

Novel mixed-valence vanadium(IV/V) molecule exhibiting unusual electron delocalization over the $[V_2O_3]^{3+}$ core †

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Condensation of methanolic salicylaldehyde and triethylenetetramine in the presence of vanadyl sulfate ($VOSO_4$) in a 3:1:2 mole ratio respectively yielded a new dinuclear mixed-valence vanadium(IV/V) Schiff-base molecule $[V_2O_3L^1] \mathbf{1}$. The crystal structure of $\mathbf{1}$ revealed the molecule to be in a bent conformation with the vanadyl units (VO) *cis* to each other and to the oxo VOV bridge. The $V(\mu-O)(\mu\text{-phenolate})V$ bridge is marginally asymmetric [$V-O_{\text{oxo}}$ 1.811(2) and 1.841(2), $V-O_{\text{phenolate}}$ 2.180(2) and 2.203(2) Å]. Normally, these geometrical properties are considered unfavourable for electron delocalization over the oxo $V-O-V$ bridge. However, remarkably, the paramagnetic molecule $\mathbf{1}$ ($\mu = 1.73 \mu_B$) features an unpaired electron delocalized over the vanadyl centres. The EPR spectra of frozen solutions and polycrystalline samples of $\mathbf{1}$ revealed extensive vanadium–vanadium interactions which are most evident in the 15-line solution EPR spectrum in dimethyl sulfoxide or acetonitrile at room temperature. Cyclic voltammograms showed a single electron loss at $E_i = 0.486$ V (with respect to the standard calomel electrode).

There is currently, considerable synthetic interest in the chemistry of vanadium because of its remarkable ability to form a variety of simple mononuclear¹ and polynuclear² compounds as well as complex clusters.³ Besides their scientific significance, many of these complexes are attractive as potential catalysts in biological⁴ and industrial⁵ processes or their simpler models. Our own involvement in vanadium chemistry reflects a recent interest⁶ in the insulin-mimicking ability exhibited by some relatively simple water-soluble vanadyl complexes.⁷

We have explored the nature of complexes formed by vanadyl species and simple Schiff-base chelates. In general Schiff bases contain reactive $N=C$ sites which can be readily reduced to produce $N-H$ functionalities that have a rather extensive chemistry. This $N-H$ chemistry can be manipulated to produce potentially versatile chelates for vanadyl species. The reaction between 2,6-diformyl-*p*-cresol, ethane-1,2-diamine and vanadyl sulfate in a template reaction yielded a Schiff-base dimer featuring a $VO_2^+ - VO_2^+$ couple.⁸ However, the larger triethylenetetramine and salicylaldehyde yields a novel dinuclear mixed-valence $[OVOVO]^{3+}$ complex with a single electron, unexpectedly, delocalized over both vanadyl centres. Herein we report the preparation, structure and electronic properties of the new dinuclear mixed-valence molecule $[V_2O_3L^1] \mathbf{1}$.

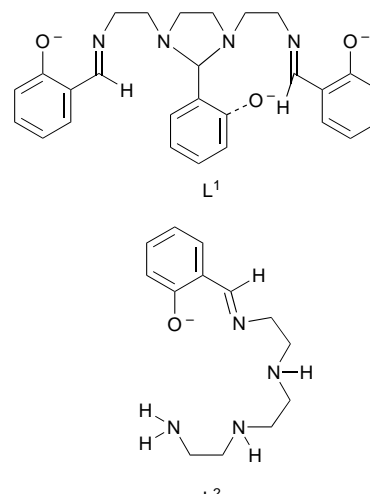
Experimental

Materials

Salicylaldehyde (99%), triethylenetetramine (tech. 60%) and $VOSO_4 \cdot nH_2O$ were obtained from BDH; methanol (95%).

Measurements

The magnetic moment of the complex was determined using a Johnson Matthey magnetic susceptibility balance, MSB1, at room temperature. The set-up used to obtain cyclic voltammograms was described previously by Bakir and McKenzie.⁸ Carbon, hydrogen and nitrogen analyses were obtained from MEDAC Ltd., Uxbridge, UK. Infrared spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer using KBr discs, UV/VIS/NIR spectra on a Perkin-Elmer Lambda 19



spectrometer; some UV/VIS spectra were recorded on an HP8451A diode-array spectrometer with the sample in acetonitrile or dimethyl sulfoxide (dmsO). The EPR spectra were recorded on an X-Band IBM/Bruker ER200DSRC electron spectrometer using a flat cell for measurements on samples in dmsO and acetonitrile.

Preparation of the dinuclear complex

Vanadyl sulfate (2 mmol) in methanol (20 cm³) and salicylaldehyde (3 mmol) in methanol (15 cm³) were mixed and then heated at 60 °C for half an hour. Triethylenetetramine (trien) (1 mmol) was then added and the resulting cloudy mixture filtered. The filtrate in a conical flask was loosely covered with paraffin film and aluminium foil and subsequently heated at 60 °C for 8 h. Dark green extensively intergrown needles of complex $\mathbf{1}$ were recovered in 12% yield after filtration (Found: C, 53.52; H, 4.42; N, 9.12. $C_{27}H_{27}N_4O_6V_2$ requires C, 53.3; H, 4.5; N, 9.2%). The IR spectrum is devoid of sulfate, amine and carbonyl absorptions but those of the imine (1630 cm⁻¹) and $V=O$ (940 cm⁻¹) are dominant. An excess of trien in the reaction mixture leads to decreasing yields of $\mathbf{1}$ and increasing deposition of a yellowish green microcrystalline diamagnetic product $\mathbf{2}$; the latter is the sole product when the ratio of

† Non-SI units employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T⁻¹, $G = 10^{-4}$ T.

vanadyl sulfate : salicylaldehyde : trien is 2 : 1 : 1. Prolonged heating of reaction mixtures containing **1** (over 1 month in a conical flask in open air or for 1.5 d under O₂) also yields **2**. Compound **2** is an oxidized product containing V^V and the proposed stoichiometry is VOL²(SO₄)·0.5CH₃OH (Found: C, 38.02; H, 5.12; N, 12.60. C_{13.5}H₂₃N₄O_{6.5}SV requires C, 37.9; H, 5.4; N, 13.1%).

X-Ray crystallography

A black crystal of complex **1** was mounted on a thin glass fibre with a coat of epoxy cement. General procedures for crystal orientation, unit-cell determination and refinement and data collection on the CAD-4 diffractometer have been published.⁹ The monoclinic cell indicated by the CAD-4 software was confirmed by the observation of *2/m* diffraction symmetry while the space group was uniquely determined by the systematic absences observed in the final data set. The data were corrected for Lorentz-polarization effects and for absorption based on ψ scans for several reflections with χ near 90°. The intensity monitors showed only statistical fluctuations, obviating the need for a decay correction. The positions of the vanadium atoms were obtained from an origin-removed Patterson function and the remainder of the structure developed by successive cycles of full-matrix least-squares refinement (based on *F*), followed by the calculation of a $\Delta\rho$ map. Near the end of the refinement, most hydrogen atoms were visible in a $\Delta\rho$ map. Those attached to C(7), C(14) and C(27) were refined with fixed isotropic displacement parameters 20% larger than those of the respective carbon atoms, while the remainder were included as fixed contributions (C–H 0.95 Å) with comparably determined isotropic displacement parameters and updated periodically. The final $\Delta\rho$ map was essentially featureless. All calculations were performed on a VAX station 3100 computer with the MOLEN¹⁰ suite of programs. The neutral atom scattering factors used include corrections for the real and imaginary portions of the effects of anomalous dispersion.¹¹ The essential crystal data are given in Table 1.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/569.

Results and Discussion

Syntheses and structure

The identity of the product **1** of the reaction between vanadyl sulfate, salicylaldehyde and triethylenetetramine in a mole ratio of 2:3:1 respectively is readily discerned from elemental (Experimental section), infrared and most convincingly single-crystal X-ray analyses. The infrared spectrum is devoid of SO₄²⁻, N–H and C=O peaks but features dominant N=C (1630 cm⁻¹) and V=O (940 cm⁻¹) absorptions which are typical of vanadyl Schiff-base complexes.¹² Fast atom bombardment mass spectrometry did not yield useful information. On the other hand, systematic variations in the reactant quantities revealed that with a ratio of vanadyl sulfate : salicylaldehyde : triethylenetetramine of 2:1:1 the reaction mixture produces a diamagnetic yellowish green vanadium(v) species formulated as **2** on the basis of IR and elemental analyses. The IR spectrum of this compound shows N–H, C=N, SO₄²⁻ and V=O absorptions at 3094, 1633, 1124 and 920–941 cm⁻¹ respectively which are consistent with its formulation.

The molecular structure of complex **1** is shown in Fig. 1 while the essential bond distances and angles are shown in Table 2. The molecular structure features a [OVOVO]³⁺ couple trapped by chelate L¹, which along with the oxygen atoms of the OVOVO framework satisfies the six-fold co-ordination

Table 1 Summary of crystallographic data

Formula	C ₂₇ H ₂₇ N ₄ O ₆ V ₂
<i>M</i>	605.42
Crystal size/mm	0.30 × 0.23 × 0.43
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	9.914(2)
<i>b</i> /Å	22.875(2)
<i>c</i> /Å	11.971(2)
β /°	106.27(1)
<i>U</i> /Å ³	2606(1)
<i>Z</i>	4
<i>D</i> _c /g cm ⁻³	1.54
μ /cm ⁻¹	7.4
Transmission factors	0.9395–0.9994
<i>T</i> /K	293
Radiation	Mo-K α (Graphite monochromated, λ = 0.710 73 Å)
Scan type	ω -2 θ
Scan range/°	0.80 + 0.34tan θ
2 θ range/°	2.0–50.0
Total no. reflections	5005
No. unique reflections	4581
<i>R</i> _{int}	0.017
No. observed data	2783 [<i>I</i> ≥ 3 σ (<i>I</i>)]
No. parameters	361
(Δ / σ) _{max} in last cycle	0.10
<i>R</i> ^a	0.033
<i>R</i> ^b	0.043
Goodness of fit ^c	1.37
$\Delta\rho$ in final ΔF map/e Å ⁻³	0.26 to –0.09

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R' = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2]^{1/2}$ with $w = 1 / (\sigma_F)^2$; $\sigma_F = \sigma(F^2) / 2F$; $\sigma(F^2) = [(\sigma_p)^2 + (0.04F^2)^2]^{1/2}$. ^c $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$ where *N*_o and *N*_v are, respectively, the number of observations and variables.

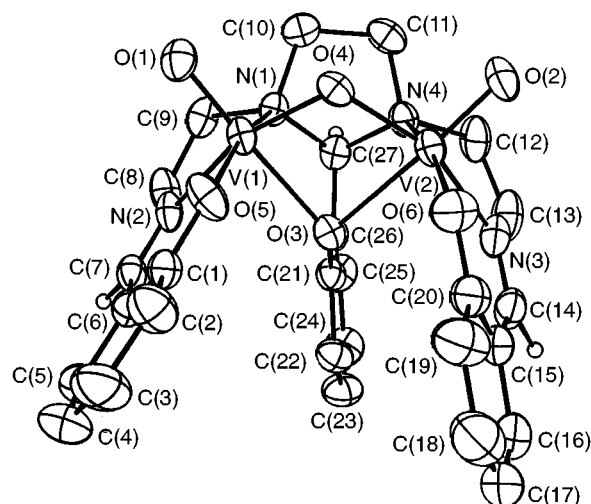


Fig. 1 A perspective view of [V₂O₃L¹]. Thermal ellipsoids for non-hydrogen atoms are drawn at the 50% probability level. Hydrogen atoms in calculated positions are omitted for clarity

requirements of the two vanadium centres. The geometry around each vanadium is distorted octahedral with the vanadium atoms displaced, to roughly similar extents, towards the terminal oxygens. Atom V(1) is 0.275(1) Å above the plane formed by N(1), N(2), O(4) and O(5) while V(2) is 0.294(1) Å above the plane of N(3), N(4), O(4) and O(6) (Fig. 1). These displacements are comparable to those found in many other vanadium compounds.¹³ The oxo VOV bridge is marginally asymmetric with V(1)–O(4) 1.811(2) Å and V(2)–O(4) 1.841(2) Å. For V₂O₃³⁺ species¹⁴ with symmetric VOV bridges the V–O distances generally fall⁸ in the range 1.77–1.825 Å while asymmetric ones have values in the range 1.7–1.95 Å. Like the V–O–V bridge, the phenolate bridge at O(3), in which the V(1)–O(3) and V(2)–O(3) distances are 2.180(2) and 2.203(2) Å

Table 2 Bond distances (Å) and angles (°) for complex **1** with estimated standard deviations in parentheses

V(1)–O(1)	1.605(3)	V(2)–O(2)	1.611(3)
V(1)–O(3)	2.180(2)	V(2)–O(3)	2.203(2)
V(1)–O(4)	1.811(2)	V(2)–O(4)	1.841(2)
V(1)–O(5)	1.900(3)	V(2)–O(6)	1.925(3)
V(1)–N(1)	2.189(3)	V(2)–N(3)	2.087(3)
V(1)–N(2)	2.108(3)	V(2)–N(4)	2.207(3)
O(4)–V(1)–N(1)	90.6(1)	O(2)–V(2)–O(4)	102.9(1)
O(4)–V(1)–N(2)	158.5(1)	O(2)–V(2)–O(6)	101.1(1)
O(5)–V(1)–N(1)	162.4(1)	O(2)–V(2)–N(3)	97.6(1)
O(5)–V(1)–N(2)	87.5(1)	O(2)–V(2)–N(4)	90.8(1)
N(1)–V(1)–N(2)	78.1(1)	O(3)–V(2)–O(4)	76.27(9)
O(2)–V(2)–O(3)	172.0(1)	O(3)–V(2)–O(6)	86.9(1)
O(1)–V(1)–O(3)	172.3(1)	O(3)–V(2)–N(3)	81.9(1)
O(1)–V(1)–O(4)	102.7(1)	O(3)–V(2)–N(4)	81.27(9)
O(1)–V(1)–O(5)	101.6(1)	O(4)–V(2)–O(6)	98.1(1)
O(1)–V(1)–N(1)	90.1(1)	O(4)–V(2)–N(3)	156.8(1)
O(1)–V(1)–N(2)	95.6(1)	O(4)–V(2)–N(4)	90.7(1)
O(3)–V(1)–O(4)	77.47(9)	O(6)–V(2)–N(3)	88.3(1)
O(3)–V(1)–O(5)	85.9(1)	O(6)–V(2)–N(4)	163.2(1)
O(3)–V(1)–N(1)	82.21(9)	N(3)–V(2)–N(4)	78.2(1)
O(3)–V(1)–N(2)	82.9(1)	V(1)–O(3)–V(2)	89.36(9)
O(4)–V(1)–O(5)	99.6(1)	V(1)–O(4)–V(2)	115.1(1)

respectively, appears to be marginally asymmetric. The bridging V–O (phenoxy) distances of **1** are longer than usual which may be indicative of strain in the molecule; normally bridging V–O (phenoxy) and V–O (alkoxy) distances, irrespective of the oxidation state of vanadium, fall in the range 1.8–2.05 Å.¹⁵ The intramolecular V···V separation in **1** is *ca.* 3.084(8) Å and falls within the range of known V···V distances in double bridged vanadium polynuclear systems.^{13,16}

Other distances in complex **1** are normal; the [V₂O₃L¹] species pack as isolated molecules with no significant intermolecular interactions. There is no significant π – π stacking among the phenolate rings.

Electronic, magnetic and redox properties

The structure of complex **1** reveals curious features of great interest to the current debate on the factors influencing vanadium–vanadium interactions. The V(μ -O)(μ -O_{phenoxy})V bridge is asymmetric, but marginally so, and the terminal V=O bonds maintain a *cis* arrangement to both each other and the oxo VOV bridge (Fig. 1). The V(1)–O(4)–V(2) and V(1)–O(3)–V(2) angles, being 115.1(1) and 89.4(1)° respectively, deviate substantially from linearity¹⁴ and are much smaller than the value of 146.6° found in a complex exhibiting *cis* OVOVO geometry.¹⁷ A comparably small V–(μ -O)–V angle [113.2(3)°] was reported recently but in this case the unusual OV–(μ -O)–VO geometry was intermediate between *cis* and *trans*.¹⁸ The preponderance of current evidence favours optimum OV···VO electronic interactions when the O=V species constitute a *trans* geometry relative to each other and are *cis* to the V–O–V bridge which is itself linear. Schulz *et al.*¹⁴ have shown that departure from V–O–V oxo bridge linearity does not affect the degree of OV···VO superexchange interactions *via* their d_{xy} (where the d^1 electron is resident) and oxygen p_x orbitals. However, π – π bonding effects in the plane perpendicular to the V=O vector (xy plane) were found to favour localized (Class I) [OVOVO]³⁺ species through their energetic influence on the populated metal d_{xy} orbital.¹⁴ The energy of this orbital is raised by such π – π interactions and may become antibonding, rather than non-bonding, under strong p_π – d_π conditions. However, the frequently encountered poor correlation between geometrical parameters and electronic interaction strength in V^{III}–V^{III},¹⁶ V^{IV}–V^{IV}¹⁹ and V^{IV}–V^V^{13,20} species calls for caution on the emphasis put on geometric considerations. More systems need to be studied to establish the major factors impacting

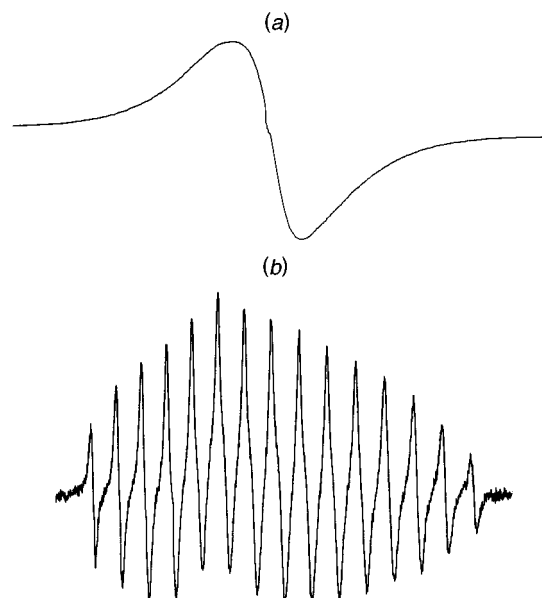


Fig. 2 The X-band EPR spectra of [V₂O₃L¹] **1** scanned over 1000 G: (a) typical profile of a polycrystalline sample at 77 K or room temperature and frozen dmso or acetonitrile solutions (77 K); frequency = 9.22 GHz, centre = 3500 G; (b) at room temperature in acetonitrile; spectrum in dmso is similar; frequency = 9.64 GHz, centre = 3300 G

upon V···V interactions. It was therefore interesting to determine the electronic behaviour of the [OV(μ -O)(μ -O_{phenoxy})VO] species **1** in view of its geometry, which appears to optimize the odds against electron delocalization on the two vanadyl centres, save for the symmetry-allowed through-space direct d_{xy} – d_{xy} overlap.¹⁴

The electronic absorption spectrum of complex **1** features Schiff-base ligand (L¹) absorptions at *ca.* 220–290 and 380 nm. These ligand absorptions are accompanied by a relatively weaker broad absorption in the range 520–1300 nm which we attribute to unresolved d_{xy} to antibonding (d_{xz} , d_{yz}) and $d_{x^2-y^2}$ transitions on the VO²⁺ centre.^{21–23}

Compound **1** is paramagnetic and the magnetic moment at 300 K is $\mu = 1.73 \mu_B$ which corresponds to one electron per molecule.

The X-band EPR spectrum of the solid complex exhibits an intense single resonance at $g = 1.97$ with a linewidth that does not change between room and liquid-nitrogen temperatures [Fig. 2(a)]. In solution, however, the spectrum [Fig. 2(b)] exhibits a well resolved 15-line hyperfine structure with relative intensities approximating 1:2:3:4:5:6:7:8:7:6:5:4:3:2:1. This spectral profile is clearly characteristic of a single unpaired electron split by two equivalent ⁵¹V nuclei ($I = \frac{7}{2}$). The coupling constant of 50 G is very similar to those reported for other delocalized V³⁺–V⁴⁺ couples.²⁴ When the solutions are frozen at 77 K the spectrum exhibits only a single broad resonance, the width of which is comparable to the 15-line pattern seen in solution. The frozen-solution spectrum is quite similar in shape to that of the pure solid complex. These data strongly suggest that the unpaired electron is delocalized over both vanadium atoms in the solid complex and in solution, both at room and liquid-nitrogen temperatures. The almost smooth increments in line intensities towards the centre of the spectrum [Fig. 2(b)] are characteristic of a delocalized (Class III) rather than partially delocalized or hopping (Class II) V₂O₃³⁺ core.²⁵

The complex appears to be quite stable in solution, since the EPR and absorption spectra showed no change upon standing for several days and over 7 months respectively. The solid compound can be heated to 573 K without evidence of decomposition. Its cyclic voltammogram in dimethyl formamide exhibits a one-electron reversible oxidation wave with $E_i = 0.486$

V vs. standard calomel electrode (SCE). This behaviour is similar to that of readily oxidized VO²⁺ species in approximate O_h environments.¹³

Conclusion

Compound **1** is a complex of a V₂O₃³⁺ species which in spite of marginal asymmetry in the OV(μ-O)(μ-O_{phenoxy})VO bridge, mutual *cis* V=O geometry, and the presence of p_π-d_π forming phenolate functionalities in the *xy* plane, features d¹ electron delocalization over both vanadyl centres (Class III V₂O₃³⁺). The occurrence of this d¹ electron delocalization against what under current thinking would be considered 'severe geometrical odds' demonstrates dramatically the limited understanding we have of the factors influencing electronic V···V coupling. For compound **1** the d_{xy} orbitals of the V=O centres have the right symmetry for mutual direct interactions.¹⁴ This seems to be the most important pathway for electronic exchange across the OV···VO bridge here.

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