

**A Macrocyclic Binuclear Vanadium(III) Complex with Di- $\mu$ -alkoxo Bridging and Pentagonal-bipyramidal Metal Co-ordination. X-Ray Crystal Structure of  $[V_2L(H_2O)_4](ClO_4)_4 \cdot 2H_2O$  ( $H_2L = 1,7,14,20$ -Tetramethyl-2,6,15,19-tetra-aza[7,7](2,6)-pyridinophane-4,7-diol)**

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The synthesis and structure of a macrocyclic binuclear vanadium(III) complex are described; complex (1) contains a planar di- $\mu$ -alkoxo bridging moiety and displays seven-co-ordinate pentagonal bipyramidal geometry around each  $V^{III}$ .

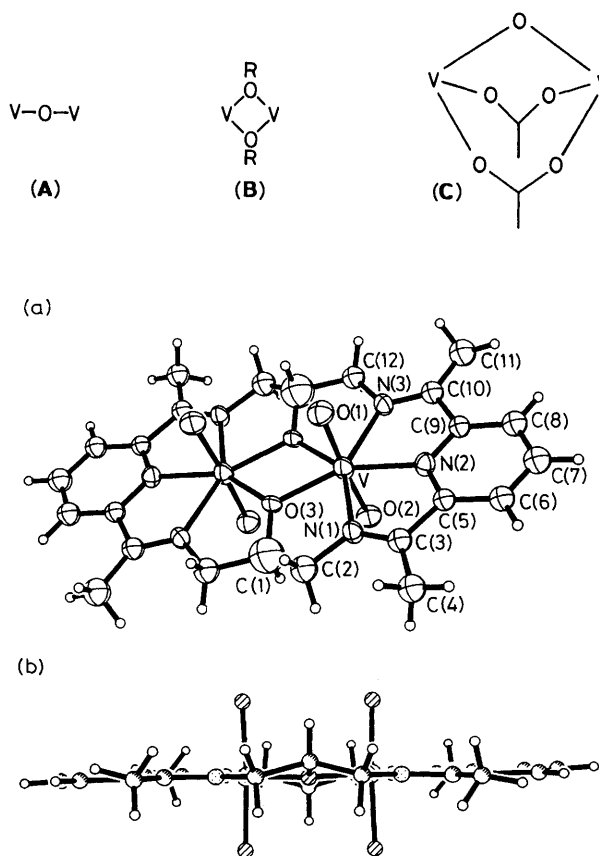
A resurgence in our interest<sup>1,2</sup> and that of other groups,<sup>3,4</sup> in vanadium chemistry has been brought about because of the recognition of vanadium in biomolecules such as marine algal bromo-peroxidases (*e.g.*, *Ascophyllum nodosum*),<sup>5,6</sup> marine ascidians,<sup>7</sup> and nitrogenase (*e.g.*, *Azobacter vinelandii*),<sup>8</sup> and in crude oils.<sup>9</sup> In order to gain an understanding of the fundamental chemistry behind these complex systems, we have embarked on a study of model systems, both mononuclear<sup>2</sup> and binuclear,<sup>10</sup> from which we aim to obtain structural, spectral, magnetic, redox, and reactivity interrelations between the oxidation states  $V^V$ ,  $V^{IV}$ , and  $V^{III}$ . Recently,<sup>10</sup> we have used open-chain binucleating ligands of type  $H_3L'$  to obtain  $\mu$ -alkoxo oxovanadium(IV) species  $[(VO)_2L'(X)]$ , where  $X = OH^-$ ,  $OR^-$ , or pyrazolate, as well as non-bridged oxovanadium(V) species  $[(VO)L']$ . The bridging alcohol fragments from 1,3-diaminopropan-2-ol or 1,5-diaminopentan-3-ol were first developed for  $[Cu_2L']^+$  complexes,<sup>11</sup> used to model type 3 Cu bio-sites. We now report a novel binuclear vanadium(III) complex of the macrocyclic Schiff-base ligand  $H_2L$ , 1,7,14,20-tetramethyl-2,6,15,19-tetra-aza[7,7](2,6)pyridinophane-4,17-diol, the latter containing two bridging alcohol groups and two 2,6-diiminopyridyl 'end' groups.

Complex (1),  $[V_2L(H_2O)_4](ClO_4)_4 \cdot 2H_2O$ , was prepared using a technique pioneered by Nelson<sup>12</sup> and developed by Fenton,<sup>13</sup> McKee,<sup>14</sup> and their co-workers, that is the transmetalation of  $[Ba(H_2L)(H_2O)_2](ClO_4)_2$  by  $VCl_3$  in methanol. After filtering off a brown precipitate, the intensely coloured mother liquor was concentrated, dissolved in water, and evaporated slowly in air to yield well formed brown crystals of (1).

The ligand  $H_2L$  presumably has a stabilizing effect for  $V^{III}$ , originating from either donor-group or geometric characteristics, since such reaction conditions would normally be expected to yield oxovanadium(IV) products. It is interesting to note that deprotonation of  $LH_2$  has occurred in the absence of added base; analogous reactions with  $Cu^{II}$  or  $Mn^{II}$  lead to partial deprotonation.<sup>13,14,15</sup>

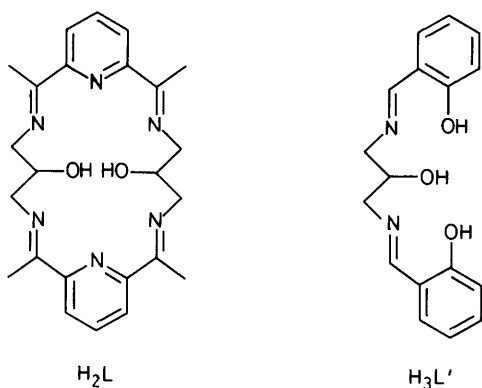
The crystal structure<sup>†</sup> of (1) shows a highly symmetrical

cation, displayed in Figure 1(a), which has a centre of inversion in the middle of the molecule, and which is surrounded by four  $ClO_4^-$  ions (not shown). The co-ordinated macrocycle is remarkably flat [Figure 1(b)], a situation which contrasts with that recently observed<sup>15</sup> in a  $Mn^{II}$  complex  $[Mn_2(HL)(Cl)_2](ClO_4)_2$ , the buckled geometry of which is no doubt related to the tetrahedral disposition of the O atom in the CHOH group present in HL. Each  $V^{III}$  in (1) has a pentagonal bipyramidal co-ordination geometry made up of two  $H_2O$  molecules in the apical positions and atoms O(3), O(3A), N(3), N(2), and N(1) of  $L^{2-}$  in the pentagonal plane, the latter atoms adopting angles at V close to the pentagonal



**Figure 1.** (a) Molecular structure of the cation  $[V_2L(H_2O)_4]^{2+}$  (1). Selected interatomic distances (Å) and angles ( $^\circ$ ): V-O(1) 2.022(6), V-O(2) 1.978(6), V-O(3) 1.992(6), V-N(1) 2.149(7), V-N(2) 2.117(8), V-N(3) 2.151(7),  $V \cdots V$  3.276(4); V-O(3)-V(A) 111.4(3), C(1)-O(3)-V 120.5(8), C(1)-O(3)-V(A) 123.4(7), O(3)-V-O(3A) 68.6(3), O(3A)-V-N(3) 73.9(3), N(3)-V-N(2) 72.1(3), N(2)-V-N(1) 71.7(3), N(1)-V-O(3) 73.8(3), O(1)-V-O(2) 176.3(3), O(1)-V-O(3) 90.4(2). (b) Side-on perspective view of (1).

<sup>†</sup> Crystal data for (1):  $C_{24}H_{40}Cl_4N_6O_{24}V_2$ , brown, crystal dimensions  $0.20 \times 0.14 \times 0.10$  mm, monoclinic,  $a = 10.773(4)$ ,  $b = 13.189(5)$ ,  $c = 14.072(6)$  Å,  $\beta = 104.78(3)^\circ$ ,  $U = 1933(1)$  Å<sup>3</sup>, space group  $P2_1/n$ ,  $Z = 2$ ,  $F(000) = 1064$ . Using  $1.40^\circ$   $\omega$ -scans at a scan rate between 3.00 and  $15.63^\circ \text{ min}^{-1}$  at 295 K, 3390 reflections were collected with  $3.5 < 2\theta < 50^\circ$ ; of these, 1743 which were unique and had  $F > 6\sigma(F)$  were used in the analysis. The data were collected on a Nicolet-R3m/V diffractometer using Mo- $K_\alpha$  radiation. The data set was corrected for Lorentz and polarization effects; a numerical absorption correction was applied. The structure was solved by direct methods. The refinement converged with  $R = 0.074$ ,  $R_w = 0.074$ . All calculations were performed on a MICROVAX 2000 computer using the least-squares refinement program SHELXTL.PLUS Revision 3.4 (Siemens Inc., 1988). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



value of  $\sim 72^\circ$ . This 7-co-ordinate geometry is not unknown for  $V^{III}$  although 6-co-ordination is normally preferred.<sup>16</sup> The apical V–O bond lengths are similar to the in-plane V–O lengths. Pertinent bridging features include a coplanar  $V_2(OR)_2$  group, V  $\cdots$  V distance of 3.276(4) Å and V–O(3)–V(A) angle of  $111.4(3)^\circ$ .

Examples of an O-donor bridging group within binuclear  $V^{III}$  complexes are still somewhat rare. The present edge-shared di- $\mu$ -alkoxo bridge (**B**) complements other recently discovered bridging modes such as corner-shared  $\mu$ -oxo (**A**)<sup>4,17,18</sup> and face-shared  $\mu$ -oxo-di- $\mu$ -carboxylato<sup>19</sup> (**C**).

The room temperature magnetic moment of (**1**) is  $1.97 \mu_B$ , per V, which is significantly reduced from the non-coupled value of  $2.83 \mu_B$ . Variable temperature measurements, which are in progress, will quantify the size of antiferromagnetic coupling. The trigonal-planar alkoxo O atoms (solid angle  $356^\circ$ ) are well set up to transmit exchange-coupling between the  $V^{III}$  ions. However, the symmetry of the 'magnetic orbitals' employed by V in  $D_{5h}$  symmetry is  $E_1''$  ( $d_{xz}^1, d_{yz}^1$  assuming V–OH<sub>2</sub> is the z-direction) which would be expected to give poor overlap with the oxygen  $sp^2$ -like orbitals and consequently should give weak exchange-coupling. This was found to be the case in a related di- $\mu$ -alkoxo bridged  $V^{III}$ –EDTA-like (EDTA = ethylenediamine tetra-acetic acid) dimer,<sup>20</sup> in which  $\mu_V = 2.75 \mu_B$ , and in a di- $\mu$ -phenoxo bridged  $V^{III}$ –acac (acac = pentane-2,4-dionato) dimer.<sup>21</sup> Complex (**1**) would appear, at this stage, to be more strongly coupled.

Studies are also in progress on the solution properties of (**1**) and on oxovanadium(IV) complexes of  $H_2L$ .

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