A Macrocyclic Binuclear Vanadium(III) Complex with Di-μ-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)

Jennifer C. Dutton, Gary D. Fallon, and Keith S. Murray*

Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia

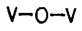
The synthesis and structure of a macrocyclic binuclear vanadium(III) complex are described; complex (**1**) contains a planar di-μ-alkoxo bridging moiety and displays seven-co-ordinate pentagonal bipyramidal geometry around each V^{III}.

A resurgence in our interest[1,2] and that of other groups,[3,4] 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*),[5,6] marine ascidians,[7] and nitrogenase (*e.g., Azobacter vinelandii*),[8] and in crude oils.[9] 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[2] and binuclear,[10] 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,[10] we have used open-chain binucleating ligands of type H_3L' to obtain μ-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,[11] 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.

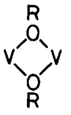
Complex (**1**), $[V_2L(H_2O)_4](ClO_4)_4 \cdot 2H_2O$, was prepared using a technique pioneered by Nelson[12] and developed by Fenton,[13] McKee,[14] and their co-workers, that is the transmetallation of $[Ba(H_2L)(H_2O)_2](ClO_4)_2$ by VCl_3 in methanol. After filtering off a brown precipitate, the 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.[13,14,15]

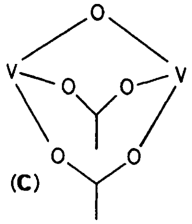
The crystal structure† of (**1**) shows a highly symmetrical cation, displayed in Figure 1(a), which has a centre of inversion in the middle of the molecule, and which is surrounded by four ClO_4^- ions (not shown). The co-ordinated macrocycle is remarkably flat [Figure 1(b)], a situation which contrasts with that recently observed[15] in a Mn^{II} complex $[Mn_2(HL)(Cl)_2]_2(ClO_4)_2$, 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



(A)



(B)



(C)

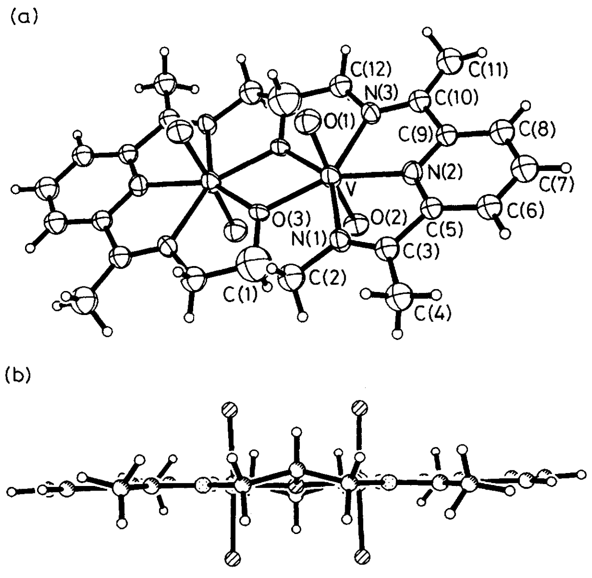
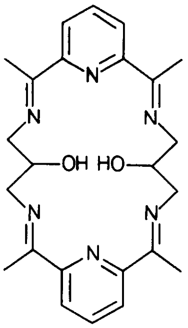


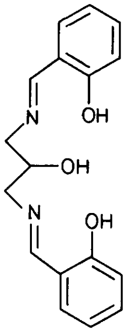
Figure 1. (a) Molecular structure of the cation $[V_2L(H_2O)_4]^{2+}$ (**1**). Selected interatomic distances (Å) and angles (°): V–O(1) 2.022(6), V–O(2) 1.978(6), V–O(3) 1.992(6), V–N(1) 2.149(7), V–N(2) 2.117(8), V–N(3) 2.151(7), V · · · V 3.276(4); V–O(3)–V(A) 111.4(3), C(1)–O(3)–V 120.5(8), C(1)–O(3)–V(A) 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**).

---

† *Crystal data* for (**1**): $C_{24}H_{40}Cl_4N_6O_{24}V_2$, brown, crystal dimensions 0.20 × 0.14 × 0.10 mm, monoclinic, a = 10.773(4), b = 13.189(5), c = 14.072(6) Å, β = 104.78(3)°, U = 1933(1) Å^3, space group $P2_1/n$, Z = 2, $F(000)$ = 1064. Using 1.40° ω-scans at a scan rate between 3.00 and 15.63° min^{-1} at 295 K, 3390 reflections were collected with $3.5 < 2\theta < 50°$; 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_α 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.



H_2L



H_3L'

value of ~72°. This 7-co-ordinate geometry is not unknown for V^{III} although 6-co-ordination is normally preferred.[16] 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 · · · V distance of 3.276(4) Å and V–O(3)–V(A) angle of 111.4(3)°.

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

The room temperature magnetic moment of (**1**) is 1.97 μ_B, per V, which is significantly reduced from the non-coupled value of 2.83 μ_B. Variable temperature measurements, which are in progress, will quantify the size of antiferromagnetic coupling. The trigonal-planar alkoxo O atoms (solid angle 356°) 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 $V{-}OH_2$ 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-μ-alkoxo bridged V^{III}–EDTA-like (EDTA = ethylenediamine tetra-acetic acid) dimer,[20] in which $\mu_V = 2.75\ \mu_B$, and in a di-μ-phenoxo bridged V^{III}–acac (acac = pentane-2-4-dionato) dimer.[21] 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.

Received, 14th September 1989; Com. 9/03941D

References

1 D. J. Machin and K. S. Murray, *J. Chem. Soc. A,* 1967, 1330; 1498.
2 J. C. Dutton, G. D. Fallon, and K. S. Murray, *Inorg. Chem.*, 1988, **27**, 34.
3 C. Floriani, *Polyhedron,* 1989, **8**, 1717, and references cited therein.
4 G. Christou, D. Heinrich, J. K. Money, J. R. Rambo, J. C. Huffmann, and K. Folting, *Polyhedron,* 1989, **8**, 1723, and references cited therein.
5 E. de Boer, K. Boon, and R. Wever, *Biochemistry,* 1988, **27**, 1629.
6 H. Vilter, *Phytochemistry,* 1984, **23**, 1387.
7 N. D. Chasteen, *Struct. Bonding* (*Berlin*), 1983, **53**, 105.
8 R. R. Eady, *Polyhedron,* 1989, **8**, 1695, and references cited therein.
9 J. G. Reynolds, E. T. Gallegos, R. H. Fish, and J. J. Komlenic, *Energy Fuels,* 1987, **1**, 36.
10 J. C. Dutton, K. S. Murray, and E. R. T. Tiekink, *Inorg. Chim. Acta*, 1989, **166**, 5.
11 W. Mazurek, K. J. Berry, K. S. Murray, M. J. O'Connor, M. R. Snow, and A. G. Wedd, *Inorg. Chem.*, 1982, **21**, 3071.
12 S. M. Nelson, *Inorg. Chim. Acta,* 1982, **62**, 39; *Pure Appl. Chem.*, 1980, **52**, 2461.
13 N. A. Bailey, D. E. Fenton, I. T. Jackson, R. Moody, and C. Rodriguez de Barbarin, *J. Chem. Soc., Chem. Commun.*, 1983, 1463; N. A. Bailey, D. E. Fenton, R. Moody, C. O. Rodriguez de Barbarin, I. N. Sciambarella, J. M. Latour, D. Limosin, and V. McKee, *J. Chem. Soc., Dalton Trans.*, 1987, 2519.
14 V. McKee and J. Smith, *J. Chem. Soc., Chem. Commun.*, 1983, 1465.
15 S. Brooker and V. McKee, *J. Chem. Soc., Chem. Commun.*, 1989, 619.
16 C. E. Holloway and M. Melnik, *Rev. Inorg. Chem.*, 1985, **1**, 75.
17 C. J. Hawkins, private communication on $[\{V(bipy)_2Cl\}_2O]^{2+}$ (bipy = bipyridine).
18 P. Chandrasekhar and P. H. Bird, *Inorg. Chem.*, 1984, **23**, 3677.
19 M. Köpper, G. Fresen, K. Wieghardt, R. M. Llusar, B. Nuber, and J. Weiss, *Inorg. Chem.*, 1988, **27**, 721.
20 R. E. Shepherd, W. E. Hatfield, D. Ghosh, C. D. Stout, F. J. Kristine, and J. R. Ruble, *J. Am. Chem. Soc.*, 1981, **103**, 5511.
21 S. Lee, K. Nakanishi, M. Y. Chiang, R. B. Frankel, and K. Spartalian, *J. Chem. Soc., Chem. Commun.*, 1988, 785.