Synthesis and Characterisation of Sulfur-rich Manganese(III) and Vanadium(IV) Complexes containing Dithioacid Ligands

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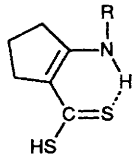
The chemistry of the bidentate $(S,S')^-$ donor ligand 2-aminocyclopent-1-ene-1-carbodithioic acid (Hacda) and its *N*-alkylated derivatives [R = Et (Heacda), Pr^n (Hpacda), or Bu^n (Hbacda)] with vanadium(IV) and manganese(III) has been studied. The vanadium(IV) complexes [V(aacda)$_4$] **1a**–**1d** are all eight-co-ordinated non-oxo species containing a VS_8 chromophore. Their ESR spectra in frozen solution (140 K) exhibit axial anisotropy with a 16-line ^{51}V hyperfine pattern. The observed order in spin-Hamiltonian parameters ($g_{\parallel} \approx 1.932$, $g_{\perp} \approx 1.985$, $A_{\parallel} \approx 175 \times 10^{-4}$ cm^{-1} and $A_{\perp} \approx 74 \times 10^{-4}$ cm^{-1}) indicates a $d_{x^2-y^2}$ ground state with a dodecahedral (D_{2d}) structure. Electrochemical studies of **1a**–**1d** show a quasi-reversible one-electron V^{IV}–V^{III} reduction at ≈ -0.7 V *vs.* saturated calomel electrode (SCE). The manganese(III) complexes [Mn(aacda)$_3$] **2a**–**2c** are all high-spin species (μ_{eff} 5.01–5.10) and exhibit two ligand-to-metal charge-transfer bands at ≈610 and 530 nm. Their cyclic voltammograms reveal the presence of two quasi-Nernstian couples: $E_{\frac{1}{2}}$(ox) = 0.1 V and $E_{\frac{1}{2}}$(red) = −0.33 V *vs.* SCE due to Mn^{IV}–Mn^{III} and Mn^{III}–Mn^{II} electron transfers respectively.

Vanadium and molybdenum both have rich oxo- and thiometalate chemistry.[1,2] This is nicely reflected in the composition[3] and structure[4] of a recently recognised iron–vanadium cofactor in a nitrogen-fixing bactarium, *Azotobacter chroococcum*, which are almost analogous to those of the iron–molybdenum cofactor of nitrogenase. Given a suitable co-ordination environment, the oxovanadium centre like its molybdenum counterpart undergoes simple acid–base chemistry with fairly acidic reagents leading to protonation and subsequent loss of oxygen[5–8] thereby generating non-oxo vanadium species. The co-ordination chemistry of non-oxo vanadium centres is a topic of current interest as such centres provide a relatively easy access to different oxidation states (+3, +4 and +5) of the metal ion.[6,9–11] The accessibility of multiple oxidation states perhaps is the key to the newly recognised role of vanadium[5,12] as a bioessential metal ion as observed in the case of molybdenum. Several model vanadium compounds, with ligands having various combinations of donor atoms, have been reported[13–16] recently with the objective to enhance our understanding of the vanadium biochromophore(s).

As an extension to our ongoing programme on molybdenum–sulfur chemistry,[17–20] we report an investigation of the co-ordination chemistry of 2-aminocyclopent-1-ene-1-carbodithioic acid and its *N*-alkylated derivatives (Haacda) with vanadium(IV). Eight-co-ordinated non-oxo (bare) vanadium compounds [V(aacda)$_4$] **1a**–**1d** containing the VS_8 chromophore have been synthesised and their spectroscopic and electrochemical properties investigated. Also reported are the syntheses and characterisation of [Mn(aacda)$_3$] complexes **2a**–**2c**.

Experimental

All reactions and manipulations of compounds were performed under an inert atmosphere of purified dinitrogen. Solvents were dried by recommended procedures[21] and distilled under nitrogen before use. Dimethylformamide (dmf, Fluka reagent grade) was treated with 4 Å molecular sieves and barium oxide for a minimum of 48 h. The sieve-dried solvent was fractionally distilled from P_2O_5 under nitrogen at reduced pressure [< 15 mmHg (*ca.* 2000 Pa)] and used within 48 h. Cyclopentanone (E. Merck), *n*-propylamine (Fluka), and *n*-butylamine (Riedel) were freshly distilled before use. The compounds Hacda,[22] Haacda,[23] [Bi(eacda)$_3$][24] and [Mn(acac)$_3$] (acac = acetylacetonate)[25] were prepared as described in the literature. All other chemicals were reagent grade and used as received.



	R
Hacda	H
Heacda	Et
Hpacda	Pr^n
Hbacda	Bu^n

Physical Measurements.—Spectroscopic measurements were made on the following spectrometers: UV/VIS (in dmf for compounds **1a**–**1d** and in dichloromethane for **2a**–**2c**), JASCO model 7850; IR (as KBr pellets), Perkin Elmer 783; ESR, Bruker ER 200D-SRC (X-band; in dmf–MeCN (1:10 v/v) solution, measured at room temperature and in frozen solution, 140 K) equipped with standard Bruker attachments as described earlier.[19] Magnetic susceptibility data were collected on powdered samples of the compounds at room temperature with a PAR 155 vibrating-sample magnetometer using mercury tetra(thiocyanato)cobaltate(II) as the susceptibility standard. Molar conductivities were measured with a Philips PR 9500 bridge.

Electrochemical experiments were carried out by using a Bioanalytical systems CV-27 controller coupled with a Houston Instruments Omnigraphic 2000 X-Y recorder. All cyclic voltammetric studies were done using either dmf (for compounds **1a**–**1d**) or CH_2Cl_2 (for **2a**–**2c**) as solvents with tetraethylammonium perchlorate (0.1 mol dm^{-3}) as supporting electrolyte and a saturated calomel electrode (SCE) as reference. The working electrode was a platinum disc. A platinum

Table 1 Analytical and IR data for the complexes

Complex	Analysis[a] (%) C	H	N	IR[b] (cm^{-1}) ν_{asym}(CSS)	ν(M–S)
1a [V(acda)$_4$]·H$_2$O	41.0	4.8	7.9	805	345
	(41.1)	(4.8)	(8.0)		
1b [V(eacda)$_4$]	48.2	6.0	7.1	805	340
	(48.3)	(6.0)	(7.0)		
1c [V(pacda)$_4$]	51.0	6.6	6.7	800	340
	(50.8)	(6.6)	(6.6)		
1d [V(bacda)$_4$]	52.9	7.1	6.2	800	345
	(52.9)	(7.0)	(6.2)		
2a [Mn(eacda)$_3$]	46.5	5.8	6.8	810	365
	(47.0)	(5.9)	(6.8)		
2b [Mn(pacda)$_3$]	49.7	6.5	6.1	805	360
	(49.5)	(6.4)	(6.4)		
2c [Mn(bacda)$_3$]	51.2	6.8	6.0	810	360
	(51.6)	(6.9)	(6.0)		

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

wire served as the counter electrode. For coulometry a platinum-mesh 'flag' working electrode was used. The supporting electrolyte solutions were deoxygenated by a stream of pure dry dinitrogen for about 10 min before introduction of the studied compounds. A nitrogen blanket was maintained over the working solutions during the experiments. Under these conditions ferrocene had $E_{\frac{1}{2}}$ at +0.46 V. Potentials are reported at 25 °C relative to the SCE and are not corrected for the liquid-junction potentials.

Elemental analyses were performed in this laboratory with the use of a Perkin Elmer 240C analyser.

Preparation of Compounds.—[V(acda)$_4$]·H$_2$O **1a**. To a magnetically stirred, freshly prepared, aqueous solution (30 cm^3) of vanadyl sulfate (0.25 g, 1.25 mmol) was added dropwise a solution of Hacda (0.8 g, 5 mmol) in acetone (50 cm^3) over a period of 30 min. The solution changed from blue to red-brown. Stirring was continued at room temperature for 3 h. The dark brown product was filtered off, washed with acetone (2 × 10 cm^3), chilled water (2 × 10 cm^3) and finally with diethyl ether and dried *in vacuo*. Yield: 0.52 g (60%). The compound is sparingly soluble in all common organic solvents except dmf. Several attempts to recrystallise it from dmf were unsuccessful.

The complexes [V(eacda)$_4$] **1b**, [V(pacda)$_4$] **1c** and [V(bacda)$_4$] **1d** were obtained similarly. The crude products were dissolved in dichloromethane and the solution filtered. To the filtrate was added hexane to the cloud point. Cooling at 0 °C gave red-brown microcrystals which were washed with hexane and methanol and finally dried *in vacuo*. Yields 50–60%.

[Mn(eacda)$_3$] **2a**. The compound [Mn(acac)$_3$][25] (200 mg, 0.56 mmol) was dissolved in benzene and cooled to 0 °C. To the cold solution was added rapidly with stirring an ice-cooled solution of Heacda (316 mg, 1.7 mmol) in chloroform (10 cm^3) resulting in an instantaneous change from amber to deep brown. The solution was stirred for *ca.* 2 min when chilled (0 °C) hexane was added to induce precipitation of a deep brown microcrystalline solid. The compound was filtered off, washed with cold (0 °C) hexane (3 × 10 cm^3), and dried under reduced pressure. Thin-layer chromatography (TLC) in dichloromethane showed only one spot. Recrystallisation from dichloromethane–hexane at 0 °C yielded shiny microcrystals. Yield: 0.22 g (64%).

The other manganese(III) compounds **2b** and **2c** were prepared similarly in varying yields (40–65%) with the use of the appropriate ligands.

All the [V(aacda)$_4$] and [Mn(aacda)$_3$] complexes are unstable even in the solid state. Useful analytical results (Table 1) were obtained only when microanalyses were performed within a few days of synthesis.

Results and Discussion

Complexes [V(aacda)$_4$] **1a**–**1d**.—Eight-co-ordinated non-oxo vanadium(IV) complexes are obtained in modest yields (50–60%) when vanadyl ion is treated with stoichiometric amounts of Haacda (1:4 molar ratio) in acetone–water [equation (1)]. The key feature of this reaction is the cleavage of

$$\mathrm{VOSO_4 + 4\,Haacda \longrightarrow [V(aacda)_4] + H_2O + H_2SO_4} \quad (1)$$

the V=O multiple bond which is otherwise very strongly π-bonded.[1] The reaction in this case probably proceeds *via* the intermediate [VO(aacda)$_2$] containing a very weak V=O terminal bond because of a steady electron influx into the metal centre from the surrounding aacda$^-$ ligands. The situation is comparable to that discussed for oxomolybdenum counterparts.[26] This in effect causes a significant reduction in the electron-accepting capacity of vanadium leading to poorer p_π–d_π donation from the multiply bonded oxygen[27] and ultimate V=O bond rupture. Choi and Wasson[28] have reported a green, unstable, very poorly characterised vanadium(IV) compound with acda$^-$ which they suggested was [VO(acda)$_2$]. All our endeavours to isolate this compound using Hacda as the ligand source have been unsuccessful.

The complex [V(acda)$_4$]·H$_2$O **1a** is almost insoluble in common organic solvents except for dmf; **1b**–**1d** are however appreciably soluble in dmf and to a limited extent in dichloromethane and chloroform, producing red-brown solutions which bleach slowly on prolonged standing. All our attempts to grow diffraction-quality crystals of these compounds by the diffusion technique were without success because of their limited stability in solution.

Pertinent IR absorption bands are listed in Table 1. The explicit feature is absence of the band in the region 2550–2430 cm^{-1}, which appears in the free-ligand spectra as the ν(S–H) vibration, thus indicating the participation of the carbodithioate group in metal–ligand bonding. In the free-ligand spectra also present is a band at ≈880 cm^{-1} due to asymmetric CSS stretching, which is diagnostic in deciding the mode of sulfur attachment to the metal centre. In the event of a disulfur chelation, ν_{asym}(CSS) appears as a single sharp band, whereas for the unidentate mode it is symmetrically split.[29] The appearance of a single sharp carbon–sulfur stretching with no evidence of splitting indicates the bidentate (*S,S'*) mode of chelation of the aacda$^-$ ligands.[26,30,31] The loss of vanadyl oxygen in the products **1a**–**1d** is confirmed by the complete absence of a strong characteristic V=O stretch in the 910–990 cm^{-1} region.[27] The spectra also contain a medium-intensity band at ≈340 cm^{-1} assignable to ν(V–S) vibration.[30,32] For more direct support of the above assignments we recorded the vibrational spectrum of [Bi(eacda)$_3$] which to our knowledge is the only structurally characterised compound with the aacda$^-$ ligand.[24] As expected, all the major bands of [Bi(eacda)$_3$] are closely matched with the corresponding bands of compounds **1a**–**1d** except for that due to ν(M–S) vibrations which appears at 325 cm^{-1} for [Bi(eacda)$_3$]. Thus we can conclude with an increased degree of confidence the presence of bidentate *S,S'* co-ordination for the ligands in the [V(aacda)$_4$] complexes, as was confirmed in [Bi(eacda)$_3$][24] by X-ray study.

The optical absorption spectra of all the vanadium(IV) complexes (Table 2) are notable for the presence of bands at ≈630 and 510 nm in the form of shoulders which are characteristic of non-oxo vanadium compounds.[6,8,33,34] No attempt will be made to interpret these poorly resolved spectra because of several uncertainties as outlined in literature.[34] Bands appearing in the UV region are due to internal ligand (π–π*) transitions.[26,30]

The ESR spectra of complexes **1a**–**1d** have been measured in the fluid (dmf–MeCN, 1:10 v/v) as well as in the frozen state (140 K). The features are almost identical for the entire series of

Table 2 Electronic spectral data for the complexes *

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})			
1a	635 (sh)	512 (sh)	395 (56 000)	300 (13 500)
1b	633 (sh)	504 (sh)	410 (55 100)	308 (14 200)
1c	630 (sh)	512 (sh)	410 (54 800)	305 (14 000)
1d	633 (sh)	508 (sh)	410 (54 400)	305 (12 500)
2a	610 (1 130)	535 (3 940)	410 (44 800)	
2b	610 (1 100)	530 (3 950)	415 (45 100)	
2c	605 (1 150)	525 (3 780)	410 (45 300)	

* Spectra for complexes **1a**–**1d** were recorded in dmf and those for **2a**–**2c** in dichloromethane.

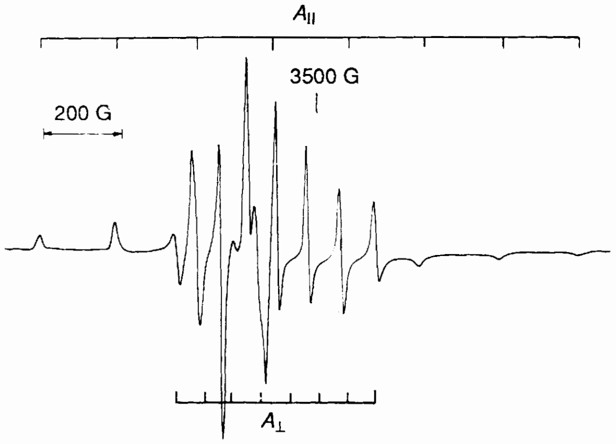


Fig. 1 Frozen-solution X-band ESR spectrum of [V(acda)$_4$]·H$_2$O at 140 K in dmf–acetonitrile (1:10 v/v). Frequency, 9.42 GHz; gain, 1.6 × 10^5; G = 10^{-4} T

compounds. A representative frozen-solution spectrum of **1a** is displayed in Fig. 1 which shows an axially symmetric anisotropy with well resolved sixteen-line hyperfine structure characteristic of an interaction between the electron spin and the vanadium nuclear spin (≈100 atom% ^{51}V, $I = \frac{7}{2}$). The measured parameters are (Table 3) $g_{\parallel} \approx 1.931$, $g_{\perp} \approx 1.985$, $A_{\parallel} \approx 175 \times 10^{-4}$ cm^{-1} and $A_{\perp} \approx 74 \times 10^{-4}$ cm^{-1}. In the same solutions, at room temperature (298 K), the compounds exhibit typical isotropic signals with an eight-line splitting pattern. The corresponding isotropic parameters are $\langle g \rangle \approx 1.971$ and $\langle A \rangle \approx 101 \times 10^{-4}$ cm^{-1}. The close agreements between the room-temperature and frozen-solution spectral parameters [$\langle g \rangle \approx \frac{1}{3}(g_{\parallel} + 2g_{\perp})$ and $\langle A \rangle \approx \frac{1}{3}(A_{\parallel} + 2A_{\perp})$] as shown in Table 3 are strong evidence that the structural identity of the parent compound is maintained in this temperature range.

For an eight-co-ordinated molecule of the type [V(S–S)$_4$] with bidentate (S,*S'*)$^-$ donor ligands either a square antiprism (D_{4d}) with a d_{z^2} ground state or a slightly distorted triangular dodecahedron (D_{2d}) with a $d_{x^2-y^2}$ ground state will be the preferred geometry.[35,36] The observed order in the spin-Hamiltonian parameters ($g_{\perp} > g_{\parallel}$ and $A_{\parallel} > A_{\perp}$) indicates a $d_{x^2-y^2}$ ground state with dodecahedral structure for the compounds **1a**–**1d**.[37,38] This interpretation is somewhat speculative in the absence of crystallographic evidence, which unfortunately we are not able to provide because of the failure to isolate diffraction-quality crystals of these compounds. Nevertheless, crystal structures of three closely comparable eight-co-ordinated non-oxo vanadium(IV) compounds, [V(S$_2$CMe)$_4$],[39] [V(S$_2$CCH$_2$Ph)$_4$][40] and [V(S$_2$CPh)$_4$],[41] have been reported with D_{2d} symmetry for the VS$_8$ chromophore.

The redox behaviour of vanadium(IV) compounds according to cyclic voltammetry in dmf with 0.1 mol dm^{-3} NEt$_4$ClO$_4$ as supporting electrolyte at a platinum-disc electrode is summarised in Table 3. Identical voltammograms are obtained in each case involving a single reduction process ($E_{\frac{1}{2}} \approx -0.7$ V *vs.* SCE), characteristic of a diffusion-controlled, quasi-Nernstian one-electron transfer as evidenced by the equal anodic and cathodic peak currents and the linear dependence of the current function on the square root of the scan rate in the range 50–500 mV s^{-1}. The peak potential separations (ΔE_p) varied between 160 and 210 mV, increasing slightly at higher scan rates, indicating a quasi-reversible behaviour [equation (2)].

$$[\mathrm{V^{IV}(aacda)_4}] \underset{}{\overset{e^-}{\rightleftharpoons}} [\mathrm{V^{III}(aacda)_4}]^- \qquad (2)$$

While these peak separations are larger than the ideal Nernstian value of 59 mV, such values are often observed for compounds of this type,[42] presumably due to uncompensated solution resistance. The one-electron nature of this process was further confirmed by exhaustive electrolysis (at potentials 200 mV more negative than the respective E_{pc}) which consumed the expected number of Coulombs.

Complexes [Mn(aacda)$_3$] **2a**–**2c**.—At ice-cold temperature simple metathetic reaction of [Mn(acac)$_3$] with stoichiometric amounts of Haacda (1:3 molar ratio) in dry aprotic solvents yielded dark brown microcrystalline materials analysing as [Mn(aacda)$_3$]. Complexes **2a**–**2c** are air sensitive and slowly decompose in solution in air. To minimise errors arising out of this instability, all physical measurements were made as soon as possible after preparation of these compounds (generally within a couple of days). In spite of repeated attempts we remain unsuccessful in isolating the complex [Mn(acda)$_3$], probably owing to the reducing nature of the Hacda ligand.[17,26,30,43] The IR spectra of the complexes have essentially the same features as those of the vanadium systems **1a**–**1d** displaying two strong bands near 810 and 360 cm^{-1} (Table 1), thus suggesting a bidentate (*S,S'*)$^-$ mode of co-ordination of the aacda$^-$ ligands.[26,30,31,44]

The manganese(III) complexes are magnetically normal. The observed moments (Table 4) are within the range expected for a high-spin d^4 ($S = 2$) system with an approximately D_3 or C_2 configuration imposed by the four-membered dithiochelate rings of the aacda$^-$ ligands.† A weak contribution from temperature-independent paramagnetism arising out of a poorer mixing of their symmetry-split ^{5}E ground term with the neighbouring excited states (^{5}T$_2$ and ^{3}T$_1$) makes the observed moments (5.01–5.10) slightly higher than the theoretical spin-only value (4.9). The complexes are ESR silent at room temperature as well as in the frozen state. This is probably as expected for a d^4 metal ion with large zero-field splitting.[45]

Electronic spectra in the visible region of the [Mn(aacda)$_3$] complexes in dichloromethane solution show two regions of absorption near 610 and 530 nm (Table 2), each associated with high molar absorptivity (ε 1100–3950 dm^3 mol^{-1} cm^{-1}). Since the ligands aacda$^-$ are not expected to be chromophoric in this range, these spectral features may be attributable to ligand-to-metal charge transfer (l.m.c.t.), probably originating from $\mathrm{S}(\pi) \longrightarrow \mathrm{Mn^{III}}$ electronic transitions. These strong charge-transfer bands probably obscure the weak spin-allowed d–d transitions which are normally expected to show up in this region by manganese(III) tris(bidentate ligand) complexes.[46,47]

Sugiura *et al.*[48] reported the isolation of a manganese form of purple acid phosphatase[49] with spectral features dominated by a charge-transfer band at 515 nm (ε 2460 dm^3 mol^{-1} cm^{-1}) which they tentatively assigned as due to $\mathrm{Mn^{III}} \leftarrow \mathrm{L}$ (L = TyrO$^-$ or CysS$^-$) charge-transfer. The close proximity of this band both in position as well as in intensity to the higher-energy charge-transfer transition observed for the [Mn(aacda)$_3$] complexes (Table 2) lends support to the notion of a metal–thiolate (cysteine) linkage in manganese biochromophores.

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† We are grateful to one of the referees for suggesting this possibility.

Table 3 ESR and electrochemical data for the $[V(aacda)_4]$ complexes

							V^{IV}–$V^{III\,c}$	
Complex	$\langle g\rangle^a$	$g_{\parallel}{}^b$	$g_{\perp}{}^b$	$10^4\langle A\rangle^a$/cm^{-1}	$10^4 A_{\parallel}{}^b$/cm^{-1}	$10^4 A_{\perp}{}^b$/cm^{-1}	$E_{\frac{1}{2}}{}^d$/V	$\Delta E_p{}^e$/mV
1a	1.971	1.931	1.985	101.0	174.9	74.1	−0.70	160
1b	1.969	1.932	1.983	102.8	169.6	70.6	−0.72	200
1c	1.968	1.929	1.984	104.9	173.8	71.8	−0.72	200
1d	1.969	1.933	1.986	105.0	176.0	73.0	−0.73	210

[a] Spectra recorded at room temperature in dmf–MeCN (1 : 10 v/v) solution. [b] Frozen-solution (140 K) spectra. [c] Solvent dmf, supporting electrolyte NEt_4ClO_4 (0.1 mol dm^{-3}), solute concentration ≈ 10^{-3} mol dm^{-3}, platinum working electrode. [d] Potentials are *vs.* SCE and are estimated from cyclic voltammetry at a scan rate of 50 mV s^{-1}, $E_{\frac{1}{2}} = 0.5\,(E_{pc} + E_{pa})$. [e] $\Delta E_p = E_{pc} - E_{pa}$.

Table 4 Magnetic moments and electrochemical data[a] for the $[Mn(aacda)_3]$ complexes

		Mn^{IV}–Mn^{III}			Mn^{III}–Mn^{II}		
Complex	μ_{eff}	$E_{\frac{1}{2}}(ox)^b$/V	$\Delta E_p{}^c$/mV	i_{pc}/i_{pa}	$E_{\frac{1}{2}}(red)^b$/V	$\Delta E_p{}^c$/mV	i_{pc}/i_{pa}
2a	5.07	0.09	180	0.95	−0.34	200	1.15
2b	5.10	0.10	200	1.05	−0.33	210	1.10
2c	5.01	0.09	140	1.00	−0.33	190	0.95

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

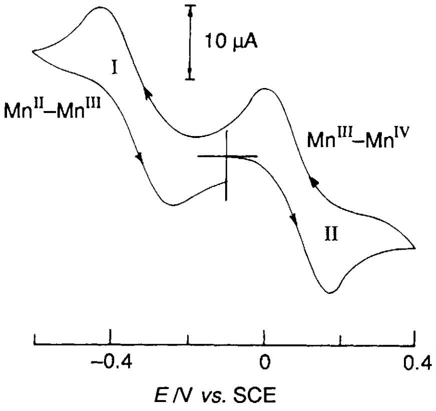

Fig. 2 Cyclic voltammogram of $[Mn(eacda)_3]$ in dichloromethane (0.85×10^{-3} mol dm^{-3}) at a platinum electrode. Scan rate 50 mV s^{-1}

All remaining bands appearing near or below 400 nm are due to intraligand transitions.

The cyclic voltammograms of the manganese (III) complexes in dichloromethane solutions (containing 0.1 mol dm^{-3} NEt_4ClO_4 as supporting electrolyte at a platinum electrode) have grossly identical features. Two one-electron-transfer waves corresponding to an oxidation (Mn^{III}–Mn^{IV}) and a reduction (Mn^{III}–Mn^{II}) are detected in the potential range 0.4 to − 1.0V *vs.* SCE as shown in Fig. 2 for the complex **2a**. The ligands are electrode inactive in this potential range. The reduction couple (couple I) has $E_{\frac{1}{2}}(red) = -0.34$ V. The oxidation process (couple II) occurs at $E_{\frac{1}{2}}(ox) = 0.09$ V. In the scan rate range 50–500 mV s^{-1} both electron-transfer processes conform to the criteria of Nernstian quasi-reversibility as observed for the vanadium complexes. Alkyl substitutions in the ligand framework do not appear to have any measurable effect on the electrochemical potentials (Table 4). In the stirred dichloromethane solutions, as shown by controlled-potential coulometry, reduction of the complexes occurred smoothly with $n = 1.0 \pm 0.1$ when the working potentials were set below (more negative) the $E_{\frac{1}{2}}(red)$ values. Attempted oxidations at potentials anodic to $E_{\frac{1}{2}}(ox)$ did not however produce any meaningful results, probably owing to some unidentified reaction(s). On the basis of coulometric results and similarities in current height data from one couple to the other, both the redox processes are diagnosed to have single-electron stoichiometry [equation (3)].

$$[Mn^{II}(aacda)_3]^- \underset{E_{\frac{1}{2}}(red)}{\overset{+e^-}{\rightleftharpoons}} [Mn^{III}(aacda)_3] \underset{E_{\frac{1}{2}}(ox)}{\overset{-e}{\rightleftharpoons}} [Mn^{IV}(aacda)_3]^+ \quad (3)$$

An almost identical pattern of electron-transfer behaviour is observed with $[Mn(S_2CNR_2)_3]$ complexes[50] which to our knowledge are probably the only other known example of a series of mononuclear manganese(III) complexes containing a MnS_6 chromophore. Closer inspection of their electrochemical data indicates that, while the redox potentials of the dithiocarbamato complexes are particularly sensitive to and tunable by alkyl group variation in the ligand framework,[50] such an effect is totally absent in the carbodithioato complexes as found in the present case (Table 4). Under identical experimental conditions (dichloromethane solution, platinum working electrode) the separation ($\Delta E_{\frac{1}{2}}$) between the potentials of the Mn^{IV}–Mn^{III} and Mn^{III}–Mn^{II} couples remains practically constant (≈0.45 V) for the MnS_6 chromophore irrespective of the type of dithio ligand ($R_2NCS_2^-$ or aacda$^-$) present.

Conclusion

Vanadium and molybdenum are diagonally placed in the Periodic Table which in many cases makes their chemistry comparable. As far as the Haacda ligands are concerned, vanadium(IV) forms eight-co-ordinated non-oxo compounds containing a VS_8 chromophore which are comparable to $[Mo(S–S)_4]$ species isolated with the same set of ligands.[17,30,32] Both $[V(S–S)_4]$ and $[Mo(S–S)_4]^+$ complexes exhibit frozen-solution ESR spectra with axial anisotropy. Interaction of these carbodithioate ligands with vanadyl ion makes the V=O bond extremely labile, leading ultimately to its fissure. This work is now being extended to the synthesis of various non-oxo vanadium compounds by introducing suitable functionalities in the Haacda ligands. Preliminary results apparently indicate a fairly good control over the tuning of the V=O bond lability by the substituents present in the ligand framework.

Acknowledgements

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