Chemistry of Molybdenum. Part 8.[1] Syntheses, Spectroscopy and Electrochemical Properties of Molybdenum Complexes containing Dithioacid Ligands†

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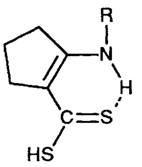
Complexes *cis*-$[Mo^{VI}O_2(aacda)_2]$ [aacda = 2-(alkylamino)cyclopent-1-ene-1-carbodithioate; alkyl = propyl (pacda) or butyl (bacda)] react with acids HX ($X = BF_4$ or PF_6) to form species $[Mo^{VI}O(aacda)_3]X$ **1a–1d**, which contain an $Mo^{VI}O$ core. Reactivity of the terminal oxo ligand of this core towards electron-donor reagents has been investigated. Non-oxo monomeric molybdenum(V) compounds $[Mo^{V}(acda)(aacda)_3]BF_4$ **2a**, **2b** and $[Mo^{V}(abt)(aacda)_3]BF_4$ **2c**, **2d** can be obtained when 2-aminocyclopent-1-ene-1-carbodithioic acid (Hacda) and *o*-aminobenzenethiol (Habt) are used for oxygen abstraction. With triphenylphosphine, however, the products are non-oxo molybdenum(IV) compounds $[Mo^{IV}(PPh_3)(aacda)_3]BF_4$ **3a**, **3b**. In frozen solution [dimethylformamide–MeCN (1:10 v/v), 140 K], compounds **2a–2d** show ESR spectra with axial symmetry. The *g* and *A* tensor parameters ($g_{\parallel} \approx 1.977$, $g_{\perp} \approx 1.975$, $A_{\parallel} \approx 51.5 \times 10^{-4}$ cm^{-1} and $A_{\perp} \approx 19.5 \times 10^{-4}$ cm^{-1}) for this series of molybdenum(V) compounds are very similar to each other indicating that the unpaired electron is located in a metal-centred orbital of essentially identical composition. Complexes **2a** and **2b** display two consecutive reversible one-electron waves in their cyclic voltammograms at $E_{\frac{1}{2}} = -0.24$ and -0.45 V *vs.* saturated calomel electrode (SCE), which correspond to Mo^{V}–Mo^{IV} and Mo^{IV}–Mo^{III} redox couples respectively. The molybdenum(IV) compounds **3a** and **3b** are seven-co-ordinate with a spin-triplet ground state (μ_{eff}, 2.48 and 2.53) and show two distinct redox waves due to the interconversion of the three $[Mo(PPh_3)(aacda)_3]^z$ ($z = +1$, 0 or -1) species. Half-wave potentials, $E_{\frac{1}{2}}$, for these processes are at -0.36 (Mo^{IV}–Mo^{III}) and -0.90 V (Mo^{III}–Mo^{II}) *vs.* SCE. The presence of the strongly π-acceptor phosphine ligand facilitates the electrochemical generation of relatively scarce molybdenum(II) species.

A large number of oxo-transfer reactions occurring in the biological world are catalysed by a group of enzymes containing molybdenum in the centre of a dissociable cofactor, the structure of which is gradually becoming clearer from extended X-ray absorption fine structure spectroscopy (EXAFS), ESR spectroscopy and chemical studies.[2] Apart from rich sulfur co-ordination the mononuclear molybdenum centre in this ubiquitous cofactor contains terminal oxo group(s). Their presence is believed to be obligatory for the oxotransferase activity of these enzymes.[3] The formal oxidation state of molybdenum in this cofactor fluctuates between +6 and +4 *via* a +5 intermediate during the turnover of these enzymes.[4] All these observations have kindled renewed interest in the co-ordination chemistry of molybdenum especially with sulfur donor ligands.[5–17]

We have recently initiated a programme to investigate the chemistry, spectroscopy, magnetism and electrochemical properties of mononuclear compounds containing molybdenum in biologically relevant oxidation states (+6, +5 and +4) using 2-aminocyclopent-1-ene-1-carbodithioic acid (Hacda) and its *N*-alkyl derivatives (Haacda) as (S–S)$^-$ donor ligands.[1,18–22] Various molybdenum-(V) and -(IV) compounds have been synthesised by oxo-transfer reactions using precursors containing the *cis*-$Mo^{VI}O_2$ moiety. It has been found that only one terminal oxo ligand in *cis*-$[MoO_2(acda)_2]$ is replaceable by proton-donor reagents.[1,21] The products have seven-co-ordinate structures with a $Mo^{VI}O$ core. The reactivity response of the terminal oxo centre of this core towards electron-donor reagents such as Hacda, *o*-aminobenzenethiol (Habt) and PPh_3 is investigated in this study. Monomeric molybdenum complexes of the type $[Mo^{V}L(aacda)_3]BF_4$ (L = acda or abt) and $[Mo^{IV}(PPh_3)(aacda)_3]BF_4$ have been synthesised using $[Mo^{VI}O(aacda)_3]BF_4$ as precursors. The magnetic, spectroscopic and electrochemical properties are also reported.



R	
H	Hacda
Pr	Hpacda
Bu	Hbacda

Experimental

Reactions and manipulations of compounds were carried out under purified dinitrogen. All solvents were reagent grade and were dried by recommended procedures[23] and distilled under nitrogen before use. Cyclopentanone (E. Merck), propylamine (Fluka) and butylamine (Riedel) were freshly distilled before use. Triphenylphosphine (E. Merck) was recrystallised from benzene. The ligands Haacda [alkyl = propyl (Hpacda) or butyl (Hbacda)][24] and the starting materials $[MoO_2(aacda)_2]$[22] (aacda = pacda or bacda) were prepared according to published methods. All other chemicals were of reagent grade and used as received.

Physical Measurements.—Infrared spectra were obtained as KBr pellets with a Perkin-Elmer 783 spectrometer and

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Non-SI unit employed: G = 10^{-4} T.

electronic absorption spectra on a Pye Unicam SP8-150 spectrophotometer. Magnetic susceptibility measurements at room temperature were made on polycrystalline samples by using a PAR 155 vibrating-sample magnetometer and electrical conductivity measurements on millimolar dimethylformamide (dmf) solutions, thermostatted at 25 °C, with a Philips PR9500 bridge. The ESR spectra in solution (1:10 v/v dmf–MeCN) were recorded at room temperature and in the frozen state (≈ 140 K) with a Bruker ER 200D-SRC spectrometer at X-band frequency with standard Bruker attachments as described elsewhere.[18]

Electrochemical experiments were performed with a Bioanalytical Systems CV 27 analyser in conjunction with a Houston Omnigraphic 2000 X-Y recorder. A standard three-electrode assembly consisting of a hanging mercury drop electrode (HMDE) as the working electrode, a platinum-wire auxiliary electrode and a saturated calomel (SCE) reference electrode was used with ferrocene ($E_{\frac{1}{2}}$ for ferrocene–ferrocenium couple +0.465 V *vs.* SCE) as an internal reference.[25] For coulometry, a stirred mercury pool was used as the working electrode. The solution used for both techniques consisted of 0.1 mol dm^{-3} tetraethylammonium perchlorate (NEt_4ClO_4) as the supporting electrolyte in freshly distilled dry dmf[18] with a metal complex concentration of $\approx 10^{-3}$ mol dm^{-3}. The solutions were degassed for *ca.* 15 min with dry nitrogen prior to making measurements at 25 °C. Potentials are quoted relative to SCE and are not corrected for the liquid-junction potentials.

Elemental analyses (C, H and N) were performed in this laboratory with a Perkin-Elmer 240C elemental analyser. Molybdenum contents were estimated as oxinate by a conventional gravimetric method.[23]

Synthesis of Compounds.—$[MoO(pacda)_3]BF_4$ **1a**. A stirred suspension of $[MoO_2(pacda)_2]$ (0.27 g, 0.5 mmol) in acetone (30 cm^3) was treated with aqueous HBF_4 (0.3 cm^3, *ca.* 31%), added dropwise over a period of 30 min. The suspension was stirred magnetically in the dark for an additional period of 2.5 h and filtered to remove any undissolved material. The volume of the solution was reduced to 5 cm^3 *in vacuo*. Addition of methanol (5 cm^3) caused precipitation of a dirty green solid which was removed by filtration. To the filtrate was added dichloromethane (5 cm^3) followed by diethyl ether (15 cm^3). Upon standing overnight in a freezer precipitation of the brown product occurred. Recrystallisation from acetone–diethyl ether gave a dark brown microcrystalline product. Yield: 0.13 g (32%). IR (KBr disc): $\nu(Mo{=}O_t)$ 920s, $\nu_{asym}(CSS)$ 800s and $\nu(Mo{-}S)$ 350m cm^{-1} (Found: C, 40.5; H, 5.3; Mo, 12.2; N, 5.2. Calc. for $C_{27}H_{42}BF_4MoN_3OS_6$: C, 40.5; H, 5.3; Mo, 12.0; N, 5.2%); Λ_M(298 K, dmf) 68 S cm^2 mol^{-1}.

$[MoO(bacda)_3]BF_4$ **1b** was obtained in 40% yield following the same procedure as for **1a** but using $[MoO_2(bacda)_2]$. IR (KBr disc): $\nu(Mo{=}O_t)$ 925s, $\nu_{asym}(CSS)$ 812s and $\nu(Mo{-}S)$ 360 m cm^{-1} (Found: C, 42.9; H, 5.7; Mo, 11.5; N, 5.0. Calc. for $C_{30}H_{48}BF_4MoN_3OS_6$: C, 42.8; H, 5.7; Mo, 11.4; N, 5.0%); Λ_M(298 K, dmf) 79 S cm^2 mol^{-1}.

$[MoO(bacda)_3]PF_6$ **1d**. To a stirred suspension of $[MoO_2(bacda)_2]$ (0.28 g, 0.5 mmol) in acetone (30 cm^3) was added dropwise aqueous HPF_6 (0.25 cm^3, *ca.* 65%) over a period of 30 min. The mixture was stirred for an additional period of 4 h in the dark. The solution was filtered and the volume was reduced to 5 cm^3. The concentrated solution was filtered again to obtain a clear dark red solution. Methanol (5 cm^3) was then added to the filtrate followed by diethyl ether (15 cm^3). On standing overnight in a freezer precipitation of the dark brown product occurred. Recrystallisation from acetone–diethyl ether gave the purified product. Yield: 90 mg (20%). IR (KBr disc): $\nu(Mo{=}O_t)$ 918s, $\nu_{asym}(CSS)$ 800s and $\nu(Mo{-}S)$ 350m cm^{-1} (Found: C, 40.0; H, 5.3; Mo, 10.7; N, 4.6. Calc. for $C_{30}H_{48}F_6MoN_3OPS_6$: C, 40.0; H, 5.3; Mo, 10.7; N, 4.7%); Λ_M(298 K, dmf) 72 S cm^2 mol^{-1}.

$[MoO(pacda)_3]PF_6$ **1c** was obtained in 22% yield following the same procedure as for **1d** but using $[MoO_2(pacda)_2]$. IR (KBr disc): $\nu(Mo{=}O_t)$ 920s, $\nu_{asym}(CSS)$ 810s and $\nu(Mo{-}S)$ 350m cm^{-1} (Found: C, 37.9; H, 5.0; Mo, 11.0; N, 5.0. Calc. for $C_{27}H_{42}F_6MoN_3OPS_6$: C, 37.8; H, 4.9; Mo, 11.2; N, 4.9%); Λ_M(298 K, dmf) 66 S cm^2 mol^{-1}.

$[Mo(acda)(pacda)_3]BF_4$ **2a**. To a stirred suspension of **1a** (0.24 g, 0.3 mmol) in methanol (25 cm^3) was added dropwise a methanolic solution (15 cm^3) of Hacda (0.15 g, 0.9 mmol) over a period of 30 min. The reaction mixture was warmed at 40 °C, and stirring was continued for a further 6 h. The solution was then cooled to room temperature, and the dark brown product which formed was filtered off, washed with chloroform–hexane (1:3 v/v) (3 × 10 cm^3) and finally dried *in vacuo*. The purity of the product was checked by TLC; yield: 0.18 g (64%). IR (KBr disc): $\nu_{asym}(CSS)$ 815s and $\nu(Mo{-}S)$ 360m cm^{-1} (Found: C, 42.0; H, 4.8; Mo, 10.3; N, 6.0. Calc. for $C_{33}H_{50}BF_4MoN_4S_8$: C, 42.1; H, 5.3; Mo, 10.2; N, 5.9%); Λ_M(298 K, dmf) 67 S cm^2 mol^{-1}.

$[Mo(acda)(bacda)_3]BF_4$ **2b** was prepared in a yield of 52%, following a similar procedure as for **2a**. IR (KBr disc): $\nu_{asym}(CSS)$ 810s and $\nu(Mo{-}S)$ 345m cm^{-1} (Found: C, 44.0; H, 5.8; Mo, 9.8; N, 5.7. Calc. for $C_{36}H_{56}BF_4MoN_4S_8$: C, 43.9; H, 5.7; Mo, 9.8; N, 5.7%); Λ_M(298 K, dmf) 65 S cm^2 mol^{-1}.

$[Mo(abt)(bacda)_3]BF_4$ **2d**. A solution of *o*-aminobenzenethiol (0.23 g, 1.8 mmol) in methanol (15 cm^3) was added dropwise to a stirred solution of **1b** (0.5 g, 0.6 mmol) in methanol (30 cm^3). The reaction mixture was then warmed gently at 40–45 °C, and the stirring was continued for a period of 4 h. The solution was then cooled to room temperature, and the dark brown product formed was filtered off, washed with chloroform–hexane (1:3 v/v) (3 × 10 cm^3) and finally dried *in vacuo*. The purity of the product was checked by TLC. Yield: 0.31 g (55%). IR (KBr disc): $\nu_{asym}(CSS)$ 815s, $\nu(Mo{-}S)$ 350m, ν(phenyl ring) 750s and 720m cm^{-1} (Found: C, 45.6; H, 5.7; Mo, 10.4; N, 5.9. Calc. for $C_{36}H_{54}BF_4MoN_4S_7$: C, 45.5; H, 5.7; Mo, 10.1; N, 5.9%); Λ_M(298 K, dmf) 69 S cm^2 mol^{-1}.

$[Mo(abt)(pacda)_3]BF_4$ **2c** was synthesised in 60% yield following an identical procedure as for **2d**. IR (KBr disc): $\nu_{asym}(CSS)$ 815s, $\nu(Mo{-}S)$ 345m, ν(phenyl ring) 750s and 720m cm^{-1} (Found: C, 43.6; H, 5.3; Mo, 10.7; N, 6.1. Calc. for $C_{33}H_{48}BF_4MoN_4S_7$: C, 43.7; H, 5.3; Mo, 10.6; N, 6.2%); Λ_M(298 K, dmf) 66 S cm^2 mol^{-1}.

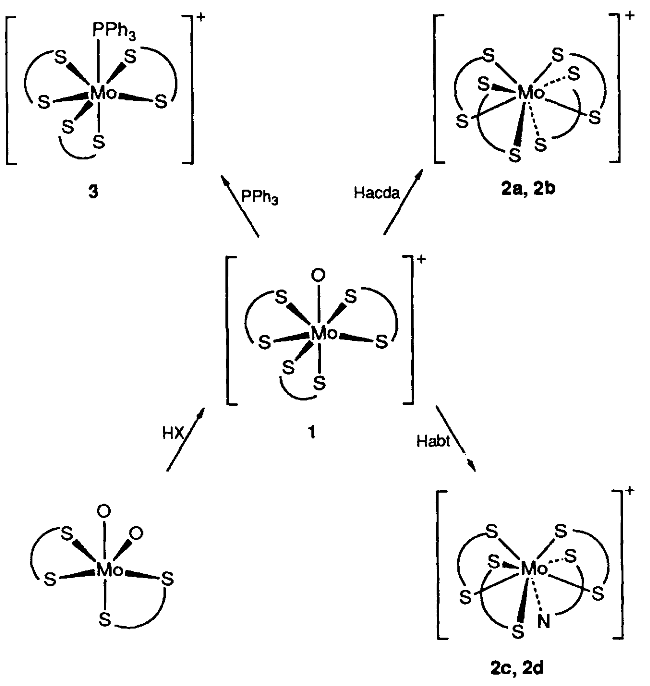
$[Mo(PPh_3)(pacda)_3]BF_4$ **3a**. A solution of triphenylphosphine (0.26 g, 1 mmol) in acetonitrile (15 cm^3) was added dropwise with constant stirring to a solution of **1a** (0.40 g, 0.5 mmol) also in acetonitrile (30 cm^3). The resulting solution was warmed to 40 °C and the stirring was continued for an additional 4 h. During this period a pale brown compound separated. The mixture was cooled to room temperature and filtered. The volume of the filtrate was reduced to *ca.* 1 cm^3 in a rotary evaporator and finally diethyl ether (10 cm^3) was added to induce precipitation. The dark brown microcrystalline compound was filtered off, washed with benzene and diethyl ether and finally dried *in vacuo*. The purity of the product was checked by TLC. Yield: 0.13 g (25%). IR (KBr disc): $\nu_{asym}(CSS)$ 810s, $\nu(Mo{-}S)$ 345m, ν(phenyl ring) 725m and 690m cm^{-1} (Found: C, 51.3; H, 5.3; Mo, 9.4; N, 4.1. Calc. for $C_{45}H_{57}BF_4MoN_3PS_6$: C, 51.7; H, 5.4; Mo, 9.2; N, 4.0%); Λ_M(298 K, dmf) 85 S cm^2 mol^{-1}.

$[Mo(PPh_3)(bacda)_3]BF_4$ **3b** was prepared in 28% yield following an analogous procedure as for **3a**. IR (KBr disc): $\nu_{asym}(CSS)$ 810s, $\nu(Mo{-}S)$ 345m, ν(phenyl ring) 725m and 690s cm^{-1} (Found: C, 53.0 H, 5.8; Mo, 8.6; N, 4.0. Calc. for $C_{48}H_{63}BF_4MoN_3PS_6$: C, 53.0; H, 5.8; Mo, 8.8; N, 3.9%); Λ_M(298 K dmf) 90 S cm^2 mol^{-1}.

Results and Discussion

Synthetic routes to the reported complexes are outlined in Scheme 1.

Complexes $[MoO(aacda)_3]X$ **1a**–**1d**. (aacda = pacda *or* bacda, X = BF_4 *or* PF_6).—These compounds are obtained in



Scheme 1 X = BF_4 or PF_6

moderate yield (20–40%) as dark brown microcrystalline solids when a suspension of $[MoO_2(aacda)_2]$[22] in acetone is allowed to react with acids HX containing non-co-ordinating anions (X = BF_4 or PF_6). Compositionally identical compounds with dithiocarbamates as ligands have been reported elsewhere.[26] The reaction involves replacement of a terminal oxo group from the *cis*-$Mo^{VI}O_2$ moiety of $[MoO_2(aacda)_2]$ precursors. The products **1a**–**1d** have seven-co-ordinate structures and contain $Mo^{VI}O$ cores. Both longer reaction times or use of excess HX are ineffective in bringing about the replacement of the remaining oxo ligand from $[MoO(aacda)_3]X$. The compounds are air-stable in the solid state and showed no sign of decomposition even after several months when stored in a desiccator. They are moderately soluble in methanol and acetonitrile but have fairly good solubilities in acetone and dmf.

The IR spectra of each of the molybdenum(VI) complexes contains a single sharp absorption at ≈ 810 cm^{-1}. For the aacda$^-$ ligands, the appearance of this band [due to $\nu_{asym}(CSS)$] strongly suggests a bidentate $(S-S)^-$ mode of chelation from these ligands.[20,22] The $\nu(Mo{=}O_t)$ absorption is observed at ≈ 920 cm^{-1} (Fig. 1) in agreement with data reported for other monooxomolybdenum(VI) derivatives.[26,27] The compounds also show absorptions at ≈ 1030, 535 and 520 cm^{-1} due to BF_4^- or at ≈ 840 cm^{-1} for PF_6^- anions.[26]

As expected the molybdenum(VI) compounds **1a**–**1d** are diamagnetic. Their molar conductivities in dmf solutions are within the range reported for 1:1 electrolytes.[28] Table 1 lists the electronic spectral data for these compounds in dmf. The spectra are relatively simple and consist of a ligand-to-metal charge-transfer (l.m.c.t.) band at ≈ 450 nm, probably originating from an $S(\pi) \longrightarrow Mo(d_\pi)$ electronic transition. Bands appearing below 400 nm arise from ligand-localized π–π^* transitions.[22]

Complexes $[Mo^VL(aacda)_3]BF_4$ (L = acda **2a**, **2b**; abt **2c**, **2d**).—These non-oxo monomeric molybdenum(V) compounds are obtained as dark brown microcrystalline solids in fairly good yield (50–60%) by an oxo-transfer reaction [equation (1)]

$$[Mo^{VI}O(aacda)_3]BF_4 + 2HL \longrightarrow [Mo^VL(aacda)_3]BF_4 + H_2O + \tfrac{1}{2}L{-}L \quad (1)$$

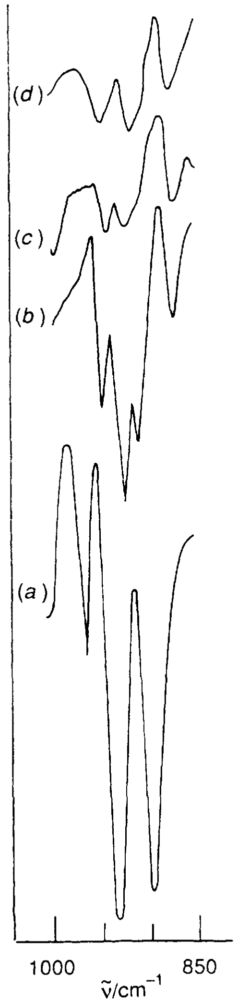


Fig. 1 Infrared spectra of (*a*) $[MoO_2(pacda)_2]$, (*b*) $[MoO(pacda)_3]BF_4$, (*c*) $[Mo(PPh_3)(pacda)_3]BF_4$ and (*d*) $[Mo(acda)(pacda)_3]BF_4$ showing gradual abstraction of oxygen atoms from the *cis*-MoO_2^{2+} precursor

using **1a** or **1b** as the precursor. The substrates Hacda and Habt play a dual role functioning both as one-electron reductants as well as co-ordinating to the metal centre. The species L–L is the oxidised form of the ligands (HL), and probably exists as the disulfide.[18]

Compounds **2a**–**2d** are air-stable in the solid state but undergo slow decomposition in solution. They have fairly good solubilities in acetone and dmf. Their molar conductivity values measured in dmf are as expected for 1:1 electrolytes.[28] Their IR spectra show all the essential features present in the corresponding precursor molybdenum(VI) compounds **1a** and **1b** except in the region 1000–850 cm^{-1} (Fig. 1), where the absence of a strong band confirms the absence of a terminal oxo group in the molybdenum(V) co-ordination sphere. The appearance of strong and sharp bands in the region 690–760 cm^{-1} evince phenyl-ring vibrations from co-ordinated abt in **2c** and **2d**.

The electronic absorption spectra of the molybdenum(V) compounds in dmf solutions are complicated by the presence of numerous peaks and shoulders (summarised in Table 1) particularly in the lower energy region (440–880 nm), each associated with high molar absorptivity. These features may be attributable to $S(\pi) \longrightarrow Mo(d_\pi)$ charge-transfer (l.m.c.t.) excitations on the basis of their high molar absorptivities (ε 2000–21 000 dm^3 mol^{-1} cm^{-1}). More intense bands of intraligand origin are also present in the UV region. These

Table 1 Electronic spectral data for the complexes in dmf solution

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
1a $[\text{Mo}^{VI}\text{O(pacda)}_3]\text{BF}_4$	452 (9100), 378 (40 000), 315 (11 000)
1b $[\text{Mo}^{VI}\text{O(bacda)}_3]\text{BF}_4$	452 (10 500), 384 (43 100), 308 (11 200)
1c $[\text{Mo}^{VI}\text{O(pacda)}_3]\text{PF}_6$	458 (9500), 380 (40 100), 315 (12 000)
1d $[\text{Mo}^{VI}\text{O(bacda)}_3]\text{PF}_6$	452 (10 300), 380 (37 200), 310 (11 500)
2a $[\text{Mo}^{V}\text{(acda)(pacda)}_3]\text{BF}_4$	824 (3700), 760 (sh), 672 (9100), 540 (20 800), 504 (sh), 400 (67 700)
2b $[\text{Mo}^{V}\text{(acda)(bacda)}_3]\text{BF}_4$	808 (3 600), 720 (sh), 656 (8700), 536 (18 900), 496 (sh), 400 (90 000)
2c $[\text{Mo}^{V}\text{(abt)(pacda)}_3]\text{BF}_4$	828 (3400), 760 (sh), 672 (8300), 540 (18 200), 504 (17 900), 424 (64 300)
2d $[\text{Mo}^{V}\text{(abt)(bacda)}_3]\text{BF}_4$	832 (3870), 760 (sh), 672 (9600), 540 (21 000), 504 (17 900), 400 (64 300)
3a $[\text{Mo}^{IV}\text{(PPh}_3\text{)(pacda)}_3]\text{BF}_4$	825 (2100), 755 (sh), 670 (5100), 540 (10 500), 515 (sh), 390 (55 300)
3b $[\text{Mo}^{IV}\text{(PPh}_3\text{)(bacda)}_3]\text{BF}_4$	828 (1900), 760 (sh), 672 (4700), 540 (10 200), 520 (sh), 384 (58 300)

Table 2 Magnetic and ESR data for the molybdenum(v) complexes

Complex	μ_{eff}	$g_{\parallel}$ [a]	$g_{\perp}$ [a]	$10^4\langle a\rangle$ [b]/cm^{-1}	$10^4 A_{\parallel}$ [a]/cm^{-1}	$10^4 A_{\perp}$ [a]/cm^{-1}	$10^4\langle a\rangle_{calc}$ [c]/cm^{-1}
2a	1.71	1.977	1.975	30.5	50.8	20.7	30.7
2b	1.65	1.974	1.975	30.1	52.8	18.4	29.9
2c	1.72	1.976	1.977	30.1	51.9	19.1	30.0
2d	1.72	1.977	1.975	30.3	51.5	19.5	30.2

[a] From frozen-solution (140 K) spectrum. [b] From room-temperature spectrum. [c] $\langle a\rangle_{calc} = 1/3\,(A_{\parallel} + 2A_{\perp})$.

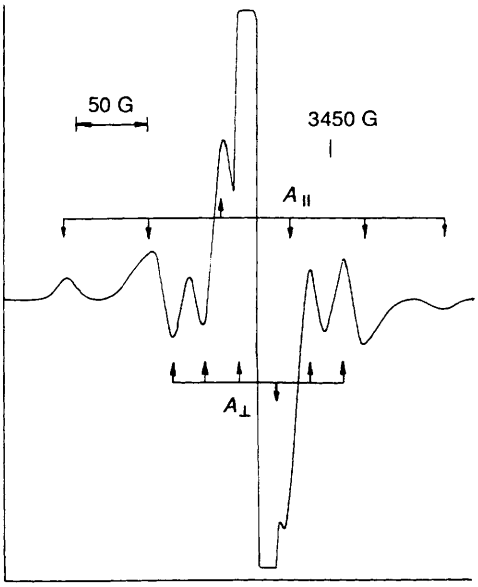


Fig. 2 X-Band frozen-solution ESR spectrum ($\approx$140 K) of $[\text{Mo(abt)(pacda)}_3]\text{BF}_4$ in 1:10 (v/v) dmf–acetonitrile solution; frequency, 9.4 GHz; gain, 4 × 10^5

intense charge-transfer and intraligand bands probably obscure possible ligand-field (d–d) transitions. The spectral nature is, however, qualitatively similar to those of the other reported non-oxo molybdenum complexes with a high degree of sulfur co-ordination.[29–32] Other than this no further attempt will be made to interpret these spectra because of their apparent complexity.

Magnetic moments and ESR parameters are listed in Table 2. The room-temperature magnetic moments for the powdered polycrystalline samples are within the range μ_{eff} 1.65–1.72, close to the spin-only value for a formally d^1 system. This feature can be interpreted as being indicative of the effective quenching of the orbital angular momentum by a low-symmetry ligand field surrounding the metal centre. The frozen solution [dmf–MeCN (1:10 v/v)] ESR spectra of the molybdenum(v) compounds at $\approx$140 K can be interpreted by assuming axial symmetry with $g_{\parallel} \approx 1.977$ and $g_{\perp} \approx 1.975$. The satellite peaks ($A_{\parallel} \approx 51.5 \times 10^{-4}$ and $A_{\perp} \approx 19.5 \times 10^{-4}$ cm^{-1}) are due to ^{95,97}Mo (25.15 atom%; $I = \frac{5}{2}$). A representative spectrum (**2c**) is shown in Fig. 2 Derived g and A tensor components listed in Table 2 are very similar for the entire series of molybdenum(v) compounds indicating that the unpaired electron is located in a molybdenum-centred orbital of essentially identical composition. Fairly low $\langle A\rangle$ and relatively high values of $\langle g\rangle$ are in conformity with a high degree of sulfur co-ordination in these compounds.[33]

The electron transfer ability of the monomeric molybdenum(v) compounds **2a** and **2b** have been studied in dmf solution (0.1 mol dm^{-3} NEt$_4$ClO$_4$) at an HMDE. Relevant data are reported in Table 3. Cyclic voltammetry in each case shows two redox couples at −0.24 (process I) and −0.45 V (process II) *vs.* SCE. Either of these couples exhibits the usual features of uncomplicated reversible one-electron charge-transfer processes ($i_{p_c}/i_{p_a} \approx 1.0$; $i_p/\sqrt{v}$ remaining independent of scan rate within the range 50–500 mV s^{-1}; ΔE_p = 60–70 mV). Controlled-potential coulometric experiments have confirmed further that both redox processes are monoelectronic.

This electrochemical behaviour is in agreement with two successive reversible metal-centred one-electron transfer steps as represented in equation (2). The ligands used are electrode inactive in the potential range of our study. The first electrode process (couple I) can be reasonably attributed to a Mo^{V}–Mo^{IV} reduction, and the second (couple II), to the Mo^{IV}–Mo^{III} one. The alkyl substituents (propyl or butyl) in the ligand framework do not appear to have any significant influence on the electrochemical potentials in the present case.

$$[\text{Mo}^{V}(\text{acda})(\text{aacda})_3]^+ \underset{\text{I}}{\overset{e^-}{\rightleftharpoons}} [\text{Mo}^{IV}(\text{acda})(\text{aacda})_3]^0 \underset{\text{II}}{\overset{e^-}{\rightleftharpoons}} [\text{Mo}^{III}(\text{acda})(\text{aacda})_3]^- \qquad (2)$$

For the remaining two molybdenum(v) complexes of the type $[\text{Mo(abt)(aacda)}_3]\text{BF}_4$, **2c** and **2d**, poorly-defined irreversible electrochemical responses are obtained. The detailed studies necessary to understand the nature of the chemical reactions following electron transfer(s) are beyond the scope of the present investigation.

Complexes $[\text{Mo}^{IV}(\text{PPh}_3)(\text{aacda})_3]\text{BF}_4$, **3a** *and* **3b**.—The reduction of complexes **1a** and **1b** in the presence of PPh$_3$ (1:2 mole ratio) at 40 °C gave dark brown molybdenum(IV)

Table 3 Summary of electrochemical data for the molybdenum-(V) and -(IV) complexes[a]

	Mo^{V}–Mo^{IV}			Mo^{IV}–Mo^{III}			Mo^{III}–Mo^{II}		
Complex	$E_{\frac{1}{2}}{}^{b}$/V	$\Delta E_p{}^{c}$/mV	i_{p_c}/i_{p_a}	$E_{\frac{1}{2}}{}^{b}$/V	$\Delta E_p{}^{c}$/mV	i_{p_c}/i_{p_a}	$E_{\frac{1}{2}}{}^{b}$/V	$\Delta E_p{}^{c}$/mV	i_{p_c}/i_{p_a}
2a	−0.24	60	1.0	−0.45	70	1.03	—	—	—
2b	−0.23	60	0.95	−0.45	70	0.98	—	—	—
3a	—	—	—	−0.36	80	0.96	−0.90	80	1.06
3b	—	—	—	−0.37	80	0.98	−0.91	70	0.99

[a] Cyclic voltammograms performed in dmf; supporting electrolyte NEt_4ClO_4 (0.1 mol dm^{-3}); solute concentration *ca.* 10^{-3} mol dm^{-3}; working electrode HMDE. [b] Potentials are *vs.* SCE and are estimated from cyclic voltammetry with scan rate of 50 mV s^{-1}, $E_{\frac{1}{2}} = 0.5\,(E_{p_c} + E_{p_a})$. [c] $\Delta E_p = E_{p_c} - E_{p_a}$.

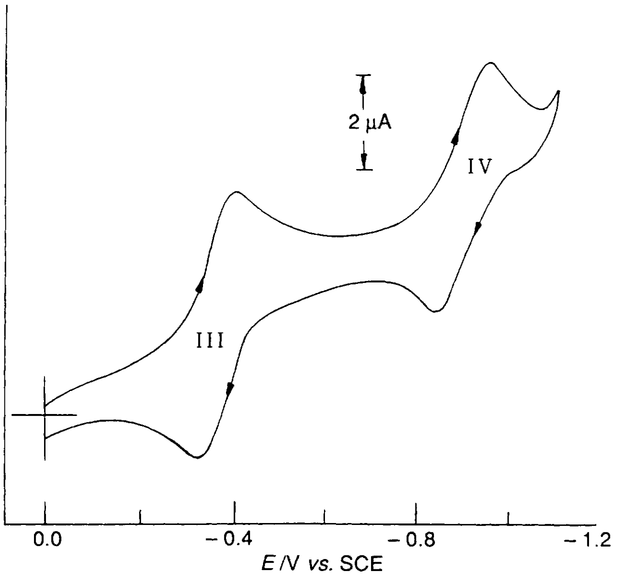


Fig. 3 Cyclic voltammogram of $[Mo(PPh_3)(pacda)_3]BF_4$ (1.2×10^{-3} mol dm^{-3}) in dmf at an HMDE. Supporting electrolyte, 0.1 mol dm^{-3} NEt_4ClO_4; scan rate, 50 mV s^{-1}

products $[Mo^{IV}(PPh_3)(pacda)_3]BF_4$ **3a** and $[Mo^{IV}(PPh_3)(bacda)_3]BF_4$ **3b** in 25–30% yield according to equation (3).

$$[Mo^{VI}O(aacda)_3]BF_4 + 2PPh_3 \longrightarrow [Mo^{IV}(PPh_3)(aacda)_3]BF_4 + O{=}PPh_3 \quad (3)$$

Besides being an oxo transfer agent, PPh_3 also functions as an incoming ligand. The compounds are air-stable in the solid state and have electrical conductivities in dmf (85–90 S cm^2 mol^{-1}) typical for 1 : 1 electrolytes.[28]

The IR spectra of these compounds display the usual pattern of absorbances associated with the $(S–S)^-$ mode of co-ordination from the aacda$^-$ ligands.[20–22] The absence of a strong band at ≈915 cm^{-1} [$\nu(Mo{=}O_t)$] (Fig. 1) together with the appearance of phenyl-ring vibrations in the range 690–750 cm^{-1} confirm the substitution of the terminal oxygen atom by PPh_3 in compounds **3a** and **3b**. These compounds also display bands at ≈1080, 540 and 520 cm^{-1} characteristic of BF_4^- vibrations.[26]

The electronic absorption spectral data of the molybdenum(IV) compounds are given in Table 1. The spectra, recorded in dmf solution, have almost identical features for both the molybdenum(IV) compounds **3a** and **3b**, and each show five absorption bands in the region 880–440 nm. Absorption manifolds of apparently similar complexity are quite common for non-oxo molybdenum-(IV) and -(V) compounds with a high degree of sulfur co-ordination,[29–32] and could possibly serve as a diagnositic feature for these types of compounds. Following the ligand-field classifications it would be reasonable to assign these bands as arising from l.m.c.t. transitions because of their high molar absorptivities (ε 1900–10 500 dm^3 mol^{-1} cm^{-1}). Bands appearing below 400 nm are due to internal ligand transitions.

The room-temperature magnetic moments of the molybdenum(IV) compounds are within the range μ_{eff} = 2.48–2.53 expected for a d^2 spin-triplet ground state. The observed moments are slightly lower than the expected spin-only value (μ_{eff} 2.83) for a d^2 ($S = 1$) system because of strong spin-orbit coupling.[34]

Electrochemical data for **3a** and **3b** are presented in Table 3. Fig. 3 shows the cyclic voltammogram of **3a** recorded at 50 mV s^{-1}. The behaviour of **3b** is very similar. Two consecutive reduction steps are observed at formal potentials of −0.36 (process III) and −0.90 V (process IV) *vs.* SCE. The shapes of the current–voltage curves for both the processes at variable scan rates (50–500 mV s^{-1}) indicate the involvement of diffusion controlled reversible electron transfer in each case. Peak potential separations (ΔE_p) are consistently within the range (70–80 mV) found for the ferrocene–ferrocenium couple. Controlled-potential coulometric tests performed in conjunction with the first reduction step ($E_w = -0.56$ V) confirm that process III involves the consumption of 1.0 ± 0.1 F of charge per mol of complex. Subsequent electrolysis at −1.15 V did not produce any meaningful result for the redox couple IV because of possible interference from post-chemical reaction(s). Single-electron involvement in process IV is, however, established by the fact that the peak heights (at E_{p_c}) are almost identical (to within 7%) with those of process III, as is evident in the voltammogram shown in Fig. 3. Since the ligands are electrode inactive in the potential range of this study (−1.5 to +0.4 V), the two one-electron transfer reactions are therefore assigned as in equation (4).

$$[Mo^{IV}(PPh_3)(aacda)_3]^+ \underset{III}{\overset{e^-}{\rightleftarrows}} [Mo^{III}(PPh_3)(aacda)_3]^0 \underset{IV}{\overset{e^-}{\rightleftarrows}} [Mo^{II}(PPh_3)(aacda)_3]^- \quad (4)$$

Taken collectively, the voltammetric results of molybdenum(IV) compounds (**3a**, **3b**) have indicated that the presence of a softer ligand such as a tertiary phosphine with strong π-electron accepting ability will greatly reduce the electron density at the metal centre, which in turn should facilitate metal-centred reduction. This simplistic approach is supported by our electrochemical results (Table 3) in which molybdenum(II) species have been generated electrochemically by a stepwise two-electron reduction of the molybdenum(IV) precursor. Similar sulfur co-ordinated molybdenum(II) complexes have previously been generated electrochemically using tertiary phosphines as ancillary ligands.[35]

Conclusion

From crystal structure analyses it has been established that terminal oxo groups in six-co-ordinated molybdenum compounds with a *cis*-MoO_2 moiety are structurally identical.[36] But so far as their reactivity is concerned the behaviour is not so straightforward. In the presence of proton donor reagents only one terminal oxo-ligand can be replaced from $[Mo^{VI}O_2(aacda)_2]$ giving seven-co-ordinate $[Mo^{VI}O(aacda)_3]^+$species. The oxo ligand of this core does not react further towards protons but can be replaced by electron-donor reagents such as thiols and phosphines. The presence of the π-acceptor PPh_3 ligand in **3a** and **3b** make these compounds interesting as precursors for the electrochemical generation of molybdenum(II) species.

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References

1 Part 7, S. B. Kumar and M. Chaudhury, *J. Chem. Soc., Dalton Trans.*, 1991, 2169.
2 J. L. Johnson, N. R. Bastian and K. V. Rajagopalan, *Proc. Natl. Acad. Sci. USA*, 1990, **87**, 3190 and refs. therein.
3 R. Hille and H. Sprecher, *J. Biol. Chem.*, 1987, **262**, 10914.
4 S. Gutteridge and R. C. Bray, *Chem. Uses Molybdenum*, 1979, **3**, 275; K. V. Rajagopalan, in *Molybdenum and Molybdenum Containing Enzymes*, ed. M. P. Coughlan, Pergamon, Oxford, 1980, p. 241.
5 S. Boyde, S. R. Ellis, C. D. Garner and W. Clegg, *J. Chem. Soc., Chem. Commun.*, 1986, 1541.
6 S. Boyde, C. D. Garner, J. A. Joule and D. J. Rowe, *J. Chem. Soc., Chem. Commun.*, 1987, 800.
7 J. P. Caradonna, P. R. Reddy and R. H. Holm, *J. Am. Chem. Soc.*, 1988, **110**, 2139.
8 G. L. Wilson, M. Kony, E. R. T. Tiekink, J. R. Pilbrow, J. T. Spence and A. G. Wedd, *J. Am. Chem. Soc.*, 1988, **110**, 6923.
9 S. J. N. Burgmayer and E. I. Stiefel, *Inorg. Chem.*, 1988, **27**, 4059.
10 S. J. N. Burgmayer, A. Baruch, K. Kerr and K. Yoon, *J. Am. Chem. Soc.*, 1989, **111**, 4982.
11 J. A. Craig and R. H. Holm, *J. Am. Chem. Soc.*, 1989, **111**, 2111.
12 K. M. Nicholas and M. A. Khan, *Inorg. Chem.*, 1987, **26**, 1633.
13 D. M. Baird, S. Falzone and J. E. Haky, *Inorg. Chem.*, 1989, **28**, 4561.
14 K. R. Barnard, A. G. Wedd and E. R. T. Tiekink, *Inorg. Chem.*, 1990, **29**, 891.
15 C. S. J. Chang, D. Collison, F. E. Mabbs and J. H. Enemark, *Inorg. Chem.*, 1990, **29**, 2261.
16 S. A. Roberts, C. G. Young, C. A. Kipke, W. E. Cleland, jun., K. Yamanouchi, M. D. Carducci and J. H. Enemark, *Inorg. Chem.*, 1990, **29**, 3650.
17 P. Subramanian, S. Burgmayer, S. Richards, V. Szalai and T. G. Spiro, *Inorg. Chem.*, 1990, **29**, 3849.
18 S. B. Kumar and M. Chaudhury, *J. Chem. Soc., Dalton Trans.*, 1991, 1149.
19 S. B. Kumar and M. Chaudhury, *J. Chem. Soc., Dalton Trans.*, 1987, 3043.
20 M. Chaudhury, *Inorg. Chem.*, 1985, **24**, 3011.
21 M. Chaudhury, *Inorg. Chem.*, 1984, **23**, 4434.
22 M. Chaudhury, *J. Chem. Soc., Dalton Trans.*, 1984, 115.
23 A. I. Vogel, *A Text-Book of Practical Organic Chemistry*, 3rd edn., Longman, London, 1973.
24 B. Bordas, P. Sohar, G. Matolcsy and P. Berencsi, *J. Org. Chem.*, 1972, **37**, 1727.
25 R. R. Gagne, C. A. Koval and G. C. Lisensky, *Inorg. Chem.*, 1980, **19**, 2854.
26 C. G. Young, J. A. Broomhead and C. J. Boreham, *J. Chem. Soc., Dalton Trans.*, 1983, 2135.
27 K. F. Miller and R. A. D. Wentworth, *Inorg. Chem.*, 1979, **18**, 984.
28 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
29 D. A. Smith, J. W. McDonald, H. O. Finklea, V. R. Ott and F. A. Schultz, *Inorg. Chem.*, 1982, **21**, 3825.
30 O. Piovesana and L. Sestili, *Inorg. Chem.*, 1974, **13**, 2745.
31 A. Nieuwpoort and J. J. Steggerda, *Recl. Trav. Chim. Pays-Bas*, 1976, **95**, 289.
32 R. D. Bereman, D. M. Biard, C. T. Vance, J. Hutchinson and J. Zubieta, *Inorg. Chem.*, 1983, **22**, 2316.
33 W. E. Cleland, jun., K. M. Barnhart, K. Yamanouchi, D. Collision, F. E. Mabbs, R. B. Ortega and J. H. Enemark, *Inorg. Chem.*, 1987, **26**, 1017.
34 B. N. Figgis and J. Lewis, *Modern Co-ordination Chemistry*, Interscience, New York, 1960.
35 J. R. Dilworth, B. D. Neaves, C. J. Pickette, J. Chatt and J. Zubieta, *Inorg. Chem.*, 1983, **22**, 3524.
36 C. J. Hinshaw, G. Peng, R. Singh, J. T. Spence, J. H. Enemark, M. Bruck, J. Kristofzski, S. L. Merbs, R. B. Ortega and P. A. Wexler, *Inorg. Chem.*, 1989, **28**, 4483 and refs. therein.

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