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Bis(tetra-*n*-butylammonium) bis[(mandelato)oxo(peroxo)-vanadate(V)] mandelic acid solvate

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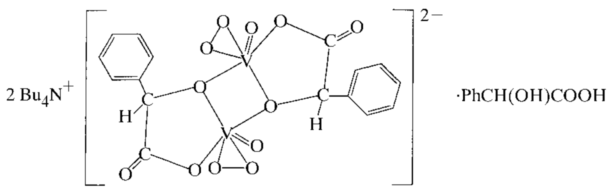
The crystal structure of the title complex, bis(tetra-*n*-butylammonium) bis(μ-α-hydroxybenzeneacetato)-$1\kappa^2O^1,O^2$:$2\kappa O^2$;$1\kappa O^2$:$2\kappa^2O^1,O^2$-bis[oxo(peroxo)vanadium(V)] α-hydroxybenzeneacetic acid solvate, $(C_{16}H_{36}N)_2[V_2O_2(O_2)_2(C_8H_6O_3)_2]\cdot C_8H_8O_3$, consists of dimeric anions with twofold rotation symmetry, cations and molecules of mandelic acid. Deprotonated hydroxyl O atoms of the mandelate dianion ligands bridge the V atoms to give a non-planar V_2O_2 ring. Each V atom has distorted pentagonal pyramidal coordination geometry, with an oxo ligand in the axial position. The mandelic acid molecule is disordered and coordinates weakly to the second axial site of each V atom through a carboxylate O atom.

Comment

Vanadium compounds are important in biochemistry and biology in many ways (Sigel & Sigel, 1995; Djordjevic *et al.*, 1995). Peroxo complexes form a new category of compounds, with effective insulin-mimetic activity (Sigel & Sigel, 1995). Vanadium peroxo complexes are formed as intermediates in oxidation reactions catalysed by haloperoxidase, which contains V in the active site (Messerschmidt *et al.*, 1997). This enzyme has been found in a variety of seaweeds (Wever *et al.*, 1991). Anions of α-hydroxycarboxylic acids also represent an interesting class of biogenic ligands. Several dinuclear vanadium monoperoxo complexes with biogenic heteroligands such as citrate (Djordjevic *et al.*, 1989), malate (Djordjevic *et al.*, 1995) and tartrate ions (Schwendt *et al.*, 1998) have been prepared recently. We report here a related complex with the mandelate dianion as ligand, namely bis(tetra-*n*-butylammonium) bis[(mandelato)oxo(peroxo)vanadate(V)] mandelic acid solvate, (I).



(I)

The crystal structure of (I) consists of dimeric anions with crystallographic twofold rotation symmetry (Fig. 1), unexceptional $(Bu_4N)^+$ cations and one molecule of neutral mandelic acid per dimeric anion. The component cations, anions and mandelic acid molecules are held together by electrostatic forces and hydrogen bonds.

The two V atoms in the anion are doubly bridged by the deprotonated hydroxyl O atoms of two mandelato ligands, O5 and O5^i [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$], to give a central V_2O_2 ring. This ring is not planar, but has a dihedral angle of folding of 151.79 (8)° about the O5$\cdots$O5^i line. Each mandelato anion also coordinates terminally to one V atom through its carboxylate group to form five-membered chelate rings. The primary coordination of V is distorted pentagonal pyramidal by six O atoms. The equatorial plane involves the peroxo group [O2 and O3, with O—O = 1.432 (3) Å], the two bridging O atoms and the carboxylate O4 atom, which have a maximum deviation of 0.10 (7) Å from this plane. The axial position is occupied by the doubly bonded oxo ligand O1, 1.89 (7) Å out of the equatorial plane, with V—O1 = 1.578 (2) Å. The V atom is displaced 0.32 (1) Å out of the equatorial plane towards the axial oxo ligand.

The neutral mandelic acid molecule is disordered about the twofold rotation axis in such a way that the O atoms coincide in the two orientations. One carboxylate O atom, on the twofold axis, is coordinated to the two V atoms in an axial position opposite the oxo ligand, the V—O8 distance being 2.550 (3) Å.

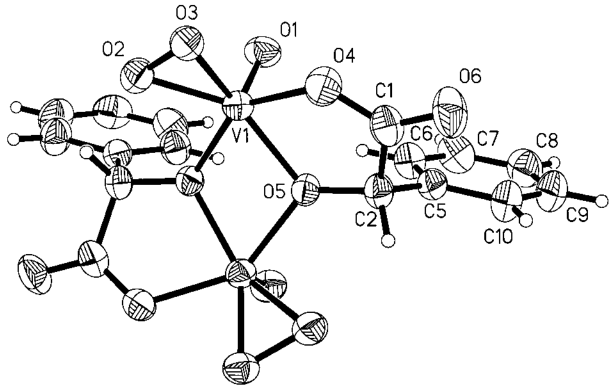


Figure 1
The structure of the dimeric anion of (I), $[V_2O_2(O_2)_2(C_8H_6O_3)_2]^{2-}$, with 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as spheres of arbitrary radii.

Experimental

A solution of NH_4VO_3 (2.5 mmol) in water (10 ml) was mixed with a solution of mandelic acid (2.5 mmol) in water (5 ml). After cooling of the solution to 273 K, H_2O_2 (30%, 5 ml) and ethanol (2.5 mmol, 10 ml) were added with stirring. Crystals were isolated after a few days at 278 K.

Crystal data

$(C_{16}H_{36}N)_2[V_2O_2(O_2)_2(C_8H_6O_3)_2]\cdot C_8H_8O_3$
$M_r = 1135.20$
Orthorhombic, *Pbcn*
$a = 19.657$ (12) Å
$b = 17.066$ (3) Å
$c = 17.670$ (5) Å
$V = 5928$ (4) Å^3
$Z = 4$
$D_x = 1.272$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 41 reflections
$\theta = 1.58$–25.1°
$\mu = 0.380$ mm^{-1}
$T = 150.0$ (1) K
Prism, dark red
0.4 × 0.3 × 0.3 mm

Data collection

Four-circle κ-axis Kuma KM-4 diffractometer with an Oxford Cryosytems Cryostream cooler
$\omega/2\theta$ scans
5680 measured reflections
5210 independent reflections
3329 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\rm max} = 25.06°$
$h = -23 \rightarrow 0$
$k = -19 \rightarrow 3$
$l = 0 \rightarrow 21$
3 standard reflections every 300 reflections intensity decay: 2.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.168$
$S = 1.034$
5210 reflections
383 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0838P)^2 + 5.65P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.663$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.399$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

V1—O1	1.579 (2)	V1—O5^i	2.000 (2)
V1—O3	1.879 (2)	C1—O4	1.290 (4)
V1—O2	1.880 (2)	C1—C2	1.517 (5)
V1—O5	1.979 (2)	O2—O3	1.432 (3)
V1—O4	1.991 (2)	C2—O5	1.410 (4)
O1—V1—O3	105.87 (12)	O2—V1—O5^i	82.09 (10)
O1—V1—O2	102.67 (12)	O5—V1—O5^i	69.57 (10)
O3—V1—O2	44.80 (10)	O4—V1—O5^i	144.53 (10)
O1—V1—O5	100.65 (11)	O4—C1—C2	114.2 (3)
O3—V1—O5	146.27 (10)	O3—O2—V1	67.55 (13)
O2—V1—O5	145.84 (10)	C5—C2—C1	112.0 (3)
O1—V1—O4	98.80 (12)	O2—O3—V1	67.65 (13)
O3—V1—O4	78.20 (10)	C1—O4—V1	119.9 (2)
O2—V1—O4	122.53 (11)	C2—O5—V1	119.08 (19)
O5—V1—O4	77.47 (9)	C2—O5—V1^i	128.5 (2)
O1—V1—O5^i	99.78 (11)	V1—O5—V1^i	105.58 (10)
O3—V1—O5^i	124.43 (10)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

All C atoms of the neutral disordered mandelic acid molecule have a site-occupation factor of 0.50, while O8 lies on the twofold rotation axis and O7 represents two different O atoms in the two disordered orientations. The H7O atom of the mandelic acid solvate molecule was refined [O7—H7O 0.86 (8) Å].

Data collection: *KM*-4 *Software* (Galdecki *et al.*, 1996); cell refinement: *KM*-4 *Software*; data reduction: *KM*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Johnson & Burnett, 1996); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1306). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (2000). C**56**, 154–155 Ivana Kutá Smatanová *et al.* • $(C_{16}H_{36}N)_2[V_2O_2(O_2)_2(C_8H_6O_3)_2]\cdot C_8H_8O_3$ **155**