The Chemistry of Molybdenum and Tungsten. Part XIII [1]. Molybdenum(V) Complexes of Dithiocarbamates and Dithioethers

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Oxotrichloromolybdenum(V) reacts with dithiocarbamates, R_2dtc^- (R_2 = Me_2, Et_2, $[CH_2]_4$) in acetonitrile at room temperature with cleavage of the terminal molybdenum–oxygen bond to yield [Mo-(R_2dtc)$_4$]$^+$, isolated as the chloride or tetraphenylborate salts; infrared spectra indicate bidentate coordination by the ligands, and these complexes appear to have dodecahedral geometry. From this same reaction can be isolated the dimeric [$Mo_2O_4(R_2dtc)_2$] species which contain a double Mo–O–Mo bridges as well as terminal Mo=O bonds, and also the [Mo_2O_3-(Et_2dtc)] complex containing a single Mo–O–Mo bridge and two terminal Mo=O linkages. With a series of dithioethers oxotrichloromolybdenum(V) yields [MoO(ligand)Cl$_3$], but the ability to complex depends critically on the structure of the dithioether. The structures of these complexes have been assigned with the aid of vibrational, electronic and electron paramagnetic resonance spectroscopy.

Introduction

From our limited, but growing, knowledge of metals in biological systems it is apparent that metals present in enzymes in their different oxidation states behave much as expected from a knowledge of their binding centres in simple model-ligand complexes, and so investigation of simple compounds of molybdenum should lead to a fair approximation of molybdenum binding in proteins. Protein can bind to a transition metal ion through oxygen, nitrogen or sulphur donors. In general, the higher oxidation states of molybdenum are more likely to bind to oxygen while the lower ones are more likely to bind to nitrogen, sulphur being intermediate. A driving force for this is the charge neutralization effect which occurs with charged oxygen and sulphur donors in contrast to the neutral nitrogen donors. The known coordination chemistry of molybdenum suggest it to have a particular affinity for sulphur, forming stable compounds. There is widespread belief that molybdenum is bound through sulphur in enzymes. Indirect evidence for this has come from epr studies of

monomeric molybdenum enzymes such as xanthine oxidase and of model complexes by Bray and Meriwether [2], Spence [3] and Dennard and Williams [4]. The sulphur could be present as cysteine sulphide and/or persulphide or inorganic sulphur.

As part of the study of the chemistry of high valent molybdenum we decided to investigate the reactions of molybdenum(V) with both charged (–S$^-$) and uncharged ($>$S) thio-donors.

Although reactions of MoOCl$_3$ with neutral ligands to give [MoOCl$_3$(LL$'$)] and [MoOCl$_3$L$_2$] are well known, reactions with anionic ligands removing one or more chlorines and giving monomeric molybdenum species are rare. Under normal conditions dimerisation occurs via oxygen or dioxygen bridges to give complexes such as [Mo$_2$O$_3$(LL$'$)$_4$] (where LL$'$ = monoanionic bidentate ligand). In fact a large number of this type of complex have been prepared with dithiocarbamate ligands [5–7]. The other types of dithiocarbamate complexes which have been extensively studied are the oxomolybdenum(VI) complexes [MoO$_2$(LL$'$)$_2$] [6] and the five-coordinate [MoO(LL$'$)$_2$] [8].

In this study molybdenum oxytrichloride was reacted with a dithiocarbamate salt under controlled anaerobic conditions in an attempt to prepare monomeric oxomolybdenum(V) compounds of the type:

(I)
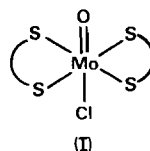
Once this step was achieved it was hoped to reduce (I) to the oxomolybdenum(IV) compound, removing the anionic chloride ligand while leaving the dithiocarbamate ligands intact. This could be done by reduction with zinc dust in tetrahydrofuran at reduced temperature giving [MoO(R$_2$dtc)$_2$(thf)]. A compound such as this could be very interesting as a model for molybdenum enzymes in that it contains a

TABLE I. Analytical and Physical Data of Dithiocarbamate Complexes.

Compound	Colour	μ_{eff}[a] B.M.	Analysis (%)[b]				Λ_M[c]
			C	H	N	S	
$[Mo(S_2CNMe_2)]Cl$	Red–brown	1.69	24.6(23.6)	4.1(3.9)	8.9(9.2)	41.1(41.9)	78
$[Mo(S_2CNMe_2)_4]BPh_4$	Red–brown	1.70	47.9(48.3)	4.9(4.9)	6.2(6.3)	27.6(28.6)	65
$[Mo(S_2CNEt_2)_4]Cl$	Red–brown	1.68	32.6(33.1)	6.5(5.5)	7.8(7.7)	35.0(35.3)	75
$[Mo(S_2CNEt_2)_4]BPh_4$	Red–brown	1.69	51.8(52.1)	5.8(5.9)	5.3(5.5)	25.3(25.3)	68
$[Mo(S_2CN\bigcirc)_4BPh_4$	Red–brown	1.70	52.3(52.8)	5.0(5.2)	5.3(5.6)	26.1(25.6)	71
$[Mo_2O_4(S_2CNMe_2)_2]$	Yellow	(d)	14.3(14.5)	2.4(2.4)	5.9(5.7)	26.3(25.7)	–
$[Mo_2O_4(S_2CNEt_2)_2]$	Yellow	(d)	21.3(21.7)	3.9(3.6)	5.4(5.1)	22.4(23.2)	–
$[Mo_2O_4(S_2CN\bigcirc)_2]$	Yellow	(d)	22.9(21.9)	3.0(2.9)	5.3(5.1)	22.7(23.3)	–
$[Mo_2O_3(S_2CNEt_2)_4]$	Purple	(d)	28.5(28.8)	5.3(4.8)	6.2(6.7)	31.2(30.8)	–

[a] Room temp. [b] Calculated values in parenthesis. [c] In 10^{-3} mol dm^{-3} nitromethane solution, in cm^2 Ω^{-1} mol^{-1}. [d] Diamagnetic.

monomeric oxomolybdenum(IV) ion which is coordinated to O and S. Also it has a neutral ligand (thf) which under suitable circumstances could be substituted bringing an enzyme substrate into direct contact with the molybdenum(IV) ion. It is tempting to suggest that in such a system electron transfer might occur giving Mo(V) and a reduced substrate.

Results and Discussion

Reaction of Oxomolybdenum(V) with Dialkyldithiocarbamate

Oxotrichloromolybdenum(V) and diethylammonium diethlydithiocarbamate react in acetonitrile at room temperature to form a purple solid which quickly turns light brown in a dark brown solution. Two products are obtained from this reaction. On filtering a yellow–brown solid residue is left and the dark brown filtrate produces a dark red–brown crystalline solid. The red–brown crystals, on the basis of analytical and spectroscopic evidence to be discussed later, are considered to be the eight-coordinate, tetrakis(diethyldithiocarbamato)molybdenum(V) chloride, $[Mo(Et_2dtc)_4]Cl$. Addition of sodium tetraphenylborate to an acetonitrile solution of $[Mo(Et_2dtc)_4]Cl$ precipitated the tetraphenylborate salt, $[Mo(Et_2dtc)_4]BPh_4$ in quantitative yield. The reaction was successfully repeated using the dimethyl- and tetramethylene-dithiocarbamates giving both the chloride and tetraphenylborate salts. We have published a preliminary report of this work [9].

$[Mo(R_2dtc)_4]X$

The compounds $[Mo(R_2dtc)_4]X$ ($R_2 = Me_2$, Et_2, $[CH_2]_4$; $X = Cl$, BPh_4) are all dark red–brown, crystalline solids (Table I). Although the reaction itself is very air and moisture sensitive the products are quite stable to the atmosphere. They are soluble in dichloromethane, chloroform and acetone but insoluble in benzene, toluene or diethylether. The conduc-

tivities of nitrobenzene solutions of the complexes (*ca.* $10^{-3}M$) give values of Λ_M in the range 65–80 cm^2 Ω^{-1} mol^{-1} indicating that they behave as 1:1 electrolytes in this solvent. The solids have magnetic moments in the range 1.68–1.72 BM at room temperature which implies that Mo(V) with one unpaired electron is present.

The series of eight-coordinate molybdenum(IV) analogues of these compounds were prepared, for comparison, by reacting $[MoCl_4(NCCH_3)_2]$ with the dithiocarbamate salt. Brown and Smith [10] have used this method to prepare the tetrakis(tetramethylenedithiocarbamato)molybdenum(IV) complex, $[Mo(Tmdtc)_4]$. These compounds are also dark red–brown crystalline solids but are diamagnetic and nonelectrolytes in solution.

The infrared spectra of the compounds have been obtained in the range 4000–200 cm^{-1} (Table II). The compounds do not show any intense bands in the 930–1000 cm^{-1} region which are characteristic of terminal Mo=O bonds, indicating their absence in these compounds. In the 200–400 cm^{-1} region there are no bands which can be assigned to metal–halogen stretching frequencies. The infrared spectra show bands which are characteristic of coordinated, bidentate dithiocarbamate ligands [10]. The spectra exhibit a strong single band in the region 1490–1525 cm^{-1} which can be assigned to the ν(CN) stretching frequency. This band lies intermediate in energy between the stretching frequencies of single C–N bonds (1250–1350 cm^{-1}) and double C=N bonds (1620–1650 cm^{-1}). This indicates that the CN bond has some double-bond character in the complexes. The resonance structures of dithiocarbamates can be represented as:
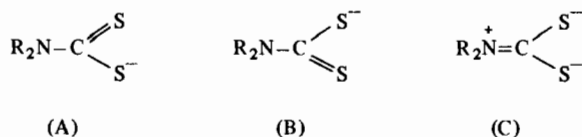
$$R_2N-C\begin{array}{c}\nearrow S \\ \searrow S^-\end{array} \qquad R_2N-C\begin{array}{c}\diagup S^- \\ \diagdown\diagdown S\end{array} \qquad R_2\overset{+}{N}=C\begin{array}{c}\diagup S^- \\ \searrow S^-\end{array}$$

(A)   (B)   (C)

TABLE II. Infrared Spectroscopic Data for Dithiocarbamate Complexes.

	$\nu(CN)$[a]	$\nu(NC_2)$	$\nu(CS_2)$	$\nu(Mo-O_t)$	$\nu(Mo-O_b)$
[Mo(S$_2$CNMe$_2$)$_4$]Cl	1510s	1210m	997m	–	–
[Mo(S$_2$CNMe$_2$)$_4$]BPh$_4$	1516s	1206m	1005m	–	–
[Mo(S$_2$CNEt$_2$)$_4$]Cl	1520s	1200m	1010m	–	–
[Mo(S$_2$CNEt$_2$)$_4$]BPh$_4$	1515m	1216m	1005w	–	–
[Mo(S$_2$CN⊃)$_4$]BPh$_4$	1505s	1201m	1000m	–	–
[Mo$_2$O$_4$(S$_2$CNMe$_2$)$_2$]	1520s	1197m	1002m	980s, 970m	755w, 475m
[Mo$_2$O$_4$(S$_2$CNEt$_2$)$_2$]	1518s	1202m	1010w	977s, 965m	750w, 480m
[Mo$_2$O$_4$(S$_2$CN⊃)$_2$]	1504s	1190m	1005m	980s, 970m	740w, 435m
[Mo$_2$O$_3$(S$_2$CNEt$_2$)$_4$]	1495m	1180m	997m	940s	760w, 450m

[a]Values given as cm^{-1}.
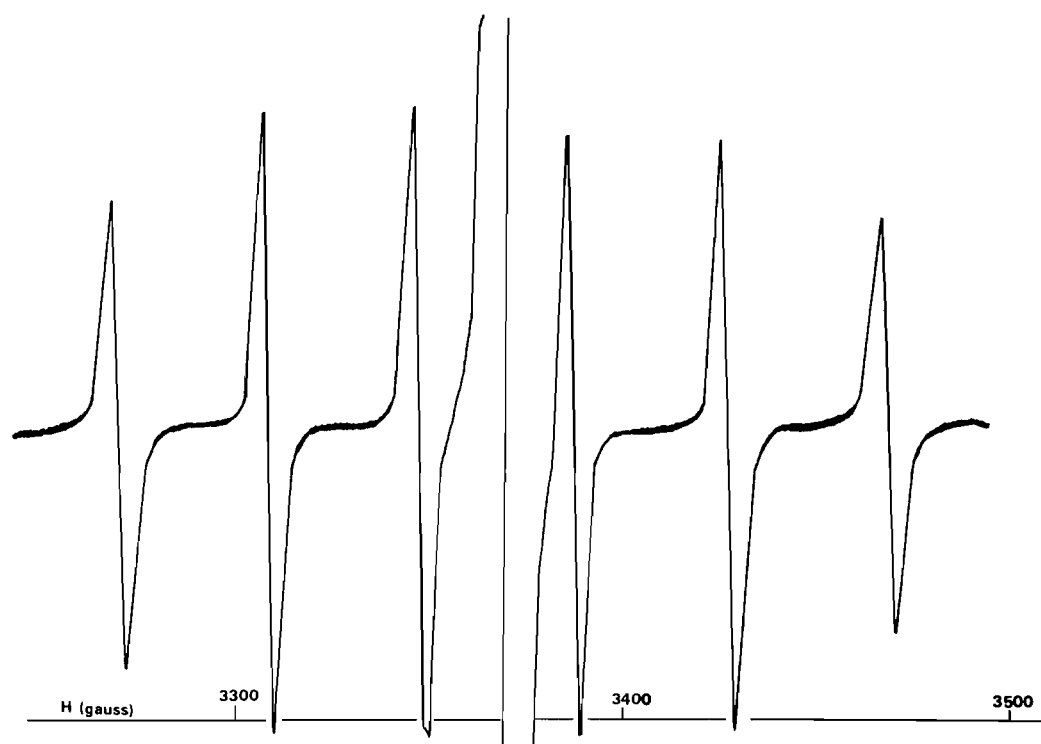

Figure 1. Epr spectrum of [Mo(Et$_2$dtc)$_4$] [BPh$_4$] in CH$_2$Cl$_2$ (293K).

Thus it seems that structure (C) contributes, to a considerable extent, to the structure of the dithiocarbamate ligands in these complexes, and this indicates bidentate coordination. Monodentate coordination would require a greater contribution from (A) or (B) and so result in lower $\nu(CN)$ frequencies. The band in the region 1160–1210 cm^{-1} can be assigned to the $\nu(NC_2)$ stretching frequency. The stretching frequency of the carbon–sulphur bonds can be found as a single band at *ca*. 1000 cm^{-1}. This, too, can be used to distinguish monodentate and bidentate coordination. With monodentate coordination splitting of the $\nu(CS_2)$ occurs to give a doublet with *ca*. 20 cm^{-1} spacing. The metal–sulphur stretching mode is found as a strong band at *ca*. 355

cm^{-1} in the molybdenum(V) complexes and 355 cm^{-1} in the molybdenum(IV) complexes. It can be seen that the $\nu(CN)$ stretching frequency is also sensitive to the oxidation state of the metal ion. On going from Mo(IV) to Mo(IV) the $\nu(CN)$ is increased by *ca*. 20 cm^{-1} indicating a greater C–N double bond character. The loss of an electron by the metal ion on oxidation results in a greater electron-withdrawing effect by the CS$_2$ group on the nitrogen lone pair electrons. Alternatively, any change in the R groups attached to the nitrogen, for example substituting electron withdrawing aryl groups for the electron releasing alkyl groups, should have the opposite effect on the C–N bond. This would result in weakening of the bond and a shift to lower energy of the $\nu(CN)$.

The e.p.r. spectra of the paramagnetic complexes in dichloromethane ($\sim 10^{-4} M$) at room temperature showed very symmetrical and sharp lines (Fig. 1). The isotropic spectra showed one strong line due to the 75% molybdenum without nuclear spin and, symmetrical about this, six satellite lines due to the 25%

molybdenum with nuclear spin of 5/2. All of the Mo(V) complexes gave the same isotropic g-value of 1.980 and isotropic hyperfine coupling constant, A_{iso}(Mo), of 35G indicating a great deal of structural similarity between the complexes. Comparison with complexes of oxygen and nitrogen donors shows a

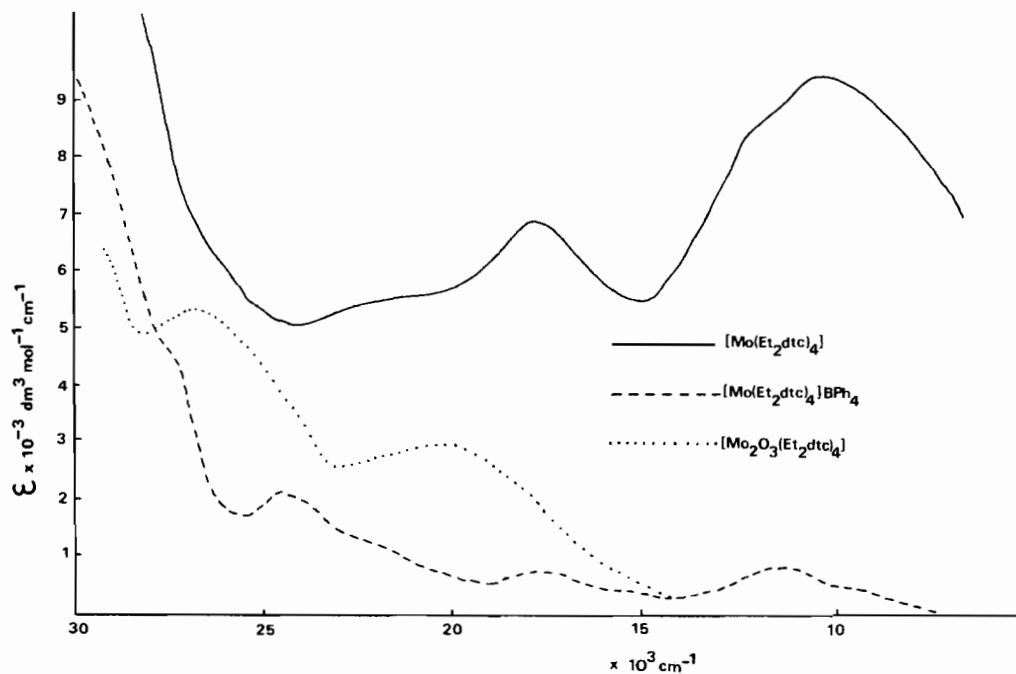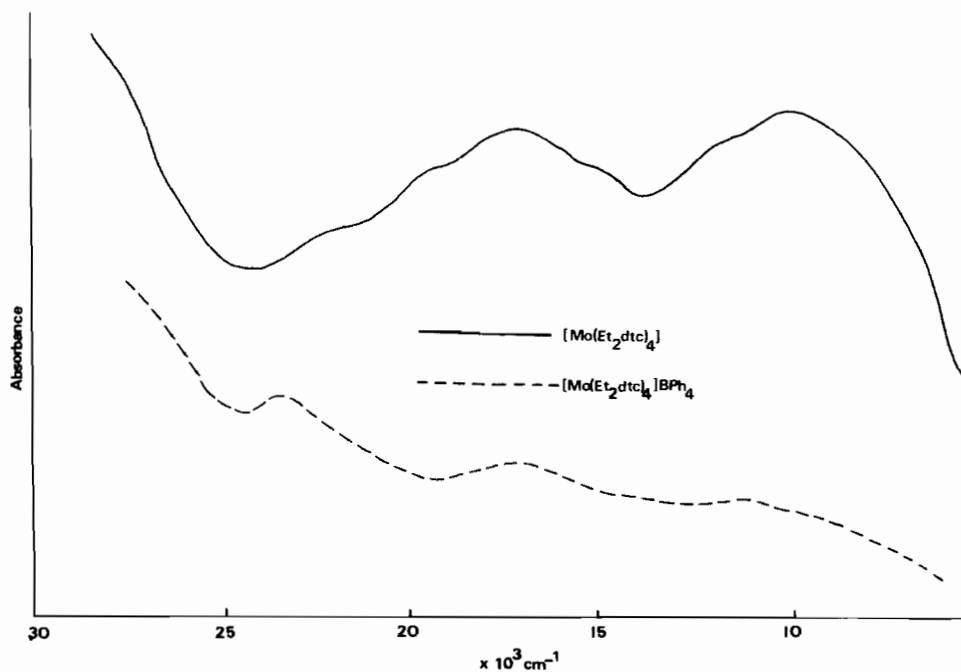

Figure 2. Solution electronic spectra.

Figure 3. Solid state electronic spectra.

higher g-value and lower A value. This is consistent with a greater amount of delocalisation of the unpaired electron from the metal ion which undoubtedly operates in these systems because of the ability of the empty orbitals on the sulphur to accept electrons. Thus the amount of coupling between the unpaired electron and the molybdenum nuclei is reduced and if sulphur had a nuclear spin we would expect to see ligand hyperfine coupling. The delocalisation gives an increase of the g-value towards the free-electron value (2.0023).

The electronic spectra of the complexes were measured in dichloromethane solution and in the solid state. The spectra of $[Mo(Et_2dtc)_4]BPh_4$ and $[Mo(Et_2dtc)_4]$ are shown in solution (Fig. 2) and in the solid state (Fig. 3). The molybdenum(IV) complex shows a number of bands in the 30–10 kK region. They are of high intensity and some are probably charge transfer transitions. The shoulders at 19.3 kK and 22.5 kK may be of d–d origin intensified by borrowing intensity from charge-transfer bands. The charge transfer bands could be due to internal ligand $\pi \rightarrow \pi^*$ transitions which are observed above 28 kK for dithiocarbamate complexes [12]. It is not clear whether the charge-transfer bonds below 28 kK are M $\rightarrow$ L or L $\rightarrow$ M; however the d–d transitions are obscured and this suggests efficient mixing of the metal and ligand orbitals. The molybdenum(V) complex show bonds of lower intensity with one of very low intensity at 24.6 kK which can be assigned to a d–d transition.

The well known eight-coordinate octacyanomolybdates [13] have been shown to be dodecahedral in structure and discussions of the bonding have generally assumed D_{2d} symmetry. An alternative structure for eight-coordination is the square anti-prism (D_{4d} symmetry). Both of these structures are obtained by distortions of the cube (Fig. 4). For a metal tetrakis chelate, in which the four identical ligands span equivalent polyhedral edges, there are three dodecahedral and two square-antiprismatic isomers possible [14]. Calculations carried out by Blight and Kepert [15] show that the potential energy minima corresponding to the stereoisomers are dependent on the normalized ligand bite "b". Energetically, there is little difference between the dodecahedral and antiprismatic structures although it is possible that the dodecahedral structure is slightly favoured by π-bonding involving the $d_{x^2-y^2}$ orbital. The e.p.r. suggests that this could be occurring in the molybdenum(V) complex enabling delocalisation into the sulphur orbitals. Dodecahedral geometry has been established for the closely related tetrakis(dithiobenzoate)molybdenum(IV) [16] and it is reasonable to assume the same basic geometry for those complexes. The geometry is presumably retained in solution since there are small differences between solid-state and solution electronic spectra.
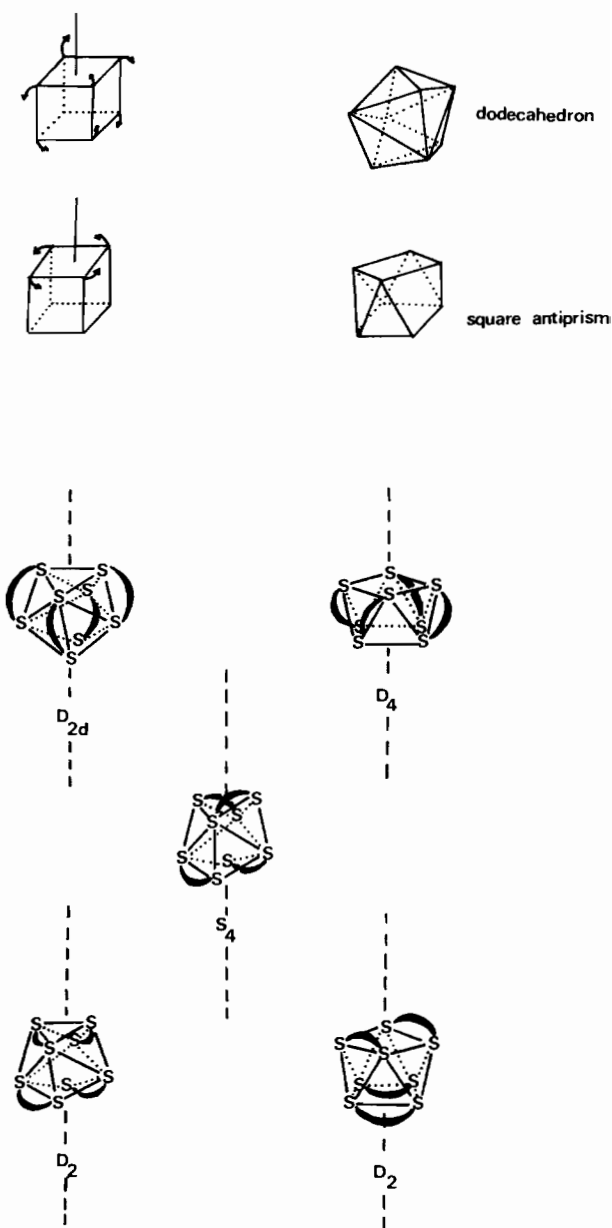

Figure 4. Structures for eight-coordination.

The reaction of oxotrichloromolybdenum with dithiocarbamates to give an eight-coordinate tetrakis-(dithiocarbamate) complex is suprising. Although carried out in mild conditions it is evident that all of the Mo–Cl bonds and, in particular, the Mo=O bond have been cleaved. This is a rare phenomenon with molybdenum, although all four Mo=O bonds in $[MoO_4]^{2-}$ have been replaced by dithiolene ligands [5]; the only analogous reaction in molybdenum(V) chemistry has been the replacement of oxygen by sulphur in some dimeric complexes to yield, for example, $[MoS(SR)(S_2CoEt)]$ [17]. While this work was in progress, Niewport [15] reported the isolation of the 8-coordinate $[Mo(Et_2dtc)_4]^+$ cation, from the

reaction of tetraethylthiuramdisulphide with a hot solution of tetrabutylammoniumpentachloromolybdate(0).

[$Mo_2O_4(S_2CNR_2)_2$]

The reaction of oxotricyloromolybdenum(V) with diethyldithiocarbamate also produced, as the major product, an orange–yellow solid. This was washed in water, followed by ethanol, and dried. The yellow solid was stable to air and moisture, diamagnetic and a non-electrolyte in nitromethane. The dimethyl- and tetramethylene-analogs were also isolated (Table I). The infrared spectra of the complexes showed a strong band at *ca.* 980 cm^{-1} and a weaker band at *ca.* 970 cm^{-1}. They can be assigned to the terminal ν(Mo=O) vibrations. The bands at *ca.* 480 and *ca.* 740 cm^{-1} can be assigned to the symmetric and antisymmetric vibrations of the Mo(μ-O)$_2$Mo bridge system [18]. The complexes also showed bands typical of bidentate coordinate dithiocarbamate ligands with ν(MoS) bands at ca. 370 cm^{-1}. The electronic spectra of the complexes were broad and poorly resolved. These complexes are the known μ-dioxobis[oxo-N,N-dialkyldithiocarbamatomolybdenum-(V)] complexes. They are dimers containing two five-coordinate molybdenum(V) ions linked by a double oxygen bridge.

[$Mo_2O_3(S_2CNEt_2)$]

The reaction of oxotrichloromolybdenum(V) with diethyldithiocarbamate initially gave a purple precipitate which quickly disappeared. An attempt was made to isolate this intermediate, and the reaction was carried out in an ice bath and filtered as soon as the purple solid formed. The purple compound was found to be air stable and diamagnetic. The infrared spectrum showed a strong band at 940 cm^{-1} assigned to terminal Mo=O stretch. Bands at 760 cm^{-1} and 450 cm^{-1} can be assigned to the anti-symmetric and symmetric stretching of the single Mo–O–Mo bridge. The ligand bands indicate a bidentate-coordinated dithiocarbamate ligand.

The electronic spectrum of the complex is similar in both the solid state and in dichloromethane solution. The band at 19.4 kK can be assigned to the $2B_2 \rightarrow 2B_1$ transition while the higher energy band at 26.4 kK is assignable to a sulphur–molybdenum charge transfer band. The compound is the μ-oxobis[oxobis(N,N-diethyldithiocarbamato)molybdenum-(V)].

[$Mo_2O_3(S_2CNEt_2)_4$]

The reaction of oxotrichloromolybdenum(V) with dialkyldithiocarbamate first produces the single oxo-bridged dimer of Mo(V) (Scheme 1).
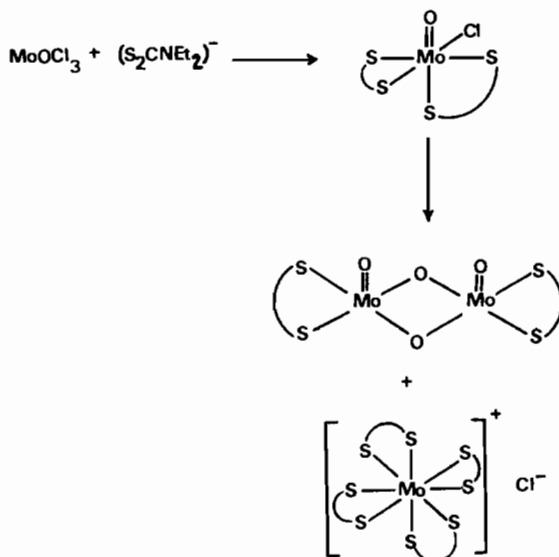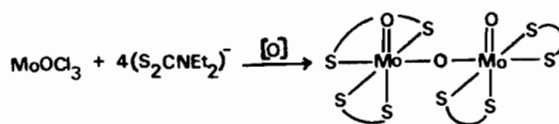
SCHEME I

A trace amount of oxygen is probably required for this. A second reaction may involve the substitution of one chloro ligand in MoOCl$_3$ by diethyldithiocarbamate to give the six-coordinate [MoOCl(S$_2$-CNEt$_2$)$_2$]. The next step involves oxygen abstraction from the six coordinate compound by the dimer with simultaneous substitution of each of the remaining chloro ligands by diethyldithiocarbamate.

Complexes with Dithioether Ligands

MoOCl$_3$ reacted with bidentate dithioether ligands in benzene to give green crystalline solids. The reactions were carried out in sealed tubes, at room temperature and over several weeks. Compounds were prepared containing ligands with both saturated and unsaturated C$_2$ backbones and a number of different alkyl substituents. No reaction occurred with the aryl-substituted ligands, PhS(CH$_2$)$_2$SPh and *cis*-PhSCH:CHSPh.

The products were extremely air-sensitive and decomposed rapidly to dark blue oils and liberating the ligand. They were insoluble in most solvents or reacted with strong donor solvents liberating the ligand. The complexes are paramagnetic having

TABLE III. Analytical and Physical Data of the Dithioether Complexes.

	Colour	μ_{eff}[a] B.M.	Analysis (%)[b]			
			C	H	S	Cl
$[MoOCl_3(MeSCH_2CH_2SMe)]$	Green	1.68	14.5(14.1)	3.0(2.9)	19.2(18.8)	31.6(31.2)
$[MoOCl_3(EtSCH_2CH_2SEt)]$	Green	1.57	19.5(19.5)	3.7(3.8)	16.9(17.4)	
$[MoOCl_3(^nPrSCH_2CH_2SPr^n)]$	Green	1.72	24.5(24.2)	4.8(4.5)	15.8(16.1)	
$[MoOCl_3(MeSCH:CHSMe)]$	Green	1.70	14.5(14.2)	2.9(2.4)	19.2(18.9)	
$[MoOCl_3(EtSCH:CHSEt)]$	Green	1.69	19.2(19.6)	3.1(3.3)	17.3(17.5)	

[a]Room temperature. [b]Calculated values in parentheses.

TABLE IV. Infrared and Electronic Spectral Data for Dithioether Complexes.

	$(Mo-O_t)$ cm^{-1}	$(Mo-S)$ cm^{-1}	$(Mo-Cl)$ cm^{-1}	E_{max}[a] solution kK
$MoOCl_3(MeSCH_2CH_2SMe)$	949s	360m	310vs, 260s	15.9(23), 13.1(13)
$MoOCl_3(EtSCH_2CH_2SEt)$	952s	365m	309vs, 255s	15.6(13), 13.3(14)
$MoCCl_3(^nPrSCH_2CH_2SPr^n)$	955vs	365m	315vs, 255s	15.8(11), 12.9(12)
$MoOCl_3(MeSCH:CHSMe)$	960s	360m	320vs, 261s	15.1(17), 13.1(12)
$MoOCl_3(EtSCH:CHSEt)$	968s	380m	312vs, 258s	15.2(21), 12.7(13)

[a]In benzene; absorption coefficients (ϵ/dm^3 mol^{-1} cm^{-1}) given in parentheses.
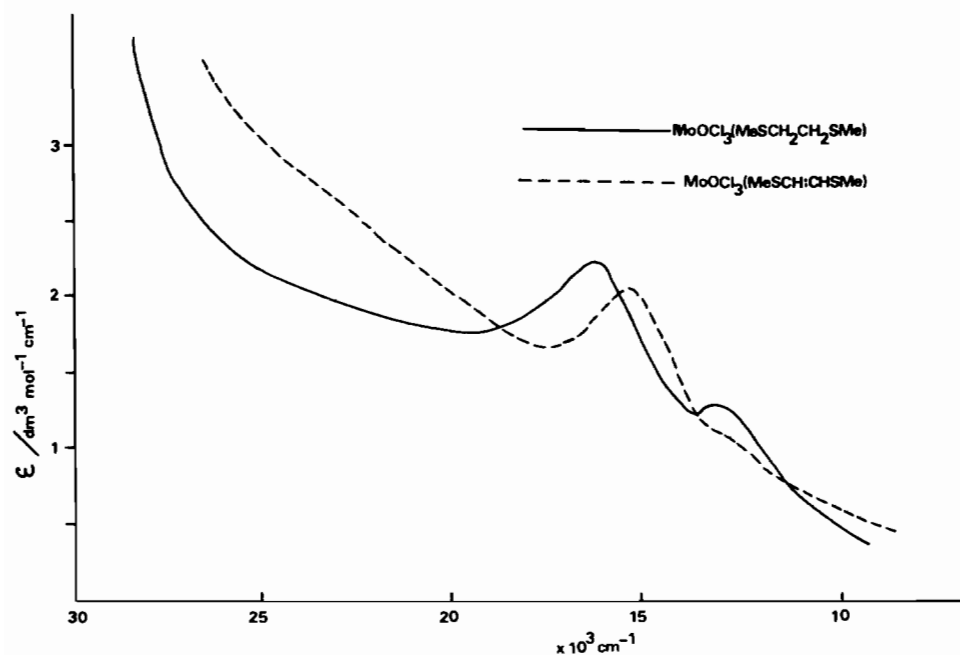

Fig. 5. Solution electronic spectra in benzene.

magnetic moments of *ca.* 1.70 B.M. indicating molybdenum(V) (Table III). It is surprising that a hard acid such as molybdenum(V) will form complexes with thioether ligands which are very soft bases (but see also ref. 16). If the reactions were attempted in donor solvents such as THF then no product was formed. Neither would the adduct $[MoOCl_3(thf)_2]$ react with dithioethers in benzene indicating a preference for the harder ether-oxygen donor. This would also explain why the extremely soft aryl-substituted ligands do not react.

The infrared spectra of the complexes (Table IV) all show a single strong band in the 940–970 cm^{-1} region which can be assigned to the $\nu(MoO)$ stretch of

the terminal molybdenum–oxygen bond. The position of this band is a little higher in energy than the corresponding diphosphine complexes [19] and this might be explained by the weaker bonding to the dithioether ligand. The ν(Mo–S) band is observed at *ca.* 365 cm^{-1}, two strong bands at *ca.* 315 cm^{-1} and 255 cm^{-1} can be assigned to the Mo–Cl stretching frequency.

The electronic spectra of the complexes were obtained in benzene solution (Table IV). The spectra are typical of monomeric oxomolybdenum(V) complexes (Fig. 5) with a low energy band at *ca.* 13 kK assigned to the $^2B_2 \rightarrow {}^2E$ transition and the band at *ca.* 15 kK assigned to the $^2B_2 \rightarrow {}^2B_1$ transition [20]. The spectral bands are not as intense as those found for other sulphur-donor complexes (*e.g.* the dithiocarbamates). This is because there are no charge-transfer bands in the region which the d–d bands can use to boost their intensity. The absence of charge transfer bands – present as sulphur → molybdenum in the dithiocarbamates – may add further support to the conclusion that the thioether donors are bonded only weakly to the molybdenum. The second transition is seen to be slightly sensitive to the nature of the dithioether ligand. On going from a saturated to an unsaturated backbone there is a slight change to lower energy.

The isotropic epr spectra of benzene solutions of the compounds showed line patterns typical of monomeric molybdenum(V) (Table V). The spectrum

TABLE V. EPR Parameters for dithioether Complexes[a].

Compound	g_{av}	A_{iso}(Mo)(G)
MoOCl$_3$(MeSCH$_2$CH$_2$SMe)	1.960	46
MoOCl$_3$(EtSCH$_2$CH$_2$SEt)	1.961	45
MoOCl$_3$(^{n}PrSCH$_2$CH$_2$SPr^n)	1.963	46
MoOCl$_3$(MeSCH:CHSMe)	1.959	44
MoOCl$_3$(EtSCH:CHSEt)	1.960	44

[a]In benzene solution *ca.* $10^{-4}M$.

of [MoOCl$_3$(MeSCH$_2$CH$_2$SMe)] is shown (Fig. 6), and is similar to those of the other compounds. The isotropic g-values, although larger than for compounds with O and N compounds, is smaller than for the dithiocarbamate complexes. This can be rationalised in terms of the weaker bonding situation with the dithioethers, thus reducing the delocalisation of the unpaired electron into sulphur orbitals. This would also mean a larger hyperfine coupling with the ^{95}Mo nuclei and this is reflected in the larger A_{iso}-(Mo) tensor. The compounds appear to be simple, monomeric octahedral complexes of molybdenum(V) with one of the following structures:

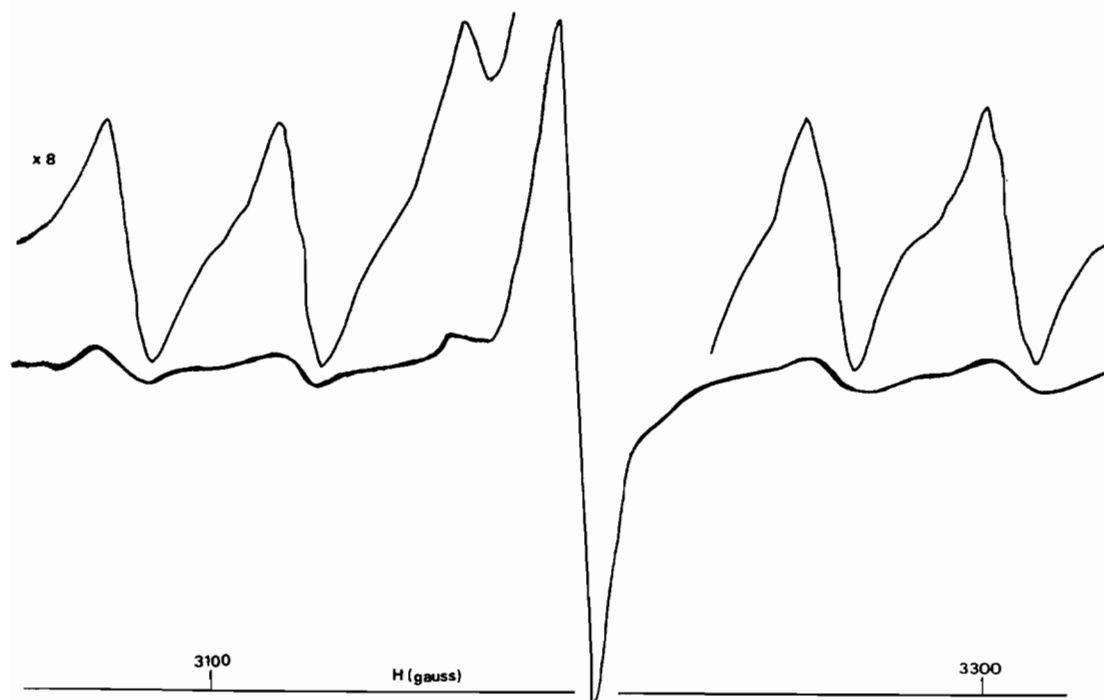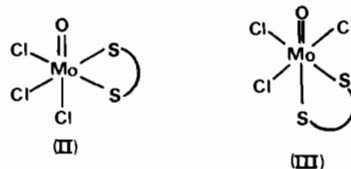Fig. 6. Epr spectrum of MoOCl$_3$(MeSCH$_2$CH$_2$SMe) in benzene.

Although the epr indicates only one species to be present in solution there is not enough evidence to suggest which of the above exists. Because of the destabilising effect of the oxo group to ligands *trans* to it, it is more likely that the isomer with chlorine *trans* to oxygen is present.

Experimental

The solvents used were dried by distillation from sodium benzophenone ketyl or, in the case of dichloromethane, from molecular sieves. All preparations were conducted under a dry nitrogen atmosphere using standard Schlenk tube and drybox techniques. Physical measurements were made as described previously [19]. E.p.r. spectra were obtained on a Varian E9 E.P.R. spectrometer using the dual cavity mode and were run in the X-band $(9.3GH_2)$ in CH_2Cl_2 or DMF at various temperatures $+ 35$ to -160 °C. The ligands were prepared by standard literature methods.

Preparation of the Complexes

$[Mo(S_2CNR_2)_4]Cl$

Oxotrichloromolybdenum (1.82 g, 0.008 mol) and the appropriate dithiocarbamate (0.04 mol) were mixed and dry, deoxygenated acetonitrile (150 cm^3) was distilled onto it giving a purple reaction mixture which quickly turned dark brown. The mixture was stirred at room temperature for 12 hours and then filtered. A yellow—brown solid residue and dark brown filtrate was obtained. The filtrate was reduced in volume to 20 cm^3 and allowed to stand at 277 K for 2 days. Dark brown needle-shaped crystals formed which were filtered, washed with benzene (5 cm^3), diethyl ether (5 cm^3) and dried *in vacuo*. Yield *ca.* 15%.

$[Mo(S_2CNR_2)_4]BPh_4$

The tetrakis(dithiocarbamate)molybdenum(V) chloride (0.0005 mol) from above was dissolved in acetonitrile (10 cm^3) and a solution of sodium tetraphenylborate (0.34 g, 0.001 mol) in acetonitrile (5 cm^3) added. After mixing at room temperature, the dark-red solution deposited dark-red crystals. They were filtered, washed with benzene (5 cm^3), diethyl ether (5 cm^3) and dried *in vacuo*. Yield was quantitative.

$[Mo_2O_4(S_2CNR_2)_2]$

The yellow—brown solid residue from the first preparation was washed in ethanol (20 cm^3) and water (20 cm^3) giving a yellow solid. This was filtered, washed with ethanol, diethyl ether and dried *in vacuo*.

$[Mo_2O_3(S_2CNR_2)_4]$

The first method was carried out at *ca.* 277 K and as soon as the mixture became purple it was rapidly filtered giving a purple solid. The complex was washed with ethanol (10 cm^3), water (10 cm^3), ethanol (10 cm^3), and diethyl ether (10 cm^3) before drying *in vacuo*.

$[MoOCl_3(RSSR)]$

$[MoOCl_3(thf)_2]$ (1 g, 0.003 mol) and benzene were placed into a reaction tube (50 cm^3), the complex partially dissolved giving a green solution. The appropriate dithioether ligand (4 cm^3) was then distilled into the tube at reduced pressure. The tube was sealed under nitrogen and left for one month. During this time the solution had turned dark blue and a green crystalline solid had formed. The product was filtered, washed with benzene (2 X 5 cm^3) and dried *in vacuo*. Yield *ca.* 15%.

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