

# Vanadium(III) Complexes with $\text{VN}_3\text{O}_3$ Co-ordination by Sexidentate Schiff-base Ligands: Synthesis, Spectra and Redox Activity

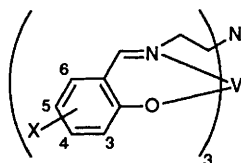
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A group of non-electrolytic red crystalline vanadium(III) complexes ( $\mu_{\text{eff}}$  2.78–2.89 in solution, 298 K) has been synthesized using sexidentate Schiff-base ligands. The complexes have a rare  $\text{VN}_3\text{O}_3$  co-ordination sphere. From the paramagnetically shifted  $^1\text{H}$  NMR spectra it is revealed that the metal co-ordination environment is distorted ( $\approx C_1$ ) due to the spatial arrangement of the ligand chelate rings. In *N,N*-dimethylformamide (dmf) solution charge-transfer band(s) together with crystal-field transitions are observed in the region *ca.* 340–600 nm. Cyclic voltammetric experiments in dmf solution at a platinum electrode reveal a quasi-reversible  $\text{V}^{\text{III}}-\text{V}^{\text{II}}$  couple [ $E_f$  -1.34 to -1.52 V vs. saturated calomel electrode (SCE)] and a reversible  $\text{V}^{\text{IV}}-\text{V}^{\text{III}}$  couple ( $E_f$  +0.21 to +0.54 V vs. SCE).

Vanadium is receiving considerable attention as a biologically important metal<sup>1</sup> and in order to understand its biological role the basic co-ordination chemistry of this element in its three accessible oxidation states (+3, +4 and +5) with relevant ligands needs to be explored. The facility with which vanadium changes oxidation state may be a key to its biological function.

In continuation of our interest<sup>2</sup> in the metal complexes of sexidentate Schiff-base ligands, we report here the synthesis, solution structure and electrochemical studies on a series of stable six-co-ordinate vanadium(III) complexes, [VL], using the ligands  $\text{H}_3\text{L}^1-\text{H}_3\text{L}^4$ .



X	Complex
H	[VL <sup>1</sup> ]
4-CH <sub>3</sub>	[VL <sup>2</sup> ]
5-CH <sub>3</sub>	[VL <sup>3</sup> ]
3,5-Cl <sub>2</sub>	[VL <sup>4</sup> ]

## Experimental

**Chemicals and Starting Materials.**—Solvents and reagents were obtained from commercial sources and used without further purification unless otherwise stated. *N,N*-Dimethylformamide (dmf), acetonitrile and diethyl ether were purified as before.<sup>3</sup> Chloroform was dried over fused calcium chloride before a final reflux and distillation. Tetrabutylammonium perchlorate was prepared as described previously.<sup>3</sup> Substituted salicylaldehydes were obtained from the appropriate phenols by the Duff reaction.<sup>4</sup> The complex [V(acac)<sub>3</sub>] (acac = acetylacetonate) was prepared following a reported method.<sup>5</sup> The Schiff-base ligands  $\text{H}_3\text{L}^1-\text{H}_3\text{L}^4$  were prepared<sup>2,6</sup> by mixing (1 : 1) the appropriate salicylaldehyde with tris(2-aminoethyl)amine in hot ethanol and then recrystallizing the crude product from chloroform. They were shown to be pure by their  $^1\text{H}$  NMR spectra [CDCl<sub>3</sub> ambient temperature:  $\text{H}_3\text{L}^1$ ,  $\delta_{\text{H}}$  2.80 (t, 6 H,  $\text{CH}_2\text{CH}_2-\text{N}=\text{}$ ), 3.50 (t, 6 H,  $\text{CH}_2\text{CH}_2-\text{N}=\text{}$ ), 6.15 (dd, 3 H,

$\text{H}^6$ ), 6.55 (m, 3 H,  $\text{H}^5$ ), 6.80 (dd, 3 H,  $\text{H}^3$ ), 7.20 (m, 3 H,  $\text{H}^4$ ), 7.75 (s, 3 H,  $\text{N}=\text{CH}$ );  $\text{H}_3\text{L}^2$ ,  $\delta$  2.30 (s, 9 H,  $\text{CH}_3$ ), 2.80 (t, 6 H,  $\text{CH}_2\text{CH}_2-\text{N}=\text{}$ ), 3.50 (t, 6 H,  $\text{CH}_2\text{CH}_2-\text{N}=\text{}$ ), 6.05 (d, 3 H,  $\text{H}^6$ ), 6.40 (d, 3 H,  $\text{H}^5$ ), 6.75 (s, 3 H,  $\text{H}^3$ ), 7.80 (s, 3 H,  $\text{N}=\text{CH}$ );  $\text{H}_3\text{L}^3$ ,  $\delta$  2.05 (s, 9 H,  $\text{CH}_3$ ), 2.80 (t, 6 H,  $\text{CH}_2\text{CH}_2-\text{N}=\text{}$ ), 3.60 (t, 6 H,  $\text{CH}_2\text{CH}_2-\text{N}=\text{}$ ), 5.95 (s, 3 H,  $\text{H}^6$ ), 6.85 (d, 3 H,  $\text{H}^3$ ), 7.10 (d, 3 H,  $\text{H}^4$ ), 7.80 (s, 3 H,  $\text{N}=\text{CH}$ );  $\text{H}_3\text{L}^4$ ,  $\delta$  2.80 (t, 6 H,  $\text{CH}_2\text{CH}_2-\text{N}=\text{}$ ), 3.60 (t, 6 H,  $\text{CH}_2\text{CH}_2-\text{N}=\text{}$ ), 6.45 (d, 3 H,  $\text{H}^6$ ), 7.30 (d, 3 H,  $\text{H}^4$ ), 7.90 (s, 3 H,  $\text{N}=\text{CH}$ ).

**Measurements.**—Solution electrical conductivity, IR and UV/VIS spectra were obtained using an Elico type CM-82T conductivity bridge (Hyderabad, India), Perkin-Elmer FT IR model 1600 and Perkin-Elmer Lambda-2 spectrophotometers respectively. Magnetic susceptibility measurements in the solution phase were made by the NMR method<sup>3,7</sup> using a PMX-60 JEOL (60 MHz) spectrometer and those in the solid state were performed using a Cahn-Faraday electromagnetic balance. The  $^1\text{H}$  NMR spectra were measured in CDCl<sub>3</sub> on either a PMX-60 JEOL (60 MHz) or a Bruker WM-400 (400 MHz) NMR spectrometer. The 400 MHz  $^1\text{H}$  NMR spectra were by the Analytical Facilities, Regional Sophisticated Instrumentation Centre, Lucknow, India. Chemical shifts are reported as positive values downfield from  $\text{SiMe}_4$  as internal standard. Cyclic voltammetric measurements at 298 K were performed under pure and dry nitrogen by using a PAR 370-4 electrochemistry system as described elsewhere.<sup>3</sup> Potentials are referenced to a saturated calomel electrode (SCE) and are uncorrected for junction potentials. A planar Beckman model 39273 platinum inlay electrode was used as the working electrode. A platinum wire-gauze working electrode was employed in the coulometric experiments when using a PAR 173 potentiostat/galvanostat and PAR 377 A cell system. The details of the cell configuration are the same as described before.<sup>3a</sup>

**Syntheses of Complexes.**—The complexes were prepared using similar methods under strictly dry and anaerobic conditions. Details are therefore given for a representative complex.

{Tris[2-(3',5'-dichloro-2'-hydroxybenzylidene)ethyl]amino-(3-)}vanadium(III).—To a solution of [V(acac)<sub>3</sub>] (0.05 g, 0.143 mmol) in acetonitrile (30 cm<sup>3</sup>) was added solid  $\text{H}_3\text{L}^4$  (0.095 g,

0.143 mmol) under magnetic stirring. The mixture was refluxed for 2 h on a water-bath, then cooled and filtered through a G-4 frit. To the dark red filtrate diethyl ether (5 cm<sup>3</sup>) was added and the solution kept in a refrigerator. After 24 h dark red crystals had formed which were filtered off, washed with acetonitrile-diethyl ether (5 cm<sup>3</sup>) (1:4 v/v) and finally dried *in vacuo* at 350 K (0.042 g, 40%) {Found: C, 45.60; H, 3.00; N, 7.60. Calc. for [VL<sup>4</sup>] (C<sub>27</sub>H<sub>21</sub>Cl<sub>6</sub>N<sub>4</sub>O<sub>3</sub>V): C, 45.45; H, 2.95; N, 7.85. Found: C, 63.85; H, 6.30; N, 10.80. Calc. for [VL<sup>1</sup>] (C<sub>27</sub>H<sub>27</sub>N<sub>4</sub>O<sub>3</sub>V): C, 64.05; H, 6.35; N, 11.05. Found: C, 65.50; H, 6.15; N, 10.15. Calc. for [VL<sup>2</sup>] (C<sub>30</sub>H<sub>33</sub>N<sub>4</sub>O<sub>3</sub>V): C, 65.70; H, 6.00; N, 10.20. Found: C, 65.45; H, 5.90; N, 10.45. Calc. for [VL<sup>3</sup>] (C<sub>30</sub>H<sub>33</sub>N<sub>4</sub>O<sub>3</sub>V): C, 65.70; H, 6.00; N, 10.20%}.

## Results and Discussion

**Syntheses.**—The complexes [VL] (L = L<sup>1</sup>–L<sup>4</sup>) were synthesised by reacting [V(acac)<sub>3</sub>] with the appropriate ligand (H<sub>3</sub>L<sup>1</sup>–H<sub>3</sub>L<sup>4</sup>) in acetonitrile and isolated as dark red crystals. Solution electrical conductivity measurements show the complexes to be non-conducting. The complexes are moderately soluble in chloroform or dmf but the solutions decompose readily in the presence of air and moisture. The magnetic moments (Table 1) in dmf solution, as well as in the solid state for a representative complex, are consistent with a d<sup>2</sup> (S = 1) electronic configuration and in excellent agreement with reported vanadium(III) complexes.<sup>8–12</sup>

The mode of co-ordination of the ligands has been confirmed by X-ray diffraction work on manganese(III) and iron(III)

complexes.<sup>13</sup> The imine structure of the ligands is clearly indicated by intense and well resolved ν(C=N) bands in the range 1602–1636 cm<sup>-1</sup> in the IR spectra of the complexes. The complexes do not exhibit a ν(V=O) vibrational band<sup>14</sup> in the range 910–1035 cm<sup>-1</sup> implying that they are not contaminated with any vanadyl(IV) species. Examples of six-co-ordinate vanadium(III) Schiff-base complexes with VN<sub>3</sub>O<sub>3</sub> co-ordination spheres (excluding the solvato complexes) are rare.<sup>15</sup>

**Solution Stereochemistry.**—Despite their paramagnetism (see above) the [V<sup>III</sup>L] complexes are EPR silent to 77 K, as expected for the non-Kramers d<sup>2</sup> (S = 1) configuration.<sup>16</sup> However since the electron relaxation of vanadium(III) is rapid, complexes of this oxidation state are detectable by <sup>1</sup>H NMR spectroscopy,<sup>17,18</sup> and the present compounds are no exception. Representative spectra are shown in Fig. 1. The spectra of [VL<sup>2</sup>] and [VL<sup>3</sup>] in the conventional diamagnetic region are complicated by the presence of free ligand as an impurity. This results from their partial decomposition in solution owing to their extreme moisture sensitivity as stated earlier.

The signal assignments for the complexes are provided (Table 2) by a combination of the expected behaviour of methyl substitution for ring proton resonances,<sup>17,18</sup> the behaviour of related complexes,<sup>15</sup> and integrated area ratios. The results reveal that, except for occasional degeneracies in shifts and instances where excessive signal broadening prohibits complete resolution, three signals of equal intensity for each substituent are observed owing to the magnetic inequivalence arising from the lack of symmetry in the molecule. These results demonstrate conclusively that in solution the complexes are severely stereochemically distorted due to the spatial disposition of the ligand chelate rings. A similar situation arises in the case of high-spin manganese(III) complexes with sexidentate Schiff-base ligands.<sup>2</sup> For the manganese(III) complexes the upfield resonances are due to the H<sup>3</sup> and H<sup>5</sup> ring protons and the downfield resonances to the H<sup>4</sup> and H<sup>6</sup> ring protons. The situation encountered here (Table 2) is just the opposite. The reason behind this lies in the ligand-to-metal spin delocalization mechanism.<sup>18</sup> The decreased symmetry observed in the solution phase is in contrast with the solid state X-ray structures for the related complexes [FeL<sup>5</sup>] and [MnL<sup>5</sup>] {H<sub>3</sub>L<sup>5</sup> = tris-[2-(5'-chloro-2'-hydroxybenzylidene)ethyl]amine}.<sup>13</sup>

**Absorption Spectra.**—The UV/VIS spectral data for the complexes in dmf solution are given in Table 2. In all cases, the expected d–d transitions are observed as tails on the charge-

**Table 1** Magnetic moment<sup>a</sup> and cyclic voltammetric data<sup>b</sup> for the vanadium(III) complexes in dmf solution

Complex	μ <sub>eff</sub> <sup>c</sup>	V <sup>III</sup> –V <sup>II</sup> couple		V <sup>IV</sup> –V <sup>III</sup> couple	
		E <sub>t</sub> /V	ΔE <sub>p</sub> /mV	E <sub>t</sub> /V	ΔE <sub>p</sub> /mV
[VL <sup>1</sup> ]	<i>d</i>	-1.46	100	+0.27	60
[VL <sup>2</sup> ]	2.89	-1.50	100	+0.26	80
[VL <sup>3</sup> ]	2.87 (3.02)	-1.52	100	+0.21	60
[VL <sup>4</sup> ]	2.78	-1.34	100	+0.54	70

<sup>a</sup> By Evans method.<sup>7</sup> <sup>b</sup> Platinum electrode; supporting electrolyte [NBu<sub>4</sub>]ClO<sub>4</sub>; all potentials are referenced to the SCE. E<sub>t</sub> = 0.5(E<sub>pc</sub> + E<sub>pa</sub>) where E<sub>pc</sub> and E<sub>pa</sub> are the cathodic and anodic peak potentials, respectively; scan rate = 50 mV s<sup>-1</sup>. <sup>c</sup> Room-temperature solid-state value in parentheses. <sup>d</sup> Due to less solubility in dmf the data could not be obtained accurately.

**Table 2** Spectroscopic data for vanadium(III) complexes

Complex	Electronic spectral data <sup>a</sup> λ/nm (ε/dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )	<sup>1</sup> H NMR shift <sup>b</sup> (δ)			
		H <sup>3</sup>	H <sup>4</sup> /4-Me	H <sup>5</sup> /5-Me	H <sup>6</sup>
[VL <sup>1</sup> ]	347(10 300), 499(sh)(760)	+5.16(2) <sup>c</sup> +5.32	+1.27 <sup>d</sup>	+3.58 +4.13 +4.28	+1.59 <sup>d</sup>
[VL <sup>2</sup> ]	345(12 200), 415(sh)(6050), 514(sh)(895)	+10.90 +13.55 +22.15	+1.68 <sup>e</sup> +2.25 +15.60	+6.00 +6.37 +6.69	-0.95 +1.18 +1.68 <sup>e</sup>
[VL <sup>3</sup> ]	361(12 250), 431(sh)(6175), 542(sh)(450)	+12.33 +13.69 +22.73	-1.92 -9.50 -13.49	+1.25 +1.83(2) <sup>c</sup>	-5.33 -1.25 +0.83
[VL <sup>4</sup> ]	370(11 880), 402(sh)(9450), 533(285), 590(sh)(150)	—	+1.17(2) <sup>c</sup> +1.53 <sup>e</sup>	—	+1.53 <sup>c</sup> +1.97 +3.47
[VL <sup>2</sup> ] <sup>+ f,g</sup>	317(20 000), 357(9000), 588(2400)	—	—	—	—
[VL <sup>3</sup> ] <sup>+ g,h</sup>	328(17 000), 374(8500), 608(2800)	—	—	—	—

<sup>a</sup> Solvent is dmf; sh = shoulder. <sup>b</sup> Solvent is CDCl<sub>3</sub>. NCH<sub>2</sub>CH<sub>3</sub> resonances: [VL<sup>1</sup>], δ -3.41; [VL<sup>2</sup>], -2.20, -14.35; [VL<sup>3</sup>], +1.25, +1.83 (overlaps with 5-methyl protons); [VL<sup>4</sup>], -3.50. Azomethine proton: [VL<sup>1</sup>], δ +28.18; [VL<sup>2</sup>], +27.81; [VL<sup>3</sup>], +27.66; [VL<sup>4</sup>], +28.25. <sup>c</sup> Signals occur with 2:1 intensity ratio because the signals from two phenyl rings overlap. <sup>d</sup> All three signals could not be located. <sup>e</sup> Overlapping H<sup>4</sup> and H<sup>6</sup> signals. <sup>f</sup> Oxidized coulometrically at +0.45 V (n = Q/Q' = 1.03 where Q is the coulomb count at the end of exhaustive electrolysis and Q' is the calculated coulomb count for a one-electron transfer). <sup>g</sup> Spectral data are taken immediately after electrolysis. Absorption coefficients (ε) are only rough estimates as decomposition of [VL]<sup>+</sup> occurs (see text). <sup>h</sup> Applied potential: +0.40 V (n = 1.07).

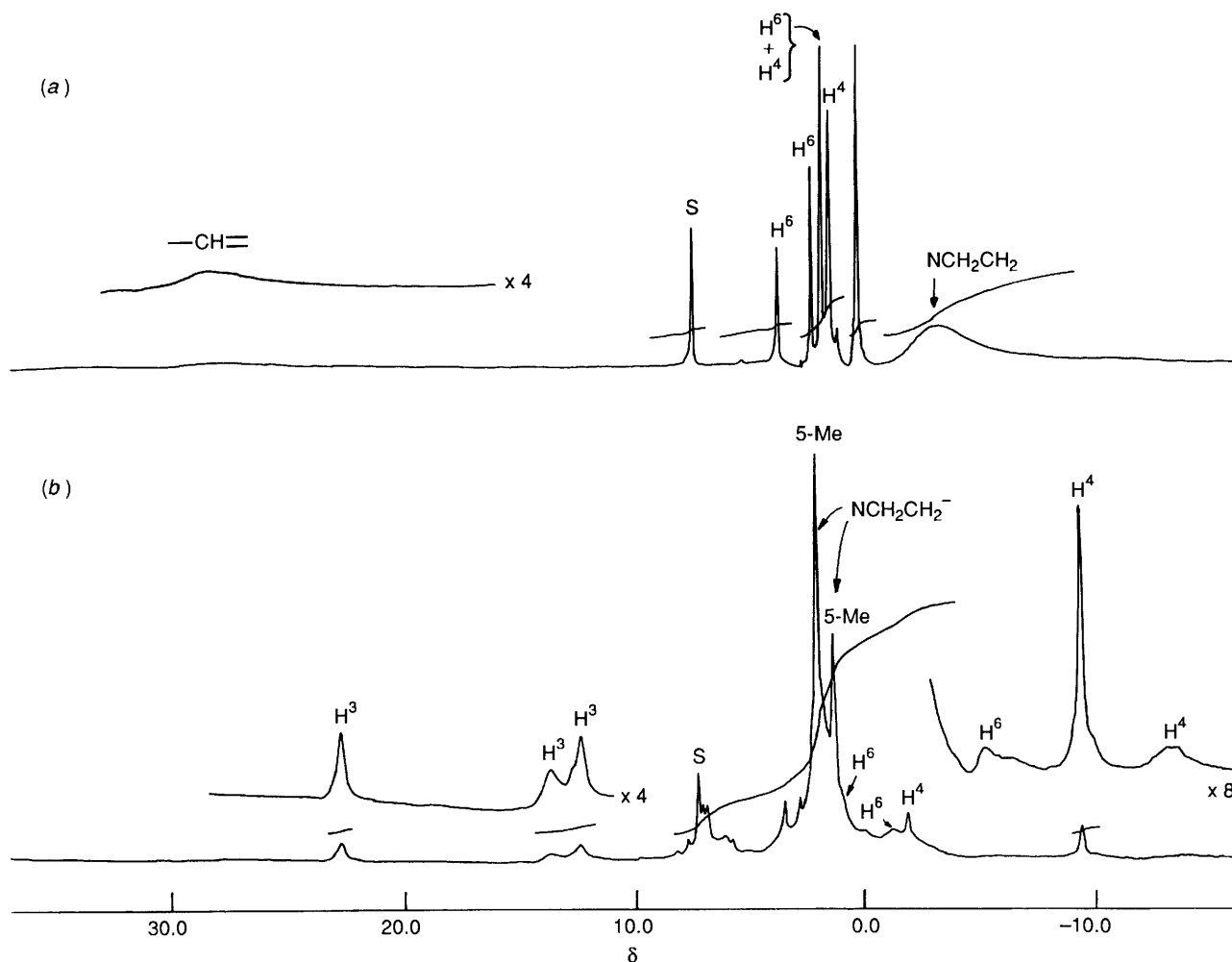


Fig. 1 400 MHz  $^1\text{H}$  NMR spectra of (a)  $[\text{VL}^4]$  and (b)  $[\text{VL}^3]$  (the peaks in the range  $\delta$  2.75–7.75 are due to free ligand resonances) in  $\text{CDCl}_3$  (solvent peaks are marked by S)

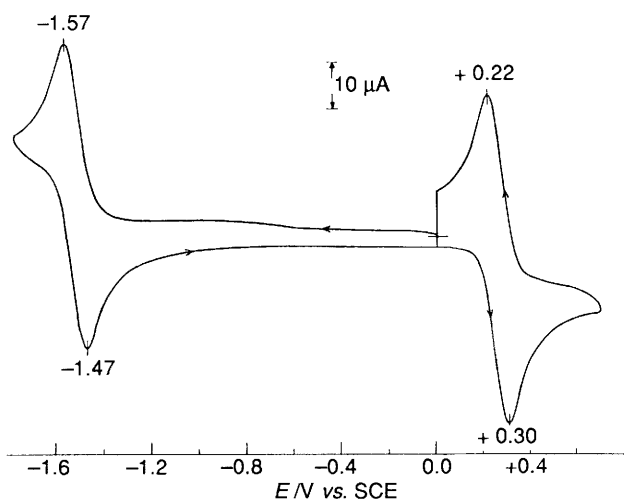


Fig. 2 Cyclic voltammogram of  $[\text{VL}^2]$  ( $2 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) in dmf solution at a platinum electrode. Supporting electrolyte  $[\text{NBu}_4]\text{ClO}_4$  ( $0.4$  mol  $\text{dm}^{-3}$ )

transfer absorptions. The complex  $[\text{VL}^4]$  exhibits two well resolved transitions, a peak at 533 nm with a shoulder at 590 nm; the peak at higher energy is considerably more intense and better resolved. The two absorptions are assigned as  $^3\text{T}_1(\text{F}) \rightarrow ^3\text{T}_2(\text{F})$  and  $^3\text{T}_1(\text{F}) \rightarrow ^3\text{T}_1(\text{P})$  (in the order of increasing energy) transitions,<sup>19</sup> implying a pseudo-octahedral arrangement of donor sites around the vanadium(III) ion. The

spectral features of the complexes are very similar to those reported for other vanadium(III) Schiff-base complexes.<sup>9,10</sup>

**Electrochemistry.**—Electrochemical experiments were carried out to investigate the suitability of  $\text{H}_3\text{L}^1\text{--H}_3\text{L}^4$  to stabilise the vanadium(III) oxidation state towards reduction, and to explore the possibility of isolating a non-oxo vanadium(IV) species. It is interesting to note that among six-co-ordinate vanadium(III) complexes with homoleptic ligands the occurrence of both the  $\text{V}^{\text{III}}\text{--V}^{\text{II}}$  and  $\text{V}^{\text{IV}}\text{--V}^{\text{III}}$  couples is rare<sup>12,20–22</sup> and within the Schiff-base family it is non-existent. Hence the electron-transfer properties of the present complexes are of considerable interest and cyclic voltammetry has indeed revealed the presence of the  $\text{V}^{\text{III}}\text{--V}^{\text{II}}$  and  $\text{V}^{\text{IV}}\text{--V}^{\text{III}}$  couples.

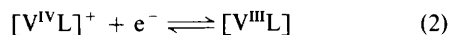
**Vanadium(III)–vanadium(II) couple.** A typical cyclic voltammogram is shown in Fig. 2. An initial cathodic scan in dmf solution reveals a well defined cyclic response due to the  $\text{V}^{\text{III}}\text{--V}^{\text{II}}$  couple [equation (1)]. The formal potentials ( $E_f$ ), calculated from the



average of the cathodic ( $E_{pc}$ ) and anodic ( $E_{pa}$ ) peak potentials, are in the range  $-1.34$  to  $-1.52$  V *vs.* SCE (Table 1). At a scan rate of  $50$   $\text{mV s}^{-1}$  the cathodic and anodic peak potential separations ( $\Delta E_p$ ) are  $100$  mV suggestive of a quasi-reversible one-electron process.

Within the group of complexes, the  $E_f$  values of the  $\text{V}^{\text{III}}\text{--V}^{\text{II}}$  couple are sensitive to the substituent X; the values increase with decreasing electron-releasing power of X (Table 1).

*Vanadium(IV)–vanadium(III) couple.* When scanned in the positive potential range the complexes display (Fig. 2) an oxidative wave with  $E_f$  values in the range 0.21–0.54 V vs. SCE (Table 1). At a scan rate of 50 mV s<sup>-1</sup> the  $\Delta E_p$  values lie in the range 60–80 mV (Table 1) showing that the electrode process [equation (2)] is nearly reversible. The stereochemistries for [VL] and [VL]<sup>+</sup> are thus likely to be grossly similar.



The one-electron stoichiometry of equation (2) is fully corroborated by constant potential coulometry for two representative cases, *viz.* [VL<sup>2</sup>] and [VL<sup>3</sup>]. The [VL<sup>2</sup>]<sup>+</sup> and [VL<sup>3</sup>]<sup>+</sup> species are dark green in solution. Under strictly dry conditions the solutions oxidized coulometrically are stable and display several absorption bands (Table 2). Significantly, the bands occur at energies lower than those of [VL<sup>2</sup>] and [VL<sup>3</sup>]. Chemical oxidation of [VL<sup>2</sup>] by AgClO<sub>4</sub>·C<sub>6</sub>H<sub>6</sub> in acetonitrile afforded a green solid of composition close to the formulation [VL<sup>2</sup>]ClO<sub>4</sub>·H<sub>2</sub>O. Freshly prepared acetonitrile solutions of the isolated species, [VL<sup>2</sup>]<sup>+</sup>, display an eight line EPR spectrum,  $\langle g \rangle$  1.99, with a peak-to-peak separation of 103 G characteristic of vanadium(IV) species. This behaviour is similar to that of Na<sub>2</sub>[V<sup>IV</sup>Cl<sub>2</sub>(dtbc)<sub>2</sub>] [dtbc = 3,5-di-*tert*-butylbenzene-1,2-diolate(2-)].<sup>8b</sup> Solutions oxidized chemically exhibit absorption spectra similar (Table 2) to those obtained by coulometric oxidation. Unfortunately, the solutions are extremely moisture sensitive and decompose within 15 min to species of unknown composition. We are attempting to isolate these solids in a pure form. The visible spectra of the oxidized complexes are notable for the presence of a strong charge-transfer band at *ca.* 600 nm, characteristic of non-oxo vanadium(IV) species.<sup>12,22,23</sup>

As for the reduction, the  $E_f$  values of the couple of equation (2) depend on X. The values decrease with increasing electron-releasing power of the substituents.

In the complexes the phenolate moieties mimic the coordination of tyrosinate while the imine functionalities provide some correspondence with the bonding of imidazole to vanadium in biological systems. From electrochemistry this work demonstrates that to maintain vanadium in the +3 oxidation state tyrosinate is the ideal ligand. In fact, vanadium(III)–transferrin is a very stable system.<sup>24</sup>

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