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Structure of Dipotassium Aquadioxotetraperoxodivanadate(V) Trihydrate

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(*Received* 2 *May* 1989; *accepted* 10 *August* 1989)

Abstract. $K_2[V_2O_2(O_2)_4(H_2O)].3H_2O$, $M_r = 412{\cdot}4$, triclinic, $P1$, $a = 6{\cdot}501$ (3), $b = 7{\cdot}882$ (3), $c = 7{\cdot}501$ (3) Å, $\alpha = 107{\cdot}18$ (5), $\beta = 95{\cdot}50$ (5), $\gamma = 116{\cdot}20$ (5)°, $V = 317{\cdot}8$ Å^3, $Z = 1$, $D_x = 2{\cdot}15$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 22{\cdot}59$ cm^{-1}, $F(000) = 204$, $T = 153$ K, $R = 0{\cdot}026$ for 1966 unique reflections. The core of the structure is a dimeric diperoxo complex of V^V atoms with purely inorganic ligands, $[V_2O_2(O_2)_4(H_2O)]^{2-}$. The coordination polyhedron of each V atom can be described as a pentagonal pyramid. Within the dimeric peroxo complex the coordination polyhedra are chemically non-equivalent and are connected to each other by sharing one O atom of the peroxo group. In the structure there is a hydrogen-bond network including O atoms of complexes and water molecules.

Introduction. Up to now, the structures of only four dimeric peroxovanadates have been determined by the single-crystal X-ray method: $(NH_4)_4[O\{VO(O_2)_2\}_2]$ (Stomberg, Olson & Svensson, 1984), $(Hbpy)[H\{VO(O_2)_2bpy\}_2].xH_2O_2.(6-x)H_2O$, $x \simeq 0{\cdot}5$ (Szentivanyi & Stomberg, 1984), $(NH_4)_3[HO\{VO(O_2)_2\}_2].H_2O$ (Campbell, Flanagan, Griffith & Skapski, 1985) and $[N(CH_3)_4]_2[V_2O_2(O_2)_4(H_2O)].2H_2O$ (Lapshin, Smolin, Shepelev, Gyepesova & Schwendt, 1989). It may be noted here that the anion composition of the latter peroxovanadate represents an analogue of that in the title compound. As part of our study of peroxovanadates, we have carried out the structural study of the present compound which provides information on the influence of the cation on the configuration of the complex anion.

Experimental. A crystal suitable for X-ray crystallography was selected from a sample prepared by dissolving 1·38 g (10 mmol) KVO_3 in 15 cm^3 of 15% H_2O_2 at 273 K. Then 8 cm^3 ethanol and several drops of H_2SO_4 solution (1 mol dm^{-3}) were added to the solution. After three months at 245 K, yellow crystals could be isolated; they were washed with ethanol and stored at 245 K in a desiccator. To prevent decomposition of the crystal investigated, dimensions 0·35 × 0·30 × 0·45 mm, the data were collected at $T = 153$ K by using a nitrogen gas stream cooling device. Reflection data were recorded using an automatic three-circle normal-beam single-crystal X-ray diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Unit-cell parameters from 14 reflections ($14 < \theta < 33°$). Intensity data were collected with the ω–2θ scan method; integrated intensity values were obtained with the modified Oatley & French (1982) profile analysis procedure. Data were collected for $2\theta < 81°$. One control reflection, monitored every 30 reflections, showed no significant variation in intensity. 2408 reflections measured, 1966 unique reflections having $I > 4\sigma(I)$ were used in the analysis; index range: $-11 \le h \le 11$, $-14 \le k \le 13$, $0 \le l \le 6$. Values of I were corrected for Lorentz and polarization effects, no absorption corrections were applied. V atoms were located by Patterson methods and all non-H atoms and H atoms were located in successive difference Fourier syntheses. Calculations were carried out on a BESM-6 computer using the locally modified crystallographic program system *RENTGEN*-75 (Andrianov, Safina & Tarnopolsky, 1974). Seven

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Table 1. *Positional and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

B_{iso} values are given for H atoms.

$$B_{eq} = [\mathrm{Det}(\beta_{ik})]^{1/3}[\tfrac{1}{4}\mathrm{Det}(a_i^*a_k^*)]^{-1/3}.$$

	x	y	z	B_{eq}/B_{iso}(Å^2)
V(1)	0·4072 (2)	0·8758 (2)	0·7591 (2)	0·84 (2)
V(2)	0·2482 (2)	0·5749 (1)	0·9630 (2)	0·99 (2)
K(1)	0	0	0	1·77 (3)
K(2)	0·6284 (2)	0·4436 (2)	0·5619 (2)	1·82 (4)
O(1)	0·2709 (5)	0·9675 (5)	0·6635 (5)	1·8 (1)
O(2)	0·4033 (4)	0·9578 (4)	1·0188 (4)	1·4 (1)
O(3)	0·6294 (4)	1·0867 (4)	0·9866 (5)	1·6 (1)
O(4)	0·4427 (4)	0·6950 (4)	0·5456 (5)	1·7 (1)
O(5)	0·6565 (4)	0·8968 (4)	0·6402 (5)	1·7 (1)
O(6)	0·1288 (4)	0·6060 (4)	0·7334 (5)	1·4 (1)
O(7)	0·0016 (4)	0·6244 (4)	0·8835 (5)	1·6 (1)
O(8)	0·5361 (4)	0·6587 (4)	0·8924 (5)	1·3 (1)
O(9)	0·5688 (4)	0·6994 (4)	1·0985 (5)	1·6 (1)
O(10)	0·1346 (5)	0·3353 (4)	0·9029 (6)	2·4 (1)
O(11)	0·1927 (5)	0·6579 (5)	1·2245 (5)	1·7 (1)
O(12)	0·7097 (5)	0·1273 (4)	0·4171 (5)	2·0 (1)
O(13)	0·7386 (5)	0·4767 (4)	0·2144 (5)	1·9 (1)
O(14)	0·1547 (7)	0·1496 (13)	0·3995 (9)	4·3 (2)
H(1)	0·28 (1)	0·64 (1)	1·32 (1)	1·7
H(2)	0·05 (1)	0·60 (1)	1·23 (1)	1·7
H(3)	0·70 (1)	0·04 (1)	0·51 (1)	2·0
H(4)	0·64 (1)	0·13 (1)	0·33 (1)	2·0
H(5)	0·66 (1)	0·33 (1)	0·11 (1)	1·9
H(6)	0·65 (1)	0·52 (1)	0·18 (1)	1·9
H(7)	0·15 (2)	0·23 (2)	0·41 (2)	4·3
H(8)	0·09 (2)	0·02 (2)	0·34 (2)	4·3

Table 2. *Selected interatomic distances* (Å), *bond angles* (°) *and hydrogen-bond geometry* (Å,°) *for* $K_2[V_2O_2(O_2)_4(H_2O)].3H_2O$

V(1)—O(1)	1·604 (5)	V(2)—O(6)	1·947 (4)
V(1)—O(2)	1·869 (4)	V(2)—O(7)	1·894 (4)
V(1)—O(3)	1·869 (4)	V(2)—O(8)	1·878 (3)
V(1)—O(4)	1·914 (4)	V(2)—O(9)	1·881 (3)
V(1)—O(5)	1·891 (4)	V(2)—O(10)	1·586 (3)
V(1)—O(6)	2·032 (3)	V(2)—O(11)	1·998 (4)
O(2)—O(3)	1·465 (4)	O(6)—O(7)	1·470 (5)
O(4)—O(5)	1·469 (3)	O(8)—O(9)	1·457 (5)

O(1)—V(1)—O(2)	104·7 (2)	O(6)—V(2)—O(7)	45·0 (2)
O(1)—V(1)—O(3)	107·1 (2)	O(6)—V(2)—O(8)	85·5 (2)
O(1)—V(1)—O(4)	105·0 (2)	O(6)—V(2)—O(9)	126·4 (2)
O(1)—V(1)—O(5)	106·6 (2)	O(6)—V(2)—O(10)	104·3 (2)
O(1)—V(1)—O(6)	100·6 (2)	O(6)—V(2)—O(11)	128·0 (2)
O(2)—V(1)—O(3)	46·1 (2)	O(7)—V(2)—O(8)	125·8 (2)
O(2)—V(1)—O(4)	148·5 (2)	O(7)—V(2)—O(9)	144·4 (2)
O(2)—V(1)—O(5)	131·9 (2)	O(7)—V(2)—O(10)	107·1 (2)
O(2)—V(1)—O(6)	84·2 (2)	O(7)—V(2)—O(11)	84·5 (2)
O(3)—V(1)—O(4)	130·9 (2)	O(8)—V(2)—O(9)	45·6 (2)
O(3)—V(1)—O(5)	89·8 (2)	O(8)—V(2)—O(10)	105·2 (2)
O(3)—V(1)—O(6)	127·4 (2)	O(8)—V(2)—O(11)	129·2 (2)
O(4)—V(1)—O(5)	45·4 (2)	O(9)—V(2)—O(10)	108·3 (2)
O(4)—V(1)—O(6)	80·6 (2)	O(9)—V(2)—O(11)	85·2 (2)
O(5)—V(1)—O(6)	123·8 (2)	O(10)—V(2)—O(11)	101·6 (2)

K(1)—O(10^{i})	2·738 (4)	K(2)—O(12)	2·710 (4)
K(1)—O(14)	2·770 (6)	K(2)—O(7^{iv})	2·744 (3)
K(1)—O(2^{ii})	2·780 (3)	K(2)—O(4)	2·762 (4)
K(1)—O(3^{iii})	2·781 (3)	K(2)—O(14)	2·765 (5)
K(1)—O(7^{ii})	2·834 (4)	K(2)—O(13)	2·824 (4)
K(1)—O(8^{iii})	2·841 (2)	K(2)—O(8)	2·843 (4)
K(1)—O(5^{iii})	2·979 (4)	K(2)—O(6^{iv})	2·902 (3)
K(1)—O(9^{iii})	3·096 (3)		

	O—H	H···O	O—H···O	O···O
O(11)—H(1)···O(4^{v})	0·94 (9)	1·75 (8)	156 (8)	2·635 (5)
O(11)—H(2)···O(13^{vi})	0·84 (7)	1·80 (7)	175 (10)	2·633 (4)
O(12)—H(3)···O(5^{vii})	1·11 (10)	1·65 (10)	174 (7)	2·753 (6)
O(12)—H(4)···O(2^{ii})	0·77 (10)	2·30 (8)	147 (8)	2·972 (5)
O(13)—H(5)···O(3^{ii})	1·05 (7)	1·75 (8)	160 (8)	2·759 (4)
O(13)—H(6)···O(9^{i})	0·82 (10)	1·96 (10)	158 (7)	2·736 (5)
O(14)—H(7)···O(12^{viii})	0·66 (13)	2·60 (11)	105 (9)	2·839 (8)
O(14)—H(8)···O(1^{vii})	0·88 (10)	2·79 (13)	94 (8)	2·983 (11)

Symmetry codes: (i) $x, y, z-1$; (ii) $x, y-1, z-1$; (iii) $x-1, y-1, z-1$; (iv) $1+x, y, z$; (v) $x, y, z+1$; (vi) $x-1, y, z+1$; (vii) $x, y-1, z$; (viii) $x-1, y, z$.

scale factors, positional parameters of all atoms and anisotropic thermal parameters of non-H atoms 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 Cruickshank's weighting scheme (Cruickshank, 1965). Final $R = 0{\cdot}026$, $wR = 0{\cdot}033$ $(\Delta/\sigma)_{max} = 0{\cdot}003$; max. and min. heights in final difference Fourier synthesis 0·7 and $-0{\cdot}4$ e Å^{-3}, respectively. The equivalent isotropic thermal parameters of water O atoms were used as B_{iso}'s for the corresponding H atoms. 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 the title compound are given in Table 2. Fig. 1 is a view of the structure along the crystallographic *b* axis. The structure consists of dimeric peroxo complexes $[V_2O_2(O_2)_4(H_2O)]^{2-}$ linked to potassium ions by anion–cation contacts. Hydrogen bonds from water molecules connect the entire structure into a complex three-dimensional network. The dimeric peroxo complex forming the core of the structure is shown in Fig. 2, where it can be seen that each V atom of the complex is six-coordinated; V(1) is surrounded by three peroxo ligands: O(2)—O(3) and O(4)—O(5) act as bidentate ligands and O(6)—O(7) as a monodentate ligand. The sixth ligand atom is the O(1) oxide ion. The second V(2) atom is connected to two bidentate peroxo ligands O(6)—O(7) and O(8)—O(9), the O(10) oxide ion and the water O(11). Thus, the coordination polyhedra of V atoms share the O(6) atom [the angle V(1)—O(6)—V(2) is 100·2 (1)°] and form the dimeric peroxovanadate in which the coordination polyhedra are chemically non-equivalent because, firstly, the bridging O(6)—O(7) peroxo group is connected to V(1) as a monodentate ligand and to V(2) as a bidentate ligand and, secondly, only V(2) coordinates a water molecule. Each coordination polyhedron can be

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52484 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

described as a pentagonal pyramid. The basal planes of the pentagonal pyramids about V(1) and V(2) consist of O(2), O(3), O(4), O(5) and O(6) about V(1) (the maximum deviation from planarity is 0·014 Å) and O(6), O(7), O(8), O(9) and O(11) about V(2) (the maximum deviation being 0·075 Å).

The O(1) apical atom of the V(1) pyramid is located 2·087 (5) Å below the basal plane and the O(10) apical atom of the V(2) pyramid 2·088 (5) Å above. The V(1) and V(2) atoms are displaced 0·485 (2) and 0·502 (2) Å, respectively, from the basal plane towards the apical O atom. The V—O_{basal} distances, 1·869 (4)–2·032 (3) Å, indicate that they are normal single bonds, while the V═O_{apical} bonds, 1·604 (5) and 1·586 (3) Å, are double bonds. The peroxo bond lengths [1·457 (5)–1·470 (5) Å] lie in the expected range. The dihedral angle between the basal planes of connected pyramids is 57·1°. The shortest non-bonded V–O distances V(1)–O(8) 2·597 (4) and V(2)–O(2) 2·606 (3) Å may indicate a tendency for both V atoms to attain a pentagonal-bipyramidal coordination. The apical atoms O(8) and O(2) are located 2·076 (4) and 2·080 (4) Å from the corresponding planes. The angles O(1)—V(1)—O(8) and O(10)—V(2)—O(2) are 167·5 (2) and 172·7 (2)°, respectively. Thus, we have established that the complex anion has a configuration similar to that recently found by us in $[N(CH_3)_4]_2[V_2O_2(O_2)_4(H_2O)].2H_2O$ (Lapshin, Smolin, Shepelev, Gyepesova & Schwendt, 1989), despite the difference in size of the K^+ and $N(CH_3)_4^+$ cations resulting in different space groups for these compounds, $P1$ and Cc, respectively. It is interesting to note the results of Stomberg & Olson. They investigated the crystal structures of $M_2[VFO(O_2)_2]$, M = K, NH_4, Cs (Stomberg, 1984; Stomberg & Olson, 1984*a*,*b*). They showed that $Cs_2[VFO(O_2)_2]$ is isomorphous with $K_2[VFO(O_2)_2]$, while $(NH_4)_2[VFO(O_2)_2]$ and $K_2[VFO(O_2)_2]$ are not isomorphous and their anions are not isostructural.

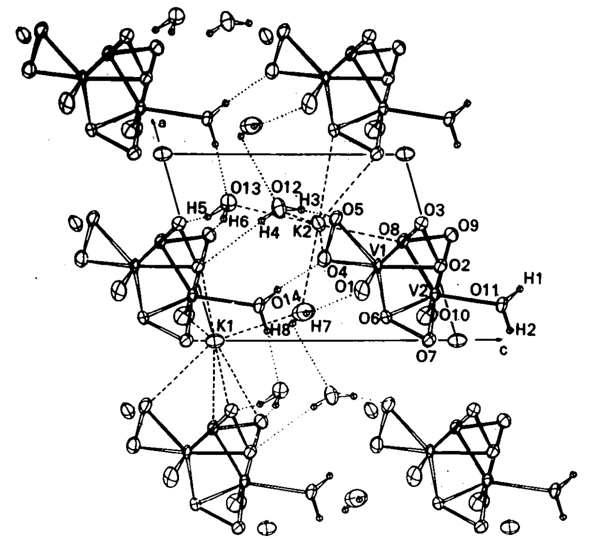

Fig. 1. View of the structure along the *b* axis. Dashed lines indicate K—O contacts and dotted lines H···O contacts.

The potassium ions occupy the corners of the cell [K(1)] and are close to the unit-cell centre [K(2)]. The K(1) and K(2) ions have eight and seven K—O contacts, respectively, within a distance of 3·2 Å. The individual K—O distances are given in Table 2. All potassium cation–anion contacts and hydrogen bonds are indicated in Fig. 1, where it can be seen that the potassium ions and peroxo complexes form layers which are arranged along [001]. Water molecules form links between the neighbouring layers. The geometry of the hydrogen bonds is reported in Table 2.

A higher temperature factor for the O(14) water atom may be explained on the basis of the average hydrogen-bond distances for water molecules. This distance for the O(14) water molecule (2·91 Å) is longer than those of the other water molecules.

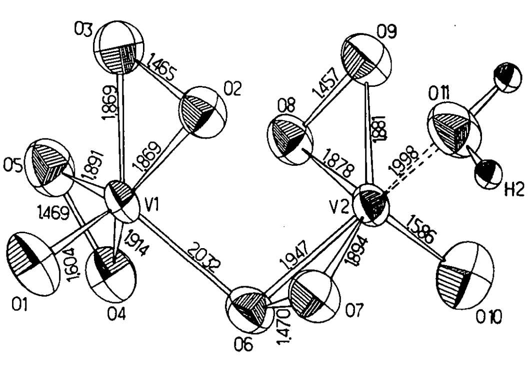

Fig. 2. The $[V_2O_2(O_2)_4(H_2O)]^{2-}$ complex. Thermal ellipsoids are drawn at the 50% probability level; H atoms are represented by spheres of aribtrary size. Bond distances are given in Å.

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Acta Cryst. (1990). C**46**, 741–745

A Coordinated Carboxylic and Carboxylate Group in Two Cu^{2+} Complexes with a Mono-*N*-functionalized Tetraaza Macrocycle

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(*Received* 20 *February* 1989; *accepted* 9 *May* 1989)

Abstract. Bis{[2-(1,4,8,11-tetraazacyclotetradecylmethyl)benzoato-*N*,*N*′,*N*″,*N*‴,*O*]copper(II)} diperchlorate pentahydrate, (I); $[Cu_2(C_{18}H_{29}N_4O_2)_2](ClO_4)_2.5H_2O$, $M_r = 1082{\cdot}967$, monoclinic, $P2_1$, $a = 9{\cdot}191\ (3)$, $b = 23{\cdot}776\ (3)$, $c = 10{\cdot}865\ (4)$ Å, $\beta = 101{\cdot}32\ (4)°$, $V = 2328{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}545$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}043$ mm^{-1}, $F(000) = 1136$, $T = 298$ K, $R = 0{\cdot}061$ for 3918 reflections with $I \geq 2\sigma(I)$. {[2-(1,4,8,11-tetraazacyclotetradecylmethyl)benzoic acid-*N*,*N*′,*N*″,*N*‴,*O*]copper(II)} diperchlorate monohydrate (II); $[Cu(C_{18}H_{30}N_4O_2)](ClO_4)_2.H_2O$, $M_r = 614{\cdot}921$, monoclinic, $P2_1/c$, $a = 11{\cdot}913\ (3)$, $b = 9{\cdot}435\ (2)$, $c = 22{\cdot}584\ (4)$ Å, $\beta = 90{\cdot}12\ (2)°$, $V = 2538{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}610$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}066$ mm^{-1}, $F(000) = 1276$, $T = 298$ K, $R = 0{\cdot}075$ for 2750 reflections with $I \geq 3\sigma(I)$. In (I) and (II), the Cu^{2+} ion is surrounded by four N and one O donor in a distorted square pyramidal geometry. The macrocyclic nitrogens form the base plane and the oxygen, stemming from the carboxylate and carboxylic acid group in (I) and (II) respectively, is in the apical position. In both cases, the macrocycles are in the *trans*-III configuration and the Cu^{2+} ion is displaced by 0·18 and 0·11 Å from the best plane of the four N atoms, respectively.

Introduction. There is a growing interest in functionalized macrocycles and their metal complexes (Busch, 1978; Kaden, 1984), because of the exceptional thermodynamic and kinetic properties of these compounds. Monosubstituted macrocycles, although difficult to obtain, are of particular interest since they allow the study of the influence of an additional donor group on the properties of an already coordinated metal ion. As described earlier (Studer & Kaden, 1986), we developed a one-step synthesis for mono-*N*-functionalized macrocycles carrying a carboxylic group in the side chain. The observation that the Cu^{2+} complex of 2-(1,4,8,11-tetraazacyclotetradecylmethyl)benzoic acid (*L*H, Fig. 1) shows a pH dependent equilibrium between a protonated uncoordinated and a deprotonated coordinated side chain in solution (Studer & Kaden, 1986) induced us to study the nature of these complexes, especially in view of the effect of the protonation state of the side chain on the coordination to the Cu^{2+}. We isolated crystals of both the protonated and the deprotonated forms of this complex and solved their structure by X-ray diffraction analysis.

Experimental. The synthesis of *L*H has been described previously (Studer & Kaden, 1986). Crystals of (I) can be isolated by adjusting the pH of the mother liquor of (II) (see below) to 8–9 and slowly evaporating the solvent. Analytical calculation for $[Cu_2(C_{18}H_{29}N_4O_2)_2](ClO_4)_2.5H_2O$ (1082·967): C 39·92, H 6·33, Cl 6·55, Cu 11·73, N 10·35, H_2O 8·32%. Found: C 40·14, H 6·05, Cl 6·55, Cu 11·8, N 10·39, H_2O 8·39%. IR(KBr): 1600, 1580

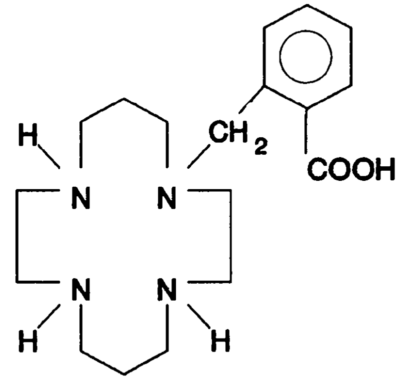

Fig. 1. The macrocyclic ligand *L*H.

0108-2701/90/050741-05$03.00

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