Chemistry of Molybdenum. Part 2.* Complexes of Molybdenum with 2-Aminocyclopent-1-ene-1-carbodithioate. Synthesis, Characterisation, and Electrochemical Studies

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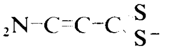
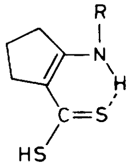
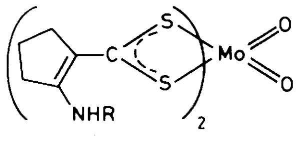
The chemistry of the bidentate (S,S$^-$) donor ligands 2-aminocyclopent-1-ene-1-carbodithioic acid (HL[1]) and its *N*-alkylated derivatives [alkyl = C_2H_5 (HL[2]), C_4H_9 (HL[3]), or cyclo-C_6H_{11} (HL[4])] with molybdenum in oxidation states +6 and +5 is described. The Mo^{VI} compounds are all *cis*-dioxo-species. Reduction of $[MoO_2(L^1)_2]$ with excess HL[1] yields $[MoO(L^1)_3]$, a monomeric Mo^V compound. The complexes are all intensely coloured due to a ligand-to-metal charge-transfer transition. Infrared electronic, e.s.r., magnetic, and electrochemical studies of these complexes are described. The results are discussed in terms of electronic structure and their relationship to the Mo centre in xanthine oxidase.

In its higher oxidation states (+3 to +6) molybdenum behaves as a typical class *a* acceptor. However, it has a strong affinity for sulphur, a fact which is reflected in its natural occurrence as a sulphide, MoS_2. There is, at present, considerable interest in the chemistry of sulphur-bonded molybdenum complexes because of the presence of such bonds in molybdoenzymes. Various dithio-ligands[1] have been used extensively to study the chemistry of molybdenum. A few of these compounds mimic very well some of the properties of molybdoenzymes.[2] In this context it appeared that an investigation on molybdenum chelates derived from the skeletal unit  $H_2N{-}C{=}C{-}C\genfrac{}{}{0pt}{}{S}{S^-}$ would be quite interesting as, in principle, chelation here may occur either from N,S$^-$ or S,S$^-$ sites. In order to explore such possibilities I have undertaken a systematic investigation on the molybdenum complexes of 2-aminocyclopent-1-ene-1-carbodithioic acid (denoted by HL[1]) and some of its *N*-alkylated derivatives. The pertinent ligands (HL[1]—HL[4]) for which a hydrogen-bonded structure (1) has been proposed by Nag and Joardar[3-6] are shown below.



(1)



HL[1]; R = H	(2a); R = H
HL[2]; R = C_2H_5	(2b); R = C_2H_5
HL[3]; R = C_4H_9	(2c); R = C_4H_9
HL[4]; R = cyclo$-C_6H_{11}$	(2d); R = cyclo $-$ C_6H_{11}

In the present paper the synthesis, characterisation, e.s.r., and electrochemical studies on some Mo^{VI} and Mo^V complexes of ligands HL[1]—HL[4] are reported.

Experimental

Preparation of Ligands.—The ligands HL[1]—HL[3] were prepared as described in the literature.[4,7] The *N*-cyclohexyl ligand, HL[4], was prepared in the customary manner[7] by dropwise addition of freshly distilled cyclohexylamine (14.85 g, 0.15 mol) to HL[1] (6.36 g, 0.04 mol) in methanol (60 cm^3) and refluxing the mixture for ~6 h. The solution was cooled to room temperature and water (180 cm^3) added. After filtration, the solution was neutralised with 2 mol dm^{-3} HCl under ice-cooling and the precipitated yellow product was collected by filtration, washed with water, and dried. The crude product was recrystallised from a (1 : 1 v/v) chloroform–acetone mixture, m.p. 185 °C, yield 5.3 g (55%). All ligands gave satisfactory analytical results.

Reagents.—All chemicals were reagent grade. Methanol,[8] acetone,[8] and *NN*-dimethylformamide (dmf)[9] were specially dried and stored over molecular sieves (Merck, type 3Å). All reactions and physical measurements were carried out under an atmosphere of purified dinitrogen using degassed solvents. $[MoO_2(acac)_2]$[10] (acac = acetylacetonate) and $[NMe_4]_2[MoOCl_5]$[11] were prepared and purified as described in literature. Tetraethylammonium bromide (Aldrich) was converted[12] to tetraethylammonium perchlorate.

Physical Measurements.—Infrared spectra (4 000—250 cm^{-1}) were recorded as KBr discs with a Beckman IR-20A spectrophotometer, electronic spectra (900—280 nm) were measured with a Pye-Unicam SP8-150 recording spectrophotometer. ^{1}H N.m.r. spectra were recorded on a Varian model T-60 spectrometer. Chemical shifts are reported in p.p.m. relative to $SiMe_4$ as internal standard. *X*-Band (~9.2 GHz) e.s.r. spectra were obtained on a Varian E-4 spectrometer at room temperature (298 K). Electrochemical measurements were made using a PAR model 370-4 electrochemistry system. Cyclic voltammetry and differential pulse polarographic measurements required the PAR 174A polarographic analyser, PAR 175 universal programmer and a PAR RE0074 XY recorder. The three-electrode measurements were carried out by using a planar Beckman model 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode, and a saturated calomel electrode (s.c.e.). All electrochemical data were obtained at 298 K in a gas-tight cell (Metrohm) under purified dinitrogen and are uncorrected for junction potential.

Preparation of Compounds.—*Bis(2-aminocyclopent-*1*-ene-*1*-carbodithioato)dioxomolybdenum*(VI), $[MoO_2(L^1)_2]$ (2a). The complex $[MoO_2(acac)_2]$ (0.66 g, 2 mmol) was dissolved in methanol (50 cm^3), the solution was filtered and the filtrate cooled in ice. To this solution an ice-cooled solution † (50 cm^3) of HL[1] (0.64 g, 4 mmol) was quickly added with stirring.

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* Part 1 can be regarded as M. Chaudhury, *J. Chem. Soc., Dalton Trans.*, 1983, 857.

† Efficient cooling of the solution is essential in order to avoid the reduction of Mo^{VI} to Mo^V.

Table 1. Analytical and physical data for the complexes

Complex	M.p.[a]/°C	Colour	Formula	Elemental analysis (%) [b]				
				Mo	C	H	N	S
(2a) [MoO$_2$(L^1)$_2$]	170—175	Maroon	C$_{12}$H$_{16}$MoN$_2$O$_2$S$_4$	21.3	32.6	3.5	6.2	—
				(21.6)	(32.4)	(3.6)	(6.3)	
(2b) [MoO$_2$(L^2)$_2$]	190—195	Cherry red	C$_{16}$H$_{24}$MoN$_2$O$_2$S$_4$	19.4	38.2	4.5	5.7	—
				(19.2)	(38.4)	(4.8)	(5.6)	
(2c) [MoO$_2$(L^3)$_2$]	172—176	Vermillion red	C$_{20}$H$_{32}$MoN$_2$O$_2$S$_4$	17.2	42.9	5.8	5.0	—
				(17.3)	(43.2)	(5.7)	(5.0)	
(2d) [MoO$_2$(L^4)$_2$]	185—190	Orange-red	C$_{24}$H$_{36}$MoN$_2$O$_2$S$_4$	15.5	47.2	5.9	4.8	—
				(15.8)	(47.4)	(5.9)	(4.6)	
(3a) [MoO(L^1)$_3$]	150—155	Black	C$_{18}$H$_{24}$MoN$_3$OS$_6$	16.1	36.6	4.3	7.1	31.0
				(16.4)	(36.9)	(4.1)	(7.2)	(32.8)
(3b) [MoO(L^1)$_3$]	148—152	Black	C$_{18}$H$_{24}$MoN$_3$OS$_6$	16.2	36.9	4.2	6.9	31.2
				(16.4)	(36.9)	(4.1)	(7.2)	(32.8)

[a] With decomposition. [b] Calculated values are given in parentheses.

The solution turned blood red from which maroon crystals deposited almost immediately. The product was quickly collected by filtration, washed with ice-cooled methanol followed by diethyl ether, and finally dried over CaCl$_2$ (yield, 72%).

Bis(2-N-*alkylaminocyclopent*-1-*ene*-1-*carbodithioato*)*dioxomolybdenum*(VI), [MoO$_2$(L)$_2$] [L = L^2 (2b), L^3 (2c), *or* L^4 (2d)]. Compounds (2b)—(2d) were obtained in good yield (60—80%) by adopting the same procedure, hence the preparation of [MoO$_2$(L^2)$_2$] is given here as an example. To a stirred methanol solution (50 cm^3) of [MoO$_2$(acac)$_2$] (0.66 g, 2 mmol) a freshly prepared solution of HL^2 (0.75 g, 4 mmol) in methanol (80 cm^3) was slowly added with stirring. The red microcrystalline compound which formed was collected by filtration, washed with methanol–ether and finally dried over CaCl$_2$.

Tris(2-*aminocyclopent*-1-*ene*-1-*carbodithioato*)*oxomolybdenum*(V), [MoO(L^1)$_3$]. *Method* (a). To a stirred filtered solution of [MoO$_2$(acac)$_2$] (0.66 g, 2 mmol) in methanol (25 cm^3), HL^1 (1 g, 6 mmol) dissolved in methanol (40 cm^3) was added. Immediately a blood red solution resulted which turned dark red on standing. The mixture was stirred at 50 °C for a period of ~1 h. During this period the colour of the mixture changed from red to black through an intermediate red-brown stage. On cooling, a shiny black crystalline product separated out which was collected by filtration, washed with cold CH$_3$OH and chloroform, and finally dried over CaCl$_2$ (yield, 40%).

Method (b). A solution of HL^1 (0.32 g, 2 mmol) in methanol (25 cm^3) was added dropwise with stirring to a solution of [NMe$_4$]$_2$[MoOCl$_5$] (0.44 g, 1 mmol) in methanol (15 cm^3). The colour of the solution changed to deep red. On cooling, a black microcrystalline compound deposited which was collected by filtration, washed with cold CH$_3$OH and CHCl$_3$, and dried over CaCl$_2$ (yield, 54%).

Analyses.—Carbon, H, and N analyses were performed by the Australian Mineral Development Laboratories, Melbourne and the microanalytical laboratory of this Institute. Molybdenum was estimated gravimetrically using quinolin-8-ol as the reagent.[13] Sulphur content was determined by peroxide fusion of the sample, followed by gravimetric estimation in the form of BaSO$_4$. Analytical data of the compounds are shown in Table 1.

Results and Discussion

Synthesis of the Complexes.—The molybdenum(VI) complexes [MoO$_2$L$_2$] (2a)—(2d) were synthesised by the reaction of [MoO$_2$(acac)$_2$] with the appropriate ligand and were obtained as microcrystalline solids, which [with the exception of (2a)] required no special precautions in handling. Solid samples showed no sign of decomposition after several months when stored in a desiccator. The compounds have poor solubilities in common solvents except dmf and dimethyl sulphoxide. Synthesis of (2a) should be carried out with care. Control of the reaction temperature to 0 °C and quick filtration of the precipitated compound ensures purity of the product. Increasing the reaction temperature (*ca.* 10 °C) and delay in filtration causes substantial reduction of the Mo^{VI} compound to a Mo^{V} species. In fact gentle heating at 50 °C leads to the formation of the black Mo^{V} compound, [MoO(L^1)$_3$], in pure form. The complex [MoO(L^1)$_3$] can also be prepared by treating a suspension of [MoO$_2$(L^1)$_2$] in CH$_3$OH or CH$_2$Cl$_2$ with excess HL^1 at ~50 °C. This compound is monomeric in nature and is probably formed by the reduction of [MoO$_2$(L^1)$_2$] with excess of ligand present in the solution. Similar reducing action of HL^1, particularly its ability to reduce Cu^{II} to its lower-valent state has been reported already.[3] Reduction of Mo^{VI} to Mo^{V} also occurs with the other ligands HL^2—HL^4, but not so easily as with HL^1. Reduction only occurs when [MoO$_2$L$_2$] (L = L^2—L^4) is refluxed with excess of the ligand in CH$_3$OH or CH$_2$Cl$_2$. However, so far isolation of these compounds in the pure form has not been possible. This is possibly due to decomposition of the ligands at the refluxing temperature. Nevertheless the electronic absorption spectra of these impure products match qualitatively with that due to [MoO(L^1)$_3$].

Another form of a monomeric Mo^{V} compound [method (b)] of HL^1, [MoO(L^1)$_3$], was synthesised by the direct reaction of [NMe$_4$]$_2$[MoOCl$_5$] with HL^1 in dry methanol.

Infrared Spectra of the [MoO$_2$L$_2$] *Complexes*.—Pertinent i.r. bands are listed in Table 2 with probable assignments. I.r. spectra of the ligands are catalogued in the literature.[4,6] It is clear from Table 2 that the bands in the region ~2 550—2 430 cm^{-1} which are present in the ligands as ν(SH) are missing in all of the metal complexes, so indicating metal–ligand bond formation through this site. Because of strong hydrogen bonding the bands due to ν(NH) could not be located in the free *N*-alkylated ligands (HL^2—HL^4)[6] and for HL^1 it appears at ~3 230 cm^{-1}.[4] The occurrence of a band at ~3 160 cm^{-1} suggests that the secondary amino-group is free from co-ordination in complexes (2b)—(2d).[6] In the case of (2a), more than one such band appeared in the region ~3 360—3 175 cm^{-1} suggesting a free primary amino-group in this complex. The free ligands display a strong band at ~880 cm^{-1} due

Table 2. Infrared data (cm^{-1}) and tentative band assignments for the complexes

Compd.	ν(N–H)	ν(Mo=O)	ν_{asym}(CSS)	ν(Mo–S)
(2a)	3 320br	905s	815s	370m
	3 175m	860s		320w
(2b)	3 160m	905s	820s	370m
		875s		320w
(2c)	3 165m	903s	805s	365m
		865s		320w
(2d)	3 165m	903s	805s	365m
		865s		320w
(3a)	3 360br			
	3 280br	935m	815s	330w
	3 180br			
(3b)	3 350br	940m	1 235m	320w
	3 270br		810s	

Table 3. Electronic and n.m.r. spectroscopic, and electrochemical data for the [MoO_2L_2] complexes

			E/V *vs.* s.c.e.^{c}	
Compd.	$\tilde{\nu}$/cm^{-1} ^{a}	δ(NH ··· S)/ p.p.m.^{b}	E_{pc} ^{d}	$E_{\frac{1}{2}}$ ^{e}
(2a)	22 220 (4.22) 26 600 (4.51) 32 000 (4.12)	10.82	−0.93	−0.91
(2b)	21 740 (4.31) 26 200 (4.54) 32 600 (4.08)	12.55	−1.05	−1.02
(2c)	21 830 (4.25) 26 000 (4.55) 32 800 (4.10)	12.66	−0.98	−0.95
(2d)	21 830 (4.33) 26 200 (4.52) 32 400 (4.11)	12.33	−1.03	−1.00

^{a} log (ε/dm^3 mol^{-1} cm^{-1}) values are given in parentheses. ^{b} Obtained from free ligand spectra. ^{c} Supporting electrolyte [NEt_4][ClO_4] (0.1 mol dm^{-3}) in dmf. ^{d} Cathodic peak potential. ^{e} Calculated from differential pulse polarographic data.

to asymmetric CSS stretching. This band is diagnostic in deciding the mode of sulphur chelation in these complexes.[6] It is generally found that in the case of disulphur chelation a single band is observed, whereas, for unidentate sulphur chelation this band is split symmetrically. For the complexes studied here, [MoO_2L_2] (2a)—(2d), a strong sharp single band at ~810 cm^{-1} assignable to ν_{asym}(CSS) is observed, thus indicating disulphur chelation. Regarding the assignment of Mo–O absorptions, two strong bands in the region ~900—860 cm^{-1} were observed for all the Mo^{VI} complexes, thus indicating *cis*-dioxo-bonding[14–16] of the oxygen atoms in these complexes.

Electronic Spectra of the [MoO_2L_2] *Complexes.*—Electronic spectral data for the various [MoO_2L_2] type complexes are shown in Table 3. Bands occurring above 23 000 cm^{-1} are due to internal ligand transitions.[6] The band at ~22 000 cm^{-1} is assignable to a ligand-to-metal Mo($d\pi$) $\longleftarrow$ L(π) charge-transfer (l.m.c.t.) transition. Such l.m.c.t. transitions are also reported[15,16] for [$MoO_2(dtc)_2$] (dtc = *NN*-dialkyldithiocarbamate) type complexes where similar (S,S$^-$) bonding occurs.

Electrochemical Studies of the [MoO_2L_2] *Complexes.*—The relevant electrochemical data for complexes [MoO_2L_2] (2a)—(2d) in the potential range +0.5 to −1.5 V *vs.* s.c.e. are summarised in Table 3. The ligands are electrode inactive in the potential range studied. All reductions are irreversible. The variable-scan cyclic voltammograms for (2d) are shown in Figure 1, which is typical of all the [MoO_2L_2] compounds. Figure 1 also includes the differential pulse polarogram of the same compound. It displays one reduction peak (E_{pc}) at −1.03 V (scan rate 0.01 V s^{-1}).

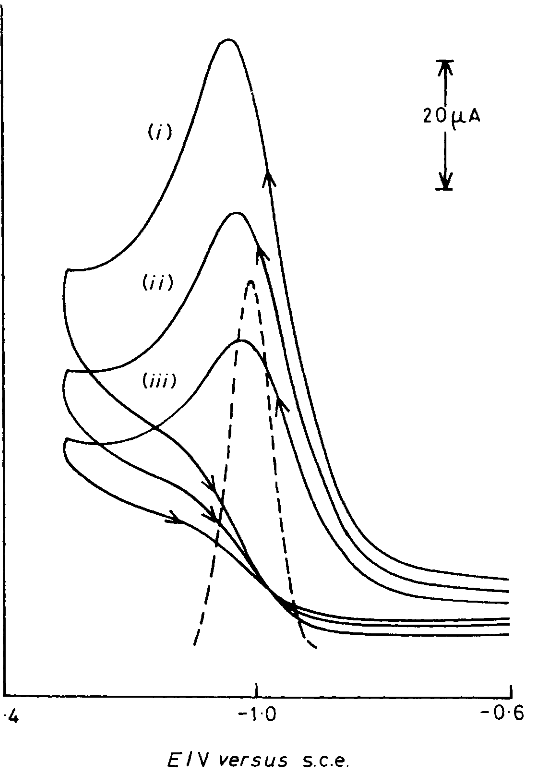

Figure 1. Cyclic voltammograms (——) of [$MoO_2(L^4)_2$] (2d) in dmf (~10^{-3} mol dm^{-3}) at a platinum electrode; scan rate, (*i*) 0.2, (*ii*) 0.1, (*iii*) 0.05 V s^{-1}. Differential pulse voltammogram (— — —) of (2d) at a scan rate of 0.01 V s^{-1}, peak-to-peak amplitude 25 mV

Attempted coulometry at potentials more negative than E_{pc} gave continuous coulomb counts due to unidentified reactions. However, on comparing the observed current height at E_{pc} with those of the authentic 1e$^-$ reductions carried out in this laboratory[17] the voltammetric response observed here appears to be a metal-centred one-electron transfer comprising the Mo^{VI} and Mo^{V} oxidation states: [$Mo^{VI}O_2L_2$] + e$^-$ $\longrightarrow$ [$Mo^{V}O_2L_2$]$^-$. The lack of anodic response even at a high scan rate (0.5 V s^{-1}) is evidently due to rapid decomposition of the reduced species [MoO_2L_2]$^-$.

The half-wave potential ($E_{\frac{1}{2}}$) was calculated from the differential pulse polarographic data utilising the equation[18] $E_{pc} = E_{\frac{1}{2}} - \Delta E/2$, where E_{pc} is the reduction peak potential and ΔE the modulation amplitude.

The most notable electrochemical feature of the [MoO_2L_2] type complexes as revealed from Table 3 is the significant change in $E_{\frac{1}{2}}$ imparted by apparently small changes in ligand structure. Such high sensitivity of the metal-centred redox potentials towards remote substitution on the ligand framework is well documented in the literature.[1,19] This change in $E_{\frac{1}{2}}$ could be interpreted as being due to the substantial ligand character of the electron-transfer orbital.[19] This explanation gains further support from the fact that the terminal oxygen atoms in [MoO_2L_2] (2a)—(2d) are extremely basic {could be replaced partially by halide ions[20] as in [$MoO_2(dtc)_2$] complexes[21]} due to the availability of high electron density on the

Table 4. Electronic and e.s.r. spectroscopic, magnetic, and electrochemical data for the $[\mathrm{MoO(L^1)_3}]$ complexes

				E/V *vs.* s.c.e.[c]			
Compound	$\tilde{\nu}$/cm^{-1} [a]	$\mu_{eff.}$/B.M.[b]	$\langle g \rangle$	E_{pc} [d]	E_{pa} [e]	ΔE_p [f]	i_{pc}/i_{pa} [g]
(3a)	12 500 (2.98) 15 500 (3.37) 22 300 (sh) 25 300 (4.47)	1.58	1.982	−0.97	−0.78	−0.19	1.21
(3b)	12 600 (3.22) 15 400 (3.55) 22 700 (sh) 25 500 (4.46)	1.65	1.985	−1.04	−0.66	−0.38	1.36

[a] log ε values are given in parentheses. [b] B.M. = 0.927×10^{-23} A m^2. [c] Scan rate 0.05 V s^{-1}; supporting electrolyte $[\mathrm{NEt_4}][\mathrm{ClO_4}]$ (0.1 mol dm^{-3}) in dmf. [d] Cathodic peak potential. [e] Anodic peak potential. [f] Difference in potentials for the cathodic and anodic peaks. [g] Ratio of the cathodic and anodic peak heights, calculated according to the method of ref. 12.

metal atom from the electron-rich ligand orbitals. In fact high electron density is located in the $-\mathrm{C}\begin{smallmatrix}\nearrow\!S\\ \searrow\!S\end{smallmatrix}$ part of the ligand due to which strong N–H ··· S hydrogen bonding occurs [4,6] and as a result the N–H ··· S proton is observed at much lower fields (δ 10.82—12.66 p.p.m.) (Table 3) in n.m.r. spectra of the ligands.

Characterisation of Mo^{V} *Complexes*.—Both the Mo^{V} compounds prepared by methods (a) and (b) gave identical analytical results. The compounds are paramagnetic and therefore should be formulated as monomeric Mo^{V} species, $[\mathrm{MoO(L^1)_3}]$. I.r. spectral features of the Mo^{V} compounds (Table 2) are similar to the Mo^{VI} compounds, thus suggesting (S,S$^-$) co-ordination. The spectra of both compounds contain a single band at ~940 cm^{-1} assignable to ν(Mo=O).[22] However, the spectrum of the Mo^{V} compound prepared by method (b) contains an additional medium intensity band at 1 235 cm^{-1} assignable to ν_{asym}(CSS) stretching due to unidentate sulphur co-ordination [23] thus suggesting the possibility that at least one of the ligands is unidentate. Hereafter the two Mo^{V} compounds will be represented as (3a) [prepared by method (a)] and (3b) [prepared by method (b)].

Electronic Spectra of (3a) *and* (3b).—A distinctive feature of the monomeric Mo^{V} compounds is their intense red colour in solution (dmf) due to electronic transitions in the region 12 000—23 000 cm^{-1} (Table 4, Figure 2). The characteristics of the Mo^{V} mononuclear oxo-complexes are the appearance of two low-energy bands at ~12 500 and 22 500 cm^{-1} (Table 4) which are essentially ligand independent and found in many such complexes.[24,25] The results are consistent with the $(4d_{xy})^1$ electronic ground state ($^2B_2$) for molybdenum(v) and the bands are assignable to $^2B_2 \longrightarrow {}^2E$ ($\mathrm{O}_{2p\pi} \longrightarrow \mathrm{Mo}_{4d_{xy}}$) and $^2B_2 \longrightarrow {}^2E$ ($\mathrm{Mo}_{4d_{xy}} \longrightarrow \mathrm{Mo}_{4d_{xz,yz}}$) transitions respectively.[24,25] Another strong band appearing at ~15 500 cm^{-1} probably originates from the ligand-to-metal (S ⟶ Mo) charge transfer.[26]

Magnetic Moment and E.S.R. Data for (3a) *and* (3b).—The magnetic moment and e.s.r. data for the monomeric Mo^{V} complexes are listed in Table 4. The $\mu_{eff.}$ values are quite close to the spin-only value for a d^1 system.

The e.s.r. spectra of complexes (3a) and (3b) are almost identical. The room temperature (298 K) spectra in the powdered form and in solution (dmf) show a single central absorption at $\langle g \rangle$~1.98 due to the resonance of molecules with even metal isotopes ($I = 0$). The observed $\langle g \rangle$ values are somewhat higher than those for the related oxo- and halogeno-species,[27] the reason for which may be the polarisable nature of sulphur ligands.[22]

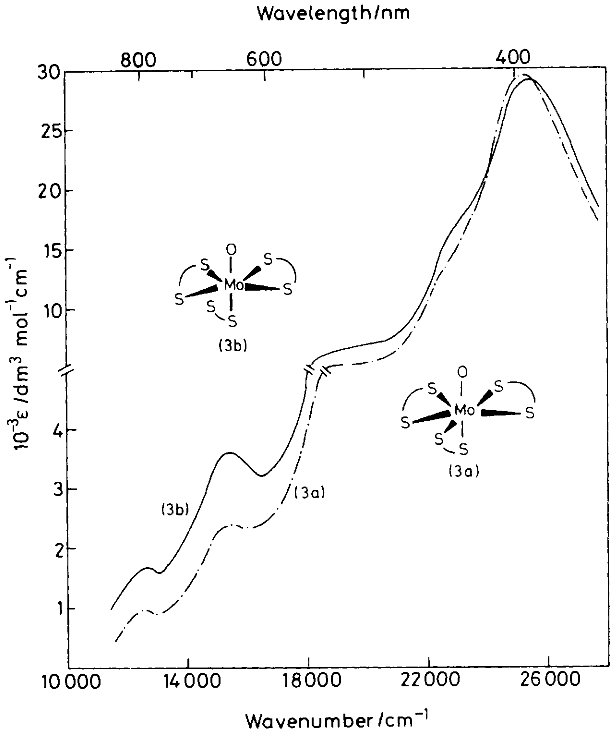

Figure 2. Electronic spectra of $[\mathrm{Mo^{V}O(L^1)_3}]$ (3a) and (3b) in dmf solution

Electrochemistry of (3a) *and* (3b).—The cyclic voltammetric traces and electrochemical data for the reduction of Mo^{V} complexes (3a)—(3b) in dmf in the range +0.5 to −1.5 V *vs.* s.c.e. are shown in Figure 3 and Table 4. In both cases reduction is essentially a quasi-reversible process.[28] The charge-transfer irreversibility is likely to be the reason for the high value of ΔE_p. In both cases the value of $i_{pc}/i_{pa} > 1$, suggesting that a post-chemical process is very much in operation.[12] This may possibly be the oxidation of the Mo^{IV} species that is formed during the cathodic scan and which is known to be very sensitive to traces of moisture and oxygen.[9] Anodic scans, beginning just slightly more positive than the reduction peak, showed no oxidation peaks in the voltage range used,

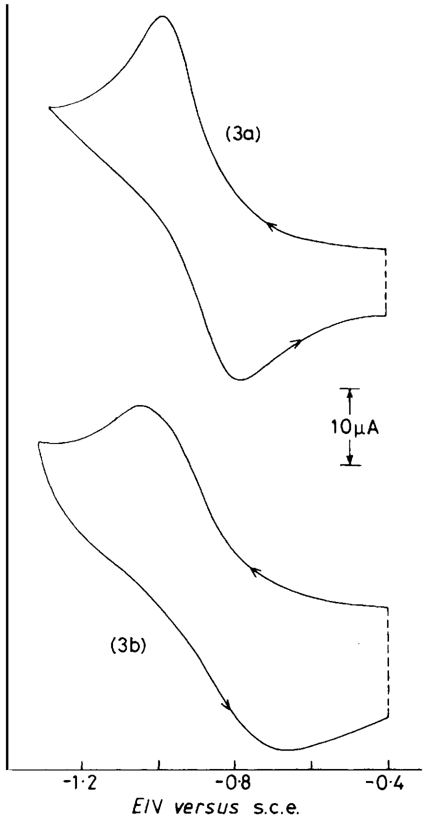

Figure 3. Cyclic voltammograms of $[Mo^{V}O(L^{1})_{3}]$ (3a) and (3b) in dmf (~10^{-3} mol dm^{-3}) at a platinum electrode; scan rate 0.05 V s^{-1}

inferring that neither of the complexes is electrochemically oxidisable to Mo^{VI} species under these conditions.

Satisfactory coulometric results were not obtained because of constant coulomb counts due to some unidentified chemical reactions, one of which may be the dimerisation of the Mo^{V} species because of their extreme moisture sensitivity in the coulometric time-scale as observed by others.[9] However, comparison of the current heights at E_{pc} with those of authentic 1e$^-$ reductions carried out in this laboratory [17] suggests that in both cases the reduction is a metal-centred one-electron process between Mo^{V} and Mo^{IV} states: $[Mo^{V}O(L^{1})_{3}] + e^{-} \longrightarrow [Mo^{IV}O(L^{1})_{3}]^{-}$. Similar electrochemical behaviour was also observed by Spence and co-workers [9] for various other monomeric Mo^{V} complexes.

The significant electrochemical feature of the two Mo^{V} complexes is the difference in their ease of reduction. Compound (3a) is reduced at a slightly more positive potential ($E_{pc} = -0.97$ V) compared to (3b) ($E_{pc} = -1.04$ V). This result correlates well with the idea that (3a) may be a seven-co-ordinate species containing one more sulphur atom co-ordinated to the central metal ion. This additional sulphur atom probably helps in lowering the energy of the electron-transfer orbital and subsequent stabilisation of the reduced species by more effective charge distribution.[29]

Thus the small differences in i.r. and electronic spectroscopic and voltammetric features of the two Mo^{V} compounds having identical chemical composition could be interpreted as being due to a difference in the co-ordination sphere surrounding the central metal ion. While (3a) is assumed to be a seven-co-ordinate species with a gross pentagonal bipyramid (D_{5h}) geometry (common for seven-co-ordinate molybdenum compounds [30]), (3b) is a six-co-ordinate octahedral (O_{h}) molecule as shown in Figure 2.

Conclusions

The binding of 2-aminocyclopent-1-ene-1-carbodithioic acid (HL^{1}) and its *N*-alkylated derivatives HL^{2}—HL^{4} with molybdenum occurs through disulphur chelation. The observed $\langle g \rangle$ values (~1.98) for the Mo^{V} compounds are quite close to the corresponding value (1.977) determined for the xanthine oxidase molecule.[31] Electrochemical studies have established that the reductions $Mo^{VI} \longrightarrow Mo^{V}$ and $Mo^{V} \longrightarrow Mo^{IV}$ occur at almost the same potential (~ −0.95 V). Reduction potentials determined for the Mo^{VI}–Mo^{V} and Mo^{V}–Mo^{IV} couples in xanthine oxidase [32] and xanthine dehydrogenase [33] respectively are also essentially equal. All these observations indicate that a close correlation may exist between the co-ordination environment surrounding molybdenum in molybdenum cofactor of xanthine oxidase and in the system studied here.

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References

1 D. A. Smith and F. A. Schultz, *Inorg. Chem.*, 1982, **21**, 3035 and refs. therein.
2 E. I. Steifel, 'Molybdenum and Molybdenum Containing Enzymes,' ed. M. P. Coughlan, Pergamon Press, Oxford, 1980, ch. 2.
3 K. Nag and D. S. Joardar, *Z. Naturforsch., Teil B*, 1975, **30**, 107.
4 K. Nag and D. S. Joardar, *Inorg. Chim. Acta*, 1975, **14**, 133.
5 K. Nag and D. S. Joardar, *Inorg. Chim. Acta*, 1975, **17**, 111.
6 K. Nag and D. S. Joardar, *Can. J. Chem.*, 1976, **74**, 2827.
7 B. Bordas, P. Sohar, G. Matolcsy, and P. Berencsi, *J. Org. Chem.*, 1972, **37**, 1727.
8 A. I. Vogel, 'A Text-Book of Practical Organic Chemistry,' Longmans, London, 1973.
9 R. D. Taylor, J. P. Street, M. Minelli, and J. T. Spence, *Inorg. Chem.*, 1978, **17**, 3207.
10 G. J.-J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Chem.*, 1976, **15**, 2612.
11 A. K. Banerjee and H. K. Saha, *Inorg. Synth.*, 1974, **15**, 100.
12 D. T. Sawyer and J. L. Roberts, jun., 'Experimental Electrochemistry for Chemists,' Wiley, New York, 1974, pp. 212, 341.
13 A. I. Vogel, 'A Text-Book of Quantitative Inorganic Analysis,' 2nd edn., Longmans, London, 1955.
14 F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 867.
15 F. W. Moore and M. L. Larson, *Inorg. Chem.*, 1967, **6**, 998.
16 R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc. A*, 1970, 1702.
17 P. Bandyopadhyay, P. K. Mascharak, and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1982, 675; P. Ghosh, P. Bandyopadhyay, and A. Chakravorty, *ibid.*, 1983, 401.
18 E. P. Parry and R. A. Osteryoung, *Anal. Chem.*, 1965, **37**, 1634.
19 G. S. Patterson and R. H. Holm, *Inorg. Chem.*, 1972, **11**, 2285.
20 M. Chaudhury, unpublished work.
21 J. Dirand, L. Ricard, and R. Weiss, *J. Chem. Soc., Dalton Trans.*, 1976, 278.
22 I. W. Boyd, I. G. Dance, K. S. Murray, and A. G. Wedd, *Aust. J. Chem.*, 1978, **31**, 279.
23 O. Piovesana and G. Cappuccilli, *Inorg. Chem.*, 1972, **11**, 1543.
24 C. D. Garner, I. H. Hillier, and F. E. Mabbs, *Chem. Phys. Lett.*, 1975, **32**, 224; C. D. Garner, L. Hill, N. C. Howlader, M. R.

Hyde, F. E. Mabbs, and V. I. Routledge, 'Proceedings of the Second International Conference on the Chemistry and Uses of Molybdenum,' ed. P. C. H. Mitchell, Climax Molybdenum Co., London, 1976, p. 14.

25 E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J. Chem. Soc.*, 1963, 4649.

26 G. R. Hanson, A. A. Brunette, A. C. McDonell, K. S. Murray, and A. G. Wedd, *J. Am. Chem. Soc.*, 1981, **103**, 1953.

27 M. I. Scullane, R. D. Taylor, M. Minelli, J. T. Spence, K. Yamanouchi, J. H. Enemark, and N. D. Chasteen, *Inorg. Chem.*, 1979, **18**, 3213.

28 R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.

29 F. A. Schultz, V. R. Ott, D. S. Rolison, D. C. Bravard, J. W. McDonald, and W. E. Newton, *Inorg. Chem.*, 1978, **17**, 1758.

30 M. G. B. Drew, *Prog. Inorg. Chem.*, 1977, **23**, 67 and refs. therein.

31 L. S. Meriwether, W. F. Marzluff, and W. G. Hodgson, *Nature (London)*, 1966, **212**, 465.

32 R. Cammack, M. J. Barber, and R. C. Bray, *Biochem. J.*, 1976, **157**, 469.

33 M. J. Barber, R. C. Bray, R. Cammack, and M. P. Coughlan, *Biochem. J.*, 1977, **163**, 279.

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