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The Coordination of Chemistry of Molybdenum and Tungsten. Part XVII [1]: Oxomolybdenum(V) Complexes Containing Sulphur and Nitrogen Donor Ligands

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The oxomolybdenum(V) complexes of the ligands N,N'-ethylene bis(thiophen-2-carbaldimine)(N_2S_2); 1,4,8,11-tetrathiocyclotetradecane(S_4), 2-mercaptobenzimidazole (N_2S) and 2-mercaptobenzothiazole-(NS_2) have been synthesized and characterized by infra-red, visible/u.v. and electron spin resonance spectroscopy, elemental analyses and magnetic moments measurements. For [$MoOCl_3(N_2S_2)$] it is shown that the ligand binds as a diimine species and the e.s.r. spectrum exhibits g = 1.95. The dimeric [$\{MoOCl_3\}_2(S_4)(THF)_2$] complex appears to be hexacoordinate and contains a bidentate sulphur bridging ligand. For both N_2S and NS_2 complexes, the ligands bind via the sulphur donor atoms and exhibit g = 1.94 valves in the e.s.r. spectrum. The complexes are synthesized from $MoOCl_3(THF)_2$ and the 'fac $MoOCl_3$' core appears to remain intact upon complexation.

Introduction

We have for some time been interested in the coordination chemistry of oxomolybdenum(V) and have made use of both the M=O moiety and the d^1 system in elucidating structural features of the complexes by infrared and electron spin resonance spectroscopy.

We report here some details of our recent work on oxomolybdenum(V) complexes which contain nitrogen and sulphur donor ligands. Electron spin resonances studies of xanthine oxidase, which contains Mo(V) have suggested the presence of Mo–S linkages [2]. More recently, EXAFS studies on xanthine oxidase [3] and sulphite oxidase [4] have confirmed the presence of sulphur and terminal oxo ligands in the coordination sphere of the molybdenum. These results make the study of Mo(V)–N/S systems all the more pertinent. The ligands employed in this study are N,N'-ethylene bis(thiophen-2-carbaldimine)-(N_2S_2), I; 1,4,8,11-tetrahiacyclotetradecane (S_4), II; 2-mercaptobenzothiazole (NS_2), III; and 2-mercaptobenzimidazole(N_2S), IV. We have previously reported the preparation and characterization [5] of ligand I,

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TABLE I. Physical and Analytical Data for the Complexes.

Compound	Colour	% Found (calculated)					
		C	H	N	S	Cl	Mo
[$MoOCl_3(N_2S_2)$]¼THF	Brown	32.2 (32.2)	2.7 (2.9)	5.9 (5.8)	11.8 (13.2)	22.4 (22.0)	21.2 (20.0)
[$(MoOCl_3)_2(S_4)(THF)$]¼THF	Yellow/green	25.9 (26.0)	4.3 (4.3)	–	14.5 (14.7)	24.7 (24.5)	22.2 (22.2)
[$MoOCl_3(NS_2)(THF)$]¼THF	Maroon	31.1 (31.6)	3.1 (3.4)	3.8 (3.0)	–	20.9 (21.5)	19.8 (19.4)
[$MoOCl_3(N_2S)(THF)$]¼THF	Dark Brown	30.7 (31.4)	3.9 (3.5)	6.3 (6.1)	–	23.3 (23.2)	19.4 (20.9)

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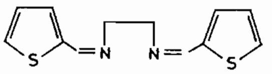
TABLE II. Infra-red Data for the Ligands and Complexes.

Compound	ν(N–H)	–HN–C=S	ν(C–O–C)	ν(M=O)
$C_7H_5NS_2$	3110	1495(s)		
	3070	1425		
	3040	1320		
$C_7H_6N_2S$	3160	1510(s)		
	3110	1465		
	3040	1355		
$[MoOCl_3(N_2S_2)]$¼THF			1065(s), 920(w)	975(s)
$[(MoOCl_3)_2(S_4)(THF)_2]$¼THF			1075(w), 920(m)	985(s)
			1040(s), 850(s)	
$[MoOCl_3(NS_2)(THF)]$½THF	3200[a]	1490(s)	1075(s), 920(w)	970(s)
		1420	1040(s), 850(s)	
		1330		
$[MoOCl_3(N_2S)(THF)]$¼THF	3350	1500(s)	1075(m), 920(m)	973(s)
	3160[b]	1455	1040(m), 850(s)	
		1360		
$MoOCl_3(THF)_2$			1045(m), 850(s)	980(s)

[a] Strong, broad band centered at 3200 cm^{-1}. [b] Weak, broad band centered at 3160 cm^{-1}.

TABLE III. Far Infra-red Spectra of the Complexes.

Compound	Ligand Absorptions		ν(Mo–Cl)				
$[MoOCl_3(THF)_2]$				350(s)	315(w)	280(w)	250(m)
$[MoOCl_3(N_2S_2)]$¼THF	395(m)	380(m)		340(s)	315(sh)	280(w)	250(m)
$[(MoOCl_3)_2(S_4)(THF)_2]$¼THF		380(w)		340(s)	310(m)		240(m)
$[(MoOCl_3)(NS_2)(THF)]$½THF	395(m)	380(m)	240(w)	340(s)	314(sh)	270(sh)	250(sh)
$[(MoOCl_3)(N_2S)(THF)]$¼THF		265(m)	255(m)	350(s)	320(s)	280(w)	270(w)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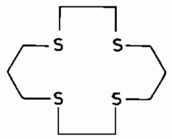
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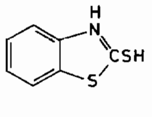
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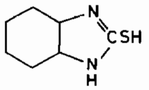

(IV)

and the inclusion of heterocyclic sulphur atoms in this Schiff base ligand makes complexation studies interesting. Moreover, transition metal complexes of the S_4 macrocycle, II, are rare [6, 7] compared with macrocycles containing nitrogen donors. We also include the NS_2 and N_2S ligands as a means of comparing these species with restricted stereochemistry as donors to molybdenum(V).

Results and Discussion

The analytical data for the complexes are listed in Table I. It can be seen that all the complexes isolated contain tetrahydrofuran (THF) as part of the composition. This is confirmed by the infrared spectra, Table II, which exhibit ν(C–O–C) bands *ca.* 1070 and 920 cm^{-1} assignable to uncoordinated THF, and *ca.* 1040 and 850 cm^{-1} assignable to coordinated THF [8]. In some complexes both coordinated and uncoordinated THF are present. Gentle heating of the complexes or prolonged pumping did not remove any THF, and more forcing conditions led to decomposition of the complexes. The employment of excess amounts of the ligand during

TABLE IV. Magnetic and Electronic Spectral Data for the Complexes.

Compound	μeff (BM)	ν_{max} (cm^{-1})		
$[MoOCl_3(THF)_2]$	1.68	13,245	19,417	27,027
$[MoOCl_3(N_2S_2)]$¼THF	1.73	13,889	20,618	–
$[(MoOCl_3)_2(S_4)(THF)_2]$¼THF	1.64	13,889	–	–
$[MoOCl_3(NS_2)(THF)]$½THF	1.87	13,333	19,230	–
$[MoOCl_3(N_2S)(THF)]$¼THF	1.43	13,459	18,519	–

TABLE V. Electron-Spin Resonance Data for the Complexes.[a]

Compound	g	A (G)
$[MoOCl_3(N_2S_2)]$¼THF	1.95	54
$[(MoOCl_3)_2(S_4)(THF)_2]$¼THF	1.95[b], 1.94	54, 56
$[MoOCl_3(NS_2)(THF)_2]$½THF	1.94	55
$[MoOCl_3(N_2S)(THF)_2]$¼THF	1.94	55

[a] Measured in methylene chloride. [b] The first signal is of greater intensity than the second signal.

complex synthesis did not result in any displacement of THF. Table II also shows the band assigned to terminal ν(Mo=O); no bands were present which could be assigned to ν(Mo–O–Mo) bridging modes. The far infrared spectra are contained in Table III, and a comparison of the spectrum of precursor molecule $MoOCl_3(THF)_2$ with those of the complexes show that the infrared bands of the $MoOCl_3$ unit are little affected by complexation.

Table IV lists the room temperature magnetic moments of the complexes and the values, μeff = 1.43–1.73 μ_β, are consistent with those of other d^1 molybdenum(V) complexes [9, 10]. The electron spin resonance parameters are listed in Table V and exhibit g values in the range 1.94–1.95. The $[\{MoOCl_3\}_2(S_4)(THF)_2]$ complex exhibits two signals at g = 1.95 and 1.94, the former being of greater intensity. The reflectance spectra of the complexes have been measured in the range 300–800 nm. The peak positions are given in Table IV and the spectra are shown in Fig. 1, from which it can be seen that all the complexes exhibit similar spectra. The low energy band in the 700–800 range is assigned to $^2B_2 \rightarrow {}^2E$ in Oh symmetry.

The complex formed with the Schiff base ligand N_2S_2, $[MoOCl_3(S_2N_2)]\cdot$¼THF leads itself to investigation by infrared spectroscopy. The ν(CN) of the imine function is a sensitive guide to the mode of coordination adopted by potentially tetradentate Schiff base ligands: coordination via both N and O

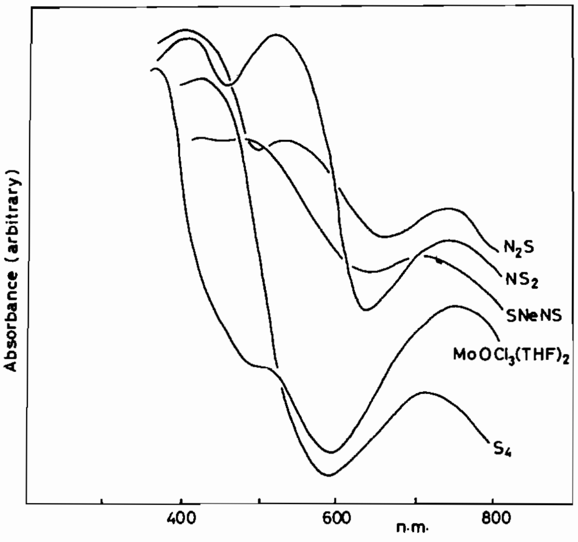
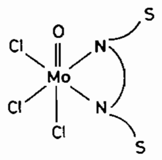


Fig. 1. Diffuse reflectance spectra of the complexes.

(or S) donors shifts the ν(C–N) to higher energy [11]. In $[MoOCl_3(S_2N_2)]\cdot$¼THF the ν(C–N) band occurs at 1638 cm^{-1}, moved to slightly higher energy than in the free ligand (1630 cm^{-1}) and thus indicates that the ligand is a neutral diimine donor. The metal–sulphur bond vibrations, expected if the sulphur atoms were coordinated could not be identified. The fact that the aromatic bands at 720 cm^{-1} and 755 cm^{-1} of the free ligand appear at the same positions in the spectrum of the complex may be taken as indirect evidence that the sulphur atoms are not involved in coordination, since coordination *via* sulphur would invariably result in a shift to lower frequencies of these bands. Furthermore, coordination of the nitrogen atoms of the imine groups relieves the strain which would be imposed by tetradentate coordination involving the two sulphur atoms. Since the number and energies of ν(Mo–Cl) bands in the infrared spectrum of this complex are almost identical to that of the $MoOCl_3(THF)_2$ starting material, we propose a similar structure, V.

The S_4 macrocyclic ligand, 1,4,8,11-tetrathiocyclotetradecane, forms the binuclear $[\{MoOCl_3\}_2$-



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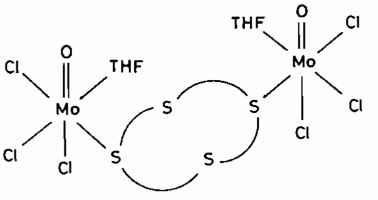

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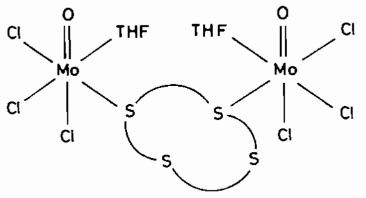


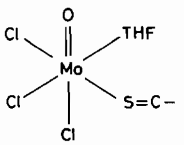
(VI)

$(S_4)(THF)_2]$, isolated as the tetrahydrofuran solvate. The magnetic and spectroscopic properties of this complex detailed earlier strongly suggest that this is a pseudooctahedral d^1 species, and from Table III it is seen that the ν(Mo–Cl) bands are very similar to that of $MoOCl_3(THF)_2$. It is possible to envisage several structures based on seven and six-coordinate geometry, and all necessarily involve a bridging S_4 ligand. We favour structure (VI) (in which the S_4 ligand is merely shown as a bidentate bridging S_2 species) for the following reasons: (a) the evidence points to six-coordinate geometry, (b) the fact that one THF per Mo is present suggests that the sulphur donors have merely displaced a coordinated THF in the parent $MoOCl_3(THF)_2$ molecule, and this is confirmed by the very similar ν(Mo–Cl) infrared profiles for the two complexes. However, whilst only one ν(Mo=O) band is observed, the e.s.r. spectrum clearly shows two signals indicating slightly different environments for each of the two molybdenum centres. Both possible structures are shown.

2-Mercaptobenzothiazole(NS_2) and 2-mercaptobenzimidazole react with $MoOCl_3(THF)_2$ in a 1:1 ratio to yield the $[MoOCl_2(NS_2)THF]$ and the $[MoOCl_3(N_2S)THF)]$ complexes respectively. Examination of the ν(C–O–C) bands again indicates the presence of coordinated and uncoordinated tetrahydrofuran, indicating that the complexes are isolated as THF solvates. The infra-red spectra both of the free ligands and their complexes show no clear indication of the ν(S–H) mode at 2550 cm^{-1}. This would suggest the presence of a thioketo form [12]. The spectrum of 2-mercaptobenzothiazole shows a strong band at 1495 cm^{-1} which is found at 1510 cm^{-1} in the spectrum 2-mercaptobenzimidazole. These bands correspond to –NH–C=S stretching vibrations resulting from the coupling of C–N stretching and the N–H deformation vibrations [13]. The bands at around 1460 cm^{-1} and 1430 cm^{-1} in the spectra of the free ligands are assigned to –NH–C=S symmetric and antisymmetric stretching vibrations, with a major contribution from the N–H deformation [14]. Examination of the infra-red spectra of the complexes shows that the bands at 1500 cm^{-1} are still present and shifted only slightly to lower frequencies. This may suggest that the thioketo structure has not been altered on complexation and a weak interaction exists between the metal ion and the sulphur atom as shown by the small shifting of the frequencies. The ligand bands at 1425 cm^{-1} and 1465 cm^{-1} are lowered on coordination also. None of the ligand spectra show a sharp band near 3430 cm^{-1}, normally attributable to ν(N–H) modes lowered by hydrogen bonding. The spectra of the complexes show the presence of broad bands between 3350 cm^{-1} and 3200 cm^{-1}, but coordinated NH bands are expected to appear at lower frequencies than uncoordinated NH bands [15] and consequently the appearance of these bands (3350 and 3200 cm^{-1}) at higher frequencies implies that the moiety cannot be coordinated. It is thus reasonable to suggest that the increase in the NH frequencies on complexation results from a substantial weakening of the hydrogen bonds of the free ligands. It seems likely that there is competition between the molybdenum and the hydrogen for the sulphur lone pairs and the weak coordination of sulphur to molybdenum lowers the energy of the hydrogen bonds and consequently increases the energy of the NH bonds. Unfortunately, ν(M–S) could not be detected in the spectra of the complexes. The possibility of disulphide formation is ruled out on the basis of the infrared (no ν(S–S) observed) and e.s.r. spectra. The latter shows no evidence for the reduction from Mo(V) to Mo(IV).

By reasoning similar to that used for the complexes described above, the ν(Mo–Cl) band profiles and the stoichiometry of the $[MoOCl_2(N_2S)(THF)]$ and $[MoOCl_3(NS_2)(THF)]$ compounds suggest that the essential features of the parent $MoOCl_3(THF)$ are retained after one coordinated THF is replaced by either an N_2S or NS_2 ligand.

Moreover, the e.s.r. spectra of both complexes exhibit g = 1.94 and indicate coordination by the sulphur, as a g = 1.95 value is observed for the diimine complex $[MoOCl_3(N_2S_2)]$. We thus assign structure VII to both $[MoOCl_3(N_2S)(THF)]$ and $[MoOCl_3(NS_2)]$.



(VII)

Experimental

Physical Measurements

Infra-red spectra were recorded in Nujol and hexachlorobutadiene mulls using Perkin-Elmer 621 and 397 spectrometers. Samples were prepared in a dry box maintained under a nitrogen atmosphere.

Diffuse reflectance spectra were measured by using a Beckmann Acta M4 spectrophotometer with barium sulphate as the blank reflector. Solution spectra were run in DMF.

Magnetic susceptibilities were measured by the Gouy method at room temperature. Mercury tetrathiocyanato cobaltate(II) $Hg[Co(CNS)_4]$ was used as a calibrant. The diamagnetic contributions were allowed for by the use of Pascal's corrections.

Electron spin resonance spectra were recorded on a Varian E9 spectrometer in tetrahydrofuran at room temperature.

Microanalytical data were obtained by the Microanalytical Service of the University of Manchester Institute of Science and Technology.

The $MoOCl_3(THF)_2$ complex was prepared by reacting 20 g (7.3×10^{-2} mole) of molybdenum pentachloride in a dry flask under a dry dinitrogen atmosphere with 130 cm^3 of dry cyclohexane. The mixture was stirred until the solid dissolved. 50 cm^3 of freshly distilled THF was then added slowly to the reaction mixture. A vigorous exothermic reaction was observed to occur and the mixture was allowed to cool to room temperature. A green solid precipitated from the solution and was isolated by standard Schlenk techniques and dried under *vacuo*. The product was stored under a sealed, dry dinitrogen atmosphere.

The complexes were prepared by the same general procedure: the $MoOCl_3(THF)_2$ complex was reacted with the ligand in a 1:1 Mo:L ratio (a 2:1 Mo:L ratio for the ligand 1,4,8,11-tetrathiocyclotetracene) in tetrahydrofuran. The mixture was mechanically shaken for 3 hours and then the solid product was isolated by filtration, washed with 3×10 cm^3 portions of tetrahydrofuran and dried *in vacuo*. The complexes were stored in sealed glass tubes under nitrogen.

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