

Structure of Bis(tetramethylammonium) Aquadioxotetraperoxodivanadate(V) Dihydrate

BY ANDREY E. LAPSHIN, YURY I. SMOLIN AND YURY F. SHEPELEV

Institute of Silicate Chemistry, Academy of Sciences of the USSR, 199 034 Leningrad, USSR

DALMA GYEPESOVA

Institute of Inorganic Chemistry, Centre for Chemical Research, Slovak Academy of Sciences, 842 36 Bratislava, Czechoslovakia

AND PETER SCHWENDT

Department of Inorganic Chemistry, Comenius University, 842 15 Bratislava, Czechoslovakia

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Abstract. $[\text{N}(\text{CH}_3)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$, $M_r = 464.28$, monoclinic, Cc , $a = 15.676$ (5), $b = 8.615$ (5), $c = 15.472$ (5) Å, $\beta = 109.25$ (1)°, $V = 1972.7$ Å³, $Z = 4$, $D_x = 1.56$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 10.7$ cm⁻¹, $F(000) = 968$, $T = 295$ K, $R = 0.024$ for 1511 unique reflections. The structure consists of $[\text{V}_2\text{O}_2(\text{O}_2)_4(\text{H}_2\text{O})]^{2-}$ anions, tetramethylammonium groups and molecules of water. The core of the structure is a dimeric diperoxo complex of V^V atoms with purely inorganic ligands. The ligands form a pentagonal pyramid around each V atom. This structure is the first example of a peroxovanadate complex with chemically nonequivalent coordination polyhedra about the V atoms.

Introduction. Peroxo complexes of transition metals are attracting attention because of their important role in catalysis and biological processes. Because of their instability, only three dimeric peroxovanadate structures have been determined by single-crystal X-ray methods: $(\text{NH}_4)_4[\text{O}\{\text{VO}(\text{O}_2)_2\}_2]$ (Stomberg, Olson & Svensson, 1984), $(\text{Hbpy})[\text{H}\{\text{VO}(\text{O}_2)_2\text{-bpy}\}_2] \cdot x\text{H}_2\text{O} \cdot (6-x)\text{H}_2\text{O}$, $x \approx 0.5$ (Szentivanyi & Stomberg, 1984) and $(\text{NH}_4)_3[\text{HO}\{\text{VO}(\text{O}_2)_2\}_2] \cdot \text{H}_2\text{O}$ (Campbell, Flanagan, Griffith & Skapski, 1985). All previously known dimeric peroxo complexes of Group 5 transition metals are characterized by the chemically equivalent coordination polyhedra of transition-metal atoms within each dimeric complex.

Experimental. Crystal selected from a sample prepared by dissolving of 0.91 g (5 mmol) V_2O_5 in 9 cm³ of a 10% solution of $\text{N}(\text{CH}_3)_4\text{OH}$. After filtration and evaporation of the solvent in a water bath, the solid vanadate was dissolved in 3 cm³ of 30% H_2O_2 and 10 cm³ ethanol was added to the solution. After 3 months at 245 K, yellow crystals could be isolated;

they were washed with ethanol and stored at 245 K in a desiccator with silica gel. To prevent decomposition in air at room temperature the crystal, dimensions $0.4 \times 0.08 \times 0.2$ mm, was coated with copal resin. Intensity data were recorded using an automatic three-circle single-crystal X-ray diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation. Unit-cell parameters from 14 reflections ($8 < \theta < 26^\circ$). The ω - 2θ scan method was used; the profiles were analysed with a modified Oatley & French (1982) procedure. Data were collected for $2\theta \leq 75^\circ$. One control reflection, monitored every 30 reflections, showed no significant variation in intensity. 1686 reflections measured, 1511 unique reflections having $I \geq 4\sigma(I)$ were used in the analysis; index range: $-21 \leq h \leq 19$, $0 \leq k \leq 14$, $0 \leq l \leq 14$. Values of I were corrected for Lorentz, polarization and absorption effects, the latter with *DIFABS* empirical absorption correction (Walker & Stuart, 1983); transmission coefficients varied from 0.759 to 1.301. The coordinates of the V atoms were found from a Patterson map and all non-H and H atoms were located in subsequent difference Fourier maps. Calculations were carried out on a BESM-6 computer using the locally modified crystallographic program system *RENTGEN-75* (Andrianov, Safina & Tarnopolsky, 1974). All parameters [layer scale factors, atomic coordinates and anisotropic (H atoms isotropic) thermal parameters] were refined by full-matrix least squares using *ORFLS* (Busing, Martin & Levy, 1962). The function $\sum w(|F_o| - |F_c|)^2$ was minimized with $w = (a + |F_o| + b|F_o|^2)^{-1}$, where $a = 2|F_o|_{\text{max}}$, $b = 2|F_o|_{\text{max}}^{-1}$. Final $R = 0.024$, $wR = 0.030$, $(\Delta/\sigma)_{\text{max}} = 0.002$, $(\Delta\rho)_{\text{max}} = 0.23$ e Å⁻³. The equivalent isotropic thermal parameters of water O atoms were used as B_{iso} 's for the corresponding H atoms. They were not refined. The average values over all equivalent

Table 1. *Positional and isotropic thermal parameters*
For non-H atoms, $B_{eq} = [\text{Det}(B_{ij})]^{1/3} [4\text{Det}(a_i^* a_j^*)]^{-1/3}$; B_{iso} values are given for H atoms.

	x	y	z	$B_{eq}/B_{iso}(\text{\AA}^2)$
V(1)	0.04668	0.13715 (5)	0.85488	1.01
V(2)	-0.04156 (4)	0.17642 (6)	0.64355 (5)	1.43
O(1)	0.1411 (2)	0.2726 (4)	0.9134 (3)	2.58
O(2)	0.0552 (3)	0.3523 (3)	0.8687 (3)	2.72
O(3)	0.1298 (2)	-0.0104 (4)	0.8409 (3)	2.42
O(4)	0.0389 (2)	-0.0314 (3)	0.7757 (3)	1.97
O(5)	0.0080 (2)	0.0705 (4)	0.9312 (3)	2.24
O(6)	-0.0689 (2)	0.2053 (4)	0.7546 (3)	2.16
O(7)	-0.1196 (2)	0.0814 (5)	0.6957 (3)	2.63
O(8)	0.0708 (3)	0.1561 (4)	0.6256 (3)	2.34
O(9)	0.0739 (2)	0.2548 (4)	0.7039 (3)	2.35
O(10)	-0.0952 (3)	0.3132 (5)	0.5793 (3)	3.37
O(11)	-0.0774 (2)	-0.0001 (4)	0.5518 (2)	2.09
O(12)	0.7538 (2)	0.0453 (4)	0.9557 (3)	2.57
O(13)	0.1744 (3)	0.1984 (5)	0.5013 (3)	3.54
N(1)	0.3658 (3)	0.1431 (4)	0.8245 (3)	2.04
N(2)	0.6300 (3)	0.1576 (4)	0.6549 (3)	1.57
C(1)	0.3430 (4)	-0.0019 (6)	0.8654 (5)	3.27
C(2)	0.4636 (3)	0.1788 (6)	0.8747 (6)	2.79
C(3)	0.3504 (6)	0.1192 (10)	0.7271 (6)	4.74
C(4)	0.3114 (4)	0.2744 (7)	0.8413 (5)	3.53
C(5)	0.6634 (4)	0.1262 (6)	0.7550 (4)	2.60
C(6)	0.6705 (4)	0.3048 (5)	0.6370 (4)	2.55
C(7)	0.5292 (3)	0.1725 (6)	0.6221 (5)	3.23
C(8)	0.6556 (4)	0.0256 (5)	0.6066 (4)	2.31
H(1)	-0.057 (4)	0.003 (7)	0.503 (5)	2.09
H(2)	-0.123 (4)	-0.100 (8)	0.535 (5)	2.09
H(3)	0.715 (5)	-0.045 (8)	0.955 (6)	2.57
H(4)	0.740 (5)	0.121 (9)	0.968 (6)	2.57
H(5)	0.147 (6)	0.179 (10)	0.551 (6)	3.54
H(6)	0.166 (5)	0.147 (9)	0.451 (6)	3.54

Table 2. *Main interatomic distances (Å), bond angles (°), and hydrogen-bond geometry (Å, °) for [V₂O₂(O₂)₄(H₂O)]²⁻*

V(1)—O(1)	1.868 (3)	V(2)—O(6)	1.919 (4)				
V(1)—O(2)	1.865 (3)	V(2)—O(7)	1.863 (4)				
V(1)—O(3)	1.883 (4)	V(2)—O(8)	1.880 (4)				
V(1)—O(4)	1.878 (3)	V(2)—O(9)	1.868 (3)				
V(1)—O(5)	1.601 (4)	V(2)—O(10)	1.591 (4)				
V(1)—O(6)	2.045 (3)	V(2)—O(11)	2.030 (4)				
O(1)—O(2)	1.466 (5)	O(6)—O(7)	1.458 (5)				
O(3)—O(4)	1.460 (4)	O(8)—O(9)	1.468 (5)				
O(1)—V(1)—O(2)	46.2 (2)	O(6)—V(2)—O(7)	45.3 (2)				
O(1)—V(1)—O(3)	90.6 (2)	O(6)—V(2)—O(8)	129.9 (2)				
O(1)—V(1)—O(4)	132.1 (2)	O(6)—V(2)—O(9)	88.4 (2)				
O(1)—V(1)—O(5)	107.4 (2)	O(6)—V(2)—O(10)	103.6 (2)				
O(1)—V(1)—O(6)	123.4 (2)	O(6)—V(2)—O(11)	129.2 (2)				
O(2)—V(1)—O(3)	131.1 (2)	O(7)—V(2)—O(8)	143.6 (2)				
O(2)—V(1)—O(4)	146.1 (2)	O(7)—V(2)—O(9)	127.5 (2)				
O(2)—V(1)—O(5)	107.6 (2)	O(7)—V(2)—O(10)	108.0 (2)				
O(2)—V(1)—O(6)	79.3 (2)	O(7)—V(2)—O(11)	84.5 (2)				
O(3)—V(1)—O(4)	45.7 (2)	O(8)—V(2)—O(9)	46.1 (2)				
O(3)—V(1)—O(5)	106.7 (2)	O(8)—V(2)—O(10)	107.7 (2)				
O(3)—V(1)—O(6)	125.4 (2)	O(8)—V(2)—O(11)	83.3 (2)				
O(4)—V(1)—O(5)	104.2 (2)	O(9)—V(2)—O(10)	105.6 (2)				
O(4)—V(1)—O(6)	82.9 (2)	O(9)—V(2)—O(11)	128.3 (2)				
O(5)—V(1)—O(6)	101.9 (2)	O(10)—V(2)—O(11)	98.7 (2)				
O(11)—H(1)—O(5 ⁱ)	0.91 (8)	H...O	1.85 (8)	O—H...O	153 (6)	O—O	2.699 (6)
O(11)—H(2)—O(12 ⁱⁱ)	1.09 (7)		1.97 (6)		113 (5)		2.603 (4)
O(12)—H(3)—O(1 ⁱⁱⁱ)	0.98 (8)		1.93 (7)		161 (8)		2.882 (5)
O(12)—H(4)—O(13 ^{iv})	0.73 (8)		2.02 (8)		166 (8)		2.738 (6)
O(13)—H(5)—O(8)	1.01 (10)		1.92 (10)		168 (6)		2.920 (7)
O(13)—H(6)—O(3 ⁱ)	0.87 (9)		1.99 (9)		171 (9)		2.852 (6)

Symmetry code: (i) $x, -y, z - \frac{1}{2}$; (ii) $x - 1, -y, z - \frac{1}{2}$; (iii) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (iv) $x + \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$.

isotropic thermal parameters of C atoms were used as B_{iso} 's for the H atoms in the tetramethylammonium ions and were not refined. Scattering factors for neutral atoms were taken from Hanson, Herman, Lea & Skillman (1964).

Discussion. Table 1 lists final atomic parameters; the main interatomic distances and bond angles for $[\text{V}_2\text{O}_2(\text{O}_2)_4(\text{H}_2\text{O})]^{2-}$ are given in Table 2.* Fig. 1 shows a projection of the atomic arrangement on the xz plane. The structure consists of dinuclear $[\text{V}_2\text{O}_2(\text{O}_2)_4(\text{H}_2\text{O})]^{2-}$ complexes linked to $\text{N}(\text{CH}_3)_4^+$ groups by anion-cation contacts. Neighbouring complexes are connected to each other by hydrogen bonds through water molecules. The geometry of the hydrogen bonds is reported in Table 2. The complex forming the core of the structure is shown in Fig. 2. Each V atom of the complex is six-coordinated in a pentagonal-pyramidal way, V(1) by three peroxo ligands: O(1)—O(2) and O(3)—O(4) act as bidentate

* Lists of structure factors, anisotropic thermal parameters, and H-atom parameters, bond distances and angles for the $\text{N}(\text{CH}_3)_4^+$ groups have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51922 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

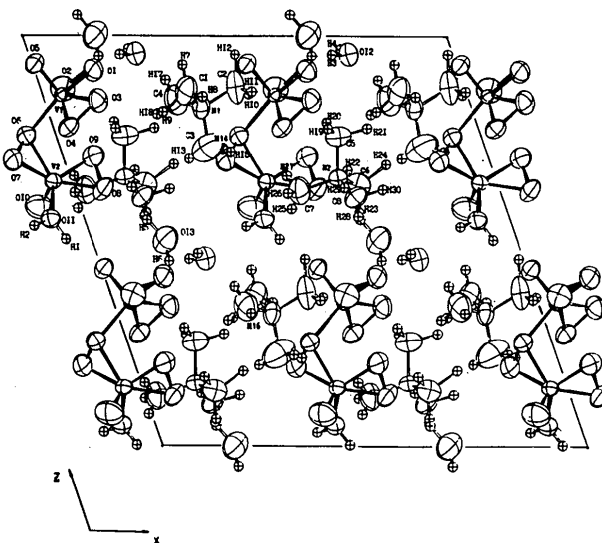


Fig. 1. Projection of the atomic arrangement of $[\text{N}(\text{CH}_3)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4(\text{H}_2\text{O})].2\text{H}_2\text{O}$ on the xz plane.

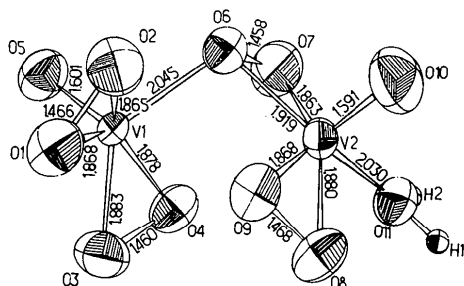


Fig. 2. The $[\text{V}_2\text{O}_2(\text{O}_2)_4(\text{H}_2\text{O})]^{2-}$ complex. Thermal ellipsoids are drawn at the 50% probability level; H atoms are represented by spheres of arbitrary size.

ligands and O(6)—O(7) as a monodentate ligand. The sixth ligand atom is the terminal O(5) oxide ion. On the other hand, V(2) is connected to two bidentate peroxy ligands O(6)—O(7) and O(8)—O(9), a water O(11) and a terminal O(10) oxide ion. Therefore, the coordination polyhedra of the two V atoms in $[V_2O_2(O_2)_4(H_2O)]^{2-}$ are not equivalent. This is the first crystal structure study of a dimeric peroxovanadate which has non-equivalent V-atom coordination polyhedra within the complex. As mentioned above, each coordination polyhedron can be described as a pentagonal pyramid. The basal planes of the pentagonal pyramids about V(1) and V(2) consist of O(1), O(2), O(3), O(4) and O(6) (the maximum deviation from planarity is 0.026 Å) and O(6), O(7), O(8), O(9) and O(11) (maximum deviation 0.114 Å), respectively. The O(5) apical atom of the V(1) pyramid is located 2.108 Å above the basal plane and the O(10) apical atom of the V(2) pyramid 2.068 Å below the basal plane. Both the V(1) and V(2) atoms are moved (0.509 and 0.479 Å, respectively) from the basal plane towards the apical O atom. The range of the V—O_{basal} distances, 1.863–2.045 Å, indicates that they are normal single bonds, while the V—O_{apical} bonds, 1.601 (4) and 1.591 (4) Å, are double bonds (Stomberg, 1984). The angle V(1)—O(6)—V(2) is 103.8 (2)° and the dihedral angle between the basal planes of connected pyramids is 60.8°. The peroxy—oxygen bond distances are in the range 1.458 (5)–1.468 (5) Å. The shortest nonbonded V—O

distances, $d[V(1)—O(9)] = 2.707$ (4) and $d[V(2)—O(4)] = 2.697$ (3) Å, may indicate a tendency for both V atoms to attain the pentagonal-bipyramidal coordination. The angle O(5)—V(1)—O(9) is 167.6 (2)° and O(10)—V(2)—O(4) is 169.6 (2)°. The apical atoms O(9) and O(4) are located 2.156 and 2.158 Å from the 'equatorial' planes.

There are two non-equivalent tetramethylammonium groups per unit cell. The N—C bond lengths are in the range 1.461–1.505 Å and the C—N—C angles vary between 107.3 and 112.2°. The average N—C distance and C—N—C angle are 1.489 Å and 109.47°, respectively.

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Euchroite, a Heteropolyhedral Framework Structure

BY RAY K. EBY* AND FRANK C. HAWTHORNE

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

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Abstract. $Cu_2(AsO_4)(OH).3H_2O$, $M_r = 337.1$, orthorhombic, $P2_12_12_1$, $a = 10.056$ (2), $b = 10.506$ (2), $c = 6.103$ (2) Å, $V = 644.8$ (2) Å³, $Z = 4$, $D_x = 3.47$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 122$ cm⁻¹, $F(000) = 648$, $T = 297$ K, $R = 0.027$ for 1061 observed reflections. The structure is a fairly open heteropolyhedral framework consisting of edge-sharing chains of octahedrally coordinated Cu^{2+} cations that are cross-linked by sharing corners with

arsenate tetrahedra. Both unique octahedra show axial Jahn–Teller-type distortions, the direction of which can be predicted from the polyhedral connectivity of the structure. The resulting arrangement is basically close-packed, but has a commensurate modulation along [010].

Introduction. Underestimation of the coordination number of Cu^{2+} has often obscured the relationships between structures, particularly those involving Cu^{2+} and non- Cu^{2+} oxyanions. In particular, common structural elements [structure modules in the hierarchical scheme of Hawthorne (1983, 1985a, 1986a)]

* Present address: Department of Geological Sciences, University of New Mexico, Albuquerque, New Mexico 87131, USA.