Crystal Structure of the Complex *cis*-Oxobis[piperidine *N*-oxido(1−)-*NO*]thiomolybdenum(VI),† containing a *cis*-$MoOS^{2+}$ Group

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The first example of a $MoOS^{2+}$ complex, *cis*-$[MoOS(C_5H_{10}NO)_2]$ [$C_5H_{10}NO$ = piperidine *N*-oxido(1−)], prepared by reaction of the corresponding *cis*-MoO_2^{2+} complex with B_2S_3, has been crystallographically characterised. The title compound crystallises in the monoclinic space group $P2_1/n$, with $a = 9.671(1)$, $b = 22.401(2)$, $c = 13.116(2)$ Å, $\beta = 95.51(1)°$, and eight molecules, comprising two crystallographically distinct species, per unit cell. The structure has been determined from 4 033 unique observed diffractometer data and refined to $R = 0.047$. The two independent molecules are virtually identical, and possess Mo–O and Mo–S bonds of length 1.723(12) and 2.106(5) Å respectively and an O–Mo–S interbond angle of 116.9(7)°. The dimensions and a selection of spectroscopic properties of the title complex are compared with those of the corresponding *cis*-$[MoY_2(C_5H_{10}NO)_2]$ (Y = O or S) complexes; *cis*-$[MoS_2(C_5H_{10}NO)_2]$ may be prepared by treating the $MoOS^{2+}$ complex with B_2S_3.

The molybdenum *K*-edge extended *X*-ray absorption fine structure (EXAFS) of the molybdoenzymes nitrogenase,[1] sulphite oxidase,[2,3] xanthine oxidase,[4] and xanthine dehydrogenase[3] has greatly improved the understanding concerning the nature, number, and distance of the atoms directly bonded to the molybdenum in these systems. An intriguing aspect of the co-ordination geometry of this metal in the oxidised state of the active form of xanthine oxidase[4] and dehydrogenase[3] is the suggestion of one terminal oxo-group (Mo=O *ca.* 1.75 and 1.70 Å, respectively), one terminal thio-group (Mo=S *ca.* 2.25 and 2.15 Å, respectively), as well as approximately three sulphur atoms at *ca.* 2.5 Å. The conversion of the active form of these enzymes into the desulpho-form upon oxidative treatment with cyanide, with the subsequent formation of thiocyanate, results in the formation of a dioxomolybdenum(VI) centre.

Complexes containing the *cis*-MoO_2^{2+} moiety are well established;[5] however, this is not the case for $MoOS^{2+}$ and MoS_2^{2+} centres. Recently, an important development in molybdenum(VI)–sulphur chemistry has been achieved by Wieghardt and co-workers[6] with the preparation and structural characterisation of *cis*-$[MoY_2(C_5H_{10}NO)_2]$ [Y = O or S, $C_5H_{10}NO$ = piperidine *N*-oxido (1−)]. The corresponding *cis*-$[MoOY(R_2NO)_2]$ [Y = O and $R_2 = Et_2$; Y = S or Se and $R_2 = Et_2$ or $(CH_2)_5$] complexes were also obtained in this study.

Herein we report an alternative preparation of *cis*-$[MoOS(C_5H_{10}NO)_2]$ and *cis*-$[MoS_2(C_5H_{10}NO)_2]$, the crystal structure of the former compound, and a comparison of selected spectroscopic properties of this material with those of the corresponding *cis*-$[MoY_2(C_5H_{10}NO)_2]$ (Y = O or S) complexes.

Experimental

Preparation of cis-*Oxobis[piperidine* N-*oxido*(1−)-NO]*thiomolybdenum*(VI), *cis*-$[MoOS(C_5H_{10}NO)_2]$.—The complex *cis*-$[MoO_2(C_5H_{10}NO)_2]$ was prepared according to the procedure of Wieghardt and co-workers.[6] The conversion into, and subsequent purification of, *cis*-$[MoOS(C_5H_{10}NO)_2]$ was performed under an atmosphere of purified dinitrogen. The complex *cis*-$[MoO_2(C_5H_{10}NO)_2]$ (7.62 g, 23.2 mmol) was dissolved in dry, degassed CH_2Cl_2 (40 cm^3). Solid B_2S_3 (0.91 g, 7.72 mmol) was added and the mixture stirred overnight, to yield a brown suspension in a red solution. The mixture was filtered, the brown residue discarded, and the red filtrate evaporated to dryness under reduced pressure to yield an orange-red powder (yield of this crude material *ca.* 70%). The crude product was recrystallised from hot, dry, degassed MeOH as orange-red needles (Found: C, 35.1; H, 6.2; Mo, 27.4; N, 8.2; S, 7.7. $C_{10}H_{20}MoN_2O_3S$ requires C, 34.9; H, 5.9; Mo, 27.9; N, 8.1; S, 9.3%).

Crystals suitable for *X*-ray diffraction measurements were obtained by dissolving a portion of the crude product in hot, dry, degassed MeOH, filtering, and then allowing the filtrate to stand at −20 °C for several hours.

U.v.-visible, ^{95}Mo and ^{13}C n.m.r. spectroscopic data (see text) were consistent with crude *cis*-$[MoOS(C_5H_{10}NO)_2]$ containing *ca.* 5% each of *cis*-$[MoO_2(C_5H_{10}NO)_2]$ and *cis*-$[MoS_2(C_5H_{10}NO)_2]$. Spectroscopically pure *cis*-$[MoOS(C_5H_{10}NO)_2]$ was conveniently obtained by column chromatography on Kieselgel 60 (0.2—0.5 mm), using degassed $CHCl_3$ as the eluant.[6] The first (purple) fraction, *cis*-$[MoS_2(C_5H_{10}NO)_2]$, was discarded; the second (orange) fraction, consisting primarily of *cis*-$[MoOS(C_5H_{10}NO)_2]$, was rechromatographed whence a further fraction of *cis*-$[MoS_2(C_5H_{10}NO)_2]$ was obtained and discarded.

Preparation of cis-*Bis[piperidine* N-*oxido*(1−)-NO]*dithiomolybdenum*(VI), *cis*-$[MoS_2(C_5H_{10}NO)_2]$.—The conversion of *cis*-$[MoOS(C_5H_{10}NO)_2]$ into *cis*-$[MoS_2(C_5H_{10}NO)_2]$ was carried out under purified dinitrogen. The complex *cis*-$[MoOS(C_5H_{10}NO)_2]$ (2.73 g 7.94 mmol) was dissolved in dried, degassed CS_2 (*ca.* 30 cm^3) to give a deep orange solution. To this was added solid B_2S_3 (0.95 g, 8.08 mmol), giving a brown suspension in a violet solution. The mixture was stirred for 3 d, and then filtered, when the brown solid was discarded. The violet filtrate was evaporated to dryness under reduced pressure to yield a deep violet solid (yield of this crude material *ca.* 75%). This product was purified by dissolution in hot, dried, degassed toluene, filtration, and standing at −20 °C for several hours (Found: C, 33.4; H, 5.9; Mo, 26.3; N,

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† *Supplementary data available* (No. SUP 23696, 29 pp.): H-atom co-ordinates, thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Atomic co-ordinates ($\times 10^4$) for *cis*-[$MoOS(C_5H_{10}NO)_2$]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	1 684(1)	2 171(1)	1 091(1)	Mo′	7 970(1)	5 214(1)	1 703(1)
S	3 599(2)	2 388(1)	555(2)	S′	5 992(2)	5 184(1)	2 256(1)
O(3)	1 759(4)	1 796(2)	2 232(3)	O(3′)	8 092(4)	5 551(2)	525(3)
O(1)	384(4)	1 794(2)	36(3)	O(1′)	8 920(4)	4 435(2)	1 823(3)
N(1)	1 447(4)	1 354(2)	241(3)	N(1′)	7 816(4)	4 341(2)	1 044(3)
C(1)	897(5)	821(2)	699(4)	C(1′)	8 359(6)	4 217(3)	40(4)
C(2)	2 087(6)	405(3)	1 004(5)	C(2′)	7 166(6)	4 184(3)	−765(4)
C(3)	2 881(7)	244(3)	104(5)	C(3′)	6 103(7)	3 715(3)	−522(5)
C(4)	3 336(6)	796(3)	−409(4)	C(4′)	5 643(6)	3 828(3)	520(5)
C(5)	2 144(6)	1 225(3)	−687(4)	C(5′)	6 856(7)	3 870(3)	1 324(5)
O(2)	318(4)	2 824(2)	998(3)	O(2′)	9 445(4)	5 458(2)	2 767(3)
N(2)	1 314(4)	3 006(2)	1 818(3)	N(2′)	8 692(4)	6 001(2)	2 523(3)
C(6)	695(6)	3 024(3)	2 801(4)	C(6′)	9 586(6)	6 442(3)	2 062(5)
C(7)	1 773(6)	3 157(3)	3 650(4)	C(7′)	8 728(8)	6 969(3)	1 714(5)
C(8)	2 499(7)	3 749(3)	3 458(5)	C(8′)	8 044(7)	7 240(3)	2 607(5)
C(9)	3 060(6)	3 730(3)	2 424(5)	C(9′)	7 226(6)	6 770(3)	3 122(5)
C(10)	1 960(5)	3 579(2)	1 565(4)	C(10′)	8 113(6)	6 249(2)	3 428(4)

8.2; S, 17.2. $C_{10}H_{20}MoN_2O_2S_2$ requires C, 33.3; H, 5.6; Mo, 26.6; N, 7.8; S, 17.8%).

Crystal Structure Determination for cis-[$MoOS(C_5H_{10}NO)_2$].—A plate crystal (dimensions *ca.* 0.54 × 0.46 × 0.11 mm, indices of principal faces 010), sealed in a glass capillary, was examined at room temperature on a Stoe-Siemens AED diffractometer, with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). Unit-cell parameters were refined from the 2θ angles of 38 reflections ($20 < 2\theta < 25°$).

Crystal data. $C_{10}H_{20}MoN_2O_3S$, $M = 344.3$, Monoclinic, $a = 9.671(1)$, $b = 22.401(2)$, $c = 13.116(2)$ Å, $\beta = 95.51(1)°$, $U = 2\,828.3$ Å^3, space group $P2_1/n$, $Z = 8$, $D_c = 1.617$ g cm^{-3}, and $F(000) = 1\,408$.

Intensity data were measured in the ω—θ scan mode by a real-time profile-fitting procedure,[7] for reflections with $7 < 2\theta < 50°$. Empirical absorption corrections were applied, based on the measurement of sets of equivalent reflections at various azimuthal angles: transmission factors range from 0.83 to 0.96 for $\mu = 10.46$ cm^{-1}.

The structure was solved by Patterson and Fourier techniques from 4 033 unique reflections with $F > 4\sigma(F)$, and refined with anisotropic thermal parameters to a minimum value of $\Sigma w\Delta^2$, with $w^{-1} = \sigma^2(F) + 0.000\,11F_o^2$. Hydrogen atoms, clearly revealed in a difference synthesis after refinement of the other atoms, were included in the refinement, subject to the riding-model constraints C–H 0.96 Å, H–C–H 109.5°, and $U(H) = 1.2U(C)$, where $U(C)$ is the equivalent isotropic thermal parameter of a carbon atom.[8] The final value of R was 0.047, with $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.053$.

Computer programs were written by W. C. (diffractometer control program) and by Professor G. M. Sheldrick (SHELXTL system) for Data General computers.

Atomic co-ordinates are given in Table 1, bond lengths and angles in Table 2.

Analytical and Spectroscopic Measurements.—Microanalyses were carried out by Mr. M. Hart and his staff in the University of Manchester Microanalytical Chemistry Laboratory. Infrared spectra were recorded, for Nujol mulls of the samples between CsI plates, in the range 4 000—200 cm^{-1} on a Perkin-Elmer 577 grating spectrometer. Raman spectra were obtained by Dr. R. S. Alexander of the Chemistry Department, Manchester University, for powdered [$MoO_2(C_5H_{10}NO)_2$] using 5 145-Å excitation from an argon-ion laser and recorded on a Cary 82 instrument, and, for powdered [$MoOS(C_5H_{10}NO)_2$], using 6 471-Å excitation from a krypton-ion laser and recorded on a Spex model 1 403 double monochromator spectrometer. U.v.–visible spectra were recorded on a Perkin-Elmer 402 spectrometer. Proton (90 MHz) and ^{13}C (20.1 MHz) n.m.r. spectra were recorded for $CDCl_3$ solutions on a Perkin-Elmer R12A and a Bruker WP-80 instrument, respectively. 26.08-MHz ^{95}Mo n.m.r. spectra were obtained by Dr. B. E. Mann using a Bruker WH-400 instrument at the S.E.R.C. high-field n.m.r. service at Sheffield University. Mass spectra were obtained for samples sublimed at *ca.* 200 °C, using 70 eV (*ca.* 1.18×10^{-17} J) electron ionisation, with an A.E.I. MS30 instrument.

Results and Discussion

The complex *cis*-[$MoOS(C_5H_{10}NO)_2$] is important as the first example of an $MoOS^{2+}$ moiety, with special relevance to the current ideas concerning the nature of the molybdenum centre in the oxidised active form of xanthine oxidase[4] and dehydrogenase.[3] The clean and efficient formation of the *cis*-$MoOS^{2+}$ and *cis*-MoS_2^{2+} groups from *cis*-[$MoO_2(C_5H_{10}NO)_2$], upon treatment with either H_2S[6] or B_2S_3, appears to be a property of the hydroxamines co-ordinated to molybdenum, $C_5H_{10}NO^-$ or $(C_2H_5)_2NO^-$,[6] and has not yet been extended to other systems. The use of B_2S_3 reported herein is similar to the synthesis of VS^{2+} from VO^{2+}; this conversion also has only been demonstrated for particular ligands co-ordinated to the metal, in this case the Schiff bases * salen and acen.[9]

The reactions of *cis*-[$MoO_2(C_5H_{10}NO)_2$] and *cis*-[$MoOS(C_5H_{10}NO)_2$] with B_2S_3 have some advantages and offer a useful alternative to the previously reported[6] preparations of *cis*-[$MoOS(C_5H_{10}NO)_2$] and *cis*-[$MoS_2(C_5H_{10}NO)_2$], by treating *cis*-[$MoO_2(C_5H_{10}NO)_2$] with H_2S. Replacement of one oxo-group in *cis*-[$MoO_2(C_5H_{10}NO)_2$] by B_2S_3 is most effectively achieved in CH_2Cl_2, and less efficiently in toluene, $CHCl_3$, or methanol. Use of a molar ratio $\geqslant 1:1$ of B_2S_3: *cis*-[$MoO_2(C_5H_{10}NO)_2$] in CH_2Cl_2 effects a significant conversion into *cis*-[$MoS_2(C_5H_{10}NO)_2$]. ^{95}Mo N.m.r. spectroscopy is a very accurate way of assessing the components of a mixture of *cis*-[$MoY_2(C_5H_{10}NO)_2$] (Y = O or S or Y_2 = OS) complexes (see below), and on this basis crude [$MoOS(C_5H_{10}NO)_2$]

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* H_2salen and H_2acen are the 1 : 2 Schiff bases formed between 1,2-diaminoethane and salicylaldehyde and pentane-2,4-dione, respectively.

Table 2. Bond lengths (Å) and angles (°) for *cis*-[$MoOS(C_5H_{10}NO)_2$]

	Molecule 1 (unprimed)	Molecule 2 (primed)		Molecule 1 (unprimed)	Molecule 2 (primed)
Mo–S	2.101(2)	2.111(2)	C(2)–C(3)	1.511(9)	1.525(10)
Mo–O(3)	1.711(4)	1.734(4)	C(3)–C(4)	1.493(9)	1.499(10)
Mo–O(1)	1.968(3)	1.970(4)	C(4)–C(5)	1.518(8)	1.503(9)
Mo–N(1)	2.142(4)	2.138(5)	O(2)–N(2)	1.432(5)	1.436(6)
Mo–O(2)	1.967(4)	1.975(4)	N(2)–C(6)	1.473(7)	1.481(7)
Mo–N(2)	2.146(4)	2.146(4)	N(2)–C(10)	1.480(7)	1.470(7)
O(1)–N(1)	1.430(5)	1.421(6)	C(6)–C(7)	1.480(8)	1.488(9)
N(1)–C(1)	1.460(7)	1.490(7)	C(7)–C(8)	1.532(9)	1.526(10)
N(1)–C(5)	1.476(7)	1.475(8)	C(8)–C(9)	1.510(10)	1.514(9)
C(1)–C(2)	1.505(8)	1.489(8)	C(9)–C(10)	1.511(8)	1.481(8)

	Molecule 1 (unprimed)	Molecule 2 (primed)		Molecule 1 (unprimed)	Molecule 2 (primed)
S–Mo–O(3)	116.2(1)	117.5(1)	O(1)–N(1)–C(5)	111.0(4)	112.0(4)
S–Mo–O(1)	112.9(1)	112.1(1)	C(1)–N(1)–C(5)	113.1(4)	111.7(5)
O(3)–Mo–O(1)	112.0(2)	112.7(2)	N(1)–C(1)–C(2)	108.4(4)	108.8(5)
S–Mo–N(1)	94.5(1)	94.6(1)	C(1)–C(2)–C(3)	111.9(5)	112.2(5)
O(3)–Mo–N(1)	91.7(2)	92.7(2)	C(2)–C(3)–C(4)	110.4(5)	109.8(6)
O(1)–Mo–N(1)	40.4(1)	40.2(2)	C(3)–C(4)–C(5)	112.5(5)	111.7(6)
S–Mo–O(2)	114.5(1)	112.5(1)	N(1)–C(5)–C(4)	108.8(4)	109.7(5)
O(3)–Mo–O(2)	113.0(2)	113.7(2)	Mo–O(2)–N(2)	76.5(2)	76.1(2)
O(1)–Mo–O(2)	84.0(1)	83.7(2)	Mo–N(2)–O(2)	63.0(2)	63.3(2)
N(1)–Mo–O(2)	124.4(1)	123.9(2)	Mo–N(2)–C(6)	120.8(3)	121.3(4)
S–Mo–N(2)	97.8(1)	96.6(1)	O(2)–N(2)–C(6)	111.4(4)	110.6(4)
O(3)–Mo–N(2)	91.9(2)	92.4(2)	Mo–N(2)–C(10)	124.4(3)	125.8(3)
O(1)–Mo–N(2)	124.3(1)	124.1(2)	O(2)–N(2)–C(10)	110.3(4)	111.4(4)
N(1)–Mo–N(2)	164.1(1)	163.9(2)	C(6)–N(2)–C(10)	112.8(4)	111.0(4)
O(2)–Mo–N(2)	40.5(1)	40.5(2)	N(2)–C(6)–C(7)	110.3(5)	108.9(5)
Mo–O(1)–N(1)	76.4(2)	76.2(3)	C(6)–C(7)–C(8)	110.6(5)	110.5(6)
Mo–N(1)–O(1)	63.2(2)	63.5(2)	C(7)–C(8)–C(9)	109.4(5)	110.4(5)
Mo–N(1)–C(1)	120.6(3)	120.7(4)	C(8)–C(9)–C(10)	112.8(5)	110.8(5)
O(1)–N(1)–C(1)	110.9(4)	111.0(4)	N(2)–C(10)–C(9)	108.0(4)	109.6(5)
Mo–N(1)–C(5)	124.2(3)	125.1(4)			

contains *ca.* 90% of this compound and *ca.* 5% each of the corresponding MoO_2^{2+} and MoS_2^{2+} compounds. Purification of the $MoOS^{2+}$ compound can be achieved by recrystallisation from MeOH and/or chromatography. Doubly chromatographed samples of *cis*-[$MoOS(C_5H_{10}NO)_2$] contained no detectable quantities of the corresponding MoO_2^{2+} and MoS_2^{2+} complexes. Thus, there is no indication that, in $CDCl_3$, the disproportionation equilibrium (1) occurs on dissolution of *cis*-[$MoOS(C_5H_{10}NO)_2$].

$$2\ cis\text{-}[MoOS(C_5H_{10}NO)_2] \rightleftharpoons cis\text{-}[MoO_2(C_5H_{10}NO)_2] + cis\text{-}[MoS_2(C_5H_{10}NO)_2] \quad (1)$$

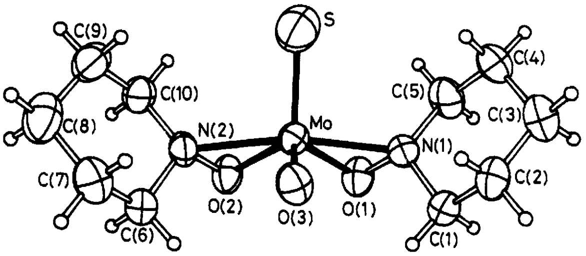

Figure 1. Molecular structure of *cis*-[$MoOS(C_5H_{10}NO)_2$]; thermal motion for one of the independent molecules is depicted by 50% probability ellipsoids

The two crystallographically independent molecules in the crystals of *cis*-[$MoOS(C_5H_{10}NO)_2$] are virtually identical; all of the non-hydrogen atoms of one molecule have been fitted to the other and the root mean square (r.m.s.) deviation is only 0.03 Å. The analytical data obtained for recrystallised samples of *cis*-[$MoOS(C_5H_{10}NO)_2$] generally suggested a Mo : S ratio of *ca.* 1 : 0.85 and the spectroscopic data (see below) indicated the presence of slightly more of the MoO_2^{2+}, as compared to the MoS_2^{2+} compound as an impurity. However, we would emphasise that the crystallographic data are consistent with the selection of a pure, single crystal of *cis*-[$MoOS(C_5H_{10}NO)_2$] for the structural study. Although the sulphur atoms *do* vibrate more than the molybdenum, oxygen, and nitrogen atoms, this seems to be *genuine* and not a result of partial oxygen/sulphur substitution. The anisotropy of the thermal ellipsoid for the sulphur atoms is not marked and, in particular, there is no large component along the Mo–S bond, as would arise from such a partial substitution. Furthermore, there is no significant residual electron density along the Mo–S bond in the final difference map.

The molecular structure of *cis*-[$MoOS(C_5H_{10}NO)_2$] (Figure 1) closely resembles that of the corresponding MoO_2^{2+} and MoS_2^{2+} complexes,[6] and involves the piperidine *N*-oxido(1–) ligands with the normal chair conformation. The co-ordination about the molybdenum in these complexes may be described as an essentially tetrahedral MoY_2O_2 [O from piperidine *N*-oxido(1–); Y = O_t and/or S_t) (t = terminal)] arrangement, but with the O–Mo–O [in this case O(1)–Mo–O(2)] interbond angle closed down [to 83.9(2)° in the $MoOS^{2+}$ complex] to accommodate the two extra Mo–N bonds, which are approximately collinear and in the same plane as the molybdenum and the ligand oxygen atoms. The planes containing the atoms S, Mo, O(3) and N(2), O(2), Mo, O(1), N(1) are essentially mutually per-

Table 3. Selected dimensions of the molybdenum environment in *cis*-[$\mathrm{MoY_2(C_5H_{10}NO)_2}$] (Y = O or S, $\mathrm{Y_2}$ = OS)

	$\mathrm{MoO_2}$ [a]	MoOS [b]	$\mathrm{MoS_2}$ [a]
Mo–Y/Å	1.7(9)	1.723(12)	
		2.106(5)	2.145(2)
Y–Mo–Y/°	119.3(3)	116.9(7)	115.0(1)
Mo–O(L) [c]/Å	1.960(11)	1.970(3)	1.956(4)
Mo–N(L) [c]/Å	2.142(5)	2.143(3)	2.151(4)

[a] Ref. 6. [b] This work. [c] L = $\mathrm{C_5H_{10}NO}$ = piperidine *N*-oxide(1–).

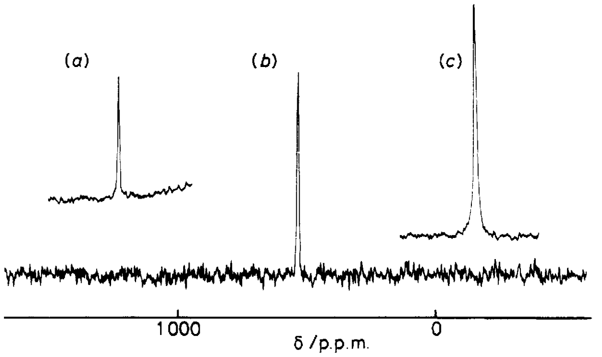

Figure 2. ^{95}Mo N.m.r. spectra of (*a*) *cis*-[$\mathrm{MoS_2(C_5H_{10}NO)_2}$], (*b*) *cis*-[$\mathrm{MoOS(C_5H_{10}NO)_2}$], and (*c*) *cis*-[$\mathrm{MoO_2(C_5H_{10}NO)_2}$] for $\mathrm{CDCl_3}$ solutions at ambient temperature; referenced to $\mathrm{Na_2[MoO_4]}$ in $\mathrm{D_2O}$ at 0 p.p.m.

pendicular (see Figure 1), and thus the former approximates to a intramolecular plane of symmetry.

Each of the intramolecular dimensions of *cis*-[$\mathrm{MoOS(C_5H_{10}NO)_2}$] (Table 2) is similar to that of the corresponding feature of the *cis*-[$\mathrm{MoY_2(C_5H_{10}NO)_2}$] molecules [6] and a selection of these dimensions is compared in Table 3. The length of the bonds from the molybdenum to the terminal oxo- and thio-groups, of 1.723(12) and 2.106(5) Å, respectively, is similar to those found in other molybdenum complexes.[5,10] This definitive characterisation of the $\mathrm{MoOS^{2+}}$ centre provides additional support for the postulate, based on the interpretation of molybdenum *K*-edge EXAFS data, that such a centre could be present in the active forms of xanthine dehydrogenase [3] and oxidase.[4] The length of these bonds in *cis*-[$\mathrm{MoOS(C_5H_{10}NO)_2}$], particularly that of Mo–S, are in better agreement with values obtained in the former [3] as compared with the latter [4] EXAFS study. The knowledge now available for this trio of *cis*-[$\mathrm{MoY_2(C_5H_{10}NO)_2}$] compounds should enable the validity of the EXAFS interpretation for such systems to be ascertained.

Given the structural similarities and the chemical variation within this group of *cis*-[$\mathrm{MoY_2(C_5H_{10}NO)_2}$] (Y = O or S, $\mathrm{Y_2}$ = OS) complexes, their spectroscopic properties are of intrinsic interest and value, especially for assessments of the purity of samples, particularly *cis*-[$\mathrm{MoOS(C_5H_{10}NO)_2}$]. The u.v.–visible and ^{1}H n.m.r. spectra of all three compounds have been reported by Wieghardt and co-workers [6] and our results are in good agreement with these data. The presence of *cis*-[$\mathrm{MoS_2(C_5H_{10}NO)_2}$] is readily ascertained by the absorption at 512 nm (ε = 1 070 dm^3 mol^{-1} cm^{-1}). Wieghardt and co-workers also reported values for ν(Mo–O) and ν(Mo–S) stretching frequencies. In the case of *cis*-[$\mathrm{MoO_2(C_5H_{10}NO)_2}$] our results are in disagreement with theirs. In the ν(Mo=O) stretching region of the i.r. spectrum, absorptions are apparent at *ca.* 914, 909, 901, and 891 cm^{-1}. Comparison with the i.r. spectrum of $\mathrm{C_5H_{10}NOH}$ and *cis*-[$\mathrm{MoS_2(C_5H_{10}NO)_2}$] suggests that the features at 909 and 891 cm^{-1} are due to ligand vibrations and thus we assign the features 914 and 901 cm^{-1} to the symmetric and antisymmetric stretching modes of the *cis*-$\mathrm{MoO_2^{2+}}$ group. This assignment is consistent with previous work [11] and the Raman data recorded for this compound; relatively intense and weak Raman effects were observed at 912 and 900 cm^{-1}, respectively. The ν(Mo=O) stretching mode of *cis*-[$\mathrm{MoOS(C_5H_{10}NO)_2}$] has been assigned to the band at 913 cm^{-1} in the i.r. spectrum (*cf.* 908 cm^{-1}, ref. 6) and 919 cm^{-1} in the Raman spectrum; the ν(Mo=S) mode of this compound is assigned to the relatively strong feature at 515 cm^{-1} in both the i.r. and Raman spectra. Wieghardt and co-workers [6] suggested that the ν(Mo=S) stretching frequencies of *cis*-[$\mathrm{MoS_2(C_5H_{10}NO)_2}$] are manifest at 524 and 498 cm^{-1} in the i.r. spectrum. Although we agree with the first of these assignments, the second, although reasonable, may be confused with ligand vibrations which we believe are manifest at 505 and *ca.* 488 cm^{-1}. Attempts to record the Raman spectrum of *cis*-[$\mathrm{MoS_2(C_5H_{10}NO)_2}$], to clarify this situation, have been unsuccessful.

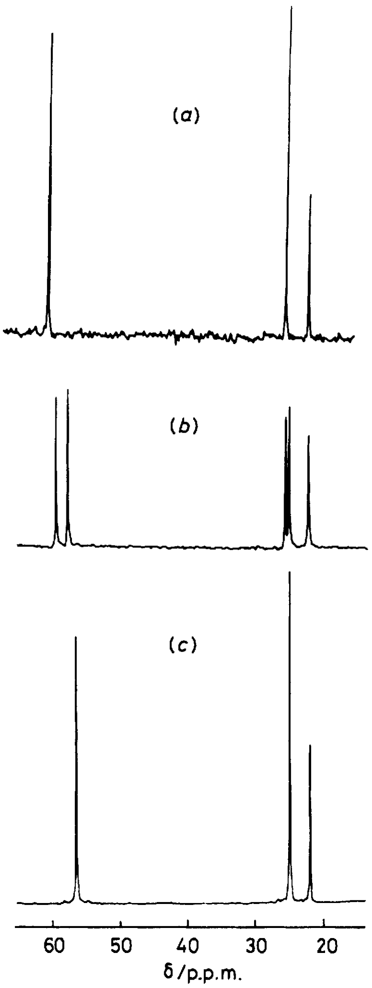

Figure 3. ^{13}C N.m.r. spectra of *cis*-[$\mathrm{MoY_2(C_5H_{10}NO)_2}$] (key as in Figure 2) for $\mathrm{CDCl_3}$ solutions at ambient temperature, referenced to $\mathrm{SiMe_4}$

Each of the three compounds produced a mass spectrum, in which a group of peaks with a mass and intensity distribution characteristic of Mo (max. *m*/*e* = 98) was clearly apparent at *m*/*e* values corresponding to those of the parent

Table 4. ^{13}C N.m.r. of *cis*-[$MoY_2(C_5H_{10}NO)_2$] (Y = O or S, Y_2 = OS) complexes in $CDCl_3$

Complex	δ/p.p.m. [a]	Relative intensity	Assignment
cis-[$MoO_2(C_5H_{10}NO)_2$]	56.6	1.7	C^1
	25.0	2.1	C^2
	22.0	1	C^3
cis-[$MoS_2(C_5H_{10}NO)_2$]	61.0	2.1	C^1
	25.8	2.3	C^2
	22.4	1	C^3
cis-[$MoOS(C_5H_{10}NO)_2$]	59.6	1.2	C(5), C(10) [b] $\}C^1$
	57.9	1.2	C(1), C(6) [b]
	25.7	1.3	C(4), C(9) $\}C^2$
	25.2	1.4	C(2), C(7)
	22.3	1	C(3), C(8) [b] = C^3

[a] Referenced to $SiMe_4$ as standard. [b] See Figure 1.

molecular ion. The molecular fragmentation was simplest for *cis*-[$MoO_2(C_5H_{10}NO)_2$] (m/e = 330), with the formation of only [$MoO_3(C_5H_{10}NO)$]$^+$ (m/e = 246) and [$MoO_2(C_5H_{10}NO)$]$^+$ (m/e = 230) being observed above m/e = 200. In the case of *cis*-[$MoS_2(C_5H_{10}NO)_2$] (m/e = 362) about nine groups of peaks, with the molybdenum profile, were observed between the parent molecular ion and m/e = 200; the most prominent of these have been taken to indicate the formation of [$MoS(C_5H_{10}NO)_2$]$^+$ (m/e = 330), [$Mo(C_5H_{10}NO)(C_5H_9NO)$]$^+$ (m/e = 297), [$MoOS_2(C_5H_9NO)$]$^+$ (m/e = 277), [$MoOS(C_5H_{10}NO)$]$^+$ (m/e = 246), [$MoS(C_5H_{10}NO)$]$^+$ (m/e = 230), and [$MoS(C_5H_{10}N)$]$^+$ (m/e = 214). The mass spectrum of *cis*-[$MoOS(C_5H_{10}NO)_2$] (m/e = 346) contains features above m/e of 200 which imply the formation of [$MoS(C_5H_{10}NO)_2$]$^+$ (m/e = 330), [$MoO(C_5H_{10}NO)(C_5H_9NO)$]$^+$ (m/e = 313), [$MoOS(C_5H_{10}NO)$]$^+$ (m/e = 246), and [$MoO_2(C_5H_{10}NO)$]$^+$ and/or [$MoS(C_5H_{10}NO)$]$^+$ (m/e = 230).

The ^{95}Mo and ^{13}C n.m.r. spectra of the *cis*-[$MoY_2(C_5H_{10}NO)_2$] (Y = O or S, Y_2 = OS) complexes (Figure 2) provide a clear distinction between these complexes. The ^{95}Mo resonance positions are −177, +537, and +1 229 (all ±2) p.p.m. (referenced to $Na_2[MoO_4]$ in D_2O at 0 p.p.m.) and show that the same variation in chemical shift with oxo-/thio-composition as manifest by the tetrahedral anions: [MoO_4]$^{2-}$, 0; [MoO_3S]$^{2-}$, +497; [MoO_2S_2]$^{2-}$, +1 067 p.p.m.[12] The similarity between the ^{95}Mo n.m.r. resonances for the two series of complexes provides a parallel with the description of the structure given earlier for the *cis*-[$MoY_2(C_5H_{10}NO)_2$] complexes.

The assignment of the ^{13}C resonances of *cis*-[$MoY_2(C_5H_{10}NO)_2$] (Y = O or S, Y_2 = OS) (see Figure 3 and Table 4) follows from that of the piperidine derivatives.[13] The data for *cis*-[$MoOS(C_5H_{10}NO)_2$], when reviewed with reference to the molecular structure (Figure 1), are consistent with inequivalence of the piperidine *N*-oxido(1−) C^1 and C^2 carbon atoms due to the $MoOS^{2+}$ core; the assignments for these C^1 and C^2 atoms then follow from the resemblance of the individual chemical shifts to those of the corresponding atoms in the MoO_2^{2+} and MoS_2^{2+} complexes.

The chemical reactions of this group of complexes are currently under investigation. Presently, we note that the reaction (2), suggested for the molybdenum centres in xanthine oxidase [4] and dehydrogenase,[3] has *not* been demonstrated for *cis*-[$MoOS(C_5H_{10}NO)_2$]

$$MoOS^{2+} + CN^- \xrightarrow[\text{oxidising conditions}]{H_2O} MoO_2^{2+} + NCS^- \quad (2)$$

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