{CuITe}$  [95] and  $\text{CuBrTe}$  [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

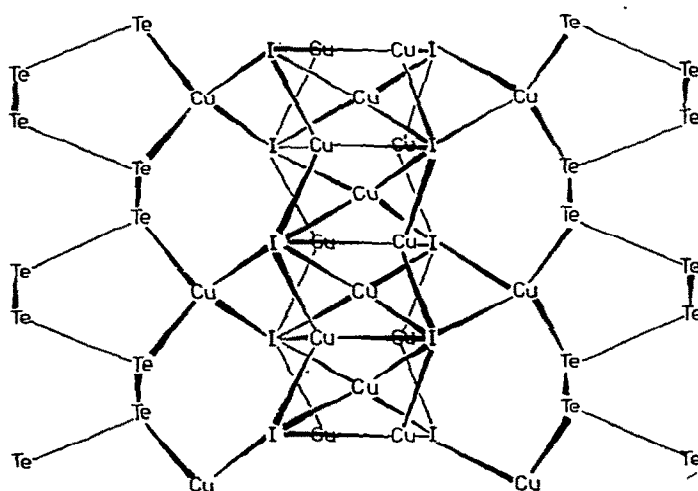


Fig. 15.  $\text{CuITe}$  showing the various Cu sites redrawn from ref. 95.

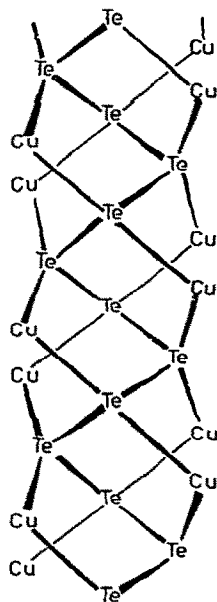


Fig. 16. The screw of Te atoms in CuTe redrawn from ref. 95.

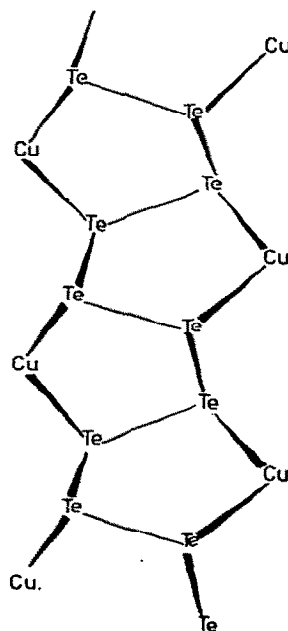


Fig. 17. The pseudo-fourfold screws of Te atoms in CuClTe<sub>2</sub> redrawn from ref. 98.

CuTe 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 CuTe [95] and those in CuClTe<sub>2</sub> (2.595(5) and 2.586(7) Å) [98].

Screws of tellurium atoms are also found in CuClTe<sub>2</sub> [98] which is one compound in the isomorphous series CuXTe<sub>2</sub> (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<sub>2</sub> (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 CuTe [95] and CuClTe<sub>2</sub> [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<sub>2</sub> (X = Cl, Br or I).



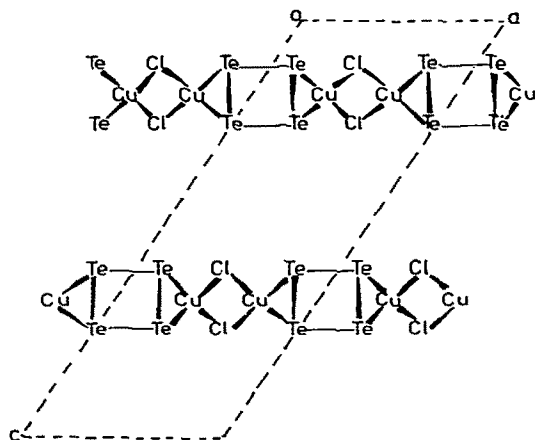


Fig. 18. The  $\text{CuClTe}_2$  layers projected down the  $b$ -axis, redrawn from ref. 98.

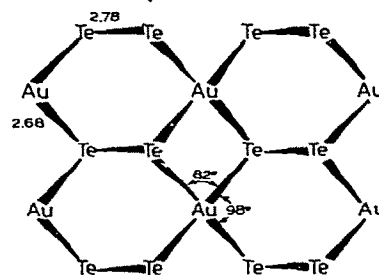


Fig. 19.  $\text{AuTe}_2$  nets in  $\text{AuTe}_2$ , redrawn from ref. 100.

#### (iv) Silver

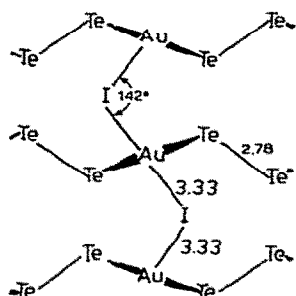
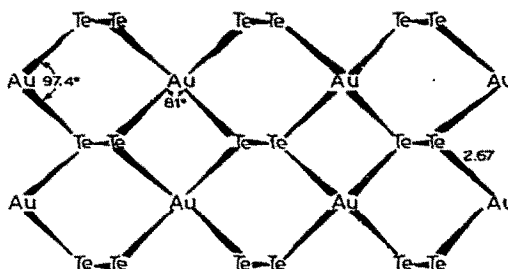
The silver compounds  $\text{Ag}_3\text{BrS}$  and the  $\beta$  form of  $\text{Ag}_3\text{IS}$  have a simple cubic lattice. Their structure is derived from the ideal antiperovskite structure by displacement of the silver ions from the centre of the faces towards the edges of the cell [99].

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

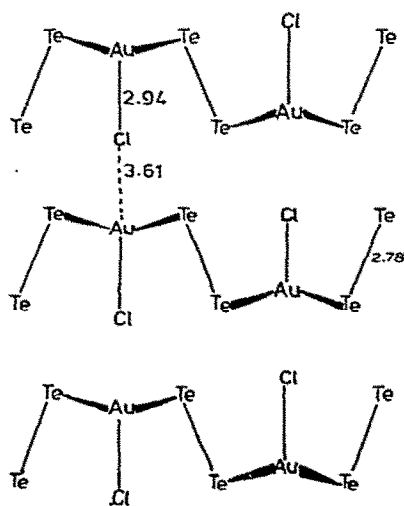
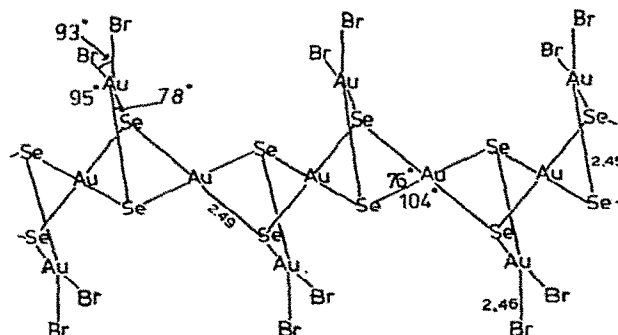
The three telluro species  $\text{AuXTe}_2$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) are all metallic conductors while the remaining gold telluro-halide  $\text{AuTe}$  has a band gap of 0.9 eV. Three of the compounds  $\text{AuTe}_2$ ,  $\text{AuBrTe}_2$  and  $\text{AuITe}$  exhibit temperature independent diamagnetism [90]. The copper compounds analogous to the  $\text{AuXTe}_2$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) series are diamagnetic, and also differ from the gold species in being semi-conductors [86]. Structural studies on  $\text{AuClTe}_2$  (which is isomorphous with  $\text{AuBrTe}_2$  [90]) and  $\text{AuTe}_2$  show that they have totally different structures from  $\text{CuClTe}_2$  [98].

The structures of  $\text{AuClTe}_2$  and  $\text{AuTe}_2$  are remarkably similar [100] (Figs. 19 to 22). The tellurium atoms occur as  $\text{Te}_2$  units in a two-dimensional net of gold and tellurium atoms. This is unlike the situation in  $\text{CuXTe}$  ( $\text{X} = \text{Cl}$  or  $\text{I}$ ) [95,96] and  $\text{CuClTe}_2$  [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  $\text{Te}-\text{Te}$

Fig. 20. The halogen bridging in  $\text{AuITe}_2$ , redrawn from ref. 100.Fig. 21.  $\text{AuTe}_2$  nets in  $\text{AuClTe}_2$ , redrawn from ref. 100.

unit. The iodine atoms in  $\text{AuITe}_2$  are equidistant from two gold atoms (3.3300(6) Å) while the chlorine atoms in  $\text{AuClTe}_2$  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  $\text{AuClSe}$  and  $\text{AuBrSe}$  [89]. The structure of the bro-

Fig. 22. The unsymmetrical halogen bridge in  $\text{AuClTe}_2$ , redrawn from ref. 100.Fig. 23. The two gold environments in  $\text{AuBrSe}$ , redrawn from ref. 101.

vide 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<sub>2</sub> [100], AuTe<sub>2</sub> [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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