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Triaqua(oxalato-*O*,*O*′)oxovanadium(IV) dihydrate

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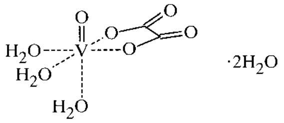
In the structure of the title compound, $[VO(C_2O_4)(H_2O)_3]\cdot 2H_2O$, the V atom of the oxovanadium(IV) cation is coordinated to one bidentate oxalate anion and three water molecules, resulting in a neutral complex. Two more water molecules are not coordinated to the V atoms but are involved in the hydrogen-bonding network, which consists of ten different hydrogen bonds.

Comment

Several different types of coordination complex of the oxovanadium(IV) cation with oxalate ligands (and also, in some cases, water) have been isolated so far. In each of the five structurally characterized compounds found in the Cambridge Structural Database (CSD, Version of 1999; Allen & Kennard, 1993), the V atom has a distorted octahedral coordination sphere. This is formed by two oxalate ligands and one water ligand in $(NH_4)_2[VO(C_2O_4)_2(H_2O)]\cdot(H_2O)$ (Oughtred *et al.*, 1976) and $[(terpy)Cu(C_2O_4)VO(C_2O_4)(H_2O)]\cdot H_2O$ (Cortes *et al.*, 1994) (terpy is 2,2′:6′,2″-terpyridine), by two oxalate ligands and by one oxalate ligand bridging two $VO(C_2O_4)_2$ units in $K_6[(VO)_2(C_2O_4)_5]\cdot 4H_2O$ (Zhou *et al.*, 1983), and by one bidentate oxalate, one water and a tetradentate oxalate ligand bridging two $[VO(C_2O_4)H_2O]$ units in $(Ph_4P)_2[(VO)_2(C_2O_4)_3(H_2O)_2]\cdot 4H_2O$ (Salta *et al.*, 1996) and $(Ph_4P)_2[(VO)_2(C_2O_4)_3(H_2O)_2]\cdot 8H_2O$ (Zheng *et al.*, 1998). In all these compounds, cations neutralize the charge of the anionic complexes. In this context, we have established the crystal structure of the title compound, (I).



(I)

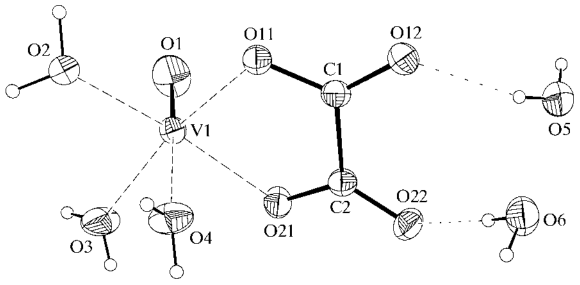


Figure 1
ORTEP (Johnson, 1965) drawing of the asymmetric unit of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

In (I), in contrast to the above-mentioned compounds, the five free coordination sites of the V atom of the oxovanadium(IV) cation are occupied by one bidentate oxalate anion and three water ligands, resulting in a neutral complex (Fig. 1). Two further water molecules are not coordinated to the V atom. The four O1—V1—O angles are distinctly larger than 90°, and this is presumably attributable to repulsion between the π electrons and the σ bonding pairs. The distance between V1 and O4, situated *trans* to O1, is markedly larger than between V1 and the other four ligands, due to the *trans* influence. Similar features are observed in the five oxovanadium(IV) oxalates found in the CSD.

The oxalate anion is considerably twisted [11.74 (9)°] around the C—C bond, leading to an elongated C—C bond length of 1.539 (2) Å. A search of the CSD for oxalates resulted in a mean torsion angle of 4.4 (2)° [standard deviation of the sample = 3.8°] and an even larger mean C—C bond length of 1.546 (1) Å.

The hydrogen-bonding system in (I) (Fig. 2) consists of ten different hydrogen bonds involving all ten H atoms of the water molecules. The acceptors of these hydrogen bonds are

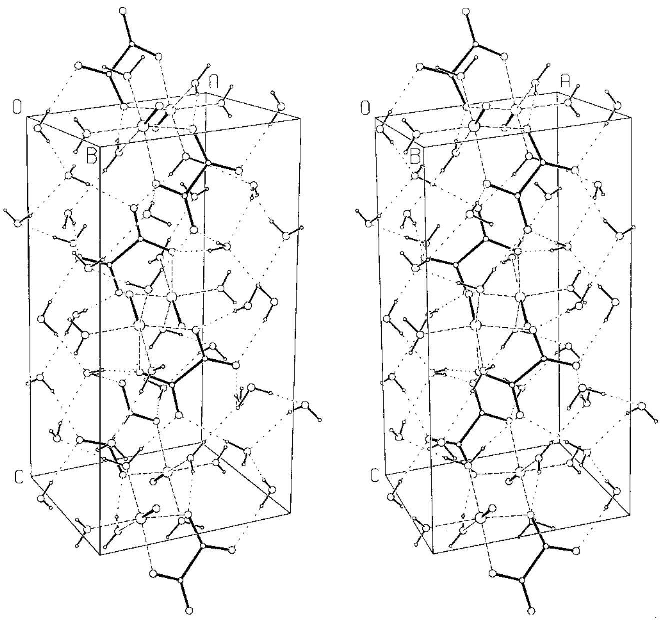


Figure 2
A stereoscopic packing diagram of the crystal structure of (I). The atoms are drawn as spheres of arbitrary radii. Covalent bonds are shown as full bonds, the five contacts to the VO^{2+} ions as dashed bonds and the hydrogen bonds as dotted bonds.

the O atoms of the two water molecules not coordinated to the V atom and the O atoms of the oxalate ligand (Fig. 2). The O atoms of the three water molecules coordinated to the V atom and atom O1 do not act as acceptors of hydrogen bonds. The metal complexes are not connected amongst themselves but are only mediated *via* water molecules.

Experimental

To a suspension of vanadium pentoxide (310 g) in water (900 g), oxalic acid dihydrate (645 g) was added and the mixture stirred at 333–353 K for 12 h, during which time vigorous evolution of CO_2 was observed. Large intensely blue single crystals of (I) separated on cooling.

Crystal data

$[VO(C_2O_4)(H_2O)_3]\cdot 2H_2O$
$M_r = 245.04$
Monoclinic, $P2_1/c$
$a = 7.152$ (2) Å
$b = 8.806$ (3) Å
$c = 14.004$ (4) Å
$\beta = 95.60$ (2)°
$V = 877.8$ (5) Å^3
$Z = 4$

$D_x = 1.854$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 31 reflections
$\theta = 3.68$–8.14°
$\mu = 1.164$ mm^{-1}
$T = 293$ (2) K
Block, intense blue
0.5 × 0.3 × 0.3 mm

Data collection

Stoe four-circle diffractometer
ω scans
3570 measured reflections
2555 independent reflections
2268 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\rm max} = 30°$

$h = -10 \rightarrow 10$
$k = -1 \rightarrow 12$
$l = -1 \rightarrow 19$
3 standard reflections every 100 reflections intensity decay: 0.2%

Table 1
Selected geometric parameters (Å, °).

V1—O1	1.5778 (14)	C1—C2	1.539 (2)
V1—O2	2.0218 (13)	C1—O11	1.2771 (19)
V1—O3	2.0093 (14)	C1—O12	1.2240 (19)
V1—O4	2.2585 (14)	C2—O21	1.2749 (18)
V1—O11	2.0144 (12)	C2—O22	1.2265 (19)
V1—O21	2.0096 (12)		
O1—V1—O4	178.03 (6)	O3—V1—O4	80.63 (6)
O3—V1—O11	162.16 (6)	O2—V1—O4	80.54 (6)
O21—V1—O2	159.04 (5)	O21—V1—O4	79.18 (5)
O1—V1—O21	101.48 (7)	O11—C1—C2	114.46 (13)
O1—V1—O11	100.03 (6)	O12—C1—C2	119.47 (14)
O1—V1—O2	98.96 (7)	O12—C1—O11	126.07 (14)
O1—V1—O3	97.48 (7)	O21—C2—C1	114.97 (13)
O3—V1—O21	92.05 (6)	O22—C2—C1	119.64 (13)
O11—V1—O2	90.80 (5)	O22—C2—O21	125.39 (14)
O3—V1—O2	89.86 (6)	C1—O11—V1	114.31 (9)
O11—V1—O4	81.89 (5)	C2—O21—V1	113.90 (9)
O21—V1—O11	81.14 (5)		
O11—C1—C2—O21	11.9 (2)	C1—C2—O21—V1	−11.86 (17)
O12—C1—C2—O21	−167.83 (14)	C2—C1—O11—V1	−5.53 (16)
O11—C1—C2—O22	−168.72 (15)	O12—C1—O11—V1	174.16 (13)
O12—C1—C2—O22	11.6 (2)	O22—C2—O21—V1	168.79 (14)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H21···O22^{i}	0.83 (3)	1.84 (3)	2.6735 (18)	173 (3)
O2—H22···O5^{ii}	0.86 (3)	1.87 (3)	2.715 (2)	170 (2)
O3—H31···O12^{iii}	0.72 (3)	1.96 (3)	2.669 (2)	174 (3)
O3—H32···O6^{ii}	0.76 (3)	1.86 (3)	2.616 (2)	173 (3)
O4—H41···O5^{iv}	0.79 (3)	2.05 (3)	2.846 (2)	177 (3)
O4—H42···O11^{v}	0.75 (3)	2.12 (3)	2.8670 (19)	169 (2)
O5—H51···O6^{vi}	0.75 (4)	2.16 (3)	2.845 (2)	151 (4)
O5—H52···O12	0.74 (4)	2.25 (4)	2.971 (2)	167 (3)
O6—H61···O22	0.84 (3)	2.02 (3)	2.851 (2)	176 (2)
O6—H62···O21^{iv}	0.77 (3)	2.03 (3)	2.7926 (19)	167 (3)

Symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $1 + x, y, z$; (iv) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (v) $1 - x, 1 - y, 2 - z$; (vi) $-x, y - \frac{1}{2}, \frac{3}{2} - z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.081$
$S = 1.064$
2555 reflections
159 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 0.1639P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.59$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.36$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.038 (2)

H atoms were refined with individual isotropic displacement parameters [O—H distances 0.72 (3)–0.86 (3) Å]. The highest peak and the deepest hole in the difference Fourier map were situated less than 0.9 Å from the V atom.

Data collection: local software; cell refinement: local software; data reduction: local software; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1392). Services for accessing these data are described at the back of the journal.

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