Macrocyclic Oxovanadium(IV) Complexes: Structure, Magnetochemistry and Electrochemistry[†]

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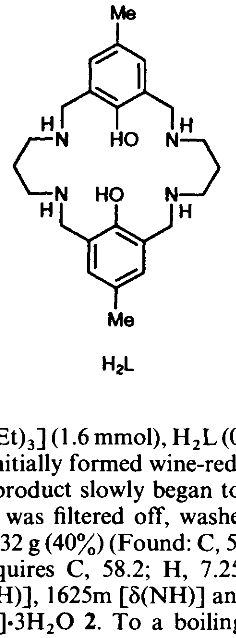
The oxovanadium(IV) complexes, $[VO(L)]\cdot H_2O$ **1**, $[VO(H_2L)(SO_4)]\cdot 3H_2O$ **2**, $[(VO)_2L(\mu\text{-}SO_4)]\cdot MeOH\cdot 3H_2O$ **3** and $[Zn(L)VO(SO_4)]\cdot 4H_2O$ **4** have been synthesised from the dinucleating tetraaminodiphenol macrocyclic ligand H_2L. The ESR and IR spectra of **1** have indicated stacking of the molecules due to $\cdots V{=}O \cdots V{=}O \cdots$ interactions. In complexes **2** and **4** the unidentate sulfate is bound to the octahedral vanadium and two of the secondary amino groups in **2** are protonated. Both of these complexes undergo oxidation to produce oxovanadium(V) species with $E_{\frac{1}{2}} = 0.40$ V (**2**), 0.455 V (**4**) *vs.* saturated calomel electrode (SCE). Fairly strong antiferromagnetic exchange interaction has been found in **3** from variable-temperature susceptibility measurements, $J = -128$ cm^{-1}. The crystal structure of **3** has been determined; tetragonal, space group $P4_122$, $a = b = 12.252(2)$, $c = 40.819(5)$ Å and $Z = 8$; refinement led to $R = 0.053$ and $R' = 0.055$ using 1825 unique reflections with $I > 3\sigma(I)$. The two octahedral vanadium centres in the complex, separated by 3.077 Å, are bridged by sulfate and have *syn* oxo configuration.

The recognition of vanadium in several biomolecules, especially in the nitrogen-fixing bacterium *Azobacter*[1] and the seaweeds that use haloperoxidases[2] to synthesise organic halides, has led to a spurt in the investigation of the bioinorganic chemistry of vanadium.[3-5] The involvement of the vanadoenzymes both in reductive ($N_2 + 6H^+ + 6e^- \longrightarrow 2NH_3$) and oxidative ($RH + H_2O_2 + HBr \longrightarrow RBr + 2H_2O$) transformations signifies the the importance of +3, +4 and +5 oxidation states in biological processes. In view of the binding of vanadium with tyrosinase in transferrin[6] and the occurrence of polyphenol pigments, tunichrome,[7] in the vanadium accumulating organisms, tunicates,[8] vanadium aryloxo(*N*,*O*-co-ordinated) complexes have received considerable attention.[4,5,9-11]

For some time we have been studying the structure-property relations in some dinuclear complexes of the tetraaminodiphenol macrocyclic ligand H_2L.[12-14] We note that although a large variety of vanadium complexes are known,[4,5,15] very few macrocyclic complexes have been reported so far.[16-19] We therefore have set out to study the chemistry of mono-, di- and poly-nuclear macrocyclic complexes of vanadium in the oxidation states +3 to +5. Herein we report our findings on the oxovanadium(IV) complexes of H_2L.

Experimental

Materials.—All chemicals were reagent grade and used as received. The ligand H_2L was prepared as reported earlier.[12,13] An ethanol solution of $[VO(OEt)_3]$ of known concentration was obtained according to the procedures described previously.[10b,20] Solvents were purified by standard methods.[21]



H_2L

Syntheses.—$[VO(L)]\cdot H_2O$ **1**. To a refluxing ethanol solution (70 cm^3) of $[VO(OEt)_3]$ (1.6 mmol), H_2L (0.66 g, 1.6 mmol) was added. From the initially formed wine-red solution an orange-yellow crystalline product slowly began to separate. After 5 h reflux the product was filtered off, washed with ethanol and dried in air; yield 0.32 g (40%) (Found: C, 57.6; H, 7.4; N, 11.15. $C_{24}H_{36}N_4O_4V$ requires C, 58.2; H, 7.25; N, 11.3%). $\tilde{\nu}$/cm^{-1} (KBr) 3260w [ν(NH)], 1625m [δ(NH)] and 850s [ν(V=O)].

$[VO(H_2L)(SO_4)]\cdot 3H_2O$ **2**. To a boiling methanol solution (30 cm^3) of H_2L (0.824 g, 2 mmol) a methanol solution (20 cm^3) of $VO(SO_4)\cdot xH_2O$ (0.434 g, 2 mmol) was added over 5 min. The resulting deep red solution was stirred at *ca.* 50 °C for 0.5 h and then filtered. The filtrate was concentrated on a rotary evaporator when pink crystals of **2** deposited, which were filtered off and recrystallized from methanol; yield 1.0 g (80%) (Found: C, 45.95; H, 6.6; N, 8.75; SO_4, 15.5. $C_{24}H_{42}N_4O_{10}SV$ requires C, 45.8; H, 6.7; N, 8.9; SO_4, 15.25%). $\tilde{\nu}$/cm^{-1}(KBr) 3210w(br) [ν(NH)], 1610m [δ(NH)], 1140s, 1120s, 1025m, 625s, 610s [ν(S–O)] and 940 [ν(V=O)]; λ_{max}/nm(ε/dm^3 mol^{-1} cm^{-1}) (MeOH) 820 (32), 520 (100) and 292 (11 300).

$[(VO)_2L(\mu\text{-}SO_4)]\cdot MeOH\cdot 3H_2O$ **3**. To a boiling methanol

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[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

solution (40 cm^3) containing H_2L (0.824 g, 2 mmol) and NEt_3 (0.404 g, 4 mmol) a methanol solution (40 cm^3) of $VO(SO_4)\cdot xH_2O$ (0.868 g, 4 mmol) was added over a period of 1 h. Refluxing of the solution was continued for 2 h, after which it was filtered and the filtrate concentrated to half of the original volume. The solution was kept at 50 °C, allowing to concentrate slowly. Bluish violet flakes that deposited on the walls of the container over a period of several hours were collected by filtration and recrystallized from methanol; yield 0.45 g (31%) (Found: C, 41.05; H, 5.95; N, 7.6; SO_4, 13.4. $C_{25}H_{44}N_4O_{12}SV_2$ requires C, 41.3; H, 6.05; N, 7.7; SO_4, 13.2%). $\tilde{\nu}$/cm^{-1}(KBr) 3200w [ν(NH)], 1610m [δ(NH)], 1220s, 1165s, 1130s, 1085s, 945m, 625m, 605s [ν(S–O)] and 970 [ν(V=O)]; λ_{max}/nm(ε/dm^3 mol^{-1} cm^{-1}) (MeOH) 665 (45), 505 (35) and 275 (7600). The mother-liquor on further concentration afforded predominantly crystals of **2**.

$[VO(L)Zn(SO_4)]\cdot 4H_2O$ **4**. A methanol solution (40 cm^3) containing **2** (0.63 g, 1 mmol), NEt_3 (0.202 g, 2 mmol) and $Zn[ClO_4]_2\cdot 4H_2O$ (0.42 g, 1.25 mmol) was stirred for 1 h. On concentration of the solution to *ca.* 10 cm^3 a light pink product deposited. This was filtered off, washed with acetone and recrystallized from methanol (Found: C, 40.3; H, 5.8; N, 7.75; SO_4, 13.7. $C_{24}H_{42}N_4O_{11}SVZn$ requires C, 40.55; H, 5.9; N, 7.9; SO_4, 13.5%). $\tilde{\nu}$/cm^{-1}(KBr) 3230w [ν(NH)], 1610m [δ(NH)], 1165s, 1115s, 1085s, 620s, 600m [ν(S–O)] and 1045s [ν(V=O)]; λ_{max}/nm(ε/dm^3 mol^{-1} cm^{-1}) (MeOH) 730 (30), 510 (105) and 290 (8700).

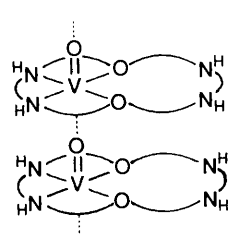
Physical Measurements.—Infrared spectra were recorded on a Perkin Elmer 783 spectrophotometer using KBr discs and UV/VIS spectra on a Shimadzu UV-160A spectrophotometer. Room-temperature magnetic susceptibility measurements were performed with an EG & G PAR 155 vibrating sample magnetometer. Variable-temperature susceptibility measurements between 80 and 293 K were carried out by the Faraday method using a Sartorius microbalance, Bruker B-E10C8 research magnet and B-VT1000 automatic temperature controller. Diamagnetic corrections were made using Pascal's constants. X-Band ESR spectra were recorded on a Varian E-109C spectrometer. Diphenylpicrylhydrazyl (dpph) (g = 2.0037) was used as an external standard. Electrochemical experiments were performed with a BAS 100B electrochemistry system. A standard three-electrode configuration was used, with platinum working and auxiliary electrodes and a saturated calomel electrode (SCE) reference. The supporting electrolyte was 0.1 mol dm^{-3} $[NEt_4][ClO_4]$.

Carbon, H and N analyses were performed on a Perkin Elmer 240C elemental analyser. Sulfate was estimated gravimetrically as $BaSO_4$.

Crystal Structure Determination of $[(VO)_2L(\mu\text{-}SO_4)]\cdot MeOH\cdot 3H_2O$.—*Crystal data*. $C_{25}H_{44}N_4O_{12}SV_2$, M = 726.6, tetragonal, space group $P4_122$, $a = b$ = 12.252(2), c = 40.819(5) Å, U = 6127.4(2) Å^3 (by least-squares refinement of diffractometer angles for 20 automatically centred reflections having 2θ range 70–100°, λ = 1.5418 Å), Z = 8, D_c = 1.575 g cm^{-3}, D_m = 1.61 g cm^{-3}. Crystal dimensions: 0.15 × 0.25 × 0.30 mm, μ(Cu-Kα) = 63.85 cm^{-1}, F(000) = 3040, T = 295 K.

Data collection and processing. Intensity data were collected with a Rigaku AFC5R diffractometer using graphite-monochromated Cu-Kα radiation (λ = 1.5418 Å) from a 12 kW rotating anode generator. Intensities of three standard reflections monitored after every 2 h showed no appreciable decay during data collection. The intensity data were corrected for Lorentz-polarization effects and for absorption.[22] A total of 2450 unique reflections were collected in the range $1 < \theta < 60°$, of which 1825 reflections with $I > 3\sigma(I)$ were used for structure determination.

Structure analysis and refinement. Systematic absence (00l; $l = 4n$) and assignment of Laue group $4/mmm$ from the intensity distribution led to the identification of the space group as $P4_122$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques using the program SHELX 76.[23] Isotropic refinement of non-hydrogen atoms followed by Fourier difference synthesis revealed the positions of the solvent molecules in the asymmetric unit. Some of the solvent molecules in **3** showed disorder. While the occupancy factors of methanol [O(11), C(11A)] and water [O(12)] were unity and that of O(9) lying on a symmetry site was 0.5, the other water molecules [O(10), O(10A) with occupancy factors of 0.25 each; O(13), O(14) with occupancy factors 0.4 and 0.6, respectively] were found to be disordered. During refinement all the solvent atoms were treated isotropically with fixed occupancy factors. In the final stage of refinement all non-hydrogen atoms of the complex molecule were made anisotropic while the hydrogen atoms were held fixed in the geometrically calculated positions with isotropic thermal parameters. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.004|F_o|^2]$, with $\sigma(F_o)$ from counting statistics gave satisfactory agreement analyses. The maximum and minimum peak heights in the final Fourier difference map were +0.55 and −0.33 e Å^{-3}, respectively. Final R and R' values are 0.053 and 0.055. Anomalous dispersion corrections were applied for the vanadium atoms and scattering factor data were taken from ref. 24. All computations were carried out on a VAX system at the Computer Centre, Indian Association for the Cultivation of Science.



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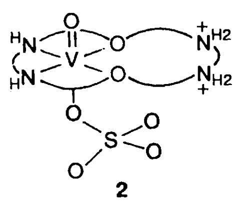

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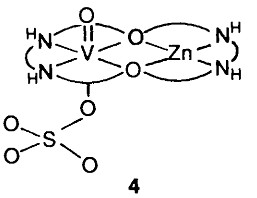

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Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis and Characterization.—The addition of 1 equivalent of H_2L to an ethanol solution of $[VO(OEt)_3]$ yields an orange-yellow compound of composition $[VO(L)]\cdot H_2O$ **1**. The formation of a vanadyl(IV) complex from a vanadium(V) precursor indicates that the ligand anion stabilizes the neutral [VO(L)] species. The mechanism of reduction of VO^{3+} to VO^{2+} is not clear at this stage. From the relatively poor yield of **1** (40%) it appears that some of the ligand has been oxidized. The IR spectrum of **1** showed no absorption between 900 and 1000 cm^{-1} indicative for a $[V{=}O]^{2+}$ stretch. However, a strong band observed at 850 cm^{-1} can be attributed to an elongated V=O bond due to V=O ··· V=O interactions in the complex. Complex **1** is probably a stacked oligomer, which is consistent with its poor solubility in common organic solvents. It should be noted that in the structurally characterized *N,N′*-propylenebis(salicylideneiminato) oxovanadium(IV) complex, [VO(salpn)],[25] where ··· V=O ··· V=O ··· interactions lead to an infinite chain structure, ν(V=O) was observed at 854 cm^{-1}.

The reaction between H_2L and vanadyl sulfate (1:1) in

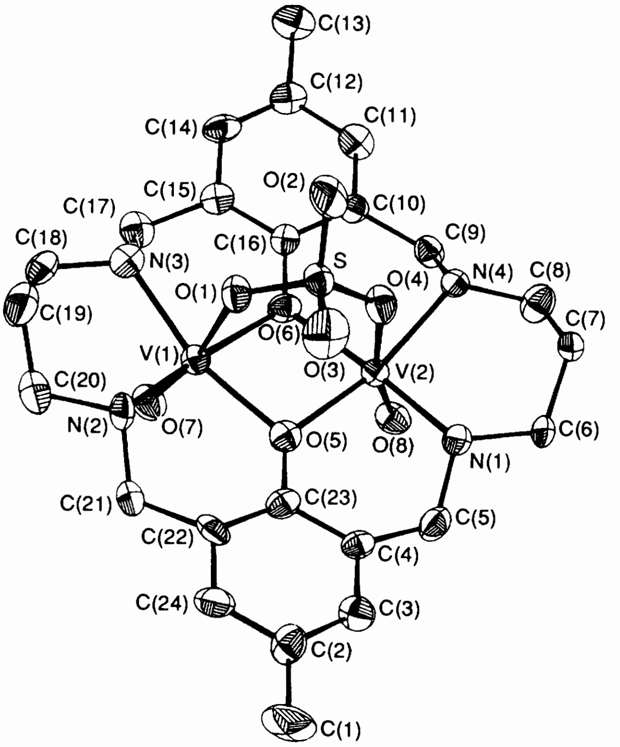

Fig. 1 An ORTEP view of [(VO)$_2$L(μ-SO$_4$)] with the atom labelling scheme

methanol affords complex **2** with the composition [VO(H$_2$L)(SO$_4$)]·3H$_2$O. Sulfate is co-ordinated to vanadium in **2** as evident from the splitting of ν_3(SO$_4$) into three components (1140, 1120, 1025 cm^{-1}) and ν_4(SO$_4$) into two components (625, 610 cm^{-1}); these are indicative of C_{3v} symmetry of monodentate sulfate.[26] The V=O stretch was observed at 940 cm^{-1}. Clearly, vanadium is six-co-ordinate in **2** and the two non-co-ordinated secondary amines are protonated.

When 1 equivalent of H$_2$L is treated with 2 equivalents of vanadyl sulfate in the presence of 2 equivalents of triethylamine the homodinuclear complex [(VO)$_2$L (μ-SO$_4$)]·MeOH·3H$_2$O **3** is obtained along with **2**. It appears that vanadyl sulfate has a propensity to form the protonated complex **2** even in the presence of a base. The presence of bridging sulfate of C_{2v} symmetry in **3** was indicated by the strong absorptions occurring at 1220, 1165, 1130 and 1085 cm^{-1} (ν_3), 945 (ν_1), and 625 and 605 cm^{-1} (ν_4). The strong ν(V=O) band was observed at 970 cm^{-1}.

The heterodinuclear complex [Zn(L)VO(SO$_4$)]·4H$_2$O **4** was obtained by treating **2** with zinc perchlorate and triethylamine (1 : 1 : 2). The IR spectral characteristics of this compound with regard to ν(SO$_4$) and ν(V=O) frequencies were similar to that of **2**, indicating an identical co-ordination environment for vanadium in the two compounds.

Structural Description of [(VO)$_2$L(μ-SO$_4$)]·MeOH·3H$_2$O **3**.—An ORTEP[27] diagram of [(VO)$_2$L(μ-SO$_4$)] with the atom labelling scheme is shown in Fig. 1. Positional parameters and selected bond lengths and angles are given in Tables 1 and 2, respectively. The molecular structure shows that each vanadium atom is co-ordinated to two secondary amine nitrogen donors and two bridging phenolate oxygens from the macrocycle and a distorted octahedral configuration is obtained through the axial co-ordination of an oxo oxygen and bridging sulfate oxygen. The V=O distance [av. 1.582(8) Å] lies within the range 1.56–1.63 Å reported for oxovanadium(IV) complexes.[28] The equatorial V–O distances [av. 2.092(2) Å] are normal. The V–O (sulfate) distances [av. 2.176(4) Å] are rather long indicating the significant *trans* influence of the vanadyl group. In **3**, the V=O groups adopt *syn* positions with respect to each other; incidentally, there are few structurally characterized *syn* dioxovanadium(IV) complexes.[10a,17,29,30] The non-bonding distance between the two terminal oxo groups is very long (4.24 Å) compared to the V $\cdots$ V distance [3.077(7) Å]. On the other hand, the distance between the two vanadium-co-ordinated sulfate oxygen atoms, O(1) and O(4), is rather short (2.40 Å). Severe distortion of the vanadium centres from a regular octahedral geometry can be judged by considering the cisoid angles, which lie between 78 and 103°, and the transoid angles, varying between 163 and 168°. The V–O–V bridge angles produced by the phenolic oxygens are 99.0(3) and 99.7(3)° whereas the S–O–V angles involving μ-SO$_4$ are 133.4(4) and 135.0(4)°. In the plane comprising N(2)N(3)O(5)O(6) atoms the donor atoms lie within 0.007 Å of the least-squares plane, but V(1) is displaced towards the vanadyl oxygen by 0.267 Å. Similarly, V(2) is displaced in the same direction from the N(1)N(4)O(5)O(6) mean plane by 0.264 Å. The dihedral angle between these two planes is 30.0(2)°. In **3** the solvent molecules are not significantly involved in intra- or inter-molecular hydrogen bonding.

Electronic Spectra.—Complexes **2**–**4** exhibited two absorption bands in methanol in the ranges 12 000–15 000 and 19 000–20 000 cm^{-1}. The Nujol mull spectrum of **1** showed a broad shoulder at 18 870 cm^{-1}. For vanadyl(IV) complexes it is generally regarded that the unpaired electron is in a d$_{xy}$ orbital and transitions occur to [d$_{xz}$, d$_{yz}$](ν_1), d$_{x^2-y^2}$(ν_2) and d$_{z^2}$(ν_3) orbitals with increasing energies.[31] Usually the band energy of ν_3 lies in the charge-transfer region. The data given in Table 3 indicate that although the energy of ν_2 is practically the same for all the complexes, the ν_1 band energy decreases in the order [(VO)$_2$L(μ-SO$_4$)] > [Zn(L)VO(SO$_4$)] > [VO(H$_2$L)(SO$_4$)].

Magnetism and ESR Spectra.—The powder ESR spectrum of **1** at 77 K showed a single line at g = 1.97. A weak resonance observed at 'half-field', 1650 G (G = 10^{-4} T) (g = 3.92) is clearly due to a $\Delta M_s = \pm 2$ transition resulting from $\cdots$V=O$\cdots$V=O stacking interactions. The room-temperature magnetic moment (μ_{eff} = 1.84) rules out the possibility of antiferromagnetic spin exchange. On the other hand, a weak ferromagnetic exchange interaction similar to that observed for [VO(salpn)] (J = 4.1 cm^{-1})[32] seems likely due to the identical ESR spectra and room-temperature magnetic moments of the two compounds. For [VO(salpn)] ferromagnetism involves a d$_{z^2}$ superexchange pathway of the spin ladder.

The eight-line ESR spectra of **2** and **4** in methanol were found to be very similar and attributable to a single $S = \frac{1}{2}$ species in which the unpaired electron in a d$_{xy}$ orbital is coupled to the nuclear spin of the vanadium nucleus ($I = \frac{7}{2}$). Their frozen glass spectra were also identical and characterized by two sets of eight lines. The spectrum of **4** in methanol glass (77 K) is shown in Fig. 2. The spin-Hamiltonian parameters given in Table 3 indicate that **2** and **4** are practically indistinguishable by ESR spectroscopy, although they can be distinguished by visible spectroscopy. Table 3 also reveals that the g and A values of these two compounds are strikingly similar to those reported for the reduced form of bromoperoxidase,[33] albeit the co-ordination environment of the active site of this enzyme is still uncertain.

Variable-temperature susceptibility measurement of the homodinuclear complex **3** was carried out between 80 and 293 K. The expression for the temperature-dependent molar susceptibility may be derived[34] from the general isotropic exchange Hamiltonian $H = -2J\vec{S_1}\cdot\vec{S_2}$ where $S_1 = S_2 = \frac{1}{2}$ for VO$^{\text{II}}$. Since the measurement was limited up to 80 K additional terms due to temperature-independent paramagnetism and contribution of mononuclear paramagnetic impurity were not considered.

Fig. 3 shows that $\chi_M T$ decreases with decreasing temperature, the effective magnetic moment per VO$^{\text{II}}$ centre decreases from

Table 1 Atomic coordinates for $[(VO)_2L(\mu\text{-}SO_4)]\cdot MeOH\cdot 3H_2O$ **3**

Atom	*x*	*y*	*z*
V(1)	0.369 80(13)	0.308 03(13)	0.166 30(4)
V(2)	0.202 48(13)	0.120 79(13)	0.166 06(4)
S	0.275 38(21)	0.217 90(19)	0.240 00
O(1)	0.352 1(5)	0.282 5(5)	0.218 7(2)
O(2)	0.335 3(6)	0.163 4(7)	0.264 6(1)
O(3)	0.191 5(6)	0.290 4(6)	0.253 2(2)
O(4)	0.220 8(6)	0.137 0(5)	0.219 0(1)
O(5)	0.206 0(5)	0.285 0(5)	0.163 5(1)
O(6)	0.364 0(5)	0.143 8(5)	0.162 2(1)
O(7)	0.400 1(5)	0.346 1(5)	0.130 2(2)
O(8)	0.171 3(5)	0.086 5(5)	0.130 1(1)
N(1)	0.038 7(6)	0.130 4(6)	0.181 2(2)
N(2)	0.348 0(6)	0.468 8(6)	0.182 1(2)
N(3)	0.533 4(6)	0.300 4(7)	0.180 9(2)
N(4)	0.227 1(6)	−0.044 2(6)	0.181 0(2)
C(1)	−0.136 9(11)	0.595 6(10)	0.177 4(3)
C(2)	−0.048 2(9)	0.513 9(9)	0.174 1(3)
C(3)	−0.067 3(9)	0.406 0(8)	0.171 4(3)
C(4)	0.013 5(8)	0.327 3(8)	0.168 0(2)
C(5)	−0.022 4(8)	0.213 2(9)	0.162 0(3)
C(6)	−0.026 0(8)	0.024 6(8)	0.181 7(3)
C(7)	0.032 8(8)	−0.066 7(8)	0.198 5(3)
C(8)	0.130 9(9)	−0.116 2(9)	0.180 8(3)
C(9)	0.313 8(8)	−0.091 3(8)	0.160 7(3)
C(10)	0.426 7(8)	−0.043 1(8)	0.165 9(3)
C(11)	0.507 0(10)	−0.119 5(9)	0.169 2(3)
C(12)	0.618 7(8)	−0.085 3(9)	0.172 3(2)
C(13)	0.706 1(8)	−0.171 3(10)	0.176 8(3)
C(14)	0.639 8(8)	0.023 1(10)	0.170 3(3)
C(15)	0.556 5(8)	0.102 9(8)	0.166 4(3)
C(16)	0.448 9(8)	0.068 6(8)	0.164 7(2)
C(17)	0.592 0(9)	0.219 5(9)	0.160 8(2)
C(18)	0.595 9(8)	0.401 8(9)	0.180 6(3)
C(19)	0.539 4(10)	0.494 3(11)	0.198 7(3)
C(20)	0.442 7(10)	0.542 7(9)	0.181 4(3)
C(21)	0.257 9(8)	0.519 4(8)	0.164 1(3)
C(22)	0.149 5(10)	0.471 0(8)	0.169 1(3)
C(23)	0.124 9(9)	0.363 8(9)	0.166 7(2)
C(24)	0.060 4(9)	0.547 5(9)	0.172 6(3)
O(9)[a]	0.500 00	0.274 0(8)	0.500 00
O(10)[b]	0.000 00	0.450 9(22)	0.000 00
O(10A)[b]	0.000 00	0.526 5(23)	0.000 00
O(11)	−0.020 5(10)	0.270 3(9)	0.253 4(3)
C(11A)	−0.011 2(20)	0.617 5(16)	0.250 5(6)
O(12)	0.227 9(9)	0.426 8(9)	0.000 3(3)
O(13)[c]	0.760 8(16)	0.035 8(18)	0.248 8(8)
O(14)[d]	0.792 7(12)	0.208 2(12)	0.229 9(4)

[a] Occupancy 0.50. [b] Occupancy 0.25. [c] Occupancy 0.60. [d] Occupancy 0.40.

Table 2 Selected bond lengths (Å) and angles (°) for $[(VO)_2L(\mu\text{-}SO_4)]\cdot MeOH\cdot 3H_2O$ **3**

V(1)–O(1)	2.173(6)	V(2)–O(4)	2.180(6)
V(1)–O(7)	1.590(6)	V(2)–O(8)	1.573(6)
V(1)–O(5)	2.029(6)	V(2)–O(5)	2.016(6)
V(1)–O(6)	2.020(6)	V(2)–O(6)	2.005(6)
V(1)–N(2)	2.091(7)	V(2)–N(1)	2.103(8)
V(1)–N(3)	2.093(8)	V(2)–N(4)	2.132(7)
V(1) • • • V(2)	3.077(7)		
N(2)–V(1)–N(3)	94.4(3)	N(1)–V(2)–N(4)	96.0(3)
O(5)–V(1)–O(6)	79.8(2)	O(5)–V(2)–O(6)	80.5(3)
N(3)–V(1)–O(6)	90.7(3)	N(4)–V(2)–O(6)	90.9(3)
N(2)–V(1)–O(5)	91.2(3)	N(1)–V(2)–O(5)	88.8(3)
O(7)–V(1)–N(2)	92.3(3)	O(8)–V(2)–N(1)	93.2(3)
O(7)–V(1)–N(3)	93.0(3)	O(8)–V(2)–N(4)	92.7(3)
O(7)–V(1)–O(5)	102.7(3)	O(8)–V(2)–O(5)	102.9(3)
O(7)–V(1)–O(6)	102.9(3)	O(8)–V(2)–O(6)	101.8(3)
O(1)–V(1)–N(3)	79.0(3)	O(4)–V(2)–N(4)	77.8(2)
O(1)–V(1)–N(2)	79.5(3)	O(4)–V(2)–N(1)	78.6(3)
O(1)–V(1)–O(6)	86.2(2)	O(4)–V(2)–O(6)	87.9(2)
O(1)–V(1)–O(5)	86.4(2)	O(4)–V(2)–O(5)	87.6(2)
O(1)–V(1)–O(7)	168.0(3)	O(4)–V(2)–O(8)	166.6(3)
N(3)–V(1)–O(5)	163.1(3)	N(4)–V(2)–O(5)	163.4(2)
N(2)–V(1)–O(6)	163.6(3)	N(1)–V(2)–O(6)	163.1(3)
V(1)–O(5)–V(2)	99.0(3)	V(1)–O(6)–V(2)	99.7(3)
S–O(1)–V(1)	135.0(4)	S–O(4)–V(2)	133.4(4)
O(1)–S–O(4)	107.4(3)		

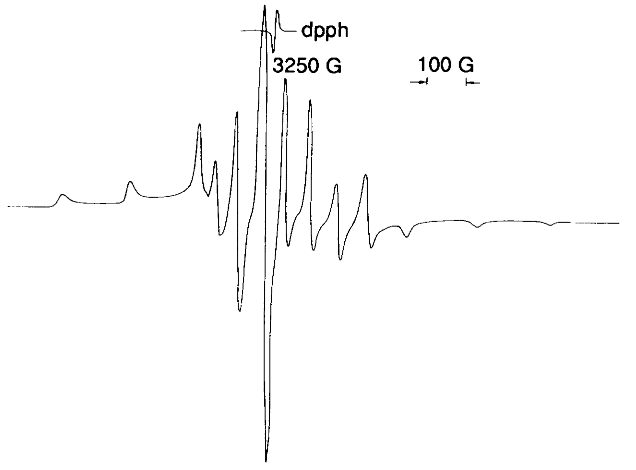

Fig. 2 The ESR spectrum of $[Zn(L)VO(SO_4)]\cdot 4H_2O$ in frozen MeOH glass at 77 K. Microwave frequency 9.109 GHz

1.28 at 293 K to 0.38 at 81 K. A good fit of data was obtained with $J = -128$ cm^{-1} and $g = 1.87$. In phenoxo, alkoxo or hydroxo bridged dimeric oxovanadium(IV) complexes, for which singlet ground states have been reported, a through space, direct overlap of d_{xy} orbitals is considered[17,18,29,35,36] as the dominant magnetic exchange pathway. Alternative pathways such as superexchange *via* $d_{x^2-y^2}$ are thought to be negligible. Despite the availability of *J* values for a fairly good number of antiferromagnetic oxovanadium(IV) complexes,[15,17,18,35–40] structure–magnetic property correlation is hampered by the paucity of structural data. Although on the basis of direct overlap of d_{xy} orbitals the extent of antiferromagnetic exchange is expected to depend approximately upon the distance between the two metal centres, the data collected in Table 4 indicate no such trend. In the four dioxovanadium(IV) complexes under consideration, while the V • • • V separation lies between 2.965 and 4.075 Å the *J* values vary between −128 and −177 cm^{-1}. However, the shortest and longest distances correspond to the two middle *J* values, while the extreme *J* values are associated with almost identical distances. It appears that aside from the distance factor, other factors such as polarizability of the donor atoms, electron density modulating behaviour of the auxiliary ligands or bridging groups and geometric distortion of the co-ordination spheres also affect subtly exchange coupling. Clearly, more work is needed in this direction. It may also be pointed out that the spin coupling in **3** is weaker compared to that observed in the dicopper(II) analogue, $[Cu_2L(ClO_4)_2]$ ($J = -412$ cm^{-1}, Cu • • • Cu 2.993 Å),[13] where superexchange occurs through $d_{x^2-y^2}$ orbitals of copper(II) and s and p orbitals of the phenoxy oxygen.

Electrochemistry.—The cyclic voltammogram of **2** (Fig. 4) shows that oxidation of $[VO(H_2L)(SO_4)]$ to $[VO(H_2L)\text{-}$

Table 3 The ESR and electronic spectral data for the complexes

				A_o	$A_{\parallel}$	$A_{\perp}$	ν_1	ν_2
Compound	g_0	$g_{\parallel}$	$g_{\perp}$	$\times 10^4$ cm^{-1}			cm^{-1}	
1	1.971 3.924							18 870
2	1.979	1.952	1.991	87	161	50	12 200	19 230
3							15 040	19 800
4	1.974	1.950	1.986	88	161	52	13 700	19 610
Bromo peroxidase *	1.969	1.948	1.979	87	160	50		

* Ref. 33.

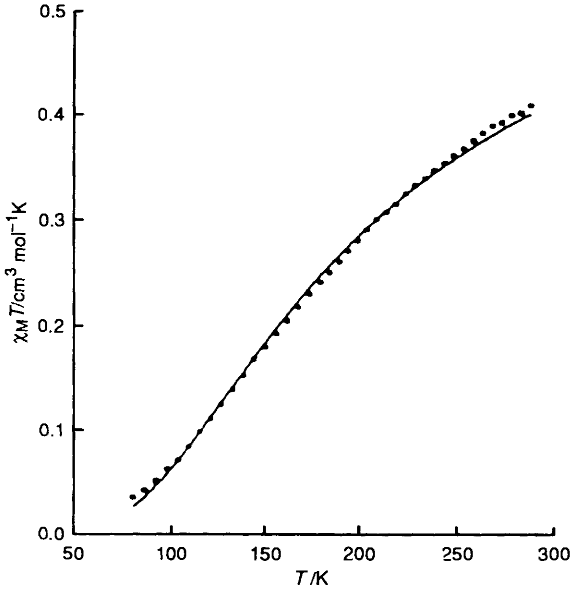

Fig. 3 Experimental (• • • •) and calculated (——) temperature dependence of $\chi_M T$ for $[(VO)_2L(\mu\text{-}SO_4)]\cdot MeOH\cdot 3H_2O$

Table 4 Variation of antiferromagnetic exchange interaction with V · · · V separation in some dinuclear oxovanadium(IV) complexes

Complex	J/cm^{-1}	V · · · V/Å	Ref.
$[(VO)_2(tpen)(\mu\text{-}OH)_2]I_2\cdot 4H_2O$ [a]	−150	2.965	29
$[(VO)_2L^1(\mu\text{-}O_2CMe)_2]I_2\cdot 2H_2O$ [b]	−144	4.075	17
$[(VO)_2(L^2)(\mu\text{-}OH)_2]Br_2$ [c]	−177	3.033	18
$[(VO)_2L(\mu\text{-}SO_4)]\cdot MeOH\cdot 3H_2O$	−128	3.077	This work
$[Cu_2L(\mu\text{-}ClO_4)_2]$	−412	2.993	13

[a] tpen = *N*,*N*,*N*′,*N*′-Tetrakis(2-pyridylmethyl)ethylenediamine. [b] L′ = 1,4,7-Trimethyl-1,4,7-triazacyclononane. [c] L^2 = 1,4,7-Triazacyclononane.

$(SO_4)]^+$ takes place reversibly at $E_{\frac{1}{2}}$ = 0.40 V *vs.* SCE. Measurements carried out at different scan rates (v = 50–500 mV s^{-1}) showed that the separation between the peak potentials remained unchanged (ΔE_p = 70 mV) and the plot of peak current *versus* $v^{\frac{1}{2}}$ was linear. It appears that co-ordination by electron-rich sulfate facilitates oxidation of oxovanadium(IV) to oxovanadium(V) at a relatively low positive potential under the same stereochemical environment. Preliminary studies revealed that a variety of redox reagents can be used to oxidize **2**. The electrochemical behaviour of the heterodinuclear complex **4** was basically similar. In this case the electron transfer occurred quasireversibly (ΔE_p = 100–120 mV, ν = 50–500 mV s^{-1}) at $E_{\frac{1}{2}}$ = 0.455 V. By contrast, the homodinuclear complex **3** did not show any electrochemical response up to +0.8 V. At more positive potentials rapid accumulation of current took place indicating decomposition of the complex.

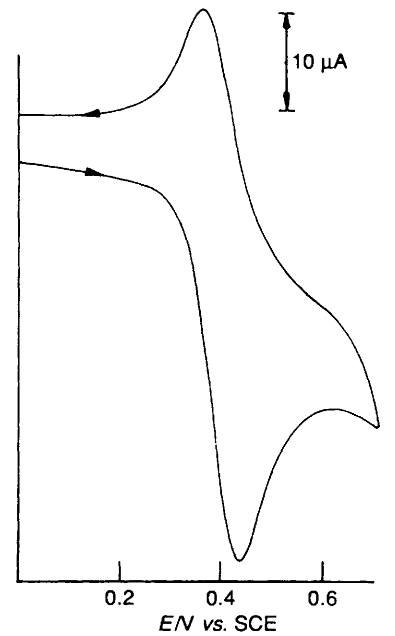

Fig. 4 Cyclic voltammogram of $[VO(H_2L)(SO_4)]\cdot 3H_2O$ in MeCN

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References

1 R. L. Robson, R. R. Eady, T. H. Richardson, R. W. Miller, M. Hawkins and J. R. Postgate, *Nature* (*London*), 1986, **322**, 388.
2 Vilter, *Phytochemistry*, 1984, **23**, 1387; E. de Boer, Y. van Kooyk, M. G. M. Tromp, H. Plat and R. Wever, *Biochim. Biophys. Acta*, 1986, **869**, 48.
3 *Vanadium in Biological Systems*, ed. N. D. Chasteen, Kluwer Academic Publishers, Dordrecht, 1990.
4 A. Butler and C. J. Carrano, *Coord. Chem. Rev.*, 1991, **109**, 61.
5 D. Rehder, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 148.
6 N. D. Chasteen, E. M. Lord, H. J. Thompson and J. K. Grandy, *Biochim. Biophys. Acta*, 1986, **884**, 84; A. Butler and H. Eckert, *J. Am. Chem. Soc.*, 1989, **111**, 2802.
7 E. M. Olta, R. C. Bruening, M. J. Smith, K. Kustin and K. Nakanishi, *J. Am. Chem. Soc.*, 1988, **110**, 6162.
8 M. J. Smith, D. Kim, B. Hornestein, K. Nakanishi and K. Kustin, *Acc. Chem. Res.*, 1991, **24**, 117.
9 A. Hills, D. L. Hughes, G. J. Leigh and J. R. Sanders, *J. Chem. Soc., Dalton Trans.*, 1991, 61, 325.
10 (*a*) C. J. Carrano, C. M. Nunn, R. Quan, J. A. Bonadies and V. L. Pecoraro, *Inorg. Chem.*, 1990, **29**, 944; (*b*) J. Kampf, M. S. Lan and V. L. Pecoraro, *Inorg. Chem.*, 1992, **31**, 2035.

11 A. Neves, A. S. Ceccato, Y. P. Mascarenhas and C. Erasmus-Buh, *J. Chem. Soc., Chem. Commun.*, 1992, 652.

12 S. K. Mandal and K. Nag, *J. Org. Chem.*, 1986, **51**, 3900.

13 S. K. Mandal, L. K. Thompson, K. Nag, J.-P. Charland and E. J. Gabe, *Inorg. Chem.*, 1987, **26**, 1391; *Can. J. Chem.*, 1987, **65**, 2815.

14 R. Das and K. Nag, *Inorg. Chem.*, 1991, **30**, 2831; K. K. Nanda, R. Das, M. J. Newlands, R. Hynes, E. J. Gabe and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1992, 897; R. Das, K. K. Nanda, K. Venkatsubramanian, P. Paul and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1992, 1253; K. K. Nanda, R. Das, K. Venkatsubramanian, P. Paul and K. Nag, *J. Chem. Soc., Dalton Trans.*, in the press.

15 A. Syamal, *Coord. Chem. Rev.*, 1975, **16**, 309; J. Selbin, *Coord. Chem. Rev.*, 1966, **1**, 293; D. Nicholls, *Coord. Chem. Rev.*, 1966, **1**, 379.

16 P. Comba, L. M. Engelhardt, J. M. Harrowfield, G. A. Lawrance, L. L. Martin, A. M. Sargeson and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1985, 174.

17 M. Koppen, G. Fresen, K. Wieghardt, R. M. Llusar, B. Nuber and J. Weiss, *Inorg. Chem.*, 1988, **27**, 721.

18 K. Wieghardt, V. Bossek, K. Volckmar, W. Swiridoff and J. Weiss, *Inorg. Chem.*, 1984, **23**, 1387.

19 J. C. Dutton, G. D. Fallon and K. S. Murray, *J. Chem. Soc., Chem. Commun.*, 1990, 64; P. Knopp, K. Wieghardt, B. Nuber, J. Weiss and W. S. Sheldrick, *Inorg. Chem.*, 1990, **29**, 363.

20 W. Prandtl and L. Hess, *Z. Anorg. Allg. Chem.*, 1913, **82**, 103.

21 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon, Oxford, 2nd edn., 1986.

22 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

23 G. M. Sheldrick, SHELX 76, *Program for Crystal Structure Determination*, University of Cambridge, 1976.

24 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

25 M. Mathew, A. J. Carty and G. H. Palenik, *J. Am. Chem. Soc.*, 1970, **92**, 3197.

26 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 3rd edn., 1978, p. 240.

27 C. K. Johnson, ORTEP II, Report ORNL-3794, revised, Oak Ridge National Laboratory, Oak Ridge, TN, 1971.

28 W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley, New York, 1988, p. 160.

29 A. Neves, K. Wieghardt, B. Nuber and J. Weiss, *Inorg. Chim. Acta*, 1988, **150**, 183.

30 H. Adams, N. A. Bailey, D. E. Fenton, M. S. L. Gonzalez and C. A. Phillips, *J. Chem. Soc., Dalton Trans.*, 1983, 371.

31 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 2nd edn., 1984, pp. 385–392.

32 R. F. Drake, V. H. Crawford, W. E. Hatfield, G. D. Simpson and G. O. Carlisle, *J. Inorg. Nucl. Chem.*, 1975, **37**, 291.

33 E. de Boer, K. Boon and R. Wever, *Biochemistry*, 1988, **27**, 1629.

34 C. O'Connor, *Prog. Inorg. Chem.*, 1979, **29**, 204.

35 A. P. Ginsberg, E. Koubeck and H. J. Williams, *Inorg. Chem.*, 1966, **5**, 1656.

36 A. Ozarowski and D. Reinen, *Inorg. Chem.*, 1986, **25**, 1704.

37 H. Okawa, I. Audo and S. Kida, *Bull. Chem. Soc., Jpn.*, 1974, **47**, 3041.

38 M. J. Heeg, J. L. Mack, M. D. Glick and R. L. Lintvedt, *Inorg. Chem.*, 1981, **20**, 833.

39 M. Julve, M. Verdaguer, M.-F. Charlot, O. Kahn and R. Claude, *Inorg. Chim. Acta*, 1984, **82**, 5.

40 J. C. Dutton, K. S. Murray and E. R. Tiekink, *Inorg. Chim. Acta*, 1989, **166**, 5.

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