Chemistry of Molybdenum. Part 6.[1] Synthesis, Spectroscopic and Redox Properties of Some Eight-co-ordinate Sulphur Chelates, $[Mo^{IV}(S_2CNR_2)_n(acda)_{4-n}]$ and $[Mo^{V}(S_2CNR_2)_n(acda)_{4-n}]Br$ (n = 2 or 3), containing MoS_8 Chromophores (acda = 2-aminocyclopent-1-ene-1-carbodithioate)

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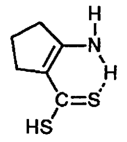
Eight-co-ordinated mixed-ligand complexes $[Mo^{IV}(S_2CNR_2)_n(acda)_{4-n}]$ **1a–1d** and $[Mo^{V}(S_2CNR_2)_n(acda)_{4-n}]Br$ **2a–2d** (n = 2 or 3) containing predominantly σ-donor S_2CNR_2 (R = Et or Pr) and π-acceptor acda (2-aminocyclopent-1-ene-1-carbodithioate) ligands have been synthesised and characterised by UV/VIS, magnetic, ESR and electrochemical studies. For the lower-energy ligand-to-metal charge-transfer bands of compounds **1a–1d** the observed spectral intensity showed an almost linear increment with the number of co-ordinated acda ligands. The molybdenum(V) compounds **2a–2d** are ESR active, and their frozen solutions (140 K) give rise to axial spectra with grossly identical features ($g_{\parallel} \approx 1.983$, $A_{\parallel} \approx 52.5 \times 10^{-4}$ cm^{-1}; $g_{\perp} \approx 1.984$, $A_{\perp} \approx 21.5 \times 10^{-4}$ cm^{-1}) consistent with the electron being localised in a metal-centred orbital of nearly constant composition for the entire series of compounds. Cyclic voltammetry indicates the existence of three molybdenum oxidation states $[Mo^{n}S_8]$ with n = III, IV and V. The $E_{\frac{1}{2}}$ values (*vs.* saturated calomel electrode) are −0.40 and −0.18 V for the $Mo^{III} \longrightarrow Mo^{IV}$ and $Mo^{IV} \longrightarrow Mo^{V}$ couples respectively and independent of whether the starting compound is a molybdenum(IV), **1a**, **1c**, or a molybdenum(V) species **2a–2d**. Of the two types of ligand systems present in $[Mo(S_2CNR_2)_n(acda)_{4-n}]^{m}$ (m = 0 or +1), acda has been found to have a profound influence in controlling the redox and charge-transfer properties.

Molybdenum is known to have specific roles in various biological electron-transfer processes.[2,3] A prominent feature of molybdenum biochemistry is the recurring presence of sulphur in the enzymatic molybdenum co-ordination sphere[4] which in part is responsible for the growing interest in molybdenum–sulphur chemistry during recent years. As a part of our interest in such chemistry[1,5–8] we have recently reported[5,6] a number of molybdenum(IV) complexes of the type $Mo(S\text{–}S)_4$ using 2-aminocyclopent-1-ene-1-carbodithioic acid (Hacda) and its *N*-alkyl derivatives (HRacda) as bidentate $(S\text{–}S)^-$ donor ligands. Both the magnetic and electrochemical properties of $[Mo(Racda)_4]$ compounds are quite interesting[5,6] compared to those of other $Mo^{IV}S_8$ species.[9–16] They undergo facile electrochemical reduction although oxidations are quite favourable with $[Mo(S_2CNR_2)_4]$ derivatives. It has been noted that dialkyldithiocarbamates are much more electron releasing compared to dithiocarboxylato ligands.[13,17] These observations have led us to extend our study to a sulphur–molybdenum system where both dithiocarbamates and dithiocarboxylates are bound simultaneously to the same metal centre. The present contribution deals with the synthesis, spectroscopy, magnetic, ESR and redox properties of a number of eight-co-ordinated molybdenum-(IV) and -(V) compounds with varying combinations of S_2CNR_2 (a predominantly σ-donor ligand)[18,19] and acda (having better π-acceptor properties).



Hacda

Experimental

All preparations and solution studies were performed under an atmosphere of purified dinitrogen with the use of freshly distilled, dry and deoxygenated solvents. The starting materials Hacda,[20] $[MoOCl_2(S_2CNR_2)_2]$,[21] $[MoO(S_2CNR_2)_3]BF_4$,[22] $[Mo(acda)_4]$[6] and $[Mo(S_2CNEt_2)_4]$[12] were prepared as described. Silica gel H from Glaxo Laboratories was used for thin-layer chromatography. All other chemicals used were of reagent grade and employed without further purification.

Physical Measurements.—Magnetic susceptibility (of powdered samples), electrical conductivity [in dimethylformamide (dmf) solutions], infrared (as KBr pellets) and electronic absorption spectral (in dmf solutions) measurements were made as described elsewhere.[1,5,6] Proton NMR spectra in $(CD_3)_2SO$ solutions were recorded on a JEOL model FX 100 spectrometer. Chemical shifts are reported in ppm relative to $SiMe_4$ as internal standard. X-Band ESR spectra in frozen solutions (dmf–MeCN 1:10 v/v) were recorded with an ER 200D-SRC model Bruker spectrometer coupled with a model ER 082 (155/45) magnet power-supply unit. The operating frequency was maintained at 9.47 GHz. The control of external magnetic field was achieved with a Bruker model ER 042 MRH microwave bridge and of temperature with a model ER 4111 VT variable-temperature unit.

The materials and the apparatus used for the electrochemical experiments have been described elsewhere.[1] A hanging mercury drop electrode (HMDE) was employed for cyclic voltammetric experiments, a stirred mercury pool for coulometric measurements together with a saturated calomel electrode as reference and a platinum-wire auxiliary electrode.

Table 1 Analytical and IR data for the complexes

	Analysis[a] (%)					IR[b]/cm^{-1}		
Complex	Mo	C	H	N	Br	$\nu(\mathrm{C\overset{\cdots}{-}N})$	ν_{asym}(CSS)	ν(Mo–S)
1a [Mo($S_2CNEt_2)_2$(acda)$_2$]	13.3	37.0	5.1	7.8	—	1525vs	830s	360m, 345w
	(13.6)	(37.3)	(5.1)	(7.9)				
1b [Mo($S_2CNEt_2)_3$(acda)]	13.5	35.8	5.3	7.5	—	1525vs	830s	360m, 340m
	(13.7)	(36.1)	(5.4)	(8.0)				
1c [Mo($S_2CNPr_2)_2$(acda)$_2$]	12.5	40.0	5.6	7.4	—	1515vs	830s	350m, 340m
	(12.6)	(40.8)	(5.8)	(7.3)				
1d [Mo($S_2CNPr_2)_3$(acda)]	12.3	41.0	6.3	7.1	—	1510vs	815s	350m, 335m
	(12.3)	(41.4)	(6.4)	(7.2)				
2a [Mo($S_2CNEt_2)_2$(acda)$_2$]Br	12.2	32.9	4.4	7.0	10.7	1520vs	820s	360m, 330m
	(12.2)	(33.5)	(4.6)	(7.1)	(10.1)			
2b [Mo($S_2CNEt_2)_3$(acda)]Br	12.4	32.4	4.7	7.3	9.9	1510vs	815s	350m, 330m
	(12.3)	(32.4)	(4.9)	(7.2)	(10.3)			
2c [Mo($S_2CNPr_2)_2$(acda)$_2$]Br	11.9	36.4	5.0	6.4	9.8	1510vs	815s	350m, 335m
	(11.4)	(37.0)	(5.2)	(6.6)	(9.5)			
2d [Mo($S_2CNPr_2)_3$(acda)]Br	11.0	37.8	5.8	6.4	9.0	1520vs	815s	355m, 330m
	(11.1)	(37.6)	(5.8)	(6.5)	(9.3)			
2e [Mo(acda)$_4$]Br	11.8	35.7	3.8	6.6	9.6	—	815s	350s, 330m
	(11.9)	(35.6)	(4.0)	(6.9)	(9.9)			

[a] Calculated values are in parentheses. [b] KBr disc.

The solvent dmf was freshly distilled and dried.[23] Tetraethylammonium perchlorate was used as supporting electrolyte at 0.1 mol dm^{-3}. All measurements were performed at ambient temperature (25 ± 2 °C) using ferrocene (+0.465 V *vs.* saturated calomel electrode)[24] as internal standard. Potentials are reported relative to the saturated calomel electrode (SCE) and are uncorrected for liquid-junction potentials. Elemental analyses for C, H and N were made in this laboratory with a Perkin-Elmer 240C elemental analyser. The molybdenum and bromine contents were estimated by conventional gravimetric methods.

Preparation of Compounds.—[Mo($S_2CNEt_2)_2$(acda)$_2$] **1a**. To a stirred dichloromethane solution (20 cm^3) of [MoOCl$_2$($S_2CNEt_2)_2$] (0.48 g, 1 mmol) was added dropwise a solution of Hacda (0.67 g, 4.2 mmol) in methanol (30 cm^3). The solution was stirred for 3 h at 40 °C and then cooled to 25 °C. Filtration of the reaction mixture followed by washing (4 × 10 cm^3) with chloroform–hexane (1:3 v/v) yielded a dark brown microcrystalline solid which was subsequently dried *in vacuo*. The purity of the product was checked by TLC. Yield 0.31 g (43%).

The compound [Mo($S_2CNPr_2)_2$(acda)$_2$] **1c** was obtained by following essentially the same procedure, in a yield of 30%.

[Mo($S_2CNEt_2)_3$(acda)] **1b**. A solution of Hacda (0.4 g, 2.5 mmol) in methanol (25 cm^3) was added dropwise with stirring to a solution of [MoO($S_2CNEt_2)_3$]BF$_4$ (0.5 g, 0.8 mmol) in CH_2Cl_2 (25 cm^3). After 3 h of stirring at *ca.* 40 °C the resulting solution was cooled to room temperature, filtered, washed four times (4 × 10 cm^3) with $CHCl_3$–hexane (1:3 v/v) and finally dried *in vacuo* to yield a black-violet powder (yield 0.26 g, 48%). The purity of the product was checked by TLC.

The compound [Mo($S_2CNPr_2)_3$(acda)] **1d** can be synthesised similarly with a yield of 26%.

[Mo($S_2CNEt_2)_2$(acda)$_2$]Br **2a**. To a well stirred solution of compound **1a** (0.45 g, 0.63 mmol) in $CHCl_3$ (20 cm^3) was added dropwise a slight molar excess of bromine in $CHCl_3$. The mixture was stirred for 3 h at ambient temperature, and the dark brown precipitate was collected. It was washed with hexane (4 × 10 cm^3) and dried under vacuum to give 0.2 g (40%) of product. The purity of the product was confirmed by TLC.

Other molybdenum(V) compounds **2b**–**2e** were prepared similarly in varying yields (30–60%) using appropriate molybdenum(IV) compounds as starting materials. For the synthesis of **2b**, **2d** and **2e** the solvent was methanol.

Recrystallisation of the above compounds were not successful because of their limited solubilities and instability in solutions. However all the compounds reported are sufficiently pure and gave satisfactory analytical results (Table 1).

Results and Discussion

Synthesis.—Non-oxo eight-co-ordinated molybdenum(IV) compounds of the type [Mo($S_2CNR_2)_2$(acda)$_2$] (R = Et, **1a**; or Pr, **1c**) and [Mo($S_2CNR_2)_3$(acda)] (R = Et, **1b**; or Pr, **1d**) are obtained in fairly good yields (30–50%) according to reactions (1) and (2) where S–S* is the oxidised form of Hacda, probably a dimer of disulphide type.[25] In the above reactions Hacda plays a dual role as a one-electron reductant as well as an incoming ligand.

$$[\mathrm{Mo^{VI}OCl_2(S_2CNR_2)_2}] + 4\mathrm{Hacda} \longrightarrow [\mathrm{Mo^{IV}(S_2CNR_2)_2(acda)_2}] + 2\mathrm{HCl} + \mathrm{H_2O} + \mathrm{S{-}S^*} \quad (1)$$

$$[\mathrm{Mo^{VI}O(S_2CNR_2)_3}]\mathrm{BF_4} + 3\mathrm{Hacda} \longrightarrow [\mathrm{Mo^{IV}(S_2CNR_2)_3(acda)}] + \mathrm{HBF_4} + \mathrm{H_2O} + \mathrm{S{-}S^*} \quad (2)$$

Molybdenum(V) compounds **2a**–**2e** are obtained by one-electron oxidation of the corresponding molybdenum(IV) compounds with stoichiometric amounts of bromine in chloroform solution according to reaction (3).

$$[\mathrm{Mo^{IV}(S_2CNR_2)_{\mathit{n}}(acda)_{4-\mathit{n}}}] + \tfrac{1}{2}\mathrm{Br_2} \longrightarrow [\mathrm{Mo^{V}(S_2CNR_2)_{\mathit{n}}(acda)_{4-\mathit{n}}}]\mathrm{Br} \quad (3)$$

All the compounds reported here have intense dark colours with varying degrees of solubility in solvents such as chloroform, acetonitrile and dmf. They are fairly stable in the solid state, but decompose slowly on prolonged standing in solution.

A few selected IR frequencies are listed in Table 1. In each case the data are consistent with the expected S,S binding mode of dithiocarbamate [ν(CN) ≈ 1525 cm^{-1}][12] and acda [ν_{asym}(CSS) ≈ 825 cm^{-1}][5,6] ligands. The absence of a strong band at ≈950 cm^{-1}, diagnostic of terminal ν(Mo=O) vibration, suggests the complete removal of oxygen from the molybdenum co-ordination sphere.

Proton NMR measurements of two representative compounds **1a** and **1b** in $(CD_3)_2SO$ gave limited information possibly because of their low solubilities and weak para-

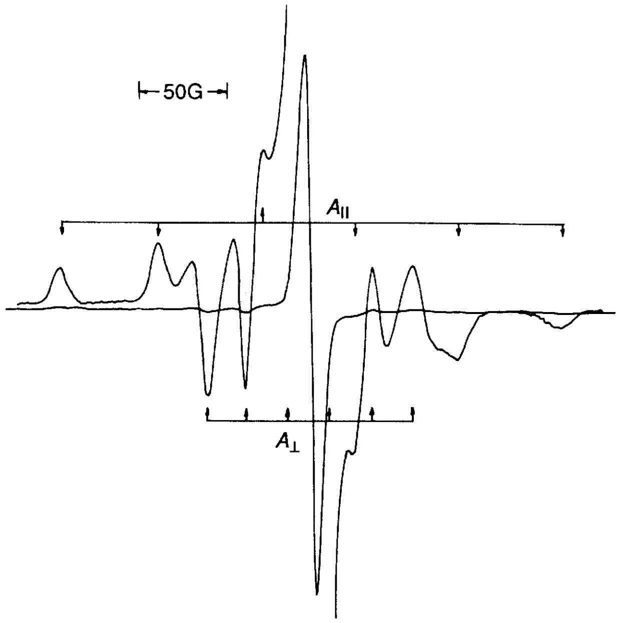


Fig. 1 X-Band ESR spectrum of $[Mo(S_2CNEt_2)_2(acda)_2]Br$ in dmf–acetonitrile (1:10 v/v) solution (concentration *ca.* 10^{-3} mol dm^{-3}) at 140 K. The satellite bands belong to odd isotopes of molybdenum

magnetism. The spectra in general contain broad bands with poor resolutions. Also recorded were the spectra of the Hacda ligand [δ 1.84(m), 2.68(t) and 2.92(t)] and $[Mo(S_2CNEt_2)_4]$ [δ 1.24(br) and 2.48(br)] for comparison. For both **1a** and **1b** broad lines at δ 1.82, 2.68 and 3.5 are obtained in addition to the lines present for $[Mo(S_2CNEt_2)_4]$. The results are in agreement with the simultaneous presence of both acda and S_2CNR_2 in the reported compounds.

While the molybdenum(IV) compounds are all non-conducting; the conductivity of the molybdenum(V) compounds (Table 2) in dmf solutions is consistent with the range reported for 1:1 electrolytes.[26]

Magnetic Properties and Electron Spin Resonance Spectra.—Unlike the $[Mo(Racda)_4]$ compounds,[5,6] the mixed-ligand molybdenum(IV) complexes **1a–1d** are all spin-paired with a small degree of associated paramagnetism (0.35–0.55). This is quite common in many eight-co-ordinated molybdenum(IV) compounds[11,14] and can be explained as due either to the presence of ferromagnetic impurities and/or to temperature-independent paramagnetism. For an eight-co-ordinated compound with d^2 configuration, the observed diamagnetism can be best explained in terms of either dodecahedral (*DD*) or square antiprismatic (*SAPR*) geometry.[27–29] Both of these geometries share a common property of a large energy gap between the lowest-lying level ($d_{x^2-y^2}$ for *DD* and d_{z^2} for SAPR)[29] and the next upper one. For ligands with small normalised bite* (*e.g.* NO_3^-, O_2^{2-}, dithiocarbamates and dithiocarboxylates), repulsion-energy minimisation calculations[28] indicate that the *DD* structure is significantly more stabilised relative to *SAPR* geometry. Most of the structurally characterised eight-co-ordinated MoS_8 compounds are dodecahedral with varying degree of distortion.[16,30,31]

Magnetic moment and ESR data for the molybdenum(V) compounds **2a–2e** are listed in Table 2. The room-temperature magnetic moments (1.68–1.72) are close to the spin-only value for a d^1 system. The ESR spectrum of $[Mo(S_2CNEt_2)_2(acda)_2]Br$ **2a** in frozen solution (dmf–acetonitrile 1:10 v/v) at 140 K (Fig. 1) shows the axial symmetry of the *g* tensor with well resolved hyperfine structure. Almost identical spectra were obtained for the remaining molybdenum(V) compounds **2b–2e**. In each case the spectrum consists of strong central lines (owing to the ≈75% Mo isotopes with $I = 0$) flanked by six parallel ($A_{\parallel} \approx 52 \times 10^{-4}$ cm^{-1}) and six perpendicular ($A_{\perp} \approx 22 \times 10^{-4}$ cm^{-1}) components of satellite bands arising from hyperfine interactions with $^{95,97}Mo$ nuclei ($I = \frac{5}{2}$, abundance ≈ 25%). The ESR parameters reported for the molybdenum(V) compounds (Table 2) are closely comparable, indicating that the unpaired electron is located in a metal-centred orbital with almost identical composition for the entire series of compounds.

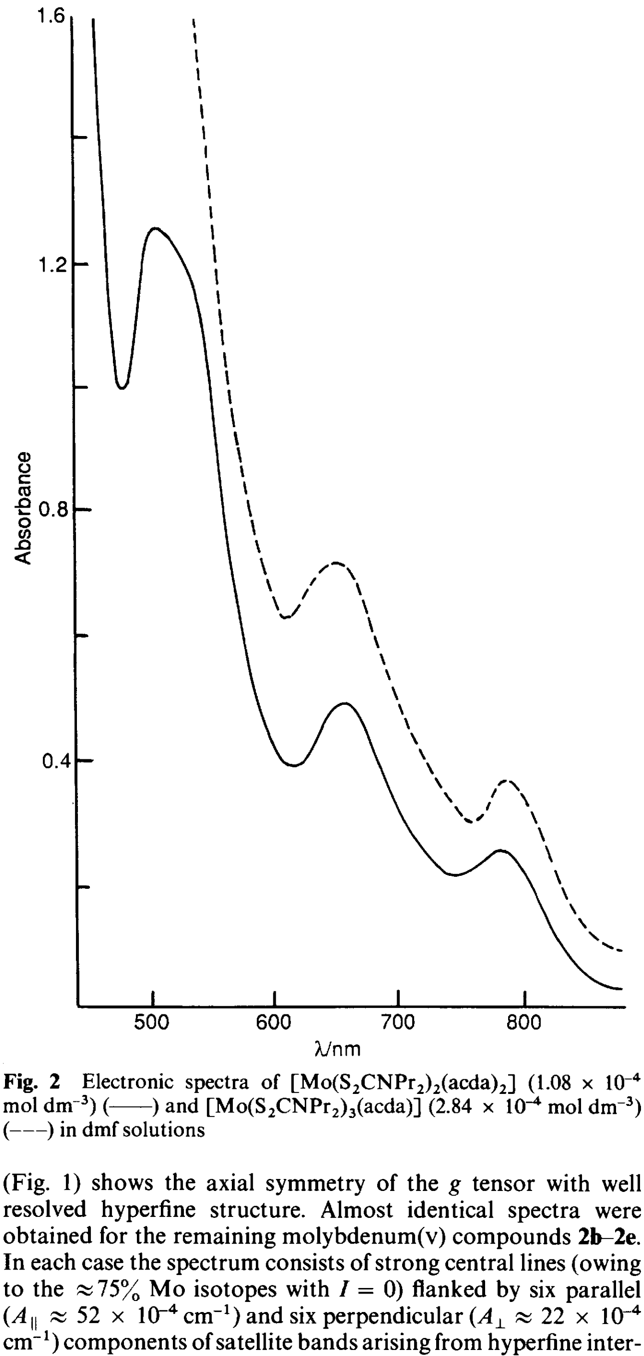


Fig. 2 Electronic spectra of $[Mo(S_2CNPr_2)_2(acda)_2]$ (1.08 × 10^{-4} mol dm^{-3}) (——) and $[Mo(S_2CNPr_2)_3(acda)]$ (2.84 × 10^{-4} mol dm^{-3}) (– – –) in dmf solutions

Electronic Absorption Spectra.—Electronic spectra of two molybdenum(IV) complexes (**1c** and **1d**) are shown in Fig. 2 as representative types. Grossly identical spectral features are also obtained with the remaining compounds **1a** and **1b**. Relevant data for all the compounds are summarised in Table 3. Complex patterns with high absorption coefficients (ε 1250–13 000 dm^3 mol^{-1} cm^{-1}) are observed at longer wavelengths (850–400 nm). The spectral features below 400 nm are due to intraligand transitions.[32] Most of the non-oxo molybdenum(IV) compounds reported so far[5,10,11,14,16,33] with MoS_8 cores show similar complicated features which were grossly treated as charge-transfer transitions. Our previous conjecture[5,6] that these low-energy transitions could possibly originate from ligand-to-metal charge transfer (l.m.c.t.) gains further ground

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* The normalised bite of a bidentate ligand is a function of both the distances between the donor atoms and the metal–ligand bond length. For ligands containing a XCS_2^- functional group, the normalised bite appears to be small.[28]

Table 2 Electrical conductivity, magnetic and ESR data for the molybdenum(v) compounds

Complex	Λ^a/S cm^2 mol^{-1}	μ_{eff}	$\langle g\rangle^b$	$g_\parallel{}^c$	$g_\perp{}^c$	$10^4\langle a\rangle^b$/cm^{-1}	$10^4A_\parallel{}^c$/cm^{-1}	$10^4A_\perp{}^c$/cm^{-1}	$10^4\langle a\rangle_{calc}{}^d$/cm^{-1}
2a	72	1.69	1.982	1.981	1.983	32.3	52.3	22.2	32.2
2b	60	1.67	—	1.983	1.984	—	52.4	21.2	31.6
2c	71	1.71	—	1.983	1.985	—	52.9	21.5	31.9
2d	81	1.72	—	1.984	1.985	—	52.6	20.7	31.3
2e	61	1.68	1.983	1.983	1.984	32.0	52.0	21.6	31.7

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

Table 3 Electronic spectral properties of the complexes

Complex	λ_{max}/nm(ε/dm^3 mol^{-1} cm^{-1})^a
1a	772 (2 800), 656 (4 350), 504 (12 950), 392 (28 500), 332 (22 100)
1b	796 (1 250), 656 (2 900), 492 (6 400), 388 (22 600), 332 (25 700)
1c	776 (2 400), 656 (4 500), 504 (11 500), 392 (39 600), 332 (26 600)
1d	788 (1 300), 656 (2 500), 504(sh), 392 (18 000), 332 (24 500)
[Mo(acda)$_4$]^b	800 (2 700), 660 (6 400), 536 (13 400), 495 (11 200), 395 (51 000)
2a	776 (4 100), 656 (5 000), 504 (12 400), 388 (21 700), 332 (21 400)
2b	798 (3 150), 672 (5 800), 528 (12 000), 392 (37 700), 336 (28 500)
2c	784 (4 300), 652 (5 500), 504 (14 000), 392 (48 100), 336 (29 100)
2d	792 (3 360), 656 (6 200), 536 (13 200), 392 (42 800), 332 (26 300)
2e	800 (3 800), 656 (7 500), 536 (14 800), 492 (15 100), 392 (44 600), 336 (31 700)

[a] Spectra recorded in dmf. [b] Ref. 6.

Table 4 Summary of electrochemical data for the compounds^a

	Mo^{III}–Mo^{IV}			Mo^{IV}–Mo^{V}		
Complex	$(E_{\frac{1}{2}})_I{}^b$/V	$\Delta E_p{}^c$/mV	i_{p_c}/i_{p_a}	$(E_{\frac{1}{2}})_{II}{}^b$/V	$\Delta E_p{}^c$/mV	i_{p_c}/i_{p_a}
1a	−0.37	90	0.97	−0.17	100	1.12
1c	−0.41	80	1.19	−0.20	110	1.14
2a	−0.39	60	0.93	−0.16	60	0.90
2b	−0.38	80	1.12	−0.18	80	0.98
2c	−0.38	90	1.07	−0.18	90	1.07
2d	−0.40	60	0.95	−0.18	80	1.05
2e	−0.39	60	0.89	−0.18	100	1.10

[a] Solvent dmf; supporting electrolyte NEt$_4$ClO$_4$ (0.1 mol dm^{-3}); solute concentration *ca.* 10^{-3} mol dm^{-3}; working electrode HMDE. [b] From cyclic voltammogram using a scan rate of 50 mV s^{-1}; $E_{\frac{1}{2}} = 0.5(E_{p_c} + E_{p_a})$. [c] $\Delta E_p = E_{p_a} - E_{p_c}$.

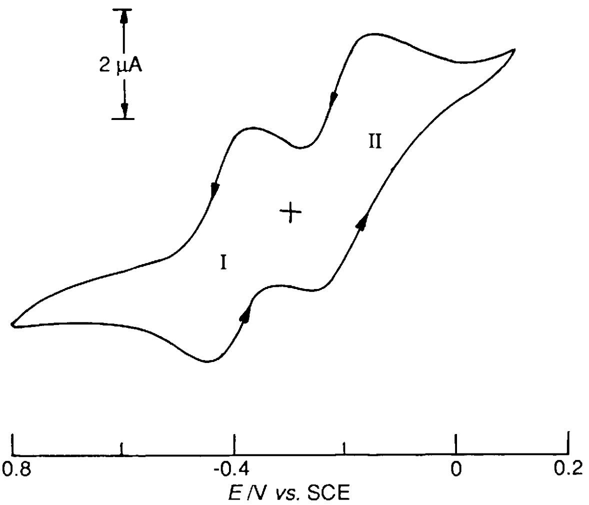

Fig. 3 Cyclic voltammogram for [Mo(S$_2$CNPr$_2$)$_2$(acda)$_2$] **1c** in dmf. Almost identical features are obtained with complexes **1a** and **2a**–**2e**. Experimental conditions: scan rate, 100 mV s^{-1}; supporting electrolyte, ≈0.1 mol dm^{-3} NEt$_4$ClO$_4$; working electrode, HMDE; complex concentration, ≈10^{-3} mol dm^{-3}

from a close scrutiny of Table 3, where a systematic variation of charge-transfer intensity is observed with the number of co-ordinated acda ligand(s). Thus, considering the molar absorption coefficient to be a rough estimation of transition probability, the value of ε for the first two low-energy transitions of **1b** and **1d** almost doubles with the increase in the number of acda ligands on going from **1b** to **1a** or from **1d** to **1c**. A similar additive effect in charge-transfer intensity has recently been reported for double helix complexes of Cu^I with poly(bipyridine) ligands.[34] Moreover, a small red shift observed in the lowest-energy c.t. band of the molybdenum(v) compounds **2a**–**2d** with respect to their molybdenum(IV) counterparts (Table 3) also suggests a l.m.c.t. type transition.[35]

For molybdenum(v) compounds, although the spectral features (Table 3) are grossly comparable to those of molybdenum(IV) compounds, the intensities of the low-energy l.m.c.t. bands do not follow the same quantitative change. For both series of compounds **1a**–**1d** and **2a**–**2d** the spectral features diagnostic of [Mo(S$_2$CNR$_2$)$_4$][10,14] are either completely absent or have lost their identity. Thus acda plays a dominant role in controlling the electronic spectral behaviour of the mixed-ligand compounds [Mo(S$_2$CNR$_2$)$_n$(acda)$_{4-n}$]$^{0,+1}$. At this stage no attempt has been made to interpret these complicated spectral features.

Electrochemistry.—Electrochemical data for the molybdenum(IV) compounds (**1a** and **1c**) as obtained by cyclic voltammetry in dmf–0.1 mol dm^{-3} NEt$_4$ClO$_4$ at a HMDE are summarised in Table 4. A typical voltammogram represented by compound **1c** is shown in Fig. 3. Both the compounds undergo a reversible one-electron reduction and a nearly reversible one-electron oxidation between +0.30 and −0.80 V (*vs.* saturated calomel electrode). The scan was initiated in each case from −0.3 V (rest potential) and the features of the voltammograms remain practically unaltered irrespective of the initial scan direction. While Hacda itself is electrode inactive, S_2CNR_2 ligands do not however interfere in the potential range of our interest. The reduction, labelled as process I [equation (4)], is presumably due to $Mo^{IV} \longrightarrow Mo^{III}$ electron transfer

$$[Mo^{III}(S_2CNR_2)_2(acda)_2]^- \underset{(E_{\frac{1}{2}})_I}{\overset{I}{\rightleftharpoons}} [Mo^{IV}(S_2CNR_2)_2(acda)_2] + e^- \quad (4)$$

and occurs at $E_{\frac{1}{2}} \approx -0.40$ V. The oxidation labelled as process II [equation (5)] is possibly due to $Mo^{IV} \longrightarrow Mo^{V}$ electron

$$[Mo^{IV}(S_2CNR_2)_2(acda)_2] \underset{(E_{\frac{1}{2}})_{II}}{\overset{II}{\rightleftharpoons}} [Mo^{V}(S_2CNR_2)_2(acda)_2]^+ + e^- \quad (5)$$

transfer with $E_{\frac{1}{2}} \approx -0.18$ V. The separation of the peak potentials (ΔE_p) for the couples (I and II) varies in the range 60–110 mV (Table 4) and is virtually independent of scan rate (50–500 mV s^{-1}). While some of these separations are larger than the ideal Nernstian value of 59 mV, such values are frequently observed for complexes of this type,[5,10] presumably due to uncompensated solution resistance. For comparison, the ΔE_p for ferrocenium–ferrocene was found to be 90 mV with this electrode configuration. In addition, plots of the peak current *versus* the square root of the scan velocity are linear, indicating the electrode processes involved in the couples (I and II) are diffusion controlled. Cathodic and anodic peak-current ratios (i_{p_c}/i_{p_a}) were close to unity in both cases and the $E_{\frac{1}{2}}$ values were independent of scan rate. Current heights for these electrochemical processes (I and II) as measured by cyclic voltammetry (Fig. 3) are almost identical indicating the involvement of identical numbers of electrons in each step. Confirmation of the overall number of electrons transferred in the reduction step (process I) came from constant-potential bulk-electrolysis experiments carried out at −0.6 V. The data are consistent with the involvement of 1 mol of electrons per mol of compounds **1a** and **1c**. Unfortunately our similar attempts to determine the electron stoichiometry of the oxidation process II proved unsuccessful. Exhaustive electrolysis past the oxidation wave (+0.05 V *vs.* saturated calomel electrode) did not yield satisfactory results because of some unidentified electrode reaction(s). However, from an analysis of voltammetric data together with coulometric confirmation of the single-electron involvement in process I, we can safely conjecture the involvement of 1 mol of electrons per mol of compounds **1a** and **1c** in process II. For the remaining two molybdenum(IV) compounds of the type $[Mo(S_2CNR_2)_3(acda)]$, **1b** and **1d**, the electrochemical behaviour is rather complicated each involving a couple of irreversible electrode processes and will not be discussed any further.

The electrochemical behaviours of the molybdenum(V) compounds **2a**–**2e** are grossly identical (Table 4), each involving two nearly reversible couples indicated by processes I and II. Their overall voltammetric features are quite similar to those of the molybdenum(IV) complexes as represented in Fig. 3. The only difference is in the nature of electron transfer in process II which is a $Mo^{V} \longrightarrow Mo^{IV}$ reduction in the present case. Each couple is judged to be a diffusion-controlled reversible process with single-electron stoichiometry on the basis of results obtained from cyclic voltammetry and constant-potential coulometry. No significant differences in $E_{\frac{1}{2}}$ values are observed for the redox couples I and II (Table 4) irrespective of whether starting compound is a molybdenum(IV), **1a** or **1c**, or a molybdenum(V) species, **2a**–**2e**.

Thus for all the $[Mo(S\text{–}S)_4]^{0,1+}$ compounds of the mixed-ligand types reported here (except **1b** and **1d**), the overall electrochemical behaviour can now be represented by Scheme 1.

$$[Mo^{III}(S\text{–}S)_4]^- \underset{(E_{\frac{1}{2}})_I}{\overset{e^-}{\rightleftharpoons}} [Mo^{IV}(S\text{–}S)_4] \underset{(E_{\frac{1}{2}})_{II}}{\overset{e^-}{\rightleftharpoons}} [Mo^{V}(S\text{–}S)_4]^+$$

$$\approx -0.40 \text{ V} \qquad\qquad \approx -0.18 \text{ V}$$

Scheme 1

For a metal-centred electrochemical process it is well known that an electron-donating ligand like the σ donor S_2CNR_2 (R = alkyl group) will favour oxidation,[10,12] while an electron-withdrawing ligand like the π acceptor acda will favour reduction [5,6] of the metal centre. Hence it should be possible to tune the redox potential of the metal centre to an appreciable extent by using appropriate combinations of ligand systems having different donor–acceptor properties. However, what we have observed here is the complete control by the acda ligand over the redox properties of the reported compounds **1a**, **1c** and **2a**–**2d**. The $E_{\frac{1}{2}}$ values of the electrochemical processes I and II (Table 4) remain practically unaltered when acda ligands in $[Mo(acda)_4]^{0,1+}$ are partially replaced by dithiocarbamate ligands. The influence of S_2CNR_2 as a ligand here appears to be almost marginal as observed in the electronic spectra. Unfortunately, right now we do not have any explanation for these interesting observations.

Conclusion

We have demonstrated here a relatively straightforward approach for the rational synthesis of mixed-ligand non-oxo compounds of molybdenum with a MoS_8 core. Of the two types of ligand systems used, acda has been found to have a domineering influence in controlling the redox and electronic spectral properties of these compounds, a fact which can possibly be explained as due to preferential edge occupancy by π-acceptor ligands in eight-co-ordinate polyhedra surrounding a metal atom with d^1 or d^2 electronic configurations.[27,36] Crystal structure data are however needed to establish this possibility. Failure to isolate diffraction-quality crystals has prevented us from confirming this hypothesis.

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