Chemistry of Molybdenum. Part 9.[1] Non-oxomolybdenum(IV) and Mononuclear Oxomolybdenum(V) Complexes with Dithioacid Ligands†

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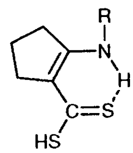
The syntheses and characterisation of a series of non-oxomolybdenum(IV) and mononuclear oxomolybdenum(V) complexes are described with 2-aminocyclopent-1-ene-1-carbodithioate (acda) and its *N*-alkyl derivatives [aacda; alkyl = ethyl (eacda), propyl (pacda) or butyl (bacda)] as the bidentate $(S–S)^-$ donor ligands. The molybdenum(IV) complexes [Mo(ox)(aacda)(acda)] (ox = oxalate) are feebly paramagnetic (*ca.* 0.9 μ_B) with a spin-paired d^2 ground state. They exhibit rich electrochemistry consisting of two reversible one-electron couples: $Mo^{IV}–Mo^{III}$ ($E_{\frac{1}{2}} \approx -0.45$ V) and $Mo^{IV}–Mo^{V}$ ($E_{\frac{1}{2}} \approx +0.54$ V), indicating conservation of the six-co-ordinated structure in $[Mo(ox)(aacda)(acda)]^z$ ($z = -1$, 0 or +1). The molybdenum(V) complexes $[MoOCl(L)_2]$ (L = acda **2a**, eacda **2b**, pacda **2c** or bacda **2d**) are paramagnetic (1.56–1.68 μ_B) with one unpaired electron. Their electronic spectra in the visible region are dominated by high intensity multiple bands arising from $S(\pi) \longrightarrow Mo(d_\pi)$ charge transfers. The cyclic voltammograms of the complexes show a reversible, one-electron $Mo^V–Mo^{IV}$ reduction and an irreversible $Mo^V–Mo^{VI}$ oxidation. In frozen solution (80 K), **2a** has an axially anisotropic ESR spectrum indicating axial co-ordination of Cl. For the remaining compounds **2b–2d** the features are much more complicated due to the hyperfine interactions from the chloro ligand providing evidence for possible equatorial co-ordination of Cl.

The mandatory presence of terminal oxo group(s) in the ubiquitous cofactor molecule of oxotransferase molybdenum enzymes has been established from extended X-ray absorption fine structure spectroscopy (EXAFS) studies.[2] The chemistry of this oxometallate bond (Mo=O) under the constraints of the protein microenvironment turns out to be extremely interesting, catalysing a large number of biological two-electron redox reactions in which an oxygen atom or a hydroxyl group is transferred to or abstracted from the substrate.[3] Mononuclear Mo^V ($4d^1$) is implicated as the intermediate metal oxidation state during the turnover process.[4] The favourable magnetic properties (^{96}Mo, $I = 0$, ≈75% and ^{95,97}Mo, $I = \frac{5}{2}$, ≈25%) of this lone molybdenum(V) centre has been extensively used as the only spectroscopic probe to explicate the metal binding sites in these complex enzymes.[5] Several model molybdenum compounds with multifunctional thio ligands have been reported recently[6–11] with a view to enhancing our understanding of the molybdenum biochromophores.

In this laboratory, for quite sometime, we have been engaged in a program aimed at credible synthesis of sulfur-rich molybdenum compounds in order to approach the biological co-ordination units found in hydroxylase-type molybdoenzymes. Accordingly, we have synthesised and examined a number of molybdenum–sulfur compounds using 2-aminocyclopent-1-ene-1-carbodithioate (acda) and its *N*-alkyl derivatives [aacda; alkyl = ethyl (eacda), propyl (pacda) or butyl (bacda)] as bidentate $(S–S)^-$ donor ligands.[1,12–17] Here we present a detailed account of the synthesis, magnetic, spectroscopic and electrochemical properties of $[Mo^{IV}(ox)(S–S)_2]$ (ox = oxalate) and $[Mo^VOCl(S–S)_2]$ complexes derived from the $(S–S)^-$ donor ligands.



R	
H	Hacda
Et	Heacda
Pr	Hpacda
Bu	Hbacda

Experimental

Materials and Methods.—The precursor compounds $[MoOCl(acac)_2]$ (acac = acetylacetonate)[18] and $[MoO(ox)(aacda)_2]$[19] and the ligands Hacda[20] and Haacda[21] were prepared following literature methods. Cyclopentanone (E. Merck), *n*-propylamine (Fluka), *n*-butylamine (Riedel) and acetylacetone (BDH) were freshly distilled before use. Reagent-grade solvents, dried and distilled by standard methods,[22] were used in all cases. All other chemicals were of reagent grade, obtained commercially and used as received.

UV/VIS spectra in solution were recorded on a Shimadzu UV-2100 spectrophotometer, while infrared spectra employed a Perkin-Elmer 783 spectrometer with samples prepared as KBr pellets. Far-infrared spectra were recorded at ambient temperature on Nujol mulls with a Nicolet-20F Fourier-transform infrared spectrometer (4 cm^{-1} resolution) employing a DTGS detector. Magnetic moments of powdered samples at room temperature were calculated from data obtained on a PAR 155 vibrating-sample magnetometer. The X-band ESR spectra in solution [dimethylformamide (dmf)–toluene (1:10 v/v)] at room temperature and in the frozen state (80 K) were recorded with diphenylpicrylhydrazyl (dpph) as a field marker on a Bruker ER 200D SRC spectrometer equipped with standard Bruker attachments as described earlier.[13] Elemental analyses (C, H and N) were performed with a Perkin-Elmer

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† *Non-SI units employed:* $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T.

240C elemental analyser by the Microanalytical Services of this Department. Molybdenum (as 8-hydroxyquinolinate) and chloride (as AgCl) contents were estimated gravimetrically using standard procedures.[23]

Electrochemical measurements were performed either with a Bioanalytical System model 100B or a CV-27 instrument. A Pt disc working- and a Pt wire auxiliary-electrode were utilised. The saturated calomel electrode (SCE) was the reference electrode and ferrocene was used as the internal standard. Bulk electrolyses were carried out with the use of a Pt-gauze working electrode. Concentrations of sample solutions were *ca.* 10^{-3} mol dm^{-3} and contained 0.1 mol dm^{-3} NEt_4ClO_4 as the supporting electrolyte. Scrupulously dried and freshly distilled deoxygenated solvents were used throughout. Details of measurements were described elsewhere.[24] Potentials are reported at 25 °C relative to SCE and are uncorrected for junction potentials. Under our experimental conditions the ferrocenium–ferrocene couple is at $E_{\frac{1}{2}} = +0.4$ V *vs.* SCE.

Preparation of the Compounds.—All manipulations in the following preparations were carried out under an atmosphere of purified dinitrogen.

[Mo(ox)(bacda)(acda)]·MeOH **1b**. A methanolic solution (15 cm^3) of Hacda (0.28 g, 1.8 mmol) was added dropwise to a stirred suspension of [MoO(ox)(bacda)$_2$]* (0.36 g, 0.58 mmol) in CH_2Cl_2 (30 cm^3) at room temperature over a period of 1 h. As Hacda was added, [MoO(ox)(bacda)$_2$] started to dissolve and the solution turned from its initial saffron colour to brown. After all the ligand had been added, a dark brown solution was obtained. It was stirred for an additional 3 h to ensure completion of the reaction. The solution was then filtered. The filtrate was concentrated to *ca.* 20 cm^3 by rotaevaporation, layered with excess diethyl ether and kept at 0 °C for ≈4 h to afford a dark brown powder. Recrystallisation from CH_2Cl_2–methanol (1:1 v/v)–Et_2O at 0 °C yielded shining microcrystals. The purity of the product was checked by TLC. Yield: 0.14 g (42%) (Found: C, 38.2; H, 4.8; Mo, 16.7; N, 4.9. Calc. for $C_{19}H_{28}MoN_2O_5S_4$: C, 38.8; H, 4.8; Mo, 16.3; N, 4.8%).

[Mo(ox)(eacda)(acda)]·MeOH **1a**. This compound was obtained in 45% yield from the [MoO(ox)(eacda)$_2$][19] precursor using an identical procedure as reported above for **1b** (Found: C, 36.9; H, 4.3; Mo, 16.9; N, 5.2. Calc. for $C_{17}H_{24}MoN_2O_5S_4$: C, 36.4; H, 4.3; Mo, 17.1; N, 5.0%).

[MoOCl(acda)$_2$] **2a**. To a freshly prepared solution of [MoOCl(acac)$_2$] (0.30 g, 0.87 mmol) in methanol (15 cm^3) was added dropwise, with constant stirring, a solution of Hacda (0.28 g, *ca.* 2 equivalents) in methanol (15 cm^3), causing slow precipitation of a dark brown solid. The mixture was stirred for an additional 30 min to ensure complete formation of the complex. The solid was filtered, washed with methanol and diethyl ether, and dried *in vacuo*. Yield: 0.31 g (77%). The compound is sparingly soluble in all common organic solvents except dmf. Several attempts to recrystallise it from dmf were unsuccessful (Found: C, 30.8; H, 3.6; Cl, 7.3; Mo, 20.6; N, 5.8. Calc. for $C_{12}H_{16}ClMoN_2OS_4$: C, 31.1; H, 3.4; Cl, 7.6; Mo, 20.7; N, 6.0%).

[MoOCl(eacda)$_2$] **2b**. A solution of Heacda (0.22 g, 1.17 mmol) in chloroform (15 cm^3) was added dropwise with stirring to a freshly prepared solution of [MoOCl(acac)$_2$] (0.2 g, 0.58 mmol) in methanol (15 cm^3). The resulting deep red solution was stirred for *ca.* 2 h, the solution volume was then reduced under vacuum to *ca.* 10 cm^3 and chilled (0 °C) diethyl ether (10 cm^3) was added to induce precipitation of a brown solid. After filtration, the product was washed with methanol. Recrystallisation from CH_2Cl_2–Et_2O gave dark brown microcrystals. Yield: 0.15 g (50%) (Found: C, 36.4; H, 4.9; Cl, 6.6; Mo, 18.4; N, 5.1. Calc. for $C_{16}H_{24}ClMoN_2OS_4$: C, 36.9; H, 4.6; Cl, 6.8; Mo, 18.5; N, 5.4%).

The following compounds were prepared similarly as described for **2b** from [MoOCl(acac)$_2$] and the appropriate Haacda ligands.

[MoOCl(pacda)$_2$] **2c**. Yield: 32% (Found: C, 39.5; H, 5.2; Cl, 6.3; Mo, 17.5; N, 5.0. Calc. for $C_{18}H_{28}ClMoN_2OS_4$: C, 39.4; H, 5.1; Cl, 6.5; Mo, 17.5; N, 5.1%).

[MoOCl(bacda)$_2$] **2d**. Yield: 30% (Found: C, 41.7; H, 5.6; Cl, 5.9; Mo, 16.5; N, 5.0. Calc. for $C_{20}H_{32}ClMoN_2OS_4$: C, 41.7; H, 5.5; Cl, 6.1; Mo, 16.7; N, 4.8%).

Results and Discussion

[Mo(ox)(aacda)(acda)]·MeOH **1a**, **1b**.—The dark brown non-oxomolybdenum(IV) complexes **1a** and **1b** are prepared by allowing a suspension of [MoO(ox)(aacda)$_2$][19] in CH_2Cl_2 to react with a solution of Hacda (1:3 mol ratio) in methanol at room temperature. Stirring the reaction mixture results in dissolution of solid [MoO(ox)(aacda)$_2$] to give a deep brown solution from which the product eventually separates as a microcrystalline solid upon addition of diethyl ether. Formation of the molybdenum(IV) complexes **1a** and **1b** probably proceeds through a multistep mechanism in which Hacda functions both as a reductant and an incoming ligand as described earlier.[15] The compounds are air stable in the solid state. They have reasonably good solubilities in CH_2Cl_2 and acetonitrile and undergo slow decomposition in solution in air. Our repeated attempts to grow diffraction-quality crystals of these compounds were without success because of their limited stability in solution.

The IR data recorded for the molybdenum(IV) complexes (Table 1) are in accord for bidentate (S–S)$^-$ chelation of the ligands. This is ascertained by the presence of a single sharp carbon–sulfur stretching at *ca.* 820 cm^{-1} due to ν_{asym}(CSS) as described previously for analogous complexes.[16,17] In the spectra of the free ligands this band appears at *ca.* 880 cm^{-1} and is split symmetrically upon co-ordination in a monodentate manner through sulfur.[25] Also consistent with the assigned mode of disulfur chelation are the presence of medium intensity bands due to ν(N–H) vibrations at *ca.* 3360, 3280 and 3155 cm^{-1} in the complexes. As reported earlier[17] the first two bands are characteristic of the primary amino group of acda and the remaining one is due to the secondary amino group of the aacda ligands. The presence of these bands verifies the proposition that the amino groups in the carbodithioate ligands remain intact and do not participate in metal co-ordination. The loss of the terminal oxo group in these products has been confirmed by the complete absence of a strong characteristic Mo=O stretch in the region 850–1000 cm^{-1}.[26] The spectra also contain a medium intensity band at 355 cm^{-1} assignable to ν(Mo–S). Additional features in the form of prominent bands at 1720, 1700, 1630 [$\nu_{asym}(CO_2)$], 1280 [$\nu_{sym}(CO_2)$] and 780 cm^{-1} [δ(OCO)] are diagnostic of the presence of a non-bridged bidentate oxalato group[27] in the molybdenum co-ordination sphere of the complexes **1a** and **1b**.

The proposed ligand attachment solely on the basis of infrared data may sound somewhat speculative in the absence of crystallographic evidence. More direct evidence in favour of disulfur chelation in **1a** and **1b**, however, comes from a closely comparable IR spectrum of [Bi(eacda)$_3$] in which the bidentate (S–S)$^-$ structure of the ligand eacda has been confirmed by X-ray crystallography.[28]

In the solid state at room temperature molybdenum(IV) complexes are diamagnetic with a small amount of associated paramagnetism. The magnetic moments of 0.85 and 0.93 μ_B for the complexes **1a** and **1b**, respectively are most likely due to the presence of ferromagnetic impurities[29] and/or temperature independent paramagnetism.[30] The measured diamagnetism is consistent with a spin-paired d^2 electronic configuration as

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* The complex [MoO(ox)(bacda)$_2$] was prepared by the reaction of [MoO$_2$(bacda)$_2$][17] with oxalic acid in 1:1 mol ratio in methanol. Details of its preparation will be reported elsewhere.[19]

Table 1 IR data (cm^{-1})* and tentative band assignments for the complexes

Complex	ν(Mo=O)	ν_{asym}(CSS)	ν(Mo–S)	ν(Mo–Cl)	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$
1a	—	820	355	—	1720 1700 1630	1280
1b	—	820	355	—	1720 1700 1635	1280
2a	955	820	351	277	—	—
2b	965	820	344 329	251	—	—
2c	970	820	344 326	249	—	—
2d	965	815	340 320	252	—	—

* As KBr disc.

Table 2 Visible electronic spectral data for the complexes

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
1a^a	826 (1540), 753 (1690), 668 (2600), 540 (4730), 506 (4425)
1b^a	831 (1200), 757 (1265), 675 (2590), 545 (5560), 511 (4990)
2a^b	800 (1625), 722 (sh), 659 (3200), 535 (6490), 497 (5180)
2b^b	825 (1260), 750 (sh), 665 (3150), 540 (6630), 512 (5450)
2c^b	832 (1230), 759 (sh), 675 (3030), 545 (6700), 509 (5680)
2d^b	830 (1180), 755 (sh), 665 (3210), 540 (6350), 510 (5600)

^{a} In CH_2Cl_2. ^{b} In dmf.

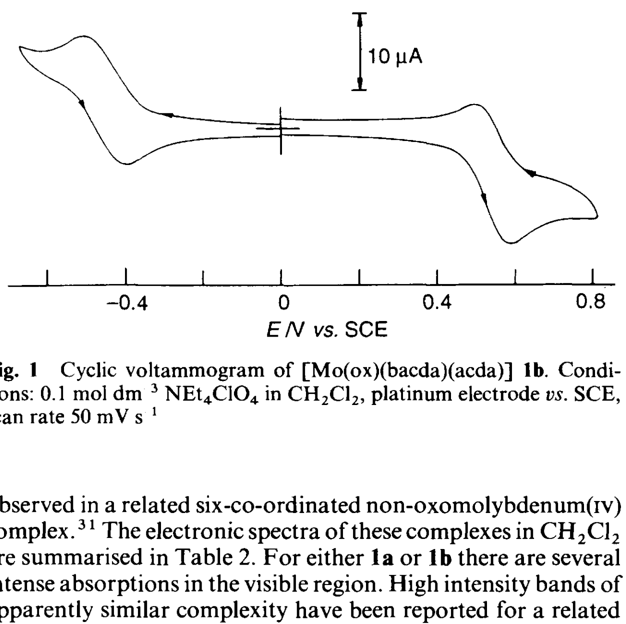

Fig. 1 Cyclic voltammogram of [Mo(ox)(bacda)(acda)] **1b**. Conditions: 0.1 mol dm^{-3} NEt_4ClO_4 in CH_2Cl_2, platinum electrode *vs.* SCE, scan rate 50 mV s^{-1}

observed in a related six-co-ordinated non-oxomolybdenum(IV) complex.[31] The electronic spectra of these complexes in CH_2Cl_2 are summarised in Table 2. For either **1a** or **1b** there are several intense absorptions in the visible region. High intensity bands of apparently similar complexity have been reported for a related system elsewhere.[31] The exact origin of these absorptions is still unknown. Nevertheless, we suggest these transitions to be ligand-to-metal charge-transfer (l.m.c.t.), $S(\pi)\rightarrow Mo(d_\pi)$, in character on the basis of their high molar absorptions (ε 1200–5560 dm^3 mol^{-1} cm^{-1}). In addition, both compounds also show intense ligand-localised bands near or below 400 nm.

Cyclic voltammograms of the complexes **1a** and **1b** at a platinum electrode in CH_2Cl_2 have nearly identical features. A typical cyclic voltammogram for **1b** is shown in Fig. 1 where two redox couples are observed at $E_{\frac{1}{2}} = -0.45$ (process I) and +0.54 V (process II) *vs.* SCE in the potential range from −1.0 to +1.0 V. The ligands are electrode inactive in this range. Analogous couples in **1a** occur at −0.43 and +0.52 V respectively. The ratios between cathodic and anodic peak currents, i_{pc}/i_{pa}, were almost unity and independent of scan rate (50–500 mV s^{-1}) for the two redox couples. Plots of i_p ($= i_{pc} + i_{pa}$) *vs.* $v^{\frac{1}{2}}$ (v is the scan rate in mV s^{-1}) in the above range were linear, and potential separations (ΔE_p) between anodic and cathodic peaks were *ca.* 110 (process I) and 95 mV (process II) while $E_{\frac{1}{2}}$ values were constant within an accuracy of ±2.5% regardless of scan rate. For comparison, ΔE_p for the ferrocenium–ferrocene couple was found to be 95 mV with this electrode configuration in CH_2Cl_2. We refer, therefore, each redox process to nearly reversible one-electron transfers without any coupled chemical reactions as shown by the reaction scheme in equation (1). The cathodic process (process I) thus corresponds to the Mo^{IV}–Mo^{III} couple, and the anodic process (process II) involves Mo^{IV}–Mo^{V} electron transfer.

$$[\mathrm{Mo^{V}(ox)(aacda)(acda)}]^+ \underset{II}{\overset{-e^-}{\rightleftarrows}} [\mathrm{Mo^{IV}(ox)(aacda)(acda)}]^0 \underset{I}{\overset{+e^-}{\rightleftarrows}} [\mathrm{Mo^{III}(ox)(aacda)(acda)}]^- \quad (1)$$

Controlled-potential coulometric experiments on the complexes at −0.65 and +0.75 V *vs.* SCE confirmed a one-electron reduction for process I and a one-electron oxidation for process II, respectively. Similar sequences of metal-centred electron transfers are already documented in the literature for a related six-co-ordinate molybdenum(IV) complex.[31]

[MoOCl(acda)$_2$] **2a** *and* [MoOCl(aacda)$_2$] **2b**–**2d**.—The mononuclear oxomolybdenum(V) complexes **2a**–**2d** are prepared in methanol at room temperature by metathesis reactions[32] involving [MoOCl(acac)$_2$] as precursor and the appropriate Haacda ligand. Recrystallisation from CH_2Cl_2–Et_2O affords (with the exception of **2a**) dark brown microcrystals in modest yield (30–50%). Compound **2a** is only slightly soluble in common organic solvents except for dmf. The other molybdenum(V) compounds **2b**–**2d** are however appreciably soluble in chloroform, CH_2Cl_2 and dmf. Conductivity measurements of fresh solutions in dmf indicate that the molecules are uncharged. On standing, however, the conductivity slowly increases because of certain unknown decomposition reaction(s). The results apparently suggest six-co-ordinate structures for **2a**–**2d** involving a chloro ligand in the molybdenum co-ordination sphere. We were unable to confirm the structures of these air-stable solids by X-ray diffraction, all efforts to grow diffraction-quality crystals of these compounds being unsuccessful owing to poor crystal growth habit and limited stability in solution. The infrared spectra of the complexes show all the essential features characteristic of the aacda moiety displaying in particular a strong band at 820 cm^{-1} (Table 1), thus suggesting a bidentate (S–S)$^-$ mode of chelation from the carbodithioate ligands. Characteristic ν(N–H) vibrations at 3325 and 3175 cm^{-1} in **2a** and at *ca.* 3160 cm^{-1} in **2b**–**2d** indicate that the amino nitrogen of the ligands are not

Table 3 Summary of electrochemical data[a] for the molybdenum(v) complexes

	$\mathrm{Mo^V}$–$\mathrm{Mo^{IV}}$				$\mathrm{Mo^V}$–$\mathrm{Mo^{VI}}$
Complex	$E_{\frac{1}{2}}/\mathrm{V}^b$	$\Delta E_p/\mathrm{mV}^c$	i_{pc}/i_{pa}	n^d	E_{pa}/V^b
2a	−0.32	110	1.10	0.96	0.84
2b	−0.35	120	0.97	0.91	0.75
2c	−0.34	110	1.15	1.10	0.74
2d	−0.36	110	1.05	0.93	0.72

[a] Conditions: solvent dmf; supporting electrolyte $\mathrm{NEt_4ClO_4}$ (0.1 mol dm^{-3}); solute concentration *ca.* 10^{-3} mol dm^{-3}. [b] From cyclic voltammetry using a scan rate of 50 mV s^{-1}; $E_{\frac{1}{2}} = 0.5\ (E_{pc} + E_{pa})$. [c] $\Delta E_p = E_{pc} - E_{pa}$. [d] Number of electrons per molecule determined by controlled-potential coulometry.

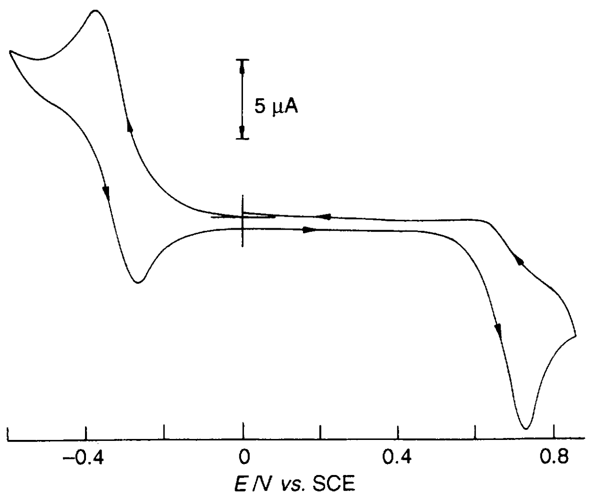

Fig. 2 Cyclic voltammogram (scan rate 50 mV s^{-1}) of $[\mathrm{MoOCl(bacda)_2}]$ **2d** in dmf (0.1 mol dm^{-3} $\mathrm{NEt_4ClO_4}$) at a platinum working electrode. Reference electrode, SCE

involved in metal co-ordination (see above). Appearance of a strong band in the region 955–970 cm^{-1} due to Mo=O terminal stretching with no evidence of Mo–O–Mo bridge vibrations indicates the mononuclear nature of the complexes.[26] Also consistent with the proposed formulations of **2a**–**2d** are the presence of characteristic metal–ligand vibrations in the regions 320–350 cm^{-1} [ν(Mo–S)] and 250–280 cm^{-1} [ν(Mo–Cl)] in the far-IR.

The electronic spectra of complexes **2a**–**2d** in dmf are presented in Table 2. In each case the spectral features are grossly similar and dominated by high intensity multiple bands with sufficient intricacy that makes their assignment less straightforward. However, their molar absorption coefficients (ε 1180–6700 dm^3 mol^{-1} cm^{-1}) are compatible with those expected for l.m.c.t. probably arising from $\mathrm{S}(\pi) \rightarrow \mathrm{Mo}(d_\pi)$ electronic transitions which appear to be a regular feature of $\mathrm{MoO^{3+}}$ complexes containing sulfur-donor ligands.[33,34] These strong l.m.c.t. bands prevent observation of weak, essentially ligand-independent d–d transitions which appear frequently in the 400–700 nm region for mononuclear oxo complexes of molybdenum(v).[35] All the remaining bands appearing near or below 400 nm are due to ligand internal transitions.

The complexes also have essentially identical redox chemistry (Table 3). Fig. 2 shows the cyclic voltammogram of **2d** at a platinum disc electrode which is typical for this series. In each case two electrochemical processes are observed in the potential window −0.6 to +1.0 V *vs.* SCE. The ligands are electrode inactive in this range. Process III, observed in the cathodic span, is reversible in the electrochemical sense (see above). Comparison with the ferrocenium–ferrocene couple as an internal standard demonstrate that they are one-electron processes consistent with the reduction to a molybdenum(iv) complex [equation (2), L = acda or aacda]. Electron-stoichiometry of

$$[\mathrm{Mo^VOCl(L)_2}] \underset{\mathrm{III}}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{Mo^{IV}OCl(L)_2}]^- \qquad (2)$$

this couple was further established by exhaustive electrolyses at potentials *ca.* 200 mV more cathodic than the respective E_{pc} values (Table 3). In the anodic range an irreversible oxidation (process IV) is observed. The oxidised species is not sufficiently stable for coulometric evaluation of the number of electrons involved in the process. Here again a metal-centred $\mathrm{Mo^V}$–$\mathrm{Mo^{VI}}$ one-electron transfer is proposed [equation (3)] from the

$$[\mathrm{Mo^VOCl(L)_2}] \xrightarrow[\mathrm{IV}]{-e^-} [\mathrm{Mo^{VI}OCl(L)_2}]^+ \qquad (3)$$

estimation of current height data (at E_{pa}, Fig. 2) which are comparable with the corresponding current parameters of couple III. The absence of a cathodic response in process IV even at a high scan rate (1.0 V s^{-1}) is not surprising in view of the lack of thermodynamically stable mononuclear compounds with $\mathrm{MoO^{4+}}$ chromophores as proposed in equation (3) for the oxidised form.

Molybdenum(v) complexes are magnetically straightforward (Table 4). Their room-temperature moments fall in the range 1.56–1.68 μ_B, as expected for a simple $S = \frac{1}{2}$ paramagnet with a d_{xy}-based ground state as proposed for monomeric $\mathrm{MoO^{3+}}$ chromophores.[35,36] The ESR spectra in solution [dmf–toluene, (1:10 v/v)] for **2a**–**2d** were measured at room-temperature to confirm the presence of a single ESR active species and then frozen for low-temperature measurements. Their spin-Hamiltonian parameters (Table 4) provide evidence for two isomeric forms of $[\mathrm{MoOCl(L)_2}]$ compounds arising from axial (L = acda) or equatorial (L = aacda) co-ordination of the chloro ligand.

The ESR criteria for the chloro ligand co-ordinating axially (antiparallel to the Mo=O bond direction) or equatorially (orthogonal to the Mo=O bond axis) is the absence or presence, respectively, of chlorine (^{35,37}Cl, $I = \frac{3}{2}$, 100%) nuclear hyperfine splitting. The ground-state configuration for octahedral $\mathrm{MoO^{3+}}$ compounds is $(d_{xy})^1$ so that if the chloro group enters an axial site (*trans* structure), very little spin-density reaches the axial ligands and ^{35,37}Cl hyperfine splitting will be very small or even absent. On the other hand if the chloro ligand enters an equatorial position (*cis* structure) it binds the molybdenum d_{xy} orbital containing the unpaired electron resulting in substantial chlorine spin-density which generates more structured ESR patterns[18,37,38] and occasionally clear chlorine hyperfine splitting.[39]

The frozen-solution ESR spectrum (80 K) of **2a** (Fig. 3) reveals well resolved axial symmetry of the g tensor, with principal values $g_\parallel = 1.982$ ($A_\parallel = 50.9 \times 10^{-4}$ cm^{-1}) and $g_\perp = 1.979$ ($A_\perp = 20.8 \times 10^{-4}$ cm^{-1}) due to ^{95,97}Mo ($I = \frac{5}{2}$) hyperfine splitting, with no indication of ^{35,37}Cl coupling. A *trans* structure with four sulfur atoms in the equatorial plane and an axially ligated chloro group (Fig. 3, inset) is thus proposed for **2a**. This interpretation is supported by the comparable ESR parameters[36] of $[\mathrm{NEt_4}][\mathrm{MoO(SPh)_4}]$ (Table 4) for which a basal plane containing four sulfur atoms has been confirmed by X-ray crystallography.[40]

The ESR spectrum for **2b** at 80 K is found to be much more complicated (Fig. 4) and has distinctly different g components: $g_\parallel = 1.994$ and $g_\perp = 1.954$. The remaining compounds **2c** and **2d** have similar ESR spectra to **2b** (Table 4) but show less well resolved features to enable the expected anisotropies to be measured with sufficient accuracy. Comparable values of g parameters obtained for $[\mathrm{MoOCl(ddp)_2}]$,[39] $[\mathrm{MoOCl(tox)_2}]$[37] and $[\mathrm{MoOCl(S_2CNEt_2)_2}]$[38] (Table 4) have been interpreted on the basis of structures with the chloro ligand occupying an equatorial site *cis* to the terminal oxo group. These results[37–39]

Table 4 Magnetic moment and spin-Hamiltonian parameters[a] for molybdenum(v) complexes

Compound	μ_{eff}/μ_B	$g_{\parallel}$	$g_{\perp}$	$10^4A_{\parallel}/cm^{-1}$	$10^4A_{\perp}/cm^{-1}$	Expected basal co-ordination
2a	1.68	1.982	1.979	50.9	20.8	S_4
$[NEt_4][MoO(SPh)_4]$[b]	—	2.017	1.979	52.3	22.3	S_4
2b	1.60	1.994	1.954			S_3Cl
2c	1.65	1.990	1.953			S_3Cl
2d	1.56	1.985	1.951			S_3Cl
$[MoOCl(ddp)_2]$[c]	—	1.990	1.950			S_3Cl
$[MoOCl(tox)_2]$[d]	—	2.006	1.953	60.7	24.1	NS_2Cl
			1.952		31.9	
$[MoOCl(S_2CNEt_2)_2]$[e]	—	1.984	1.945	61.4	24.1	S_3Cl
			1.958		27.5	

[a] Calculated from frozen (80 K) solution spectra. [b] Ref. 36. [c] Ref. 39, Hddp = diethyldithiophosphoric acid. [d] Ref. 37, Htox = quinoline-8-thiol. [e] Ref. 38.

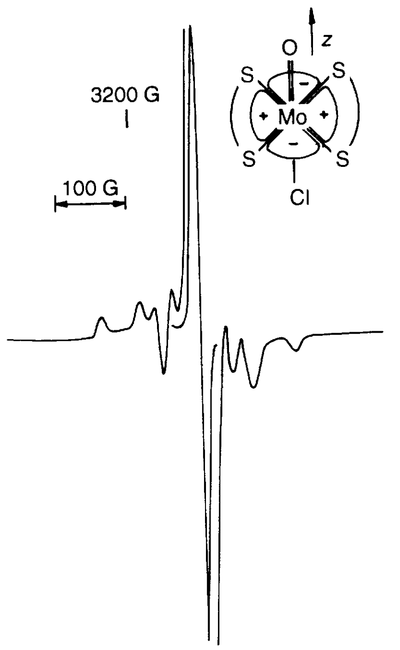

Fig. 3 Frozen-solution X-band ESR spectrum of $[MoOCl(acda)_2]$ **2a** at 80 K in dmf–toluene (1 : 10 v/v). Frequency, 9.09 GHz; gain, 5.0 × 10^2

have prompted us to assign a *cis* structure (Fig. 4, inset) with a S_3Cl mode of basal co-ordination for **2b**–**2d** despite a recent report[41] that in addition to their positions in the co-ordination sphere, the nature of the sulfur donor type also has an influence in controlling the *g* values of molybdenum(v) complexes. Nevertheless, our interpretations gain further ground as $[MoOCl(tox)_2]$ has been confirmed to have an equatorial plane with NS_2Cl co-ordination by X-ray crystallography.[42]

Conclusion

Non-oxomolybdenum(iv) complexes have been synthesised by oxo-transfer reactions using Hacda as reagent which functions both as a reducing agent as well as an incoming ligand. The compounds **1a** and **1b** display rich electrochemistry. Electron-transfer reversibilities in this multi-component redox system [equation (1)] indicate conservation of the six-co-ordinate structure throughout the $[Mo(ox)(aacda)(acda)]^z$ ($z = -1$, 0 or +1) series. The frozen-solution (80 K) ESR spectra of the molybdenum(v) complexes show interesting features providing convincing evidence for two structural types. In complexes **2b**–**2d**, with proposed *cis* structure, the steric bulk of the alkyl substituent in the ligand framework probably enforces one aacda ligand to bind the metal centre spanning one equatorial and one axial site.

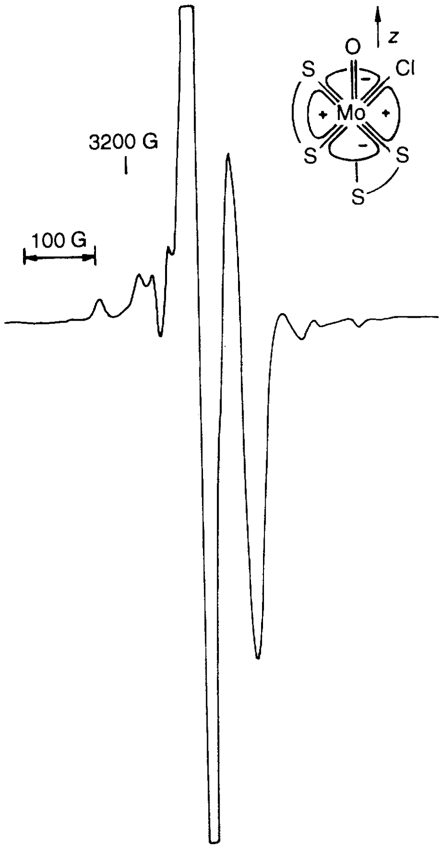

Fig. 4 Frozen-solution X-band ESR spectrum (80 K) of $[MoOCl(eacda)_2]$ **2b** in dmf–toluene (1 : 10 v/v). Frequency, 9.09 GHz; gain, 2.0 × 10^2

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