Adducts of Molybdenum(v) Trichloride Sulphide

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The compound $MoCl_3S$ reacts with methyl cyanide to give $MoCl_3S,MeCN$ and $MoCl_3S,2MeCN$, which have been characterised as containing six-co-ordinate molybdenum with bridging Mo–S–Mo and terminal Mo=S bonds respectively. The complex $MoCl_3S,2MeCN$ reacts with other ligands; 1,4-dioxan and 1,2-bis(methoxy)-ethane give adducts $MoCl_3S,2diox$ and $MoCl_3S,bme$, while pyridine gives the salt $[Hpy][MoCl_4S,py]$ and 1,10-phenanthroline reduces molybdenum to the quadrivalent state in forming $MoCl_2S,phen$. Direct reaction of $MoCl_3S$ with py gives $MoCl_3S,3py$ (one py being in the lattice). The salts WCl_3S and $MoCl_3S$ did not react with any of the ligands tried even after prolonged reaction periods.

THE chemistry of molybdenum(v) trichloride oxide and tribromide oxide has been studied in some detail,[1-5] but reported work with the corresponding trihalide sulphide and selenide has been limited to their preparation.[6,7] Some adducts of WCl_3S have been prepared [7] from WCl_4S by reduction with various ligands. We now report attempts to prepare complexes of $MoCl_3S$, $MoCl_3Se$, and WCl_3S by direct reaction of the trihalide sulphides or selenides with ligands.

EXPERIMENTAL

As the compounds are very moisture sensitive, the preparative and handling procedures were carried out by means of conventional vacuum-line or dry-box methods. All ligands and solvents were rigorously dried and distilled on the vacuum line before use. The compounds $MoCl_3S$, $MoCl_3Se$, and WCl_3S were prepared by heating the appropriate pentahalide with either Sb_2S_3 or Sb_2Se_3.[7]

Conductivity measurements were carried out in cells specially adapted to eliminate air and moisture; molecular weights were determined by the elevation of b.p. method; oxidation states were determined by titration with cerium(iv) sulphate.

Preparations.—Analytical data are given in the Table. (i) *Molybdenum*(v) *trichloride sulphide–methyl cyanide* (1/1) *and* (1/2). The compound $MoCl_3S$ (2 g) and MeCN (50 cm^3) were sealed in an evacuated ampoule, and the mixture heated gently under reflux for 48 h. A green solution formed together with a green precipitate and the latter ($MoCl_3S,MeCN$) was isolated by filtration *in vacuo*. Evaporation of the solution gave a dark green powder of composition $MoCl_3S,2MeCN$. The magnetic moment (in B.M.) of $MoCl_3S,MeCN$ was determined over a temperature range: $\mu = 1{\cdot}07$ (298); 1·04 (273); 1·03 (253); 1·03 (233); 1·00 (193); 0·99 (173); 0·98 (153); 0·97 (133); and 0·94 113 K).†

(ii) *Molybdenum*(v) *trichloride sulphide*–1,4-*dioxan* (1/2) *and* –1,2-*bis*(*methoxy*)*ethane* (1/1). The adduct $MoCl_3S,2MeCN$ (2 g) was heated under reflux in a sealed ampoule with neat ligand (50 cm^3; diox or bme) for 16 h. The green solids obtained on evaporation of the excess of ligand still contained some MeCN (i.r. spectral evidence) so they were heated for a further period with two further successive quantities of fresh ligand.

(iii) *Pyridinium tetrachlorothiomolybdate*(v)*–pyridine* (1/1). The adduct $MoCl_3S,2MeCN$ (2 g) and pyridine (py) (1 : 4 mol ratio) were heated gently in a sealed ampoule with benzene (50 cm^3). The green solution formed initially gradually turned brown and deposited a green solid, $[Hpy][MoCl_4S,py]$, which was isolated by filtration, washed with benzene, and pumped free from solvent. An intractable tar remained when the brown solution was evaporated.

(iv) *Molybdenum*(v) *trichloride sulphide–pyridine* (1/3). The compound $MoCl_3S$ (2 g) was heated gently under reflux for 24 h with py (50 cm^3) in a sealed ampoule, and the green solution evaporated to leave $MoCl_3S,3py$.

(v) *Molybdenum*(iv) *dichloride sulphide*–1,10-*phenanthro-*

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† 1 B.M. = $0{\cdot}927 \times 10^{-23}$ A m^{-2}.

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[6] D. Britnell, G. W. A. Fowles, and R. Mandyczewsky, *Chem. Comm.*, 1970, 608.

[7] D. Britnell, G. W. A. Fowles, and D. A. Rice, *J.C.S. Dalton*, in the press.

line (1/1). The adduct $MoCl_3S,2MeCN$ (2 g) was allowed to react with 1,10-phenanthroline (phen) (1 : 2 mol ratio) in dichloromethane solution at room temperature. The green solution which formed initially gradually turned red, and red crystals of $MoCl_2S$,phen were formed as the solvent was removed by the pump.

(vi) *Other attempted preparations.* (*a*) Only non-stoicheiometric materials were obtained from the reaction of $MoCl_3S,2MeCN$ with PPh_3, tetrahydrofuran (thf), Et_2O, and $MeSCH_2CH_2SMe$. (*b*) Non-stoicheiometric materials also resulted when $MoCl_3S,MeCN$ was heated under reflux with py, diox, thf, and bme. (*c*) The compounds $MoCl_3Se$ and WCl_3S were heated under reflux with all the ligands referred to under reactions of $MoCl_3S,2MeCN$, but despite prolonged reflux periods no reaction took place; analysis showed the products to be unchanged $MoCl_3Se$ and WCl_3S.

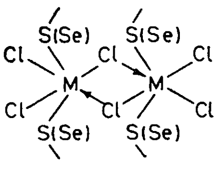
Analytical and i.r. data (400—200 cm^{-1}) of the complexes prepared from $MoCl_3S$

Complex	Analyses/(%)												Colour	μ/ B.M.	$\tilde{\nu}$(Mo=S) / cm^{-1}	*M* [a]	Oxidation state	I.r. spectra [b]	Diffuse-reflectance spectra ($10^{-3}\tilde{\nu}/cm^{-1}$)
	Found						Calc.												
	Mo	S	Cl	C	H	N	Mo	S	Cl	H	H	N							
$MoCl_3S,MeCN$	35·0	12·3	38·2	9·0	1·0	5·1	34·9	11·6	38·7	8·7	1·1	5·1	Green	1·07			5·2	*340*s, 285m, 270m	37·2(sh), 30·0, 21·8, 10·5, 8·0(sh)
$MoCl_3S,2MeCN$	29·9	9·7	33·8	13·2	2·0	6·7	30·3	10·1	33·7	15·2	1·9	8·8	Green	1·85	480	330	4·9	*320*s, br, 285(sh), 245w	37·0, 24·0, 13·0
$MoCl_3S$,2diox	23·7	7·4	26·4	22·1	3·7		23·4	7·8	26·0	23·4	3·9		Green	1·71	475	400	5·0	*320*s, br, 285s	37·0, 34·2, 29·0, 22·2, 15·6
$MoCl_3S$,bme	29·0	8·9	31·9	13·0	2·8		29·6	9·9	32·8	14·8	3·1		Green	1·68	470		5·2	*315*,s br	37·5, 34·2, 30·0, 18·0
$MoCl_3S$,3py	19·9	6·5	22·0	37·4	3·2	8·6	20·4	6·8	22·6	38·2	3·2	8·9	Green	2·01	475	280 [c]	4·8	*320*s, 300s, 280(sh)	37·6, 31·8, 26·2, 22·0, 16·0
[Hpy][$MoCl_4S$,py]	21·8	7·0	32·8	29·0	2·6	7·3	22·4	7·5	33·1	28·0	2·4	6·5	Green	1·74	490	[d]	5·1	340s, 322s, 255	36·0, 28·6, 36·4, 21·0, 7·0
$MoCl_2S$,phen	25·3	6·6	18·4	39·6	2·7	8·3	25·4	8·5	18·7	38·0	2·1	7·4	Red	1·99	460		3·8	*335*s, 330s, *295*s, 235w	44·6, 37·0, 23·6, 19·0, 14·5

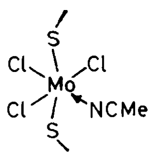
[a] Measured by elevation of b.p. in benzene solution. [b] Italicised bands suggest probable Mo–Cl modes. [c] Dissociation to $MoCl_3S$,py and py. [d] 1 : 1 Electrolyte in MeCN.

RESULTS AND DISCUSSION

The trichloride and tribromide oxides of molybdenum and tungsten have the $NbCl_3O$ structure with six-co-ordinate metal atoms bridged by both chlorine and oxygen atoms,[8,9] although there is a modification of $MoCl_3O$ which contains terminal oxygen atoms. The sulphur and selenium analogues under discussion also have the $NbCl_3O$ structure, (I).[10] Hence it is interesting to note that while the trihalide oxides react directly with a number of ligands, often under relatively mild conditions,[4] the trihalide sulphide and selenide are appreciably less reactive. The compounds $MoCl_3Se$ and WCl_3S, for instance, did not react with any of the ligands tried, even after prolonged periods under reflux, and only MeCN and py reacted with $MoCl_3S$. This reduced activity suggests that the M–S–M bridging is more resistant to attack by donor ligands than the comparable M–O–M bridges.



(I)



(II)

$MoCl_3S$ Complexes were prepared by direct reaction with MeCN and py, and the methyl cyanide complex was used as a starting material for other complexes. Thus methyl cyanide can be replaced by diox, 1,2-bis(methoxy)ethane, py, and phen to give well defined complexes, although with triphenylphosphine, diethyl ether, thf, and 1,2-bis(methylthio)ethane the products were non-stoicheiometric. The Table lists the products, their analytical data, and their i.r. spectra in the 200—400 cm^{-1} region, together with the peak at *ca.* 480 cm^{-1} tentatively assigned to a ν(Mo=S) stretching mode.[4]

(i) $MoCl_3S,2MeCN$ *and* $MoCl_3S,MeCN$.—The 1 : 2 adduct is monomeric in benzene solution and behaves as a non-electrolyte in methyl cyanide. The room-temperature magnetic moment (1·85 B.M.) rules out any interaction through neighbouring molybdenum atoms, so the structure would appear to be a simple six-co-ordinate monomer. This requires a terminal Mo=S bond and the i.r. spectrum shows a peak at 480 cm^{-1} that can be tentatively assigned to ν(Mo=S). There is no such peak in the spectrum of the 1 : 1 adduct, on the other hand, and this implies a Mo–S–Mo bridging system rather than a terminal Mo=S bond. Insolubility of the adduct in the usual solvents ruled out measurements of molecular weight and conductance but is consistent with a polymeric structure, (II). The low room-temperature magnetic moment (1·07 B.M.) and the other magnetic data (see Experimental section) indicate some Mo–Mo interaction and this could possibly be by way of the bridging sulphur atom.

In the reaction of WCl_3O with py[4] two analogous complexes (WCl_3O,2py and WCl_3O,py) were also obtained, the 1 : 2 adduct being a six-co-ordinate monomer and the 1 : 1 adduct an oxygen-bridged polymer that shows magnetic interaction.[4]

(ii) $MoCl_3S$,bme *and* $MoCl_3S$,2diox.—The i.r. spectra of both complexes contain bands associated with ν(Mo=S) and that of the diox complex shows both modified and unmodified COC stretching frequencies,

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showing the ligand to be unidentate.[4,11] The diox complex is monomeric in benzene solution and is clearly six-co-ordinate. The bme complex is also likely to be a monomer with a chelating ligand molecule. Thus the room-temperature magnetic moment of 1·68 B.M. rules out Mo–Mo interactions, and the i.r. spectrum shows the ligand to be in the *gauche* chelating form.[12]

(iii) $MoCl_3S,3py$ *and* $[Hpy][MoCl_4S,py]$.—The direct reaction of $MoCl_3S$ with py gives $MoCl_3S,3py$ as product, whereas $MoCl_3S,2MeCN$ reacts with py to give a product with analysis corresponding to the overall composition $MoCl_4S,2py$. The complex $MoCl_3S,3py$ appears to be six-co-ordinate $MoCl_3S,2py$ with the third molecule of py in the lattice; an analogous situation has been reported for $TiCl_3,4py$.[13] The i.r. spectrum shows the presence of both co-ordinated and unco-ordinated py molecules,[14] but no bands attributable to Hpy^+. When the complex was dissolved in benzene, molecular-weight measurements indicated dissociation, but conductivity measurements on methyl cyanide solutions showed the species to be non-conducting. $MoCl_4S,2py$, on the other hand, appears to be a pyridinium salt, $[Hpy][MoCl_4S,py]$, since it behaves as a 1 : 1 electrolyte in methyl cyanide solution [15] and its i.r. spectrum shows both the pyridinium cation and co-ordinated py to be present. The Hpy^+ proton presumably comes from one of the excess of pyridine molecules.[16]

(iv) $MoCl_2S,phen$.—Oxidation-state titrations show molybdenum to be present in the quadrivalent state in this complex; the magnetic moment (1·99 B.M.) is well below the spin-only value but very similar to that of $[MoBr_4(pdma)_2]$ [pdma = *o*-phenylenebis(dimethylarsine)].[17] The complex behaves as a non-electrolyte in methyl cyanide solution, and we suggest that it may contain six-co-ordinate molybdenum through bridging chlorine atoms. Thus the i.r. spectrum shows a Mo=S bond to be present, which rules out Mo–S–Mo bridging, and the complex low-frequency spectrum is consistent with both terminal and bridging Mo–Cl bonds being present; the usual bands of co-ordinated phen are found but there is no evidence for a protonated cation.

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