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PREPARATION AND CHARACTERIZATION OF SOME TRIHALOSULPHIDONIOBIUM(V) AND TETRAHALOSULPHIDOTUNGSTEN(VI) COMPLEXES

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Summary

Complexes of the type $MSX_3 \cdot 2L$ (where $M \equiv$ Nb, Ta or W; $X \equiv$ Cl or Br and $L \equiv$ MeCN or Ph_3PO) and $WSCl_4 \cdot L$ (where $L \equiv$ MeCN and Ph_3PO) have been prepared by the direct reaction of MSX_3 and $WSCl_4$ with ligands. $NbSCl_3 \cdot Et_2S$ was prepared by the direct reaction of $NbSCl_3$ with Et_2S. These complexes have been characterized by microanalysis, IR and Raman spectra, ESR, magnetic susceptibility and electrical conductivity measurements, and X-ray powder diffraction.

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1. Introduction

Transition metal oxohalides react with monodentate (L) and bidentate (B) ligands containing oxygen, sulphur and nitrogen as donor atoms to yield complexes of the type $MOX_3 \cdot 2L$ and $MOX_3 \cdot B$. A large number of compounds of general formula $MOX_3 \cdot 2L$ (where $M \equiv$ Nb, Ta, Mo or W and L is an oxygen donor ligand *e.g.* R_3PO, R_3AsO, R_2SO, $RCOOR'$, $RR'CO$, RCOOH or ROH) have been prepared by the direct reaction of metal(V) oxohalide and ligand and also by oxygen abstraction reactions [1 - 8]. $WOCl_4 \cdot Ph_3PO$ has been prepared by the direct reaction of $WOCl_4$ and Ph_3PO in MeCN–C_6H_6 [9].

The reactions of metal(V) trihalosulphides have received much less attention than those of the analogous metal(V) trihaloxides. However, niobium(V) trichlorosulphide reacts with methyl cyanide, 2,2′-bipyridyl, 1,10-phenanthroline, dimethoxyethane, 1,4-thioxan, tetrahydrothiphene, pyridinum chloride and tetraphenylarsonium chloride to give complexes containing six coordinate niobium [10]. The reaction of $NbSCl_3$ with Ph_3PS results in the formation of the 1:1 adduct of $NbSCl_3 \cdot Ph_3PS$ [11, 12].

The reaction of tetrahydrothiophene (tht) with $NbSBr_3$ and $NbSCl_3$ results in the formation of $NbSBr_3 \cdot 2tht$ and $Nb_2X_4S_3 \cdot 4tht$ respectively [13]. $TaSX_3$ reacts with monodentate diethyl sulphide, tetrahydrothiophene and methyl cyanide to form $TaSX_3 \cdot 2L$ and with bidentate ligands such as 1,2-

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bis(phenylthio)ethane to form $TaSX_3 \cdot B$ [14]. Ph_4PCl reacts with $NbSCl_3$ and $WSCl_3$ to form $Ph_4P[NbSCl_4]$ and $[Ph_4]_2[WSCl_4]_2$ respectively [15].

2. Experimental details

The complexes were prepared and handled in a drybox filled with oxygen-free dinitrogen.

2.1. *Materials*

$NbCl_5$ (Koch-Light), $NbBr_5$ (Alfa), $TaCl_5$ (Alfa), $TaBr_5$ (Alfa), $MoCl_5$ (Alfa), WCl_6 (Alfa), Sb_2S_3 (Alfa), B_2S_3 (Alfa), Ph_3PO (BDH), $(Me_2N)_3PO$ (BDH), Ph_2SO (Aldrich), Et_2S (Ralph-N-Emanuel), MeCN (Hopkin and Williams), CH_2Cl_2 (BDH), CS_2 (Hopkin and Williams) and Analar C_6H_6 (BDH) were purified and dried by standard methods.

2.2. *Analytical determination*

Analysis of niobium, tantalum, molybdenum, tungsten, chlorine, bromine, sulphur, carbon, hydrogen, nitrogen and phosphorus were carried out in the microanalytical laboratory of this department by Mr M. Hart.

2.3. *Preparation of compounds*

2.3.1. *Preparation of metal halosulphides*

$WSCl_4$ and $MSCl_3$ (where $M \equiv Nb$, Ta or Mo) were prepared by the reaction of metal halides with boron sulphide in a sealed tube. $MSBr_3$ (where $M \equiv Nb$ or Ta) were prepared by the direct reaction of the metal halide with antimony sulphide in carbon disulphide at room temperature. The analyses of the metal halosulphides are summarized in Table 1.

TABLE 1

Physical properties and analytical data of halosulphides

Halosulphide	*Colour*	*Melting point* (°C)	*Analysis*					
			Calculated %			*Found %*		
			M	*S*	*X*	*M*	*S*	*H*
$NbSCl_3$	Green	110[d]	40.4	12.82	46.78	46.17	12.6	46.4
$NbSBr_3$	Reddish-brown		25.47	8.79	65.79	25.7	7.9	64.7
$TaSCl_3$	Yellow	110[d]	56.65	10.01	33.33	56.7	10.3	33.3
$TaSBr_3$	Orange	—	39.95	7.06	52.98	39.4	5.95	53.7
$MoSCl_3$	Black	200[d]	40.93	13.64	45.38	40.2	13.5	46.7
$WSCl_4$	Deep red	145	51.37	8.94	39.68	51.8	8.7	39.9

[d] Decomposition.
M ≡ Nb, Ta, Mo, W.
X ≡ Cl, Br.

2.3.2. *Preparation of $MSX_3 \cdot 2MeCN$*

Acetonitrile complexes of MSX_3 (where M ≡ Nb or Ta; X ≡ Cl or Br) were prepared by the direct reaction of the metal(V) trihalosulphide with a large excess of ligand. The resultant precipitate was filtered off under strictly anhydrous conditions and the soluble products remaining in solution were isolated by vacuum evaporation of the solvent.

2.3.3. *Preparation of $WSCl_4 \cdot MeCN$*

$WSCl_4 \cdot MeCN$ was prepared by the direct reaction of a warm carbon tetrachloride solution of $WSCl_4$ with the stoichiometric amount (1:1 molar ratio) of acetonitrile in carbon tetrachloride. The red soluble complex was isolated by vacuum evaporation of the solvent.

2.3.4. *Reaction of $MoSCl_3$ with MeCN*

$MoSCl_3$ was allowed to react with acetonitrile under reflux for two weeks. At the end of this period the brown solid was filtered off under strictly anhydrous conditions and vacuum dried. The excess of solvent was removed from the green filtrate by evaporation. The brown and green complexes correspond respectively to (1:1) and (1:2) ratios of molybdenum(V) chlorosulphide to ligand.

2.3.5. *Preparation of $WSCl_4 \cdot Ph_3PO$*

$WSCl_4 \cdot (Me_2N)_3PO$ was prepared by the direct reaction of a red solution of $WSCl_4$ in a mixture of carbon tetrachloride–benzene with the stoichiometric amount (1:2 molar ratio) of Ph_3PO in benzene. The red solution was concentrated to half of its original volume and when left in a drybox for three days resulted in the formation of deep brown crystals of the complex.

2.3.6. *Preparation of $WSCl_3 \cdot 2Ph_3PO$*

$WSCl_3 \cdot 2Ph_3PO$ was prepared by the direct reaction of a red solution of $WSCl_4$ in MeCN–C_6H_6 with the stoichiometric amount (1:2 molar ratio) of Ph_3PO in MeCn–C_6H_6. The deep brown solution was left in a drybox for 12 h, by which time the green crystals of complex were deposited.

2.3.7. *Reaction of $WSCl_4$ with $(Me_2N)_3PO$*

$WSCl_4 \cdot (Me_2N)_3PO$ was prepared by the direct reaction of a red solution of $WSCl_4$ in carbon tetrachloride with the stoichiometric amount (1:1 molar ratio) of ligand in dichloromethane. The dark red solution was concentrated to half its original volume and when left in a drybox for one week no precipitate was observed. The brown-black solid complex was obtained by evaporation of all the solvent under reduced pressure.

2.3.8. *Preparation of $NbSCl_3 \cdot 2Ph_3PO$*

$NbSCl_3 \cdot 2Ph_3PO$ was prepared by the following routes:

(a) by the reaction of green acetonitrile solution of $NbSCl_3$ with the stoichiometric amount (1:2 molar ratio) of Ph_3PO in dichloromethane. The green solution was concentrated to half of its original volume and when left in a drybox for one day resulted in the formation of green crystals of the complex;

(b) by the reaction of acetonitrile solution of $NbSCl_3 \cdot 2MeCN$ with two-fold excess of Ph_3PO in benzene. The green solution was left in a drybox for two days by which time the green crystals of the complex had formed.

2.3.9. *Preparation of* $NbSBr_3 \cdot 2Ph_3PO$

$NbSBr_3 \cdot 2Ph_3PO$ was prepared by the following routes:

(a) by the reaction of reddish-brown acetonitrile solution of $NbSBr_3$ with the stoichiometric amount (1:2 molar ratio) of Ph_3PO in dichloromethane. The resultant green solution was concentrated to half of its original volume and when left in a drybox for one week no precipitate was observed. The green complex was separated by evaporation of all the solvent under reduced pressure;

(b) by the reaction of a dichloromethane solution of $NbSBr_3 \cdot 2MeCN$ with the stoichiometric amount (1:2 molar ratio) of Ph_3PO in dichloromethane. The resultant green solution was concentrated to half of its original volume and when left in a drybox for one week resulted in the formation of a green crystalline complex.

2.3.10. *Reaction of* $NbSCl_3$ *with* $(Me_2N)_3PO$

$NbSCl_3 \cdot 2(Me_2N)_3PO$ was prepared by the reaction of acetonitrile solution of $NbSCl_3$ with the stoichiometric amount (1:2 molar ratio) of hexamethylphosphoramide in acetonitrile. The resulting green solution was concentrated to half its original volume and when left in a drybox for one week resulted in the formation of a dark green crystalline complex.

2.3.11. *Reaction of* $NbSCl_3$ *with* Ph_2SO

$NbSCl_2 \cdot Ph_2SO$ was prepared by the reaction of an acetonitrile solution of $NbSCl_3$ with the stoichiometric amount (1:2 molar ratio) of diphenyl sulphoxide in dichloromethane. The resultant green solution was first concentrated to half of its original volume, and when left in a drybox for one week no precipitate was observed. The pale green complex was obtained by vacuum evaporation of all the solvent.

2.3.12. *Preparation of* $NbSCl_3 \cdot Et_2S$

$NbSCl_3$ was reacted with a large excess of diethyl sulphide to form a reddish-brown solution. The solution was filtered under strictly anhydrous conditions and the brown complex was isolated by vacuum evaporation of the excess diethyl sulphide.

2.3.13. *Reaction of* $MoSCl_3$ *with* Ph_4AsCl

$(Ph_4As)(MoSCl_4)$ was prepared by the direct reaction of a dichloromethane suspension of $MoSCl_3$ with the stoichiometric amount (1:1 molar ratio) of Ph_4AsCl in dichloromethane which results in the formation of brownish-green complexes.

2.4. *Physical measurements*

The analyses of the complexes are summarized in Table 2.

2.4.1. *IR spectra*

IR spectra were recorded using Perkin–Elmer model 257 (4000 - 625 cm^{-1}) and Perkin–Elmer model 225 (625 - 200 cm^{-1}) instruments. Nujol mulls were prepared in a drybox.

2.4.2. *Raman spectra*

Raman spectra of powdered samples were recorded using a Cary-82 laser Raman spectrophotometer.

2.4.3. *X-ray powder photographs*

Photographs were obtained using a Debye–Scherrer Camera with a diameter of 5.37 cm. In all cases Cu Kα radiation was used.

2.4.4. *Melting point*

The melting points of compounds were determined using either a Gallenkamp melting point apparatus or an electrically heated oil bath. The samples were loaded in capillary tubes in a dinitrogen atmosphere and covered with parafilm.

2.4.5. *Electronic spectra*

Utraviolet/visible spectra (200 - 850 nm) were recorded for solutions using Unicam SP800 and Perkin–Elmer 402 utraviolet/visible spectrophotometers.

2.4.6. *Electron spin resonance*

Electron spin resonance spectra were recorded on a Varian "V 4502" electron spin resonance spectrophotometer using a 2 band Klystron source. The samples, as powders or solutions, were loaded into a silica tube of about 1 mm in diameter in a dry dinitrogen atmosphere. The tube was sealed by parafilm to protect the compounds from moist air.

2.4.7. *Mass spectral measurements*

Mass spectra of some of the complexes were recorded on an AEI 12 mass spectrometer at a nominal excitation of 70 eV.

2.4.8. *Magnetic susceptibility*

The magnetic susceptibilities were determined using the Gouy method. Two independent determinations of magnetic susceptibility were carried out for each sample at room temperature.

TABLE 2

Complexes	*Colour*	*Analysis*													
		Calculated (%)							*Found (%)*						
		M	*S*	*X*	*C*	*H*	*N*	*P*	*M*	*S*	*X*	*C*	*H*	*N*	*P*
$WSCl_4 \cdot MeCN$	Red	46.10	8.04	35.56	6.02	0.75	3.51		45.80	8.40	35.20	6.00	0.70	3.90	
$NbSCl_3 \cdot 2MeCN$	Green	29.64	10.23	33.98	15.32	1.92	8.93		29.30	10.00	34.40	13.70	1.90	8.30	
$NBSBr_3 \cdot 2MeCN$	Brown	20.80	7.15	53.69	10.73	1.34	6.26		20.3	6.8	55.1	9.9	1.3	5.9	
$TaSCl_3 \cdot 2MeCN$	Purple	45.08	7.97	26.52	11.95	1.49	6.97		44.9	6.8	27.7	11.2	1.4	6.9	
$MoSCl_3 \cdot MeCN$	Brown	34.84	11.61	38.65	8.71	1.08	5.08		35.5	11.2	26.3	7.5	0.9	3.9	
$MoSCl_3 \cdot 2MeCN$	Green	30.33	10.11	33.64	15.16	1.89	8.84		27.6	4.9	33.2	15.4	2.0	8.9	
$WSCl_4 \cdot Ph_3PO$	Brown	28.90	5.04	22.29	33.99	2.37	—	4.86	30.50	4.60	22.20	36.00	2.40		5.10
$WSCl_3 \cdot 2Ph_3PO$	Green	20.92	3.70	12.0	49.40	3.40		7.04	21.3	3.70	12.50	49.40	3.40		7.20
$WSCl_4(Me_2N)_3PO$	Brown-black	34.37	5.98	26.54	13.46	3.36	7.85	5.77	34.5		24.8	13.7	3.5	7.6	5.82
$NbSCl_3 \cdot 2Ph_3PO$	Green	11.79	4.06	13.49	54.88	3.83	—	7.86	11.80	4.10	13.30	55.20	3.80		7.70
$NbSBR_3 \cdot 2Ph_3PO$	Green	10.09	3.47	26.05	46.9	3.25	—	6.73	10.5	1.9	25.40	46.7	3.3		6.7
$NbSCl_3 \cdot 2(Me_2N)_3PO$	Green	15.77	5.4	18.06	24.42	6.4	14.25	10.51	17.1	2.6	17.8	25.1	6.4	14.5	10.0
$NbSCl_2 \cdot Ph_2SO$	Green	15.5	16.0	11.83	48.0	3.33			16.6	13.5	12.8	43.3	3.4		
$NbSCl_3 \cdot Et_2S$	Brown	28.92	19.90	33.12	14.93	3.11			27.8	18.4	31.6	15.1	3.2		
$(Ph_4P)(MoSCl_4)$	Brownish-green	14.7	4.90	21.74	44.10	3.06		11.84	14.3	1.9	22.7	43.8	3.0		11.0

3. Results and discussion

Halosulphidometal complexes may be prepared by the direct reaction of the metal halosulphide with the ligand or by the reaction of acetonitrile complexes of the metal halosulphide with other ligands.

The reactions of $WSCl_4$ and MSX_3 (where $M \equiv Nb$, Ta or Mo; $X \equiv Cl$, or Br) with the unidentate nitrogen donor acetonitrile have resulted in the formation of two types of complexes: $WSCl_4 \cdot MeCN$ and $MSX_3 \cdot 2MeCN$.

$WSCl_4 \cdot MeCN$ was prepared by the direct reaction of $WSCl_4$ with a slight excess of the ligand in CCl_4. The red crystalline complex of $WSCl_4 \cdot MeCN$ is extremely sensitive to moisture and its red colour changes to blue on exposure to moisture. It dissolves in CCl_4, C_6H_6, CH_2Cl_2 and acetonitrile to form a red solution. It had no definite melting point and turned to deep brown at 110 °C under atmospheric pressure.

The complexes $MSX_3 \cdot 2MeCN$ (where $M \equiv Nb$ or Ta; $X \equiv Cl$ or Br) were prepared directly by adding an excess of acetonitrile to the corresponding metal(V) halosulphide, the resultant precipitate was filtered under extremely anhydrous conditions. Acetonitrile complexes of metal(V) halosulphides are very soluble in acetonitrile yet insoluble in most of the usual organic solvents. Its extreme instability in acetonitrile solution prevented some studies from being carried out. $NbSCl_3 \cdot 2MeCN$ had no definite melting point and decomposed between 120 and 130 °C under atmospheric pressure.

Tungsten(VI) tetrahalosulphides react with triphenylphosphine oxide at room temperature in CCl_4–C_6H_6 to form deep brown crystalline $WSCl_4 \cdot Ph_3PO$. This complex is moisture sensitive and slightly soluble in CH_2Cl_2 and C_6H_6 but insoluble in CCl_4; it has no definite melting point and decomposed at 130 °C.

$NbSX_3 \cdot 2Ph_3PO$ was prepared either by addition of trihalosulphidoniobium(V) or acetonitrile complexes of $NbSX_3$ to Ph_3PO in acetonitrile–dichloromethane.

Triphenylphosphine oxide complexes of metal halosulphides are more stable in air than metal halide, metal halosulphide and acetonitrile complexes and show no visible signs of decomposition on exposure to air for several hours. $NbSX_3 \cdot 2Ph_3PO$ was insoluble in any of the usual organic solvents.

The chemistry of metal halosulphide complexes is not well established and there are some unresolved problems. Among the more important of these problems are the similarities in the IR, ESR and electronic spectra of halosulphide and halooxide complexes. These similarities are even more surprising in that they are also present in the system for which we have crystal structure data, *i.e.* $WSCl_3 \cdot 2Ph_3PO$ [16] where, although there is disorder between the sulphur and chlorine atoms, there is no doubt that the formulation of these compounds is correct. Another major problem is the poor analysis obtained for these complexes where in some cases no sulphur was detected although some sulphur fragments were detected by mass spectral studies. Therefore it may be that routine methods of sulphur analysis are not good enough for halosulphide systems, whereas they are quite adequate for systems where sulphur is a constituent atom in the ligand. It has been reported that in the analysis of some Ta–S–Ta systems in which sulphur is present in two different chemical environments no sulphur was detected for one of these sites, but was quantitatively estimated for the other sites [17].

The IR spectra of some halosulphide complexes of niobium indicate the existence of terminal M=S or bridging M—S—M sulphur modes and some of these assignments have been confirmed by the crystal structure studies.

$TaSX_3 \cdot 2L$ (where $X \equiv Cl$ or Br; $L \equiv MeCN$, dimethyl sulphide or tetrohydrothiophene showed strong absorption in the range of 504 - 510 cm^{-1} and $TaCl_3(PhSCH_2CH_2SPh)$, which crystallizes in the monoclinic system with space group $P2_1/c_1$, showed very strong absorptions at 508 and 512 cm^{-1} which are assigned to the tantalum–sulphur stretching vibration [14]. The Nb=S bond length in monomeric $NbSCl_3 \cdot Ph_3PS$ is shorter than in the dimer because of the *trans* chlorine influence in the dimer, but this difference is not reflected in the IR and Raman spectra, which both show single bands at 536 and 537 cm^{-1} respectively [12].

Drew and coworkers have shown that the reaction of acetonitrile complexes of niobium(IV) chloride and bromide with Sb_2S_3 results in the formation of dihalosulphidoniobium(IV) complexes. $[\{NbSCl_2(MeCN)_2\}_2]2MeCN$ and $[\{NbSCl_2(MeCN)_2\}_2]MeCN$ were found to be crystallized in the triclinic system with $P\bar{1}$ space group and to contain niobium–sulphur bridging [18]. The absorptions at 476, 470(s) (doublet) and 330(sh) cm^{-1} in the spectrum of $[\{NbSCl_2(MeCN)_2\}_2]$, and the strong absorptions at 468 and 321 cm^{-1} in the IR spectrum of $[\{NbSBr_2(MeCN)_2\}_2]$ have been assigned to $\overline{\mathrm{Nb{-}S{-}Nb{-}S}}$ vibrations. The same workers have also shown that the reaction of niobium(V) trihalosulphide with tetrahydrothiophene results in the formation of complexes of the type $NbSBr_3 \cdot 2tht$ and $Nb_2S_3X_4 \cdot 4tht$ (where $X \equiv Cl$ or Br). The existence of terminal Nb=S and bridging Nb—S—Nb have been confirmed by crystal structure studies of $NbSBr_3 \cdot 2tht$ and $Nb_2S_3X_4 \cdot 4tht$ respectively [13].

The reaction of $NbSCl_3$ with Ph_4PCl results in the formation of $Ph_4P[NbSCl_4]$ which crystallizes in the tetragonal system with space group $P4/n$. The absorptions at 552 and 548 cm^{-1} in the IR spectra of $Ph_4P[NbSCl_4]$ and $Ph_4P[Nb^{34}SCl_4]$ respectively have been assigned to (Nb=S) stretching vibrations [15]. The reaction of $WSCl_3$ with Ph_4PCl in CH_2Cl_2 results in the formation of dimeric $[Ph_4P]_2[WSCl_4]_2$ tungsten–chlorine bridging at 241(vw) and 231(m) cm^{-1} and terminal W=S bonding at 572 cm^{-1} [3]. The absorptions at 526, 512, 469 and 578 cm^{-1} in the IR spectra of $[WSCl_5]^-$, $[W^{34}SCl_5]^{2-}$, $[WSCl_5]^{2-}$ and $[WSBr_5 \cdot BBr_3]^{2-}$ respectively are assigned to the W=S stretching vibrations [15].

Holm *et al.* [20] have compared the difference in the IR spectra of $MS(S_2CNEt_2)_3$, where $M \equiv Nb$ and Ta, and have concluded that $\nu(M{=}S) \leqslant 490$ cm^{-1}. Finally, by crystal structure studies of $NbS(S_2CNEt_2)_3$ and comparison with the other known crystal structures of halosulphide complexes of niobium(V), they have reported that the absorptions at 493 and 479 cm^{-1}, in the spectra of $NbS(S_2CNEt_2)_3$ and $TaS(S_2CNEt_2)_3$, may be assigned to ν(M=S) stretching vibrations [19].

Sharma and Shivahare [21] have assigned the absorptions at 570 - 530 and 390 - 365 cm^{-1} in the spectrum of NbTPMA and absorptions at 365 - 345 cm^{-1} in the IR spectrum of NbTPA to ν(Nb—S) modes (where TPMA ≡ thiopicolinmethylamide and TPA ≡ thiopicolinanilide).

Britnell and coworkers have assigned the absorption in the range of 518 - 560 cm^{-1} in the IR spectra of halosulphidetungsten complexes of the type $WSX_4 \cdot L$, $2WSX_4 \cdot B$ and $WSCl_3 \cdot B$ to the terminal W=S stretching vibration [22]. Reaction of $MoSCl_3$ with MeCN results in the formation of $MoSCl_3 \cdot 2MeCN$ and $MoSCl_3 \cdot MeCN$, in which the former has a terminal Mo=S stretching vibration at 480 cm^{-1}, while there is no such a peak in the spectrum of the 1:1 adduct; this implies a Mo–S–Mo bridging system rather than a terminal Mo=S bond [23].

The observed IR spectra of $WSCl_4 \cdot MeCN$, $NbSCl_3 \cdot 2MeCN$, $NbSBr_3 \cdot 2MeCN$ and $TaSCl_3 \cdot 2MeCN$ show medium strong intensity bands at 535, 532, 524 and 438 cm^{-1} respectively, which may be assigned to M=S stretching vibrations. The observed IR spectra of $NbSCl_3 \cdot 2Ph_3PO$, $NbSCl_3 \cdot 2(Me_2N)_3PO$, $NbSBr_3 \cdot 2Ph_3PO$, $MoSCl_3 \cdot 2Ph_3PO$ and $NbSCl_2 \cdot 2Ph_2SO$ in the range of 600 - 400 cm^{-1} are very confused, and because vibration frequencies in the spectra of complexes resemble the frequencies in the free ligand, it is not possible to assign particular bands to metal–sulphur vibrations. However the medium band at 509 cm^{-1} in the IR and at 515 cm^{-1} in the Raman spectra of $NbSCl_3 \cdot 2Ph_3PO$, which is absent from the IR and Raman spectra of the free ligand and corresponding halooxide complex, may be assigned to the Nb=S stretching vibration.

The IR spectra of $MoSCl_3 \cdot 2Ph_3PO$ shows a doublet band at (455, 446) and 420 cm^{-1} of medium intensity which is less intense in the spectra of the free ligand and corresponding halooxide complex. The IR spectra of the mixture ($MoSCl_3 \cdot 2Ph_3PO$) and ($MoOCl_3 \cdot 2Ph_3PO$) shows an independent increase in the intensity of a doublet band in both oxo and thio complexes, while no change in absorption at 420 cm^{-1} is observed. Therefore the absorption at 420 cm^{-1} for $MoSCl_3 \cdot 2Ph_3PO$ is not due to the ligand and is probably due to the Mo=S stretching modes, but it is not possible to find with any certainty what changes have occurred on coordination.

The IR spectrum of the product obtained by the reaction of $NbCl_5 \cdot MeCN$ with Sb_2S_3 shows a strong absorption at 542 cm^{-1} which is not present in the spectra of $NbCl_5 \cdot MeCN$ or Sb_2S_3. Therefore this band may be assigned to Nb=S stretching vibration.

It has been established that alkylcyanides coordinate to metal halides through the lone pair electrons of the nitrogen atom. The position of the C≡N stretching frequencies in the IR spectra of the complexes has been utilized to elucidate the mode of bonding of the nitrile group on coordination: the C≡N stretching mode is almost always shifted to higher frequency

TABLE 3

IR data of halosulphidometal complexes

Complexes	*M—X*		*M=S*		*P=O*		*CH_3 deformation C—C stretching and C≡N*
	IR (cm^{-1})	*Raman* (cm^{-1})	*IR* (cm^{-1})	*Raman* (cm^{-1})	*IR* (cm^{-1})	*Raman* (cm^{-1})	
$NbSCl_3 \cdot 2MeCN$	338		532				2280, 2310
$NbSBr_3 \cdot 2MeCN$	240		524				2280, 2300
$TaSCl_3 \cdot 2MeCN$	330		438				2280, 2316
$WSCl_4 \cdot MeCN$	325		535				2280, 2300
$NbSCl_3 \cdot 2Ph_3PO$	318	333	509	515	1172, 1160	1167	
$NbSBr_3 \cdot 2Ph_3PO$	244	250			1160		
$NbSCl_3 \cdot 2HMPA$	314				1135		
$WSCl_4 \cdot Ph_3PO$	330, 310				1135		
$WSCl_3 \cdot 2Ph_3PO$	321, 315, 310				1153	1157	
$WSCl_4 \cdot HMPA$	338; 332						
$MoSCl_3 \cdot 2Ph_3PO$	322, 294	348, 298	420		1156	1163	

[24]. In the recorded IR spectrum, the two strong absorptions of free MeCN at 2291 and 2250 cm^{-1}, which are assigned to a combination of symmetric CH_3 deformation and C—C and C≡N stretching vibrations [25], have shifted to higher frequencies upon coordination as shown in Table 3. In all of the spectra of acetonitrile complexes observed in this study, the ν(C≡N) is shifted to higher frequencies and is found to be at 2280 cm^{-1}.

The IR spectra of $NbCl_5 \cdot MeCN$ shows two strong absorptions at 2318 and 2290 cm^{-1} which are shifted to 2306, 2280 cm^{-1} and 2302, 2280 cm^{-1} in the IR spectra of products obtained by the reaction of $NbCl_5 \cdot MeCN$ with Sb_2S_3 and Sb_2O_3 respectively.

The observed IR spectra of Ph_3PO and $(Me_2N)_3PO$ show strong absorptions at 1185 and 1205 cm^{-1} respectively, which are assigned to the ν(P=O) stretching vibration. Brown *et al.* [26] have reported that the position of the ν(P=O) stretching vibration is shifted to lower frequencies on coordination owing to an overall decrease in pπ–dπ bonding.

The (P=O) stretching vibrations of halosulphidometal complexes are summarized in Table 3. The IR spectra of $WSCl_4(Me_2N)_3PO$ show five strong absorptions at 1190, 1072, 994, 980 and 967 cm^{-1} and it is difficult to decide which one is the ν(P=O) stretching vibration; by comparison with the IR spectrum of $(Me_2N)_3PO$, the absorptions at 967 or 980 cm^{-1} may be assigned to the ν(P=O) vibration. If this is not the case, then either of these absorptions may be assigned to the ν(W=O) vibration, but such an assignment then presents a problem since such absorptions are also found in $WSCl_3 \cdot 2Ph_3PO$. Another factor to note is that the P=O vibration and the C—N stretching vibration may overlap at 1072 cm^{-1}.

The assignment of the (C—S) frequency in Et_2S is complicated and the frequencies associated with the (C—S) stretching vibration have been assigned at 640, 660, 693, 746 and 781 cm^{-1} [27]. The absorptions at 720 and 580 cm^{-1} for $NbSCl_3 \cdot Et_2S$ are probably due to C—S stretching modes but it is difficult to say which modes these are, or what changes have occurred on coordination.

The observed IR and Raman spectra show the expected metal–halide vibrations which are summarized in Table 3.

The niobium(V) and tantalum(V) complexes of type $NbSX_3 \cdot 2Ph_3PO$ and $WSCl_4 \cdot MeCN$ have formally a d^0 electron configuration, so pure d–d transitions are not possible and the absorption bands in the spectra are due to charge transfer. The spectra of complexes were recorded in acetonitrile solution. The extinction coefficient, using the Beer-Lambert Law, was calculated to be 3.87×10^3, 3×10^3 and 3×10^3 for $WSCl_4 \cdot MeCN$, $NbSCl_3 \cdot 2Ph_3PO$ and $NbSBr_3 \cdot 2Ph_3PO$ respectively.

Conductivity measurements of 10^{-3} molar solutions of $WSCl_4 \cdot MeCN$ in acetonitrile gave values of 9 - 4 ohm^{-1} cm^{-2} mol^{-1} which suggest that the complex is a non-electrolyte in acetonitrile solution.

ESR measurements of $WSCl_3 \cdot 2Ph_3PO$ shows two signals which, on the basis of their intensity, are assigned to $g(\perp) = 1.755$ and $g(\|) = 1.589$ and this suggests that tungsten has formally a d^1 electron configuration.

The reaction of $NbSCl_3$ with Ph_2SO in acetonitrile results in the formation of a green compound whose elemental analysis corresponds to $NbSCl_2 \cdot Ph_2SO$. However, the ESR spectrum suggests that niobium has formally a d^1 electronic configuration. Magnetic susceptibility measurements on $WSCl_3 \cdot 2Ph_3PO$ indicate that it is paramagnetic with $\mu_{eff} = 1.67\ \mu_B$.

The mass spectral studies on some of the halosulphidometal complexes show the following mass peaks:

(i) $NbSCl_3 \cdot 2(Me_2N)_3PO$: 277 ($NbS^{35}Cl_3 \cdot OP$), 199 ($NbS^{37}Cl_2$), 162 ($NbS^{37}Cl$), 160 ($NbS^{35}Cl$).

(ii) $NbSBr_3 \cdot 2Ph_3PO$: 253 ($NbSBr \cdot OP$), 125 (NbS).

(iii) $WSCl_4(Me_2N)_3PO$: 286 ($WS^{35}Cl_2$), 288 ($WS^{35}Cl^{37}Cl$), 251 ($WS^{35}Cl$), 253 ($WS^{37}Cl$).

The X-ray powder diffraction results for complexes prepared in this study suggest that $WSCl_3 \cdot 2Ph_3PO$, $WSCl_4 \cdot MeCN$ and $NbSCl_3 \cdot 2Ph_3PO$ are isostructural.

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