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Valence Delocalisation in a Triad of Binuclear $[L(O)V^{IV}OV^{V}(O)L]^-$ Species electrogenerated from Structurally Characterised Divanadium(V) Analogues (L = tridentate ONO ligand)†

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In $[L(O)VOV(O)L]^-$, the one-electron reduced form of structurally characterised [L(O)VOV(O)L] (L = azobenzene-2,2′-diolate), metal valence is delocalised at 300 K but is localised at one centre at 77 K with average hyperfine coupling constants of ≈50 and ≈100 G respectively; the estimated rate constant is ≈4 × 10^{10} s^{-1} (300 K) and the activation energy is ≈3 kcal mol^{-1}.

Authentic complexes of the $[OV^{V}OV^{V}O]^{4+}$ cation are rare.[1-4] Herein we examine the redox behaviour of a [L(O)VOV(O)L] triad (L = L^1 **1**, L^2 **2** or L^3 **3**), with special reference to valence delocalisation in the mixed-valence congeners formed by one-electron reduction. Complexes **1**[3] and **2**[1] are known but **3** is new‡ and its crystal structure§ is shown in Fig. 1. The diphenolic azo compound binds in the ONO fashion and the metal geometry is square pyramidal, the base being constituted of ONO from the tridentate ligand and the bridging oxygen atom which lies on a crystallographic two-fold axis. Each metal atom is displaced from the base towards the oxo apex by 0.47 Å. Atoms O(4) and O(4a) are *trans* directed lying on opposite sides of the V–O–V plane.

In CH_2Cl_2 (0.1 mol dm^{-3} NEt_4ClO_4, platinum electrode) a one-electron cyclic voltammetric response due to the $[V_2O_3L_2]$–$[V_2O_3L_2]^-$ couple is observed. The $E_{\frac{1}{2}}$ values are 0.21, 0.23 and 0.30 V for **1**–**3** respectively *vs.* the saturated calomel electrode. Constant-potential coulometry at −0.1 V affords $[V_2O_3L_2]^-$ quantitatively and upon reoxidation at 0.6 V $[V_2O_3L_2]$ is fully regenerated. The cyclic voltammogram

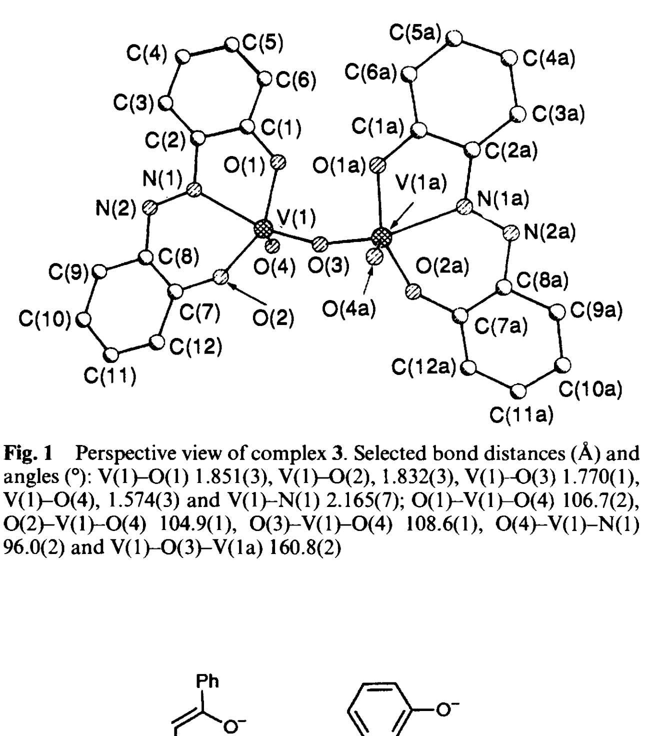
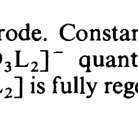
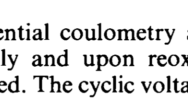


Fig. 1 Perspective view of complex **3**. Selected bond distances (Å) and angles (°): V(1)–O(1) 1.851(3), V(1)–O(2), 1.832(3), V(1)–O(3) 1.770(1), V(1)–O(4), 1.574(3) and V(1)–N(1) 2.165(7); O(1)–V(1)–O(4) 106.7(2), O(2)–V(1)–O(4) 104.9(1), O(3)–V(1)–O(4) 108.6(1), O(4)–V(1)–N(1) 96.0(2) and V(1)–O(3)–V(1a) 160.8(2)



L^1



L^2 X = CH
L^3 X = N

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† *Non-SI units employed:* G = 10^{-4} T, cal = 4.184 J, $\mu_B \approx 9.274\,02 \times 10^{-24}$ J T^{-1}.

‡ An equimolar mixture of azobenzene-2,2′-diol and oxobis(pentane-2,4-dionato)vanadium(IV) on stirring in methanol at room temperature in air for 6 h afforded a deep brown solution which upon evaporation to dryness yielded complex **3** in 80% yield (Found: C, 49.90; H, 2.60; N, 9.60. Calc. for $C_{24}H_{16}N_4O_7V_2$: C, 50.15; H, 2.80; N, 9.75%). IR (KBr): ν_{VO} 995s, ν_{VOV} 775s cm^{-1}.

§ Crystal data. $C_{24}H_{16}N_4O_7V_2$, $M = 574.3$, orthorhombic, space group *Pcnb* (no. 60), $a = 7.392(2)$, $b = 12.868(2)$, $c = 24.371(7)$ Å, $U = 2318(1)$ Å^3, $Z = 4$, $D_c = 1.646$ g cm^{-3}, Mo-Kα radiation (λ = 0.710 73 Å), crystal dimensions 0.30 × 0.26 × 0.38 mm, μ(Mo-Kα) = 8.61 cm^{-1}, $F(000) = 1160$, 188 parameters(p), 2263 unique reflections(n), 1402 reflections with $I > 3\sigma(I)$, $R = \Sigma|F_o - F_c|/\Sigma|F_o| = 0.0432$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}} = 0.0485$, goodness of fit $\{= [\Sigma w(|F_o| - |F_c|)^2/(n - p)]^{\frac{1}{2}}\} = 1.02$. Data were collected in the range $2 \leqslant 2\theta \leqslant 55°$ by the ω-scan method on a Nicolet R3m/V four-circle diffractometer, and corrected for Lorentz-polarisation effects and absorption (maximum, minimum relative transmission factors 1.00, 0.97). The structure was solved by direct methods and refined by full-matrix least squares {weighting scheme $w^{-1} = [\sigma^2(|F_o|) + 0.0002|F_o|^2]$} using the SHELXTL-PLUS program on a MicroVAX-II computer.[5] Hydrogen atoms were included at calculated positions ($U = 0.08$ Å^2). Atomic coordinates, thermal parameters and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Magnetic and ESR data for $[V_2O_3L_2]^-$ in CH_2Cl_2

		300 K		77 K					
Compound	μ_{eff}/μ_B	g	A/G	$g_{\parallel}$	$g_{\perp}$	$g_{av}{}^a$	$A_{\parallel}$/G	$A_{\perp}$/G	$A_{av}{}^b$/G
1^-	1.75	1.975	50.0	1.952	1.983	1.973	173.6	61.4	98.8
2^-	1.80	1.977	50.3	1.950	1.979	1.969	174.3	63.3	100.3
3^-	1.78	1.980	49.9	1.960	1.980	1.973	174.3	64.2	100.9

[a] $g_{av} = \frac{1}{3}(2g_{\perp} + g_{\parallel})$. [b] $A_{av} = \frac{1}{3}(2A_{\perp} + A_{\parallel})$.

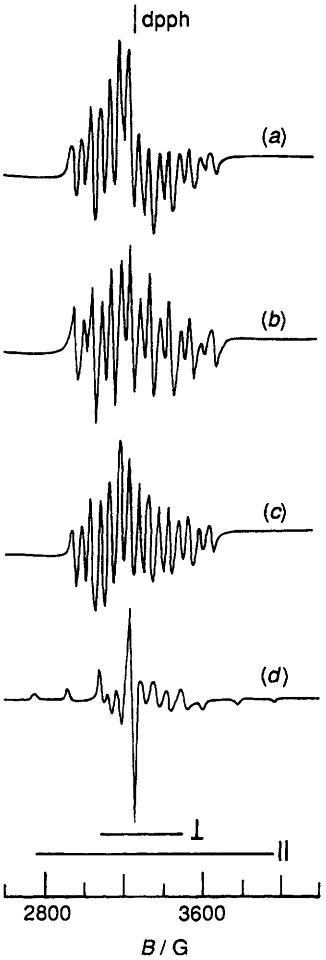

Fig. 2 X-Band ESR spectra of electrogenerated $[V_2O_3L_2]^-$ in CH_2Cl_2 solution: (*a*) 1^- at 300 K; (*b*) 2^- at 300 K; (*c*) 3^- at 300 K; (*d*) 1^- at 77 K (the ⊥ and || designations apply to this spectrum only). dpph = Diphenylpicrylhydrazyl

of $[V_2O_3L_2]^-$ (initial scan anodic) is the same as that of the parent complex (initial scan cathodic).

The magnetic moments of the electrogenerated $[V_2O_3L_2]^-$ species determined by the Evans method[6] (300 K) in CH_2Cl_2 solution correspond to one unpaired electron (Table 1) and their ESR spectra consist of 15 lines (Fig. 2). Thus the unpaired electron is interacting with both $^{51}V(I = \frac{7}{2})$ nuclei in fluid solution at 300 K. In a frozen glass (77 K) parallel and perpendicular components characteristic[7,8] of a localised $V^{IV}O$ centre are observed (Fig. 2, Table 1). As expected[9] the average hyperfine coupling constant is doubled in going from the former to the latter state (Table 1).

Is the unpaired electron in fluid solutions of $[V_2O_3L_2]^-$ fully delocalised (Robin–Day Class III)[10] or is it hopping corresponding to Class II? Although a definitive answer to this question cannot be given at this stage, there are indications that Class II provides a better description. For full delocalisation a systematic increase in the height of successive hyperfine lines is expected as the central line is approached from either side. In practice however an alternating line-height effect is observed (Fig. 2) which is suggestive[9] of hopping. The ESR spectra of fluid solutions of $[V_2O_3L_2]^-$ broaden considerably upon cooling, allowing only a rough estimate[11] of the rate constant ($\approx 4 \times 10^{10}\ s^{-1}$ at 300 K) and activation energy (≈ 3 kcal mol^{-1}). For Class II species it is expected that the frozen solution spectrum would show coupling to only one metal centre because the electron is effectively trapped at one site. Further studies are in progress.

To our knowledge this work represents the first demonstration of a *thermally controllable valence delocalisation* phenomenon apparently of Class II type, in oxidic mixed-valence vanadium(IV,V) species. The room-temperature formation (aqueous solution) of a delocalised $[V_2O_3]^{3+}$ core in equilibrium with mononuclear species bonded to nitrotriacetic acid has been reported.[12] The ESR spectra of the $[V_2O_3]^{3+}$ complex of quinolin-8-ol did not reveal any clear sign of valence delocalisation.[13]

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