Studies of Molybdenum and Tungsten Thiolates

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The i.r. and electronic spectra and magnetic properties of a range of Group VIB metal thiolates, $M(SR)_3$ [M = Mo or W; R = Me, Et, Bu, or Ph] are reported. It is concluded that these compounds probably have polymeric chain structures with metal–metal interaction occurring between adjacent octahedra.

IN previous papers,[1,2] we reported the existence of a series of polymeric chromium(III) alkoxides[1] and thiolates,[2] with the latter being the more stable to hydrolysis and exchange reactions. With the exception of molybdenum(III) tris(benzenethiolate),[3] no simple alkoxides or thiolates have been reported for the heavier members of Group VIB.

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[1] D. A. Brown, D. Cunningham, and W. K. Glass, *J. Chem. Soc. (A)*, 1968, 1563.

[2] D. A. Brown, W. K. Glass, and B. Kumar, *J. Chem. Soc. (A)*, 1969, 1510.

[3] R. N. Jowitt and P. C. H. Mitchell, *Inorg. Nuclear Chem. Letters*, 1968, 40.

Most transition metal thiolates reported to date are apparently polymeric, ranging from hexameric Ni(SEt)$_2$ [4] and its palladium analogue, which probably has a similar structure,[5] to the more highly polymeric thiolates such as those of copper(II) [6] and chromium(III).[2] In many of these highly polymeric compounds, carbon and hydrogen analyses are often found to be low,[1,2] probably due to incomplete decomposition or combustion but metal analyses are always reproducible and close to theoretical. Similar difficulties arise in the molybdenum (and tungsten) thiolates reported in this paper.

Direct *X*-ray and supporting spectroscopic evidence was obtained previously for polymeric layer lattice structures for both chromium(III) alkoxides and thiolates with essentially octahedral co-ordination about the chromium atoms. In the case of Cr(OMe)$_3$ we suggested a layer-type lattice with chromium atoms occupying two thirds of the octahedral sites between alternate layers of alkoxide groups which is very similar to the structure of CrCl$_3$.[7] Although we were unable to obtain good *X*-ray photographs for the molybdenum (and tungsten) thiolates the spectroscopic and magnetic evidence presented below shows a close similarity with that for the analogous halides suggesting again similar polymeric structures for both series involving approximately octahedral co-ordination, but with much stronger metal–metal interaction compared to the chromium(III) series. This similarity of spectroscopic and structural properties suggests a general analogy between thiolate (and alkoxide) groups and the halogens such that the former may be regarded as pseudohalogens.

TABLE 1

Compound	Calculated (%) C	H	S	Metal	Found C	H	S	Metal	Method [a]
Mo(SMe)$_3$	15·2	3·8	40·5	40·5	14·7	2·9	28·1	40·3	(a)
					15·8	2·95	27·9	40·5	(b)
Mo(SEt)$_3$	25·8	5·4	34·4	34·4	19·8	4·0	31·8	34·2	(a)
					22·4	4·7	22·9	34·3	(b)
					18·55	3·95	34·2	34·2	(d)
Mo(SBu)$_3$	39·7	7·45	26·45	26·45	36·2	7·3	21·65	25·95	(d)
Mo(SC$_5$H$_{11}$)$_3$	44·45	8·15	23·7	23·7	38·1	6·35	15·5	23·55	(c)
Mo(SPh)$_3$	51·1	3·6	22·7	22·7	49·2	3·6	21·0	22·5	(b)
					47·2	3·7	21·7	22·3	(a)
					47·55	3·9	15·8	22·0	(c)
Mo(SClPh)$_3$ [b]	41·05	2·3	18·2	18·2	39·3	2·15	19·1	17·9	(d)
Mo(SBrPh)$_3$ [c]	32·75	1·8	14·55	14·55	29·45	2·1	13·9	14·1	(c)
W(SMe)$_3$	11·15	2·9	29·0	56·95	9·07	2·6	20·8	55·6	(b)
W(π-C$_6$H$_5$Me)(CO)$_2$SMe	31·7	2·9	8·45	48·6	30·15	2·7		48·1	

[a] See text for methods of preparation (a)—(d). [b] Chlorine analysis: Found: 18·4; Calc. 20·25%. [c] Bromine analysis: Found: 27·5; Calc. 36·4%.

Four methods of preparation were used for Mo(SR)$_3$ and W(SR)$_3$, all involving oxidative decarbonylation of metal carbonyls and related complexes: (a) reaction of an (tricarbonyl)arenemetal with a dialkyl or diaryl disulphide; (b) reaction of the hexacarbonylmetal with a dialkyl or diaryl disulphide; (c) reaction of the hexacarbonylmetal with the thiol or thiophenol; (d) reaction of the (tricarbonyl)arenemetal with the thiol or thiophenol. In general, methods (a) and (b) gave products with the best analyses. In most of the reactions, black-yellow coloured solutions developed and, in some cases, even when the solid thiolate was removed, a black-yellow carbonyl-containing solution remained; however, all attempts to isolate products from these solutions gave only unstable oils. The molybdenum(III) thiolates obtained ate dark red-brown or black while the tungsten(III) thiolates are brown-black in colour; they are insoluble in normal organic solvents and possess offensive odours characteristic of the parent disulphide or thiol. All the thiolates are hydrolytically stable to both water and dilute acids and thermally stable up to 300 °C. Thus the Mo^{III} and W^{III} thiolates show very similar properties to those of the Cr^{III} thiolates, again suggesting polymeric structures. Analytical results for this series are given in Table 1. In all cases, metal analyses are excellent but carbon analyses range from 0·60 to 3·3% below theoretical with the discrepancy increasing as the size of the alkyl group increases. This effect has been observed before and is probably due to incomplete decomposition. In the case of Mo(SPh)$_3$, a thermal gravimetric analysis of its combustion in air showed that even at 860 °C about 2% of the sample was unreacted. The problem appears to be much worse in the case of the tungsten compounds so we have only included the lowest member of this series in the Table.

Electronic Spectra.—The reflectance spectra of powder samples of the molybdenum and tungsten thiolates measured between 30 000 cm^{-1} and 10 000 cm^{-1} are given in Table 2, together with the Δ values; for comparison, the previously reported spectra of related polymeric and simple octahedral compounds are also given. In the case of MoCl$_3$ in which the molybdenum atoms are known to be approximately octahedrally

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[4] P. Woodward, L. F. Dahl, E. W. Abel, and B. C. Crosse, *J. Amer. Chem. Soc.*, 1965, **87**, 5251.

[5] R. G. Hayter and F. S. Humiec, *J. Inorg. Nuclear Chem.*, 1963, **26**, 807.

[6] D. C. Bradley and C. H. Marsh, *Chem. and Ind.*, 1967, 361.

[7] N. Wooster, *Z. Krist.*, 1930, **74**, 363.

co-ordinated,[8] the bands in the region 12 000—14 000 cm^{-1} were assigned to quartet–doublet transitions ($^2E_{2g}$, $^2T_{1g} \longleftarrow {}^4A_{2g}$) occurring within the t_{2g} subshell, whilst the band at *ca.* 19 000 cm^{-1} was assigned to the $^4T_{2g} \longleftarrow {}^4A_{2g}$ transition (frequency ν_1) which is equal to the ligand field parameter (10 *Dq*). We assign the bands *ca.* 13 000 and 19 000 cm^{-1} observed in our [Mo(SR)$_3$] series similarly giving a Δ value for Mo(SMe)$_3$ of 19 750 cm^{-1} compared with our previously reported value of 16 500 cm^{-1} for Cr(SMe)$_3$;[2] this increase in Δ value is normal between first and second row transition elements.[9] For a d^3 ion in an octahedral field, additional bands should be observed at higher energies corresponding to the transitions $^4T_{1g}(F) \longleftarrow {}^4A_{2g}$ and $^4T_{1g}(P) \longleftarrow {}^4A_{2g}$ (frequencies ν_2 and ν_3 respectively). Allowing for interaction between the two $^4T_{1g}$ states, it is possible in principle to calculate all the above transition energies;[10] however, for most of the polymeric compounds reported in Table 2, *e.g.* CrCl$_3$, MoCl$_3$, Cr(SMe)$_3$ the frequency ν_3 is not observed (and sometimes ν_2 is also missing) and so calculations of the nephelauxetic ratio are not possible.

TABLE 2

U.v.–vis. and Δ value data/cm^{-1} of some chromium, molybdenum, and tungsten compounds

Compound	$\left.\begin{matrix}2T_{2g}\\ ^2E_g\end{matrix}\right\} \longleftarrow 4A_{2g}$	$4T_{2g} \longleftarrow 4A_{2g}$ (ν_1)	$4T_{1g}(F) \longleftarrow 4A_{2g}$ (ν_2)	$4T_{1g}(P) \longleftarrow 4A_{2g}$ (ν_3)	Δ
CrCl$_3$	13 150	13 700	18 900		13 700
CrCl$_6{}^{3-}$		13 180	18 700		13 180
Cr(H$_2$O)$_6{}^{3+}$	15 000	17 400	24 600	37 800	17 400
Cr(OMe)$_3$		17 000	24 200		17 000
Cr(SMe)$_3$		16 667	25 000		16 667
MoCl$_3$		19 300			19 300
MoCl$_6{}^{3-}$	9 650	19 200	24 000		19 200
Mo(SMe)$_3$	13 500	19 750	30 350	35 600	19 750
Mo(SPh)$_3$	14 700	21 100	29 300	37 600	21 100
W(SMe)$_3$	13 000	30 500	35 150		30 500

In the case of the Cr^{III} compounds the Δ values lie in the sequence: Δ(OMe) ~ Δ(H$_2$O) > Δ(SMe) > Δ(Cl); whereas for Mo^{III}: Δ(SMe) ~ Δ(Cl). The sequence of Δ values for the Cr^{III} compounds is in agreement with previous series[9] and the higher value for the thiolate group compared to chloride agrees with some recent studies of pseudohalide complexes of transition metals[11] including the benzenethiolate group. A number of opposing factors such as (a) relative electronegativities of the donor atom, (b) M $\longrightarrow$ L π bonding (d_π-p_π or d_π-d_π) and (c) L $\longrightarrow$ M bonding (p_π-d_π) can influence Δ. For Cr^{III}, it appears that factors (a) and (c) outweigh (b) and it is noteworthy that the importance of L $\longrightarrow$ M π-bonding in first-row transition metal alkoxides has already been suggested.[12] From the more limited data for Mo^{III}, it appears that factor (b) becomes important and causes the Mo–S bond to become relatively stronger and more covalent compared to the Mo–Cl bond than in the comparable Cr^{III} series.

Magnetic Properties.—The room temperature magnetic moments are given in Table 3, together with those of the corresponding molybdenum and tungsten trihalides. In all cases the moments (μ_{eff}) lie in the range 0·81—1·53 B.M. and again where comparison is possible with previous results, as in the case of Mo(SPh)$_3$, agreement is good. These moments are all less than the theoretical moment for one unpaired electron (1·73 B.M.) and much lower than the theoretical spin-only moment of 3·88 B.M. for a d^3 ion M^{III}. Even allowing for the effect of spin-orbit coupling, the reduction is very large and suggests strong interaction between the molybdenum centres. It is interesting to note that for both Mo(SMe)$_3$ and MoCl$_3$[8] the susceptibility increases with decreasing temperature in typical antiferromagnetic manner. Application of the Curie–Weiss law and extrapolation of $1/\chi'_M$ to zero for Mo(SMe)$_3$ gives θ = 220 K and this θ value provides a corrected room-temperature moment of 0·79 B.M. A correction of this type with such a large θ value is of little theoretical significance[13] but it is important to note that unlike the previous case of Cr(SMe)$_3$, it is not possible to correct the magnetic moment to even approach the theoretical value for Mo^{III} of 3·88 B.M. The similar electronic spectra and magnetic properties of Mo(SMe)$_3$ and MoCl$_3$ suggests a similar type of structure for both. The latter compound is known to exist as a chain polymer with each

TABLE 3

Magnetic susceptibilities and magnetic moments of some molybdenum and tungsten compounds at 293 K

Compound	Magnetic susceptibility $\chi'_g \times 10^6$ c.g.s.	Magnetic moment μ_{eff} (θ = 0)
Mo(SMe)$_3$	0·33	0·81
Mo(SBu)$_3$	0·44	0·91
Mo(SC$_5$H$_{11}$)$_3$	0·79	1·17
Mo(SPh)$_3$	0·77	1·10
Mo(SClPh)$_3$	1·19	1·53
W(SMe)$_3$	0·79	0·90
MoI$_3$	0·67	0·49
MoBr$_3$	1·24	1·11
WBr$_3$	0·88	0·94

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[8] J. Lewis, D. J. Machin, R. S. Nyholm, P. Pauling, and P. W. Smith, *Chem. and Ind.*, 1960, 259.

[9] A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, 1968.

[10] E. König, *Structure and Bonding*, 1971, **9**, 175.

[11] B. R. Hollebone and R. S. Nyholm, *J. Chem. Soc.* (*A*), 1971, 332.

[12] D. C. Bradley, *Progr. Inorg. Chem.*, 1960, **2**, 303.

[13] B. N. Figgis and J. Lewis, 'Modern Co-ordination Chemistry,' Interscience, New York, 1960.

Mo^{3+} ion being surrounded by distorted octahedra which share faces such that adjacent Mo^{3+} ions are only 2·77 Å apart.[14] The fact that the corrected room temperature magnetic moment of $Mo(SMe)_3$ remains so low is in accord with the above type of structure in which quite strong Mo–Mo interaction can occur; thus in contrast to $Cr(SMe)_3$, the reduction in moment of the molybdenum compounds arises not only from superexchange *via* bridging thiolate groups but also from direct overlap of molybdenum orbitals which, even in the absence of structural differences in the parent compounds, will have a greater radial extension than those of chromium.

Infrared Spectral Studies.—The features normally expected of methyl compounds are observed in the i.r. spectra of $Mo(SMe)_3$ and $W(SMe)_3$ (Table 4). A broad band in the 650—750 cm^{-1} region was assigned to a metal–sulphur–carbon stretching mode. The spectra are very similar to $Cr(SMe)_3$.

The u.v. and visible spectra of molybdenum and tungsten thiolates suggests that the metal ion is surrounded octahedrally by thiolate ligands, albeit with some distortion. It was decided to analyse and assign the skeletal modes on this basis, the thiolate ions being regarded as point masses. Six fundamentals would be expected: ν_1, ν_2, and ν_5 being Raman-active, ν_3 and ν_4 i.r.-active, and ν_6 forbidden. It was found impossible to record the Raman spectra of these compounds. In the three-constant Urey–Bradley force field, *K*, *H*, and *F* represent the force constants (units of 10^5 dyn cm^{-1}) for bond stretching, angle deformation, and interaction between non-bonded atoms respectively: ν_3 and ν_4 were assigned here by analogy [1,2] and used to evaluate *K* and *F*, *H* being assumed as 0·0 mdyn $Å^{-1}$.

TABLE 4

Infrared spectra/cm^{-1} of $Mo(SMe)_3$ and $W(SMe)_3$

$Mo(SMe)_3$ observed	Assignment	$W(SMe)_3$ observed
194	ν_4	198
450	ν_3	450
290		320
275sh		
320	$\nu_5 + \nu_6$	390
735	Metal–S–C stretching	700
945	CH_3 rocking vibration	945
1295	CH_3 symmetrical bending	1305
1410	CH_3 asymmetrical bending	1415
2902	CH_3 symmetrical stretching	2915
2960	CH_3 asymmetrical stretching	2975

For $W(SMe)_3$, force constants $K = 3·10$, $H = 0·0$, $F = 0·66$ (all values in mdyn $Å^{-1}$) predicted bands at 455, 358, 452, 197, 229, and 162 cm^{-1} respectively for ν_1, ν_2, ν_3, ν_4, ν_5, and ν_6. ν_3 and ν_4 were observed at 450 and 198 cm^{-1} respectively, and the observed band at 390 cm^{-1} could be assigned to $\nu_5 + \nu_6$ on this basis.

With $Mo(SMe)_3$, force constants of $K = 2·58$, $H = 0·0$, and $F = 0·50$ mdyn $Å^{-1}$ predicted the six fundamentals ν_1—ν_6 at 406, 325, 454, 194, 199, and 141 cm^{-1} respectively. Observed bands at 450 and 194 cm^{-1} were assigned to ν_3 and ν_4 respectively, and at 320 cm^{-1} to $\nu_5 + \nu_6$. On this analysis, ν_3 is essentially a pure metal–sulphur stretching mode, and ν_4 a sulphur–molybdenum–sulphur bending mode. In both these cases, as expected, the *K* value is higher than that obtained for $Cr(SMe)_3$ which is in agreement with the Δ values obtained from the electronic spectra of $Mo(SMe)_3$ and $Cr(SMe)_3$.

CONCLUSION

Although we were not able to obtain direct *X*-ray structural evidence, the reported electronic spectra, magnetic properties, and vibrational analysis of the molybdenum thiolates are consistent with polymeric chain structure with local octahedral co-ordination about the metal atoms and definite metal–metal interaction between adjacent octahedra. In a previous paper we suggested a tentative mechanism for the oxidative decarbonylation reaction used in the preparation of these compounds involving a stepwise displacement of the carbonyl groups from the initial carbonyl complex. It is noteworthy that the last compound reported in Table 1 supports this view since it was formed by reaction between (π-toluene)$W(CO)_3$ and dimethyl disulphide. This stable product of empirical formula, [(toluene)$W(CO)_2(SMe)$], is probably a dimer since it is diamagnetic. In other words, initial displacement of one carbonyl group occurs probably followed by dimerization thereby precluding the formation of a stable thiolate; however, the frequent observation of carbonyl-containing solutions during the above preparations of the polymeric thiolates suggests a general mechanism involving the above type of intermediate.

EXPERIMENTAL

In the measurement of i.r. spectra, Nujol and Fluorolube mulls and KBr, CsBr, and KI discs were used in conjunction with a Perkin-Elmer 457 spectrometer and a Grubb-Parsons interferometer. All values are quoted to ±2 cm^{-1}, except for the far-i.r. (±4 cm^{-1}). The u.v. spectra of powders were obtained with a Unicam SP 500 spectrophotometer equipped with a diffuse reflectance attachment. We thank Dr. S. M. Nelson for his co-operation: the susceptibilities of the compounds were measured at The Queen's University of Belfast. The Microanalytical Laboratory of this Department carried out C, H, N, and S analyses. Molybdenum and tungsten were analysed using standard gravimetric methods with oxine. Molybdenum was also determined on a Hilger and Watts Atomspek atomic absorption spectrometer. Numerical calculations were run on the I.B.M. 360/50 computer of University College, Dublin.

Preparation of Molybdenum and Tungsten Thiolates.—Two typical preparations are recorded below.

Molybdenum(III) *Tris*(*methanethiolate*).—(a) *Reaction of* (*arene*)*tricarbonylmetal with* Me_2S_2. $C_7H_8Mo(CO)_3$ (2·7 g) were refluxed under nitrogen using a magnetic hot plate

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[14] H. G. Schnering and H. Woehrle, *Naturwiss.*, 1963, **50**, 91.

with Me_2S_2 (25 ml, dry). The solution turned from a wine-red tint to a black colour within 30 min. Fine black powdery crystals were deposited. After 3 h, the reaction mixture was digested with sodium-dried ether, and the solution filtered through a G4 sintered glass crucible. The black residue was washed three times with sodium-dried ether, refluxed with carbon disulphide (50 ml, dry) for 1 h, and filtered. The residue was dried under vacuum in a desiccator followed by drying in a pistol at 100 °C and 0·5 mmHg pressure. Yield of $Mo(SMe)_3$: 2·5 g.

(b) *Reaction of the hexacarbonylmetal with* Me_2S_2. The mixture in benzene quickly turned yellow, and finally black. The product was isolated and purified as above. Yield of $Mo(SMe)_3$: 2·0 g; based on $Mo(CO)_6$, 2·7 g.

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