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THIO-, SELENO-, AND TELLUROHALIDES OF THE TRANSITION METALS

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I. Introduction

Thio-, seleno-, and tellurohalides are classes of compounds with only sparse coverage in the chemical literature. Over the past 20 years, however, there has been a gradual increase in activity in these areas of chemistry, although the papers published so far have been the almost exclusive preserve of a small number of research groups.

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This review summarizes the preparation and chemistry of known thio-, seleno-, and tellurohalides of the transition-metal elements, the compounds being dealt with element by element and group by group. For the purposes of the review we have adopted the definition of transition elements as those which, as elements, have partly filled *d* or *f* shells in any of their commonly occurring oxidation states. This means that copper, silver, and gold are included. However, whereas the Group I elements may lose one or two *d* electrons to give ions or complexes in the II and III oxidation states, this is no longer possible for Group II, and zinc, cadmium, and mercury compounds have been omitted. Tables I, II, and III list the compounds considered. No thio-, seleno-, or tellurohalides have yet been prepared for scandium, zirconium, hafnium, technetium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, or palladium. For the remaining elements

TABLE I

KNOWN TRANSITION-METAL THIOHALIDES[a]

Group IIIA	Group IVA	Group VA	Group VIA	Group VIIA	Group VIII
	$TiSCl_2$	VSCl	CrSBr	$MnSCl_2$	
	TiSCl	(VSBr)?	$CrSI_{0.83}$		
YSHal		$NbSCl_3$	$MoSCl_3$		
		$NbSBr_3$	$MoSBr_3$		
		$NbSCl_2$	$MoSCl_2$		
		NbS_2X_2	MoS_2Cl_3		
		$Nb_3S_3Cl_8$	MoS_2Cl_2		
			MoS_2Br_2		
			MoSX		
			$Mo_2S_4Cl_5$		
			$Mo_2S_5X_3$		
			$Mo_3S_7Cl_4$		
			$Mo_3S_7Br_4$		
			Mo_6SBr_{10}		
			$Mo_6S_{14}I_8$		
LaSHal		$TaSCl_3$	WSF_4	$ReSCl_4$	PtS_nCl_m
MSBr		$TaSBr_3$	$WSCl_4$	$ReSCl_3$	PtS_nBr_m
		$TaSCl_2$	$WSBr_4$	$ReSCl_2$	
		TaS_2Cl_2	$WSCl_3$	$ReSBr_2$	
			$WSCl_2$	ReS_2Br	
			WS_2Cl_2	ReS_3Cl	
			$WOSCl_2$	$Re_2S_3Cl_4$	
			$WSSeCl_2$		

[a] M = La, Ce, Pr, Sm, Gd, Tb, Dy, Ho, Er, Yb, Lu; Hal = F, Cl, Br, I; X = Cl, Br, I; *m* and *n* = integers that depend on the ratio of reactants and temperature.

TABLE II

KNOWN TRANSITION-METAL SELENOHALIDES[a]

Group IIIA	Group IVA	Group VA	Group VIA	Group VIIA	Group VIII	Group IB
			$CrSeI$ Cr_2CuSe_3Br	$MnSeBr_2$ $MnSeI_2$ $MnSeCl$ $MnSe_2Cl_2$ Mn_2SeBr_2		$CuSe_2Cl$ $CuSe_3Br$ $CuSe_3I$ $CuCr_2Se_3Br$
$YSeF$		$NbSeCl_3$ $NbSeBr_3$ $NbSe_2X_2$	$MoSeCl_3$ $MoSeCl_2$ $Mo_3Se_7Cl_4$ $Mo_3Se_7Br_4$ Mo_6SeBr_{10} Mo_6SeI_{10} $Mo_6Se_{14}I_8$			
$LaSeF$		$TaSeBr_3$	$WSeF_4$ $WSeCl_4$ $WSeBr_4$ $WSeBr_3$ $WSeBr_2$ $WOSeCl_2$ $WSSeCl_2$	$ReSeCl_2$ $ReSeBr_2$ $Re_3Se_2Cl_5$		$AuSeCl$ $AuSeBr$

[a] X = Cl, Br, I.

TABLE III

KNOWN TRANSITION-METAL TELLUROHALIDES[a]

Group IIIA	Group IVA	Group VA	Group VIA	Group VIIA	Group VIII	Group IB
			$CrTe_{0.73}I$			$CuTeX$ $CuTe_2X$ Ag_3TeBr Ag_5Te_2Cl $AuTeI$ $AuTe_2X$

[a] X = Cl, Br, I.

the most usual preparative routes for thio and seleno derivatives are:

1. Direct combination of the elements (a method often used to prepare chalcogenide halides of the main group elements)
2. The halogenation of a metal sulfide or selenide
3. The reaction of a metal halide with sulfur, selenium, a sulfide or a selenide (such methods being mainly employed for the early transition elements)

4. Hydrothermal synthesis at high temperature and pressure in an autoclave (this route has been employed exclusively for the later transition elements).

At present the number of tellurohalides known is limited, and it is perhaps too soon to list "general" methods for their preparation.

II. Group IIIA

A. YTTRIUM

The series of yttrium thiohalides YSX (X = F, Cl, Br, I) have been synthesized, and X-ray crystallographic studies have yielded comprehensive data on their space groups and unit cell parameters (*29*). Yttrium thiofluoride, prepared by the reaction of Y_2S_3 with YF_3 (at 900°–1200°C) (*29*) or other fluorinating agents (*52*), has both α- and β-forms, which are tetragonal and hexagonal, respectively (*27*, *29*, *75*). The β-form has been studied by three-dimensional X-ray diffraction and shown to consist of compact layers of (YS_2) and (YF_2) units parallel to the (001) plane (Fig. 1) (*75*).

Yttrium selenofluoride may be prepared using YF_3 and Y_2Se_3 (*25*, *26*) and is known to exist in at least three forms: orthorhombic (*33*), monoclinic (*34*) and one that is either hexagonal or rhombohedral (*26*). The orthorhombic polytype has selenium atoms at the vertices of a slightly distorted octahedron. Each selenium has 4-fold coordination, and the three-coordinate fluorines are each at the center of a yttrium

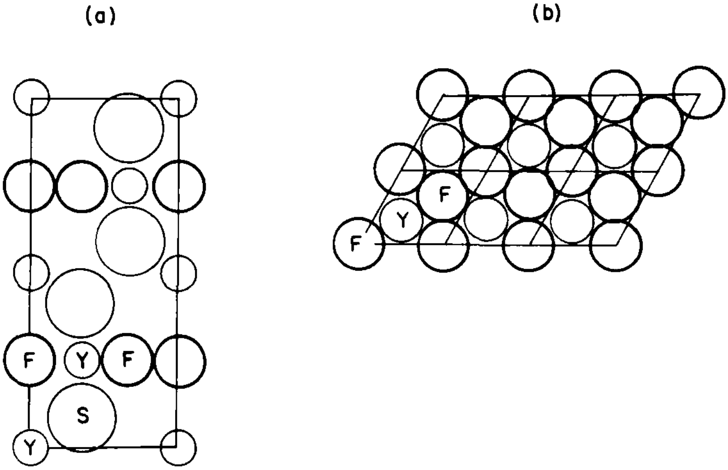

FIG. 1. Crystal structure of β-YSF (*75*). (a) View of the structure in the diagonal plane (110). (b) Planar layer of YF_2 at $z = \frac{1}{4}$. Reproduced with permission.

isosceles triangle. The yttrium atoms have 7-fold coordination. The main feature of the structure is the planar Y–F groups along two diagonals of the projected selenium hexagons (*33*), Comparison of this two-layer orthorhombic polytype with the four-layer monoclinic polytype (Fig. 2) has been made (*34*). More recently, structures of other

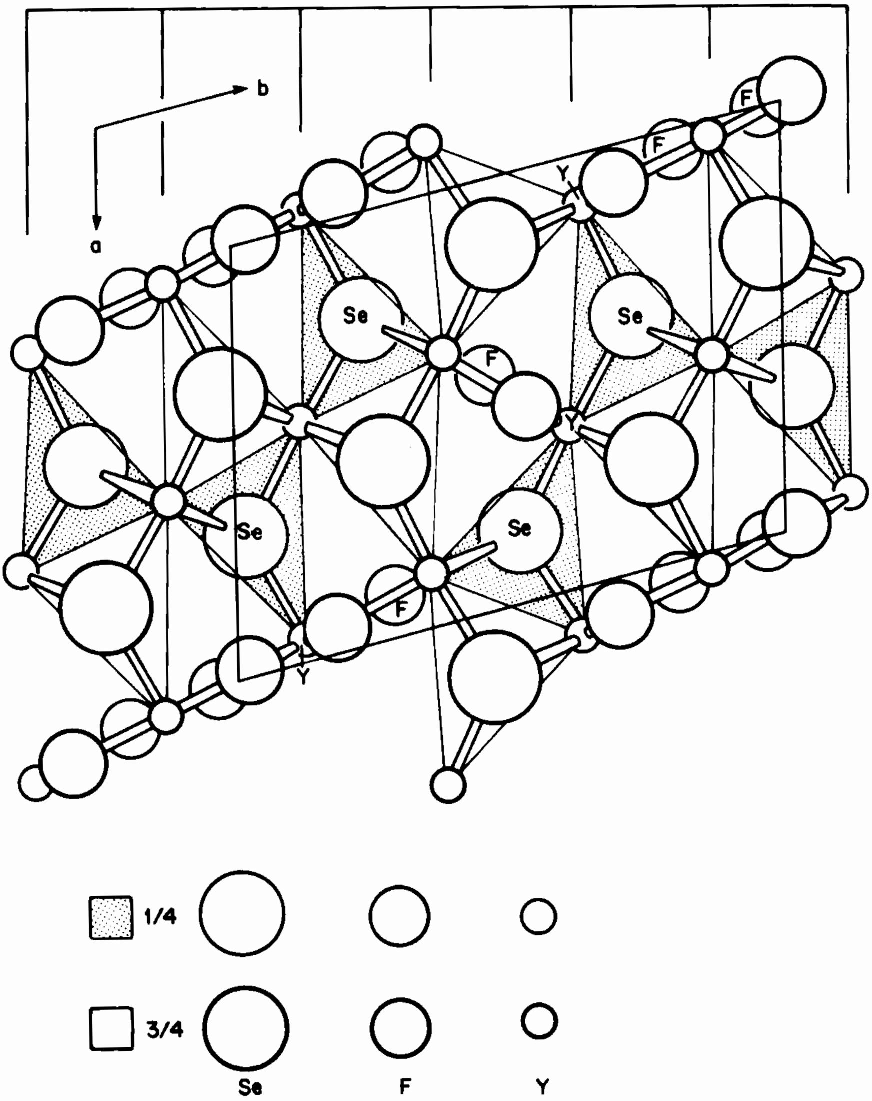

FIG. 2. Projection on the $x0y$ plane of the structure of four-layer monoclinic polytype of YSeF (*34*). Reproduced with permission.

polytypes have been studied by lattice imaging using electron microscopy (*88*).

B. LANTHANUM

The series of compounds LaSX (X = Cl, Br, I), each of which is orthorhombic (*23*, *27*), may be made by the reaction of metallic lanthanum with sulfur and the appropriate halogen at 500°C (*27*). Lanthanum thiofluoride (LaSF), however, has only been prepared by reaction of LaF_3 with La_2S_3 (*5*, *29*, *44*, *89*) or La_3S_4 and sulfur at high temperature (*78*). This gray-white solid, which melts at 1810°C (*89*), possesses a tetragonal structure of the PbClF type (*27*, *44*, *78*). The infrared spectrum has been compared with those of CeSF, PrSF, and NdSF (*5*). The thiochloride and thioiodide of lanthanum are of unknown structure whereas LaSBr has three structures, all of which are characterized by alternate layers of bromine ions and La_4S tetrahedra (*28*). A number of other analogous lanthanide and actinide thiobromides have also been reported (Table I) (*28*).

Light gray LaSeF has been prepared by routes analogous to those used to prepare LaSF (*24*, *78*) and has been identified in three forms, tetragonal (*24*), hexagonal (*32*), and orthorhombic (*78*). The tetragonal structure is of the PbClF type and contains layers of $(LaF)_n$ and Se (*24*). The hexagonal form consists of layers of selenium anions and planes of lanthanum and fluoride ions. Each lanthanum and fluorine occupies the center of an equilateral triangle formed by the other ions. The selenium and fluorine anions together form a rhombohedral stacking sequence (*32*). The corresponding chloride, bromide, and iodide are not known.

III. Group IVA

TITANIUM

Low yields of $TiSCl_2$ were obtained by bubbling hydrogen sulfide through solutions of titanium tetrachloride in CS_2 at 20°–65°C (*35*). The product was reported to be oxygen and moisture sensitive and to decompose into TiS_2 and $TiCl_4$ at temperatures above 400°C. This work has been repeated by Riera and Uson (*74*), and no evidence for $TiSCl_2$ was obtained, although very small yields of insoluble, air- and water-sensitive TiSCl were produced. This had infrared peaks at $550\ cm^{-1}$ and $370\ cm^{-1}$, which were assigned to Ti–S and Ti–Cl stretching frequencies, respectively. Attempts to prepare TiSCl by reaction of $TiCl_4$ with As_2S_3, Sb_2S_3, or MoS_2 also proved to be unsuccessful (*74*). Mixtures of TiSCl and $TiSCl_2$ appear to be produced from reaction of $TiCl_3$ with sulfur in benzene in an autoclave. The brown product can be used as a catalyst in the production of crystalline polypropylene (*85*).

IV. Group VA

A. VANADIUM

The vanadium thiochloride (VSCl) has been prepared by the reaction of vanadium trichloride with antimony trisulfide at 380°–390°C. The thermal conditions for the reaction require careful control. The infrared spectrum and magnetic susceptibility have been obtained (*3*). An attempt to prepare the analogous thiobromide has been less successful, the product always containing less than the theoretical amount of bromine (*3*).

B. NIOBIUM

Reaction of niobium pentachloride with both antimony trisulfide and sulfur has been used to prepare a complex series of species that includes predominantly $Nb_3S_3Cl_8$, a red-brown solid believed to be a cluster compound (*38*). These materials appear to originate from the disproportionation of $NbSCl_3$, formed as an intermediate in the reaction. Niobium thiotrichloride, $NbSCl_3$, has been isolated as golden-yellow, air-sensitive crystals from the reaction of $NbCl_5$ with Sb_2S_3 at room temperature in carbon disulfide (*38*, *39*), and the analogous compounds $NbSBr_3$, $NbSeCl_3$, and $NbSeBr_3$ have been prepared by the same method (*39*). $NbSCl_3$ has also been prepared by the reaction of $NbCl_5$ with B_2S_3 (*4*). The infrared spectra of the thiohalides exhibit metal–sulfur stretches in the region of 550 cm^{-1} (Table IV) (*4*).

TABLE IV

METAL–SULFUR STRETCHING FREQUENCIES (IN CM^{-1}) FOR NIOBIUM AND TANTALUM THIOHALIDES MSX_3 (M = Nb, Ta; X = Cl, Br) (*39*)

Compound	$\nu(M = S)$
$NbSCl_3$	552
$TaSCl_3$	463
$NbSBr_3$	542
$TaSBr_3$	448

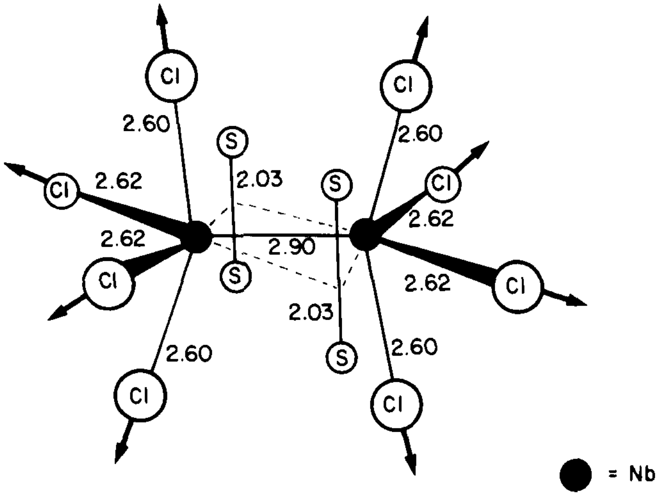

FIG. 3. Coordination polyhedron of an Nb_2 pair in the NbS_2Cl_2 structure (*79*). Reproduced with permission.

A series of compounds, NbX_2Y_2 (X = S, Se; Y = Cl, Br, I), has been prepared (*76*, *77*, *79*) by reaction of the elements at ~ 500°C. Niobium dithiodichloride has also been made by heating a 1:1 mixture of niobium metal and S_2Cl_2 (*76*). These niobium dithiodihalides contain bridging S_2 groups, and the structure of single crystals of NbS_2Cl_2 has been determined (*79*) and can be described in terms of $Nb_2(S_2)_2$ groups linked to one another via chlorine atoms (Fig. 3).

Vibrational studies of the octahedral cages $[Nb{-}(S_2)_2{-}Nb]$ in the thiohalides NbS_2X_2 (X = Cl, Br, I) show metal—(S_2) bridging vibrations at <400 cm^{-1} and sulfur—sulfur stretches that are both infrared and Raman active at 500–600 cm^{-1} (*61*, *63*). This high S—S stretching frequency has been accounted for in later theoretical studies (*60*). The frequencies associated with S—S, Nb—S, and Nb—X are listed in Table V.

Niobium thiodichloride, $NbSCl_2$, is the product of the reaction of $NbCl_4$ with M_2S_3 (M = As, Sb) at 250°C under an atmosphere of argon (*54*) and the reaction of $NbCl_5$ with sulfur in benzene (*83*). In the latter study a series of compounds $Nb(S_2)_mCl_n$ (m = 1–3, n = 1–4) were also produced by interaction of Nb(V) chloride with elemental sulfur in melts at 240°–300°C in a vacuum and the products were examined by infrared spectroscopy. Intense absorptions at 535 cm^{-1} were attributed to stretching vibrations of S—S bonds coordinated to the metal. All the products from the melts are unstable hydrolytically, insoluble in

TABLE V

FREQUENCIES (IN CM^{-1}) OF INFRARED AND RAMAN VIBRATIONS OF NIOBIUM THIOHALIDES NbS_2X_2 (X = Cl, Br, I) (*61*, *63*)

	Compound				
	NbS_2Cl_2		NbS_2Br_2		NbS_2I_2
Assignments	IR	Raman	IR	Raman	IR
S—S	558s	592vs	585s	585vs	575s
	582sh		580sh		570sh
Nb—S	377m		370m		358m
	362vs		358vs		348vs
		336s		328s	
	323vs		320s		315s
		317m		310m	
		252m		243s	
		188m		183w	
	166s		174s		169s
Nb—X	295vs		205vs		148s
		285m		170w	
	255sh				
	250vs		190vs		131s
	245sh				
			143sh		
	218w		140m		

the usual organic solvents, decomposed by mineral acids, and dissolve in a mixture of potassium hydroxide and hydrogen peroxide with separation of elemental sulfur (*83*).

C. TANTALUM

The first identification of a tantalum thiohalide was made by Boehland and Schneider, who studied the reaction of $TaCl_5$ with PhNCS in hexane and heptane (*10*). These reactions yielded $TaCl_5 \cdot PhNCS$, which was totally converted to $TaSCl_3 \cdot PhNCCl_2$ on refluxing. Heating a mixture of $TaCl_5$ with Sb_2S_3 to 120°C produces a material of empirical formula $TaSCl_3$ (*38*, *39*). This has been separated into a black residue and white and yellow sublimates by heating to 140°C for 14 days. Yellow $TaSCl_3$ produced by the reaction of $TaCl_5$ with Sb_2S_3 in dry CS_2 (*38*) or by direct reaction of stoichiometric amounts of $TaCl_5$ and B_2S_3 at 80°C (*4*) has also been shown to be thermally unstable and, on heating, decomposes producing a white sublimate, $TaCl_5$, and a black residue of $TaSCl_2$. The metal–sulfur stretching frequency in

$TaSCl_3$, 463 cm^{-1}, is similar to the Nb—S frequencies of analogous niobium compounds (Table IV) (*39*). Both $TaSBr_3$ and $TaSeBr_3$ have been synthesized by reaction of the appropriate antimony chalcogenide with $TaBr_5$ in CS_2 (*39*). The dithiodichloride, TaS_2Cl_2, has been reported as the product from the reaction of $TaCl_5$ and sulfur in benzene (*83*).

V. Group VIA

A. CHROMIUM

There have only been two reports of chromium thio-, seleno- and tellurohalides (*46*, *71*). Black CrSBr may be prepared from Cr_2S_3 and $CrBr_3$ in a sealed ampoule at 870°C, and $CrSI_{0.83}$ and CrSeI and $CrTe_{0.73}I$ are the products from the reaction of iodine and the respective metal chalcogenide at 400°C (*46*). All are hexagonal, and all three compounds are readily hydrolyzed. The preparation of single crystals of $CuCr_2Se_3Br$ has been reported (*71*).

B. MOLYBDENUM

The variety of, and number of publications concerning, molybdenum thio-, and selenohalides is surpassed only by those on the corresponding tungsten species. Compounds with molybdenum in the oxidation states 3, 4, 5, and 6 have been successfully synthesized.

The series of molybdenum(III) thiohalides, MoSX (X = Cl, Br, I), has recently been reported (*58*, *59*). Each is prepared by heating a mixture of sulfur, powdered molybdenum metal, and the appropriate molybdenum dihalide. All are cubic with tetrahedral Mo_4 clusters, which are bridged together by the halogen atoms. The thiobromide structure has been studied in detail (Fig. 4) (*59*).

Black molybdenum thiodichloride, $MoSCl_2$, may be prepared in three ways, by the reaction of antimony trisulfide with $MoCl_4$ at 140°C for 7 days (*15*), from the disproportionation of $MoSCl_3$ (*15*) or by the direct chlorination of MoS_2 in a flow system (*40*, *70*). Of these three routes the first has been reported to give the best yields.

Involatile, dark green, $MoSCl_3$ may be prepared by the reaction of $MoCl_5$ with sulfur at 140°C for 3 weeks (*15*) or in carbon disulfide at room temperature (*73*). Alternatively, it can be made by reaction of $MoCl_5$ and sulfur with antimony trisulfide at 170°C for 7 days (*14*, *15*) or in CS_2 at 25°C for 3 days (*73*). Another method is the reaction of stoichiometric quantities of $MoCl_5$ with B_2S_3 at 190°C (*4*). It has also

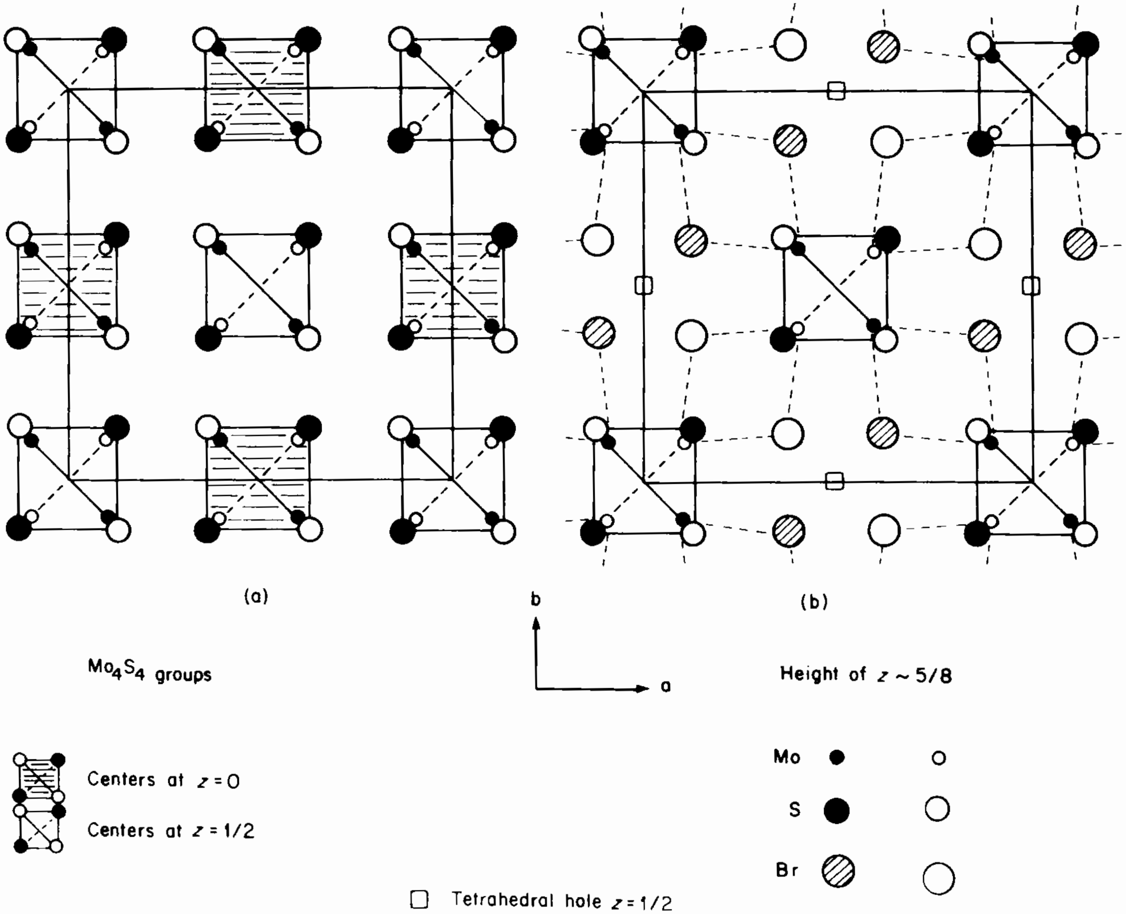

FIG. 4. Crystal structure of MoSBr (*59*). (a) Disposition of Mo_4S_4 group in the lattice. (b) Projection of the atoms lying between $z = \frac{1}{4}$ and $\frac{3}{4}$ on the (001) plane. Reproduced with permission.

TABLE VI

MAGNETIC MOMENTS (B.M.) AND FREQUENCIES OF INFRARED VIBRATIONS (CM^{-1}) OF MOLYBDENUM AND TUNGSTEN THIOHALIDES AND MOLYBDENUM THIOCHLORIDE COMPLEXES (*14, 16*)

	$MoSCl_3$	$MoSCl_3 \cdot MeCN$	$MoSCl_3 \cdot 2MeCN$	$MoSCl_3 \cdot 2diox$	$MoSCl_3 \cdot bme$	$MoSCl_3 \cdot 3py$	$[Hpy][MoSCl_4,py]$	$MoSCl_2 \cdot phen$	$WSCl_3$	$WSCl_4$	$WSBr_4$
μ(B.M.)	0.75	1.07	1.85	1.71	1.68	2.01	1.74	1.99	0.54		
$\nu(M = S)^a$ (cm^{-1})			480	475	470	475	490	460		569s	555s
Infrared spectra, other bands	383(sh)	340s^b	320s,br^b	320s,br^b	315s,br^b	320s^b	340s^b	335s^b	373s	392(sh)	395w
	364m	285m	285(sh)	285s		300s	322s	330s	334s	355s	346w
	320m	270m	245w			280(sh)	255	295s	298w	306s	250m
	271w							235w		284w	

[a] M = Mo, W.

[b] Designated as probable Mo—Cl bands [see Britnell *et al.* (*16*)].

been found as the ultimate product in the decomposition of alkylthiolates prepared using the reagents $RSSiMe_3$ (R = Me, Et, *t*-Bu) as follows:

$$MoCl_5 \xrightarrow{RSSiMe_3} MoCl_4(SR)$$

$$MoCl_4(SR) \xrightarrow{decomp} MoSCl_3$$

where rate *t*-Bu > Et > Me (*11*). The infrared spectrum of $MoSCl_3$ (*14*) is devoid of bands above 383 cm^{-1} (Table VI), which indicates a polymeric structure containing Mo—S—Mo bridges. The compound is paramagnetic, and this has been attributed to the interactions between electrons on adjacent metal atoms through nonlinear bridging systems. X-Ray powder photographs show $MoSCl_3$ to be isomorphous with $MoOCl_3$ and $NbOCl_3$, which have six-coordinate metal atoms bridged by both chlorine and oxygen atoms (*16*).

On prolonged reaction with neat donor solvents (*16*), acetonitrile and pyridine, the adducts $MoSCl_3 \cdot nMeCN$ (n = 1 or 2) and $MoSCl_3 \cdot 3py$ are formed. The $MoSCl_3 \cdot nMeCN$ adducts contain Mo—S—Mo bridges and terminal Mo═S bonds. On the basis of magnetic measurements and infrared spectra (Table VI), each adduct appears to have a monomeric structure based on six-coordinate molybdenum atoms. The complex $MoSCl_3 \cdot 2MeCN$ will react with other ligands, 1,4-dioxane and 1,2-bis(methoxy)ethane, to form $MoSCl_3 \cdot 2diox$ and $MoSCl_3 \cdot bme$. With pyridine the pyridinium salt, $[Hpy]^+[MoSCl_4py]^-$, is formed, and 1,10-phenanthroline has been found to reduce molybdenum(V) to molybdenum(IV) forming $MoSCl_2 \cdot phen$. Reactions of $MoSCl_3$ alone with these ligands did not proceed, and it appears that Mo—S—Mo bridges are more resistant to attack by donor ligands than Mo—O—Mo bridges.

In 1967 MoS_2Cl_2 was reported (*72*) as the product when S_2Cl_2 was passed over molybdenum metal heated to 500°C. Sharma *et al.*, (*81*) in an attempt to prepare $MoOS_2$, bubbled H_2S through a solution of $MoOCl_4$ in dry benzene. The brown precipitate they obtained was also tentatively identified as MoS_2Cl_2. Later, by passing H_2S through $MoCl_4$ in CS_2, Britnell *et al.* (*15*) obtained the same compound. In spite of the fact that this compound has been reported three times, it has still not been conclusively characterized.

If a large excess of S_2Cl_2 is heated with molybdenum pentachloride at 250°C low yields of MoS_2Cl_3 are produced (*36*), Marcoll *et al.* (*51*) have solved the structure of this compound, which contains (S_2) bridging groups (Fig. 5). It is clearly related to that of NbS_2Cl_2 (Fig. 3).

After volatiles were removed from mixtures of $MoCl_3$ and sulfur which had been heated to 450°C for 24 hours the residue was found to

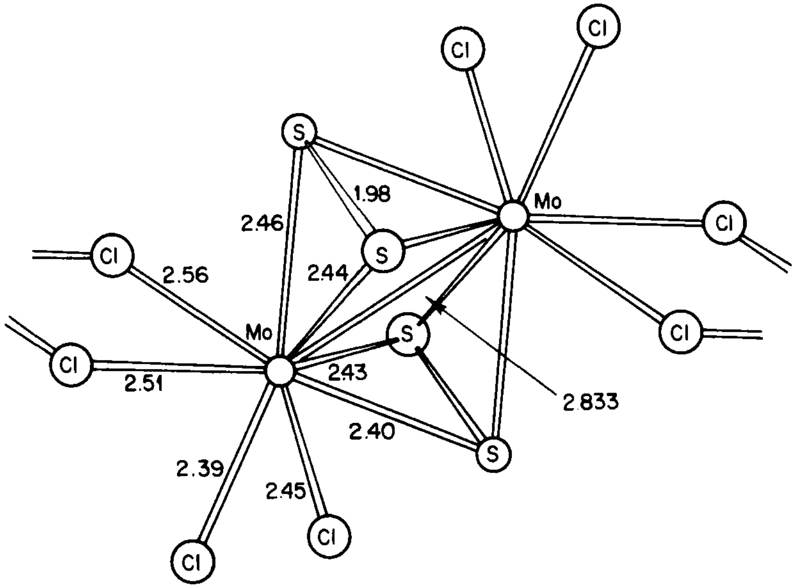

FIG. 5. Crystal structure of MoS_2Cl_3 (*51*). Reproduced with permission.

be a single compound which decomposed at 530°C evolving sulfur chlorides and forming MoS_2 (*55*). The compound, $Mo_3S_7Cl_4$, has been studied crystallographically and contains not only bridging (S_2) groups, but also a sulfur atom in the center of a triangle of molybdenum atoms (Fig. 6) (*51*).

$Mo_3S_7Br_4$, a brown, air-stable, amorphous powder, has been prepared by heating $MoBr_2$ with sulfur at 300°C (*57*). Its infrared spectrum has been recorded but not interpreted.

$Mo_2S_4Cl_5$, a brown microcrystalline solid, results when MoS_3 is treated with S_2Cl_2 at 350°C. The same reaction at 450°C produces red $Mo_2S_5Cl_3$, which may also be prepared by the reaction of molybdenum metal with excess S_2Cl_2 at 450°C (*72*). Both compounds are air-stable and are oxidized to MoO_3 at 250°C. The analogous bromine-containing compound, $Mo_2S_5Br_3$, may be prepared in a similar fashion from S_2Br_2. Both this and $Mo_2S_5Cl_3$ have been shown to contain Mo—S—Mo bridges and (S_2) groups by infrared spectroscopy (Table VII) (*61*, *63*). The reaction of $[Mo_6Cl_8]Cl_4$ and dimeric $MoCl_2$ with sulfur at 380°–400°C gives $Mo_3S_7Cl_4$ (*53*).

The compound Mo_6SBr_{10} is formed when molybdenum powder, $MoBr_5$, and sulfur are heated to 1100°C (*62*), and $[Mo_6I_8]S_{14}$ results from the reaction of MoI_3 or MoI_2 with sulfur (*47*).

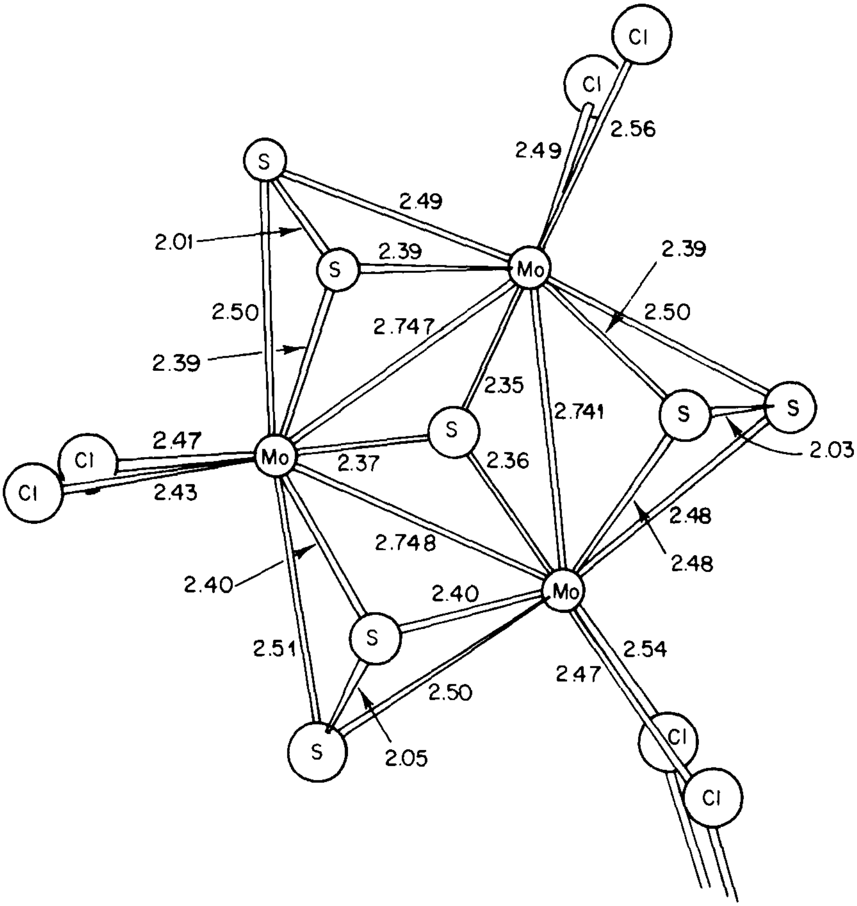

FIG. 6. Crystal structure of $Mo_3S_7Cl_4$ (*51*). Reproduced with permission.

Selenohalide chemistry of molybdenum is not as extensive as that of the thiohalides. Black $MoSeCl_2$ is produced during the disproportionation of $MoSeCl_3$ or by the action of Sb_2Se_3 on $MoCl_4$ (*15*). Attempts to prepare $MoSeBr_2$ from $MoSe_2$ and bromine result only in the formation of molybdenum tribromide and selenium tetrabromide (*56*). Molybdenum selenotrichloride ($MoSeCl_3$) is a maroon solid prepared by treating $MoCl_5$ with Sb_2Se_3 (*15*). Attempts to prepare complexes with py, phen, diox, and bme have failed (*16*). Both $Mo_3Se_7Cl_4$ and $Mo_3Se_7Br_4$ have been prepared, the former from $MoCl_3$ (*55*) or

TABLE VII

FREQUENCIES (IN CM^{-1}) OF INFRARED AND RAMAN VIBRATIONS OF MOLYBDENUM THIOHALIDES $Mo_2S_5X_3$ (X = Cl, Br, I) (*61*, *63*)

	Compound				
	$Mo_2S_5Cl_3$		$Mo_2S_5Br_3$		$Mo_2S_5I_3$
Assignments	IR	Raman	IR	Raman	IR
S—S			560(sh)	565vs	550(sh)
	560vs	570vs	555vs	555(sh)	545vs
Mo—S	397w	420m	395w	395w	390w
	368w	368m	360w	366m	362w
	335w	332m	335m	320m	335w
	315vs		315vw		305s
	295(sh)				295(sh)
	280(sh)	288s	278m	280s	272w
			250(sh)		250vw
	192w	176m	185w	180m	180w
	168m		165s		165m
Mo—X	405w	417w	335m	341w	215m
	340vs	343vw	253vs	257m	140vs
	305vs	306(sh)	227vs	224w	118vs
	257vs	245s	170s	165w	
	240m	235(sh)	150w	155w	

$[Mo_6Cl_8]Cl_4$ (*53*) and selenium and the latter from $MoBr_3$ and selenium (*57*). A compound $[Mo_6I_8]Se_{14}$ results from the reaction of MoI_3 or MoI_2 with selenium (*47*), and Mo_6SeBr_{10} and Mo_6SeI_{10} are formed when molybdenum powder, the appropriate metal halide, and selenium are heated to 1100°C (*62*).

All attempts to prepare molybdenum tellurohalides have failed (*15*).

C. TUNGSTEN

More work has been published on the thio- and selenohalides of tungsten than on any other transition element.

The first reported preparation of a tungsten thiochloride was by Smith and Oberholtzer (*84*), who obtained it from the reaction of red-hot tungsten metal with sulfur monochloride. Brown $WSCl_2$ has been reported as being formed when $WSCl_3$ disproportionates at 275°C. $WSBr_2$ has been prepared from the reaction of WBr_5 with Sb_2S_3 (*15*). Tungsten thiotrichloride itself has been synthesized by heating finely divided, intimately mixed WCl_5 and Sb_2S_3 at 120°–150°C for 7 days

(*14*, *15*). Tungsten thiotrichloride, $WSCl_3$, is a black involatile solid which appears, from its infrared spectrum, to contain W—S—W bridges (*14*) (see Table VI). $WSCl_3$ does not form complexes with py, phen, diox, or bme (*16*).

Red, air-sensitive, $WSCl_4$ is the most studied transition-metal thiohalide; it can be prepared by many methods, such as the action of chlorine on WS_2 or WS_3 in a flow system (*15*), by treating WCl_6 with Sb_2S_3 (*14*, *15*) or sulfur (*14*, *15*, *37*, *86*), by heating a mixture of WCl_5 and sulfur (*15*), or by the reaction of WCl_5 with $RSSiMe_3$ (R = Me, Et, *t*-Bu) and the subsequent decomposition of the product $WCl_5(SR)$ (*11*). The rate of decomposition of the alkylthiolates is in the order *t*-Bu > Et > Me (*11*).

$WSCl_4$ is a diamagnetic compound that readily sublimes under vacuum to form triclinic crystals. The crystal structure has been studied (*30*). Each tungsten atom is strongly bonded to a sulfur atom and four chlorine atoms in a square-based pyramidal arrangement with the sulfur apical. Two of these $WSCl_4$ units form a dimer with two weak W—Cl bridges trans to the tungsten—sulfur bonds (Fig. 7).

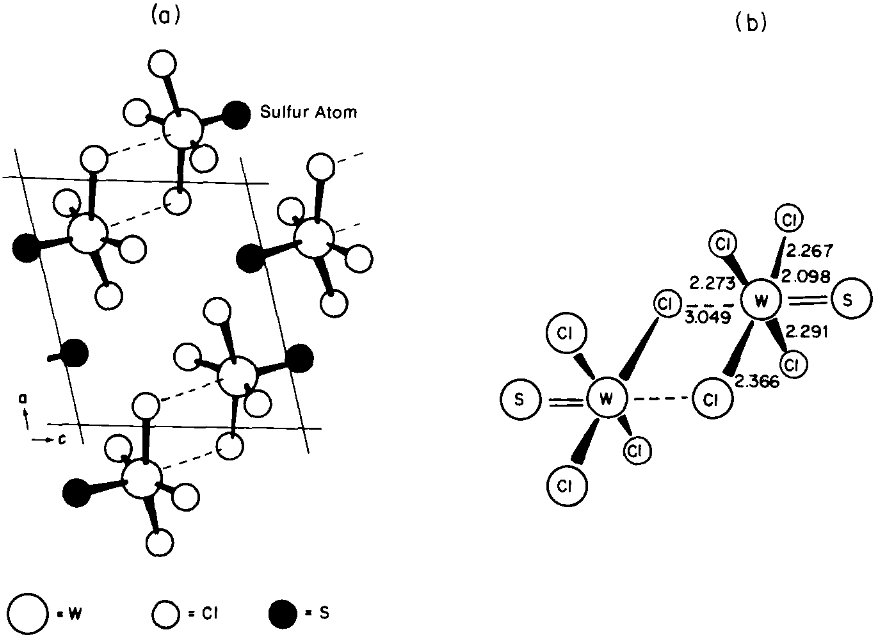

FIG. 7. Crystal structure of $WSCl_4$ (*30*). (a) The contents of the unit cell in the b projection. (b) The $(WSCl_4)_2$ dimer, showing bond lengths. Reproduced with permission.

The mass spectrum of $WSCl_4$ (*82*) comprises a fragmentation pattern, similar to those of $MoOCl_4$, $WOCl_4$, and $WOBr_4$, in which the parent ion, $WSCl_4^+$, is only 1% abundant and the most abundant ion is $WSCl_3^+$. As $WSCl_3$ is involatile, the $WSCl_3^+$ ion could only have been formed by the fragmentation and ionization of $WSCl_4$. The infrared spectrum of tungsten thiotetrachloride has been reported (*14*), the main features being strong bands at 569 cm^{-1} and 355 cm^{-1} assigned to W═S and W—Cl stretching modes respectively (Table VI).

Tungsten thiotetrabromide, $WSBr_4$, may be prepared from the reaction of antimony trisulphide with WBr_6 (*14, 15*) or WBr_5 (*15*), along with $WSBr_2$, and from the reaction of WBr_6 with elemental sulphur (*15*). It dissolves and forms adducts in donor solvents and its infrared spectrum (*14*) has a strong band at 555 cm^{-1} assigned to a ν(W═S) (Table VI).

WS_2Cl_2, a blue-black amorphous solid, first reported as the final product when H_2S was bubbled through $WOCl_4$ in dry benzene (*81*), has since been prepared by bubbling H_2S through WCl_6 in CS_2 at 18°C (*15*) and by the reaction of $WSCl_4$ with Sb_2S_3 in CS_2 at room temperature (*39, 73*). The last reaction, $WYCl_4$ (Y = O, S, Se) with $Sb_2Y'_3$ (Y′ = O, S, Se) in CS_2, has also been employed to prepare $WOSCl_2$, $WOSeCl_2$, and $WSSeCl_2$ (*39, 73*). Best yields are obtained when Y′ is lower in the group than Y.

The selenohalides of tungsten are less well known than the thiohalides. Attempts to prepare $WSeBr_2$ by brominating WSe_2 only resulted in the formation of WBr_6 and $SeBr_4$ (*56*), and, so far, $WSeBr_2$ has been prepared only during the disproportionation of $WSeBr_3$ (*15*). Tungsten selenotribromide may be prepared when WBr_5 is heated with Sb_2Se_3. The analogous reaction employing WCl_5 results in the formation of $WSeCl_3$ (*15*). Both $WSeCl_4$ and $WSeBr_4$ are known and may be synthesized by heating a mixture of the appropriate tungsten hexahalide and Sb_2Se_3 (*15*). The infrared spectra of both compounds have been recorded (*15*), and that of $WSeCl_4$ has a strong band at 396 cm^{-1} assigned to W═Se while the equivalent feature is absent from the $WSeBr_4$ spectrum.

The compounds WXY_4 (X = S, Se; Y = Cl, Br) react with a number of ligands, containing nitrogen, oxygen, phosphorus, and sulfur donor atoms, to form the six-coordinate adducts $WXY_4 \cdot L$ and $2WXY_4 \cdot L'$ (L = unidentate; L′ = bidentate) in which the terminal W = X is retained (*17*). With tetrahydrofuran, 1,4-dioxane and acetonitrile all four compounds form 1:1 adducts. With pyridine and 1,4-oxathian, 1:1 adducts are formed by the chlorides only, the bromides forming 1:2 complexes, $WXBr_4 \cdot 2py$, with pyridine. The reactions of all four compounds with 2,2′-bipyridyl result in nonstoichiometric products that were not characterized. With 1,2-bis(methylthio)ethane WSY_4 reacts to form both WSY_4·mte and $2WSY_4$·mte. When $WSeCl_4$ was allowed to react with a large excess of acetonitrile evidence was obtained for the adduct WCl_4·NCMe·NCSeMe, in which the selenium atom was incorporated into an acetonitrile molecule. The adduct, however, was not isolable. Under severe conditions, such as high temperature or a large excess of ligand, reduction to tungsten(V) or even tungsten(IV) took place. With excess 1,2-bis(methylthio)ethane $WSCl_4$ formed $WSCl_3$·mte which has a band at 535 cm^{-1} in its IR spectrum assigned to $\nu(W{=}S)$. Such a band does not occur in the IR spectrum of $WSCl_3$, which is thought to contain W—S—W bridges (Table VI). Excess 2,2′-bipyridyl also reduces W(VI) to W(V) forming $WSCl_3$·bipy from $WSCl_4$. At high temperatures triphenylphosphine reduces WXY_4 to W(IV) by abstracting the chalcogen atom and incorporating it in a PPh_3 molecule forming WX_4·PPh_3·P(Y)Ph_3.

The reaction between $WSCl_4$ and 1,2-bis(methoxy)ethane results in oxygen abstraction and the resultant formation of $WSCl_4$·$WOSCl_2$·bme, which has been investigated by X-ray crystallography (*12*). The $WSCl_4$ and $WOSCl_2$ units are linked through the oxygen atom, both tungsten atoms having a distorted octahedral environment (Fig. 8).

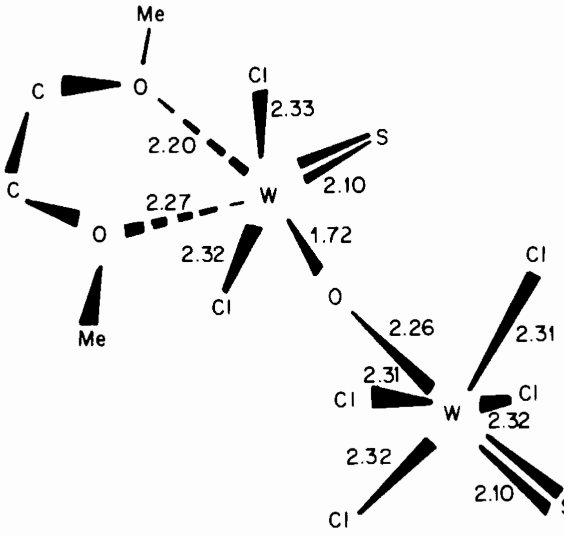

FIG. 8. Crystal structure of $WSCl_4$, $WOSCl_2$, dme (*12*). Reproduced with permission.

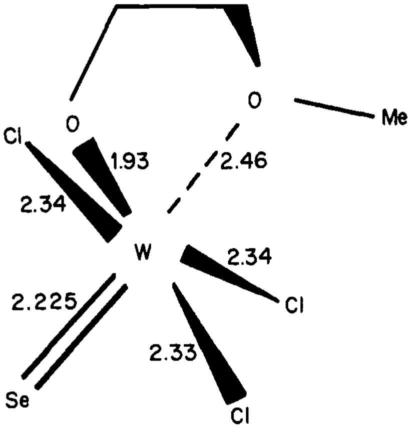

FIG. 9. Crystal structure of $C_3H_7Cl_3O_2SeW$ (*13*). Reproduced with permission.

The analogous reaction with $WSeCl_4$ results in selective demethylation and the formation of selenotrichlorotungsten(VI)-(2-methoxy) ethoxide (Fig. 9) (*13*).

Excepting yttrium and lanthanum, which are usually classed as lanthanides, not transition metals, tungsten is the only transition element for which thiofluoride species have been reported (*1*, *18*, *45*, *48–50*). Gaseous SF_6, when admitted to a tungsten effusion cell at 1600 K, reaches an equilibrium. The equilibrium mixture was investigated by mass spectrometry, and among those species identified were WSF_3^+, WSF_4^+, $WS_2F_2^+$, and $WOSF_2^+$ (*45*). ^{19}F NMR studies of the reaction of $WSCl_4$ in acetonitrile with HF have revealed the existence of WSF_4, $WSFCl_4^-$, $WSF_2Cl_3^-$, $WSF_3Cl_2^-$, WSF_4Cl^-, WSF_5^-, and $W_2S_2F_9^-$ (*1*, *18*); and with XeF_2, WSF_4, WSF_3Cl, WSF_2Cl_2, and $WSFCl_3$ are formed (*1*). These species are all extremely unstable and readily form oxyfluorotungsten anions.

The reactions of inorganic sulfides with WF_6 in acetonitrile have been studied by ^{19}F NMR (*48*). It was found that short-lived monothiofluoride species were formed when sulfur replaced two fluorines on the tungsten atom. The greatest yields were obtained using H_2S, and the species were also formed when K_2S, Na_2S, Bu_2S, Ph_2S, Me_2S_2, and thiourea were used. Attempts to prepare WSF_4 by passing H_2S through WOF_4 in MeCN and through $K_2WO_2F_4$ in DMSO yielded no product.

In spite of the observations of WSF_4^+ and $WS_2F_2^+$ (*45*) mass spectrometrically and of $WSCl_xF_y^-$ ($x + y = 5$) by ^{19}F NMR (*18*), only recently has any thiofluoride been isolated as a solid compound (*1*). Thus yellow

WSF_4 is the main product of the reaction of WF_6 with Sb_2S_3 at 300°C ($3WF_6 + Sb_2S_3 \rightarrow 3WSF_4 + 2SbF_3$). Crystals of WSF_4 melt at ~ 90°C and, on exposure to the atmosphere, HF and H_2S are rapidly evolved. The main features of the infrared spectrum of the solid include strong peaks at 699, 673, and 643 cm^{-1} which can be attributed to $\nu(W—F)$ for three terminal fluorines. The W=S bond is evidenced by an intense peak at 577 cm^{-1} in the IR and at 580 cm^{-1} in the Raman, which are close to that for $\nu(W{=}S)$ in $WSCl_4$. Observation of peaks at 534 and 514 cm^{-1} in the infrared, which can be assigned to W—F—W bridge vibrations, suggest that the structure is polymeric, and it has been suggested that it may be the same as that of WOF_4 (*1*). ^{19}F NMR spectra of WSF_4 in MeCN show the characteristic singlet at τ, −85.1 ppm. Solutions of WSF_4 in MeCN decompose slowly over several weeks to give WF_6 and WS_3 (*1*).

WSF_4 has also been recently obtained by condensation of the product formed by the reaction of a tungsten filament with SF_6 at 200 torr (*20*):

$$3W + 2SF_6 \xrightarrow{>500°C} 2WSF_4 + WF_4$$

The WSF_4 was identified by its ^{19}F NMR spectrum.

The adduct $WSF_4 \cdot MeCN$ was prepared when the reaction between H_2S and WF_6 in MeCN was recently reexamined (*50*). It has also been observed in the products of reaction of WSF_4 with $BuNH_2$ or H_2O in MeCN (*19*). The complex melted at 106°C with partial decomposition, and H_2S was evolved on exposure to air (*50*). $WS_2F_2 \cdot 2MeCN$ was also isolated when H_2S was passed through a solution of $WSF_4 \cdot MeCN$ in acetonitrile for a prolonged period. The replacement of the acetonitrile molecule of the complex by ethanol, phenol, 1,2-ethanediol, acetylacetone, diethylamine, and BuSH has been examined by ^{19}F NMR (*49*). It was found that the new complexes were formed less readily than their oxyfluoride counterparts. The adduct $WSF_4 \cdot H_2O$ has been observed as a product of the reaction of WSF_4 with H_2O in MeCN (*19*).

The first transition-metal selenofluoride, $WSeF_4$, has recently been prepared by the reaction of stoichiometric quantities of WF_6 and Sb_2Se_3 at 350°C (*2*). The amber solid quickly decomposes in the atmosphere, liberating HF and H_2Se. The infrared spectrum is very similar to that of WSF_4, with strong peaks at 690, 661, and 629 cm^{-1} [$\nu(W—F)$], 366 cm^{-1} [$\nu(W{=}Se)$] and 540 and 517 cm^{-1} [W—F bridging modes]. ^{19}F NMR spectra in CH_3CN gave rise to a singlet at $\tau = -87.9$ ppm ($\tau = 0$ ppm. for $CFCl_3$), $J_{W-F} = 36 \pm 1Hz$, which was assigned to $WSeF_4$(*2*).

As with molybdenum, all attempts to prepare tungsten tellurohalides have been unsuccessful (*15*).

VI. Group VIIA

A. MANGANESE

Manganese selenochloride, MnSeCl, a green crystalline solid, has been prepared by the direct chlorination of MnSe (*6*). It decomposes in air and water, and upon heating to 90°C *in vacuo* gray $MnSe_2Cl_2$ is formed.

Manganese thiodichloride, $MnSCl_2$, can be made by heating MnS and chlorine in a bomb for 35 hours. It is reported to be slightly soluble in water (*7*). Brown $MnSeBr_2$, prepared by heating MnSe and bromine in a bomb, is readily hydrolyzed on exposure to air and is thermally unstable. At 70°C *in vacuo* Mn_2SeBr_2 is formed. This yellow-gray material is reported to turn brown at 100°C, but its empirical composition remains unchanged (*6*). Manganese selenodiiodide ($MnSeI_2$), prepared by heating a mixture of MnSe and iodine to 160°C for 20 hours, has also been obtained (*6*).

B. RHENIUM

Direct chlorination of ReS_2 results in the formation of a small amount of nonvolatile, brown, $ReSCl_2$ as a minor product (*87*). The compounds $ReSCl_2$ and $ReSBr_2$ have also been observed in DTA studies of the reaction of the appropriate trihalide with sulfur. The related ReS_2Br has also been detected in the reaction of Re Br_3 with sulfur (*80*). Rhenium thiodichloride, along with $Re_2S_3Cl_4$, has been isolated following the direct chlorination of Re_2S_7 in a flow system (*42*) and from the rhenium–sulfur–chlorine system (*31*). The thiochlorides, ReS_3Cl and $ReSCl_4$ (m.p. 80 ± 2°C), have been isolated from ReS_2–S_2Cl_2 and the $ReCl_3$–S_2Cl_2 systems (*31*). Rhenium thiotrichloride, $ReSCl_3$, prepared from the reaction of $ReCl_5$ with Sb_2S_3 in carbon disulfide at low temperatures, has also recently been isolated (*39*).

The reactions of $ReSCl_2$ with hydrogen and steam at 350°C have been studied. With hydrogen, hydrogen chloride is formed leaving ReS and with steam, HCl is again formed while amorphous ReOS remains (*41*).

Three rhenium selenohalides have been reported. Brown $ReSeCl_2$ is formed when $ReSe_2$ is heated, under chlorine, in a sealed quartz ampoule (*56*), or when $ReCl_3$ and Se combine (*80*). The related bromide, $ReSeBr_2$, has also been observed in DTA studies (*80*). Brown, $Re_3Se_2Cl_5$ is the product when a mixture of $ReSe_2$ and Re_3Cl_9 is heated to 700°C (*56*), and air-stable, dark violet $Re_3Se_2Br_5$, is produced by the analogous reaction using $ReBr_3$ or by heating $ReSe_2$ to 600°C under an atmosphere of bromine (*56*).

VII. Group VIII

PLATINUM

There has been only one report of a thiohalide of platinum (*8*). Heating a mixture of PtX_2 ($X = Cl, Br$), and sulfur produces a series of compounds PtX_mS_n, where m and n depend upon the ratio of reactants and the reaction temperature.

VIII. Group IB

A. COPPER

Copper seleno- and tellurohalides may be prepared in polycrystalline form by the reaction of stoichiometric amounts of copper(I) halide with selenium or tellurium in a sealed ampoule at 300–350°C. However, separation from other phases often causes difficulties. Many can be obtained as single crystals by the reaction of the respective elements, binary compounds, or both with the appropriate hydrogen halide acid under hydrothermal conditions (*65*, *66*, *68*), or by chemical transport during the reaction of the appropriate copper(I) halide with selenium or tellurium in a temperature gradient (*22*). The compounds that have been prepared are listed in Table VIII with X-ray photographic and

TABLE VIII

X-RAY CRYSTALLOGRAPHIC AND SPECTRAL REFLECTION DATA FOR COPPER CHALCOGENIDE HALIDES (*22*, *64*, *65*)

		Unit cell dimensions					
Compound	Symmetry	a (Å)	b (Å)	c (Å)	β^0	Z	Optical band gaps (eV)
$CuSe_2Cl$	Monoclinic	7.62	4.68	30.73	91.6	12	1.6
$CuSe_3Br$	Orthorhombic	7.64	4.49	14.23		4	~2.0
$CuSe_3I$	Rhombohedral[a]	14.083		14.187		18	
CuTeCl	Tetragonal	15.53		4.78		16	1.4
CuTeBr		16.417		4.711			
CuTeI		17.07		4.83			
$CuTe_2Cl$	Monoclinic	8.168	4.195	15.187	134.9	4	1.2
$CuTe_2Br$		8.358	4.951	15.704	135.1		
$CuTe_2I$		8.672	4.881	16.493	135.0		

[a] Referred to a hexagonal cell.

optical band gap data. All the compounds are air-stable and exhibit temperature-independent diamagnetism, which implies that copper is present as Cu(I). The tellurium compounds are stable in alkali but decompose in concentrated HNO_3 and H_2SO_4. The selenium compounds are readily decomposed by alkali.

A recent single-crystal determination on CuTeBr (*21*) has shown that the structure consists of infinite spirals of tellurium atoms with bromine tetrahedra interspersed. Two basic types of disordered copper atoms occur: one where the copper atom is at the center of the bromine tetrahedron, the other where the copper lies in two possible sites in a distorted tetrahedral environment with tellurium and two bromine atoms as nearest neighbors.

B. SILVER

Differential thermal analytical investigations of the $AgCl–Ag_2Se$, $AgCl–Ag_2Te$, $AgBr–Ag_2Se$, and $AgBr–Ag_2Te$ systems have led to the discovery of two peritectic compounds, Ag_3TeBr and Ag_5Te_2Cl (*9*).

C. GOLD

Both AuSeCl and AuSeBr are known; the former is produced when a gold selenium mixture is heated to 200°C under an atmosphere of chlorine, and the latter when AuSe is heated under bromine (*70*). Each compound crystallizes in the orthorhombic system.

Hydrothermal synthetic methods analogous to those used in the preparation of copper chalcogenides have been used to prepare gold halide tellurides (*65*, *67*, *69*). The compounds are listed and preparative conditions are summarized in Table IX. All are insoluble in dilute acid and alkali and decompose in concentrated HNO_3 and H_2SO_4.

Earlier X-ray diffraction data for $AuTe_2X$ (X = Cl, Br, I) from powders has been more recently refined by single-crystal studies on $AuTe_2Cl$ and $AuTe_2I$. The compound $AuTe_2Cl$ is orthorhombic, space group Cmcm, with $a = 4.020$, $b = 11.867$, $c = 8.773$ Å, $z = 4$; and $AuTe_2I$ is orthorhombic, space group Pmmb, with $a = 4.056$, $b = 12.579$, $c = 4.741$ Å, $z = 2$. The structures consist essentially of corrugated two-dimensional nets of Au and Te atoms with interleaved halogens. This explains their metallic conductivity. The Te atoms form pairs coordinated to four Au atoms, and each Au is coordinated to four Te atoms (*43*). The iodine, AuTeI is monoclinic, with $a = 7.245$, $b = 7.622$, $c = 7.313$ Å and $\beta = 106.3°$ (*65*).

TABLE IX

PREPARATIVE CONDITIONS FOR GOLD HALIDE TELLURIDES (*65*)

Compound	Starting materials (grams)	Solvent	Temperature (°C)	Time (days)
$AuTe_2Cl$	5.9 Au 1.9 Te 1.0 Cl	HCl	100–400	10
$AuTe_2Br$	13.9 Au 5.1 Te 5.7 Br	HBr	150–350	10
$AuTe_2I$	6.2 Au 4.0 Te	HI	150–450	10
AuTeI[a]	6.2 Au 4.0 Te 8.0 I	HI		

[a] The corresponding AuTeCl and AuTeBr were not obtained.

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Note Added in Proof

Preparative routes to, and the properties of, transition metal thio-, seleno-, and tellurohalides are the subject of an informative article by Rice (*1*) which serves as a useful complement to this review.

The series of thiochlorides Mo_6YCl_{10} (Y = S, Se, Te) has recently been prepared (*2*) from the reaction between molybdenum dichloride, molybdenum metal and the elemental chalcogen at 1000°C in a silica reactor for about 24 hours. The compounds produced are isostructural with Nb_6I_{11} being of space group Pccn. with $z = 4$. The X-ray structure of octahedral crystals of dark red Mo_6SeCl_{10} has been determined, this reveals a central $(Mo_6X'_8)$ unit in which the selenium atom is statistically distributed among the eight X′ positions.

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