Preparation of Halide Sulphides and Halide Selenides of Molybdenum and Tungsten

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A study has been made of a number of methods for the preparation of halide sulphides and halide selenides of molybdenum and tungsten in several oxidation states and the relative merits of the methods are discussed. The method of most general application is reaction of Sb_2S_3 or Sb_2Se_3 with the appropriate halide. In the case of $WSCl_4$ the best preparative method is by reaction of sulphur with WCl_6. Halide sulphides and selenides of molybdenum(IV) and tungsten(IV) are formed in the thermal decomposition of the corresponding quinquevalent compounds. The properties of these compounds are reported. Attempts to make similar tellurium compounds have been unsuccessful.

HALIDE OXIDES of molybdenum and tungsten are well documented[1] but in contrast there are few reports of comparable halide sulphides and none of the analogous halide selenides. Thus $WSCl_4$ was prepared by the reaction of sulphur with tungsten(VI) chloride,[2] and MoS_2Cl_2 and WS_2Cl_2 by reaction of H_2S with the tetrachloride oxide ($MOCl_4$);[3] MoS_2Cl_2 was also prepared by reaction of S_2Cl_2 with the metal or sulphide.[4] Successful routes that lead to the preparation of halide oxides of molybdenum and tungsten include chlorination of the oxides[5-7] and abstraction of oxygen by halides from either Sb_2O_3 or SO_2.[8-11] We now report a systematic study of analogous preparative procedures for the halide sulphides and selenides. This extends considerably our preliminary communication[12] reporting the use of Sb_2S_3 for the preparation of several molybdenum and tungsten halide sulphides.

Analytical and preparative details of molybdenum and tungsten halide sulphides and selenides

			Analyses (%) Found			Calc.								
Product	Colour	Preparative route	M	Y[b]	X[b]	M	Y[b]	X[b]	Yield % [a]	Reaction temperature, θc/°C	Reaction time	Sublimation temperature, θc/°C	Reaction vessel	Other products
$WSCl_4$	Red	$WS_2 + Cl_2$	51·3	8·7	39·8	51·4	8·9	39·7	14	150—160	1 h		Flow tube	WCl_6
		$WS_3 + Cl_2$	51·0	8·8	39·6	51·4	8·9	39·7	20	150—160	1 h	170	Flow tube	WCl_6
		$Sb_2S_3 + WCl_6$	51·4	8·9	39·7	51·4	8·9	39·7	95	140	3 d		(*ii*)	$SbCl_3$
		$S + WCl_6$ [c]	51·4	8·7	39·3	51·4	8·9	39·7	20	100	1 h	170	(*i*)	S_2Cl_2 plus mixed $W_2S_2Cl_3$ species
		$S + WCl_6$	51·5	8·8	39·6	51·4	8·9	39·7	95	100	3 h		(*i*)	S_2Cl_2
		$H_2S + WCl_6$ in CS_2	51·4	8·9	40·2	51·4	8·9	39·7	70	18			Flask	
$WSBr_4$	Brown	$Sb_2S_3 + WBr_6$	34·3	5·8	59·4	34·3	6·0	59·7	92	140	7 d		(*ii*)	$SbBr_3$
		$S + WBr_6$ [d]	37·6	6·2	55·8	34·3	6·0	59·7		90	7 d		(*i*)	S_2Br_2
		$Sb_2S_3 + WBr_5$ [e]	34·3	6·0	59·7	34·3	6·0	59·7	40	140	10 d		(*ii*)	$WSBr_2$, $SbBr_3$
$WSeCl_3$	Green	$Sb_2Se_3 + WCl_6$	45·4	19·5	35·0	45·4	19·5	35·1	90	120	7 d	170	(*ii*)	$SbCl_3$
		$Sb_2Se_3 + WCl_5$	45·3	19·3	35·2	45·4	19·5	35·1	40	120	7 d	170	(*ii*)	$SbCl_3$, $WSeCl_2$, WCl_6
$WSeBr_4$	Red	$Sb_2Se_3 + WBr_6$	31·6	13·5	54·5	31·6	13·6	54·9	85	120	14 d		(*ii*)	$SbBr_3$
$WSCl_3$		$Sb_2S_3 + WCl_5$	57·4	9·5	33·2	57·1	10·0	33·0	80	120	7 d		(*ii*)	$SbCl_3$
$WSeBr_3$	Red-brown	$Sb_2Se_3 + WBr_5$	36·2	15·3	46·3	36·6	15·7	47·7	80	120	14 d		(*ii*)	$SbBr_3$
$WSCl_2$	Brown	Disproportionation of $WSCl_3$	63·3	10·8	25·1	64·1	11·2	24·7	40	275	4 d		(*ii*)	$WSCl_4$
$WSBr_2$	Brown	$Sb_2S_3 + WBr_5$ [e]	48·5	8·2	42·3	49·0	8·5	42·6	30	140	10 d		(*ii*)	$WSBr_4$, $SbBr_3$
$WSeBr_2$		Disproportionation of $WSeBr_3$	42·9	17·7	37·3	43·5	18·7	37·8		220	4 d		(*ii*)	$WSeBr_4$
WS_2Cl_2	Blue-black	$H_2S + WCl_6$ in CS_2	57·7	18·9	22·9	57·7	20·1	22·2	Very low	18				
$MoSCl_3$	Green	$Sb_2S_3 + MoCl_5$ [b]	40·9	13·4	45·0	41·0	13·6	45·4	95	40 [f] then 140	7 d		(*ii*)	$SbCl_3$
		$S + MoCl_5$ [d]	37·2	11·2	44·0	41·0	13·6	45·4		140	21 d		(*i*)	S_2Cl_2
$MoSeCl_3$	Maroon	$Sb_2Se_3 + MoCl_5$	35·5	27·5	36·9	34·1	28·1	37·8	85	140	14 d		(*ii*)	$SbCl_3$
$MoSCl_2$	Black	$Sb_2S_3 + MoCl_4$	47·9	15·9	35·3	48·3	16·1	35·6	80	140	7 d			$SbCl_3$
		Disproportionation of $MoSCl_3$	47·8	16·1	35·4				30	260	5 d		(*ii*)	S, $MoCl_4$
$MoSeCl_2$	Black	$Sb_2Se_3 + MoCl_4$	38·7	31·6	28·4	39·0	32·1	28·9	90	120	14 d		(*ii*)	$SbCl_3$
		Disproportionation of $MoSeCl_3$	38·6	31·8	28·0				40	260	2 d		(*ii*)	Se, $MoCl_4$
MoS_2Cl_2		$H_2S + MoCl_4$ in CS_2	41·8	28·0	30·0	41·6	27·8	30·7	18					

[a] Based on the amount of halide used. [b] Y = S or Se and X = Cl or Br. [c] $WSCl_4$ Collected in section (B) of a type (*i*) reaction tube; remaining in section (C) was a non-stoicheiometric product. [d] Unsatisfactory analyses were obtained in spite of repeated experiments. [e] Two products formed; in section (B) of the tube $WSBr_4$ was collected, and $WSBr_3$ remained in (C). [f] Vigorous initial reaction; the mixture was kept at below 40 °C until the initial reaction had ceased.

EXPERIMENTAL

Conventional vacuum-line and dry-box techniques were used to handle the samples. The molybdenum and tungsten halides required as starting materials were prepared as previously described.[13]

Preparations.—The following general methods have been used to prepare the halide sulphides and selenides, and

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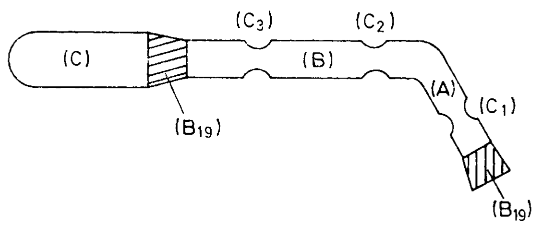
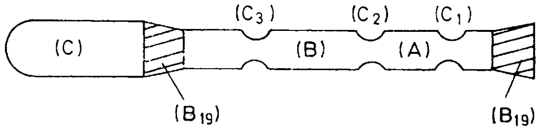
specific conditions necessary for the preparation of particular compounds are listed in the Table.

(a) *Reaction of a metal halide with sulphur.* Sulphur (3·5 g) was mixed in a dry-box with sufficient metal halide to make a 1 : 3 molar ratio. The mixture was placed in section (C) of a type (*i*) reaction tube, which was evacuated and sealed at (C_1). Sections (B) and (C) of the tube were placed in a furnace while (A) was at room temperature for the reactions with tungsten(VI) chloride and molybdenum(V) chloride and liquid dinitrogen temperature for the tungsten(VI) bromide experiments. A liquid gradually collected in section (A), and when no more liquid was produced the tube was sealed at (C_2) while (A) was cooled in liquid dinitrogen. The tube was then replaced in the furnace so that section (C) was at the furnace temperature while (B) was at room temperature. A final liquid product was collected in (B) and the halide sulphide was isolated by sealing the tube at (C_3). The compound $WSCl_4$ was further purified by vacuum sublimation in a type (*ii*) tube.

(*i*)



(*ii*)



From the Table it can be seen that this method was tried for WCl_6, WBr_6, WCl_5, and $MoCl_5$, but only with WCl_6 was a high-yield pure compound ($WSCl_4$) obtained; the conditions for formation of $WSCl_4$ were similar to those previously reported.[2]

(b) *Reactions of metal halides with either* Sb_2S_3 *or* Sb_2Se_3. Finely powdered Sb_2S_3 or Sb_2Se_3 (6·0 g) was mixed with sufficient metal halide to give a 1 : 3 molar ratio and placed in a type (*ii*) reaction tube which was evacuated and sealed at (C_1). Sections (C) and (B) were placed in a furnace while (A) was maintained at room temperature. A white solid collected in section (A), and this was removed by sealing the tube at (C_2). The remaining material was broken up by shaking the tube, which was returned to the furnace, and when further white solid collected in section (B), this again was removed by sealing the tube at (C_3). The final halide sulphide or selenide remaining in (C) was used without further purification, except in the case of $WSCl_4$ and $WSeCl_4$ which were further purified by sublimation at 170 °C in a type (*ii*) tube.

(c) *Chlorination of molybdenum and tungsten sulphides.* Powdered sulphide (2·0 g) contained in a silica boat was placed in a long tube complete with stopcocks at either end. The tube was pumped for some hours, flamed to remove moisture and occluded air, and then purged with dry dinitrogen. Dichlorine was passed through the tube while the contents of the boat were heated to 150—160 °C, and after 1 h the product which collected along the sides of the tube was removed. This method of preparation yielded some $WSCl_4$ with WS_2 and WS_3, but only $MoCl_5$ with MoS_2 and MoS_3.

(d) *Reaction of metal halides with dry hydrogen sulphide.* The metal halide (5·0 g) was placed in a flask fitted with inlet and outlet taps. The system was evacuated and dry carbon disulphide (100 cm³) was distilled into the flask. The reactants were allowed to warm to room temperature, dry hydrogen sulphide was bubbled through the carbon disulphide, and the mixture was continually stirred. Two stages of reaction were observed with tungsten(VI) chloride. During the first stage a red solution was formed which on evaporation yielded $WSCl_4$. When more H_2S was passed through the solution a black precipitate formed whose analysis approximated to WS_2Cl_2. In the similar reaction with molybdenum(V) chloride only MoS_2Cl_2 was formed.

(e) *Thermal decomposition of molybdenum*(V) *and tungsten*(V) *halide sulphides and selenides.* The compounds were placed in section (C) of a type (*ii*) reaction tube. Section (C) was placed in a furnace and the volatile products collected in (A) and (B) which were at room temperature; the involatile molybdenum(IV) and tungsten(IV) halide sulphides and selenides remained in section (C). The mode of decomposition was confirmed by conventional weight-loss measurements using a modified thermal-gravimetric balance.

RESULTS AND DISCUSSION

The halide sulphides and selenides of molybdenum and tungsten that have been prepared are listed in the Table. From the Table and the Experimental section it can be seen that, with the exception of the preparation of $WSCl_4$ from sulphur and tungsten(VI) chloride, the most useful preparative route for species containing the metal in the V or VI oxidation state is from the appropriate metal halide and Sb_2Y_3 ($Y = S$ or Se) This paper contains the first report of halide selenides; our attempts to prepare compounds containing tellurium failed.

(a) *Tungsten*(VI) *Compounds*.—The compounds $WSCl_4$, $WSBr_4$, $WSeCl_4$, and $WSeBr_4$, like the corresponding halide oxides, are very sensitive to moisture and evolve H_2Y ($Y = S$ or Se) on exposure to moist air. All can be sublimed *in vacuo*, the order of volatility being $Cl > Br$ and $Se > S$, and all are soluble in benzene, carbon tetrachloride, and carbon disulphide but insoluble in n-pentane and hexane. In general they dissolve in donor solvents to give solutions from which simple adducts can be obtained.[14] With 1,2-dimethoxyethane, however, they undergo unusual reactions. Thus $WSCl_4$ abstracts oxygen to form $WOSCl_2$ [15] while with $WSeCl_4$ there is cleavage of a carbon–oxygen bond and an alkoxide is formed.[16]

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[14] D. Britnell, G. W. A. Fowles, and D. A. Rice, unpublished work.

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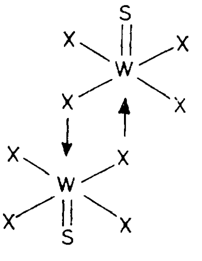
[16] D. Britnell, M. G. B. Drew, G. W. A. Fowles, and D. A. Rice, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 501.

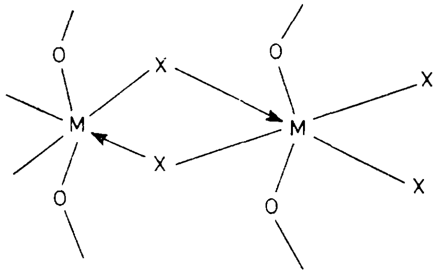
The molecular structures of $WSCl_4$ and $WSBr_4$[17] are very similar. In the dimeric structures each tungsten is six-co-ordinate, being bonded to four chlorine atoms in a plane with a terminal W=S at right angles to this plane. The two WSX_4 units link through unsymmetrical chlorine bridges; thus for $WSCl_4$, W–Cl (bridge) = 3·05 and W–Cl (terminal) = 2·28 Å. Since $WSeCl_4$ and $WSCl_4$ are isomorphous, as are $WSBr_4$ and $WSeBr_4$, then presumably $WSeX_4$ (X = Cl or Br) contain terminal tungsten–selenium bonds. It was previously reported[12] that i.r. spectra of $WSCl_4$ and $WSBr_4$ contain bands that may be assigned to ν(W=S) at 569 and 555 cm^{-1} respectively.* The i.r. spectrum of $WSeCl_4$ had a band at 396 cm^{-1} which we tentatively assign to ν(W=Se), although a similar band was not shown by $WSeBr_4$. These tungsten(VI) compounds are all weakly paramagnetic and have moments that fall slightly with temperature. For samples of $WSCl_4$ prepared from spectroscopically pure tungsten, μ = 0·4 B.M. at 25 °C and falls to 0·2 B.M. at −180 °C;† the results for $WSBr_4$ were similar. Since we have eliminated the possibility of the effect being caused by a paramagnetic impurity in the starting material, the results must be attributed to tungsten(V) impurities or in part at least to temperature-independent paramagnetism (t.i.p.). Similar behaviour was seen in a number of other tungsten(VI) species.[18] Although WS_2Cl_2 was formed in the reaction between H_2S and WCl_6, the yield was so low that investigations were limited to characterisation by analysis.



(A)

(b) *Molybdenum*(V) *and Tungsten*(V) *Compounds*.—The compounds $MoSCl_3$, $WSCl_3$, and $MoSeCl_3$ can be readily prepared in a pure state, but $WSeBr_3$ can be obtained only if the specified reaction conditions (Table) are strictly observed; if the temperature is a little higher then disproportionation takes place with formation of $WSeBr_2$ and $WSeBr_4$. Reactions of WCl_5 with Sb_2Se_3 and of WBr_5 with Sb_2S_3 did not give the hoped for $WSeCl_3$ and $WSBr_3$, the analytical data indicating that disproportionation had occurred. Attempts made to prepare $WSCl_3$ by photolysis of $WSCl_4$ in tetrachloroethylene were unsuccessful, even though similar conditions produce WCl_5 from WCl_6.[19]

These halide sulphides and selenides of quinquevalent molybdenum and tungsten (MYX_3) are much less reactive than the sexivalent compounds (MYX_4), being only slowly hydrolysed in moist air. They are insoluble in all non-polar solvents, and even with neat donor solvents only $MoSCl_3$ shows any appreciable reaction. Thus on prolonged reaction $MoSCl_3$,NCMe, $MoSCl_3$-2NCMe, and $MoSCl_3$,3py can be obtained (py = pyridine).[14] The 1 : 1 methyl cyanide adduct has a room-temperature magnetic moment of 0·90 B.M., while the 1 : 2 adduct has a moment of 1·90 B.M. Similar behaviour is shown by $WOCl_3$ which forms 1 : 1 and 1 : 2 adducts with py that have room-temperature moments of 0·79 and 1·47 B.M. respectively.[20] The compound $WOCl_3$ is known to have the $NbOCl_3$ structure (B),[21] and it has been suggested that in $WOCl_3$,py the chlorine bridges are broken but that oxygen bridges are only broken when $WOCl_3$,2py is formed.



(B)

The parallel reactivity of $WOCl_3$ and $MoSCl_3$, and the complete lack of reactivity of $WSCl_3$ and $MoSeCl_3$, suggest that these MYX_3 compounds have the $NbOCl_3$ type of structure rather than that of the monoclinic form of $MoOCl_3$ in which there are terminal metal–oxygen bonds.[22,23] Moreover the i.r. spectra showed no bands that can be assigned to ν(M=S), so that M–S–M linkages would appear to be present. The magnetic properties (see SUP 21106) also fit with the proposed structure and indicate appreciable magnetic interaction is taking place. Thus the moments of $MoSCl_3$ and $MoSeCl_3$ fell with temperature, as found with $WOCl_3$ and $MoOBr_3$ ($NbOCl_3$ structure), while that of $WSCl_3$ was appreciably lower than the spin-only value; the monoclinic form of $MoOCl_3$ does not show this behaviour.[24] *X*-Ray powder photographs were inconclusive because although $MoSCl_3$ and $WSCl_3$ are isomorphous they are not isomorphous with $MoSeCl_3$, and

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* I.r. spectral and magnetic data are to be found in Supplementary Publication No. SUP 21106 (4 pp.). For details see Notice to Authors, No. 7, *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full-size copies).

† 1 B.M. = 0·927 × 10^{-23} A m^2.

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none of the three is isomorphous with either form of $MoOCl_3$.

(c) *Molybdenum*(IV) *and Tungsten*(IV) *Compounds.*—The compounds $MoSCl_2$ and $MoSeCl_2$ are readily prepared from $MoCl_4$ and Sb_2S_3 or Sb_2Se_3, while the tungsten species (Table) are best obtained as the involatile fraction from the thermal-disproportionation reaction of the appropriate tungsten(V) halide sulphide or selenide, the other product being the corresponding tungsten(VI) derivative. Thermal decomposition of the comparable molybdenum(V) compounds is not so simple, since while $MoSCl_2$ and $MoSeCl_2$ are formed the other compounds are molybdenum(IV) chloride and either S or Se. All the compounds are insoluble in a wide range of solvents but are slowly hydrolysed by moisture. The magnetic properties indicated that appreciable magnetic exchange is taking place, while their *X*-ray powder photographs showed they are not isomorphous with the corresponding dihalide oxides $MOCl_2$ (M = Mo or W) which have the $MoOCl_2$ structure.[25]

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