

Table 1. Selected geometric parameters (Å, °)

Re—N3	1.723 (4)	N1—C5	1.342 (6)
Re—N2	2.052 (4)	N1—C1	1.357 (6)
Re—N1	2.204 (4)	N2—C6	1.296 (6)
Re—C11	2.372 (2)	N2—C7	1.452 (6)
Re—C13	2.382 (3)	N3—C13	1.375 (6)
Re—C12	2.414 (3)	C1—C6	1.443 (7)
N3—Re—N2	95.0 (2)	N3—Re—C12	90.97 (15)
N3—Re—N1	165.2 (2)	N2—Re—C12	94.86 (13)
N2—Re—N1	73.8 (2)	N1—Re—C12	80.70 (13)
N3—Re—C11	102.00 (15)	C11—Re—C12	87.90 (10)
N2—Re—C11	162.76 (11)	C13—Re—C12	166.80 (5)
N1—Re—C11	89.93 (12)	C1—N1—Re	115.3 (3)
N3—Re—C13	102.07 (15)	C6—N2—Re	120.8 (3)
N2—Re—C13	86.14 (13)	C13—N3—Re	171.6 (3)
N1—Re—C13	86.97 (13)	N1—C1—C6	112.7 (4)
C11—Re—C13	87.38 (9)		

The highest electron-density peak ($1.04 \text{ e } \text{Å}^{-3}$) lies near the C14 atom.

Data collection: *SHELXTL-Plus90* (Sheldrick, 1990). Cell refinement: *SHELXTL-Plus90*. Data reduction: *SHELXTL-Plus90*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1115). Services for accessing these data are described at the back of the journal.

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Disodium bis[μ -2-hydroxy-2-methylpropanoato(2-)]-O¹,O²:O²:O¹,O²-bis-[dioxovanadate(V)] heptahydrate

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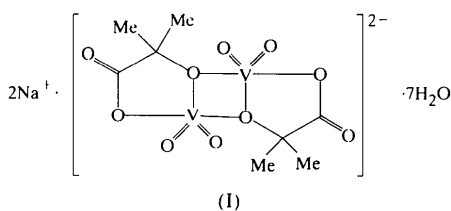
(Received 6 July 1999; accepted 19 August 1999)

Abstract

The title complex, Na₂[V₂O₄(C₄H₆O₃)₂]·7H₂O, contains the {[V{OC(CH₃)₂COO}(O₂)]₂}²⁻ complex anion in which two five-coordinate inversion-related vanadium centres are doubly bridged by hydroxyl-O atoms and each vanadium centre has distorted trigonal bipyramidal geometry. In the crystals, there are also two Na⁺ cations and seven molecules of water of crystallization.

Comment

Vanadium(V) complexes are of interest because they can act as models for enzyme inhibitors (Crans *et al.*, 1990, 1991). In the structure of ribonuclease A inhibited by vanadate and uridine, reported by Kostrewa *et al.* (1989), the V^V complex has a trigonal bipyramidal geometry. Hambley *et al.* (1992) prepared the diammonium complex of bis(μ -2-ethyl-2-hydroxybutyrato-O,O,O')dioxovanadium(V), which they reported was stable at room temperature. The title compound, (I), is also very stable and exists as a dimer of two five-coordinate vanadium centres doubly bridged by hydroxyl-O atoms. The V atoms are related by an in-



version centre in the V_2O_2 core. The geometry about the V atom is a distorted trigonal bipyramid with the oxo-O atoms occupying equatorial positions together with the alkanolate donor of a chelating ligand. The axial positions are occupied by a terminal carboxylate and the bridging bond between vanadium and the alkanolate group of the adjacent V centre. The structures of several other vanadium(V) alkoxides are known (Bu_4N) $_2$ [$VO_2(C_4H_6O_3)$] $_2$, (II) (Smatanová *et al.*, 1998), (NH_4) $_2$ [$V\{OC(CH_2CH_3)_2COO\}(O_2)_2$], (III) (Hambley *et al.*, 1992), $K_2[VO(O_2)(C_6H_6O_7)]_2$, (IV) (Djordjevic *et al.*, 1989), $VO(OCH_2CH_2Cl)_3$, (V) (Preibsch & Rehder, 1990), $K_2[VO_2(C_6H_6O_7)]_2$, (VI) (Wright *et al.*, 1995), and $K_2(NH_4)_4[VO_2(C_6H_4O_7)]_2$, (VII) (Zhou *et al.*, 1995). The $V=O$ bonds of (I) (1.619 and 1.624 Å) are quite similar to those of (II) (1.607 and 1.622 Å), (III) (1.617 and 1.611 Å), (IV) (1.601 Å) $_2$, (VI) (1.623 and 1.611 Å) and (VII) (1.620 and 1.625 Å), but longer than those in (V) (1.584 Å). The bridging $V-O$ (alkanolate)

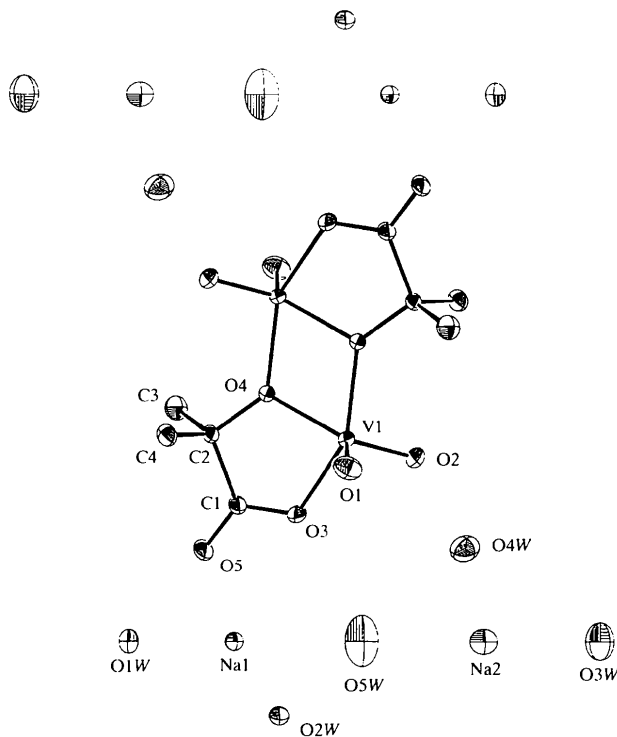


Fig. 1. The molecular structure of (I), showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

distances of (I) (1.958 and 1.990 Å) are consistent with the corresponding $V-O$ bond lengths in (II) (1.960 and 1.975 Å), (III) (1.973 and 1.984 Å), (IV) (1.991 and 2.031 Å), (VI) (1.957 and 2.013 Å) and (VII) (1.961 Å).

In the title compound, the Na^+ ions and three of the seven water molecules are located on a mirror plane. There is a complex network of hydrogen bonds and $Na^+ \cdots O$ contacts between the Na^+ ions, which are located on a mirror plane, and water molecules, as well as the carbonyl O of the vanadium complex.

Experimental

Compound (I) was prepared by dissolving $NaVO_3$ (1.83 g, 0.015 mol) in hot distilled water (50 ml). To this solution at room temperature, $HOC(CH_3)_2COOH$ (1.56 g, 0.015 mol; 2-hydroxy-2-methylpropanoic acid) was added. The resulting solution was kept in a stoppered flask for a week and then allowed to evaporate at room temperature. Pale-yellow crystals appeared after about a week.

Crystal data

$Na_2[V_2O_4(C_4H_6O_3)_2] \cdot 7H_2O$	Mo $K\alpha$ radiation
$M_r = 542.162$	$\lambda = 0.71070 \text{ \AA}$
Orthorhombic	Cell parameters from 3409 reflections
$Pnma$	$\theta = 3.1-31.4^\circ$
$a = 8.7320(1) \text{ \AA}$	$\mu = 0.992 \text{ mm}^{-1}$
$b = 21.7160(3) \text{ \AA}$	$T = 293(2) \text{ K}$
$c = 11.2460(2) \text{ \AA}$	Prism
$V = 2132.51(5) \text{ \AA}^3$	$0.30 \times 0.25 \times 0.22 \text{ mm}$
$Z = 4$	Pale yellow
$D_x = 1.695 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Nonius KappaCCD diffractometer	2861 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.040$
Absorption correction: empirical (Blessing, 1997)	$\theta_{max} = 31.44^\circ$
$T_{min} = 0.766$, $T_{max} = 0.804$	$h = -12 \rightarrow 0$
42859 measured reflections	$k = 0 \rightarrow 31$
3409 independent reflections	$l = 0 \rightarrow 16$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.043$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$\Delta\rho_{max} = 0.624 \text{ e \AA}^{-3}$
$wR(F^2) = 0.121$	$\Delta\rho_{min} = -0.530 \text{ e \AA}^{-3}$
$S = 0.958$	Extinction correction: none
3409 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
149 parameters	
H atoms constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0763P)^2 + 1.7082P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected geometric parameters (\AA , $^\circ$)

V1—O1	1.6193 (16)	Na1—O1W	2.378 (2)
V1—O2	1.6242 (14)	Na1—O2W	2.3934 (16)
V1—O3	1.9896 (13)	Na1—O1W ⁱⁱ	2.463 (2)

V1—O4	2.0043 (12)	Na1—Na2 ⁱⁱ	3.6806 (16)
O3—C1	1.291 (2)	Na2—O4W2	2.400 (14)
O4—C2	1.4333 (18)	Na2—O3W	2.416 (4)
O4—V1 ⁱ	1.9583 (12)	Na2—O4W1	2.440 (3)
O5—C1	1.234 (2)	Na2—O2W ⁱⁱ	2.4685 (19)
C1—C2	1.523 (2)	Na2—O5W	2.533 (5)
O5—Na1	2.4145 (15)		
O1—V1—O2	108.03 (9)	O3—V1—O4	76.49 (5)
O1—V1—O3	98.04 (8)	C1—O3—V1	119.93 (11)
O2—V1—O3	95.87 (7)	C2—O4—V1	118.48 (9)
O1—V1—O4	120.15 (7)	V1 ⁱ —O4—V1	108.21 (5)
O2—V1—O4	131.77 (7)	O3—C1—C2	115.80 (14)
O4 ⁱ —V1—O4	71.79 (5)	O4—C2—C1	104.53 (12)

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

No attempt was made to model the water H atoms. The Na⁺ ions were located on a mirror plane at $(x, \frac{1}{4}, z)$. Three and a half water molecules were also located at or near the same mirror plane. One water molecule (O4W) was disordered over two sites and was modelled with site occupancies of 0.83 and 0.17.

Data collection: COLLECT (Nonius, 1998). Cell refinement: DENZO (Otwinowski & Minor, 1996). Data reduction: DENZO. Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELX97 (Sheldrick, 1998). Molecular graphics: ZORTEP (Zsolnai, 1995). Software used to prepare material for publication: SHELX97.

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[*trans*-Bis(en)dioxosmium(VI)] *trans*-bis(en)dioxosmium(VI)[aqua- η^1 - sulfato- η^2 -sulfatoiron(II)][diaquabis- (η^1 -sulfato)iron(II)] hexahydrate†

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Abstract

Aqueous ferrous ion reacts reversibly with *trans*-[Os(en)₂O₂]²⁺ producing an intensely blue complex ion which, in the presence of sulfate ion, produces the title complex, [OsO₂(C₂H₈N₂)₂]₂[Os₂Fe₄O₄(SO₄)₈-(C₂H₈N₂)₄(H₂O)₆].12H₂O, from H₂O/CH₃OH solution. The X-ray structure shows the unit cell to contain two discrete [Os(en)₂O₂]²⁺ ions and two counter-ions having the basic linear core [(SO₄)₂-Fe-O-Os(en)₂-O-Fe-(SO₄)₂]²⁻. Using sulfate ions as bridges, the latter ions form an infinite one-dimensional planar ribbon-like array separated by cations. In this array, the osmyl bond is lengthened [average 1.845 (7) Å] with respect to that of the parent ion [average 1.734 (7) Å], while the Fe—O bond is shortened to an average of 1.800 (6) Å with respect to the usual single-bond distance of 2.05 Å. Sulfate ions serve as bridges between linear cores and are also chelated to a single ferrous ion. The strength of the bonds in the linear Fe—O—Os—O—Fe core as judged by bond-length changes suggests extensive electron delocalization between the metal centers.

Comment

Some years ago, two related reactions of *trans*-[Os(en)₂O₂]²⁺ were observed (Murmman, 1977). Intensely colored species were reversibly formed with Fe²⁺ and with the photolyzed product of [Mo(CN)₈]⁴⁻, i.e. [Mo(CN)₇(OH₂)³⁻. The former reaction was studied spectrophotometrically and found to involve two steps forming 1:1 and 1:2 Os—Fe complex ions. It was presumed that these interactions involved coordination of the oxo-O atoms of the highly oxidized osmium complex with a metal ion in a reduced state, but no structural or compositional data are available. These compounds

† Systematic chemical name: poly[bis[*trans*-bis(ethylenediamine)dioxosmium(VI)] [[hexaaqua-3 κ^2 O,4 κ O,5 κ^2 O,6 κ O-tetrakis(ethylenediamine)-1 κ^4 N,N',2 κ^4 N,N'-tetra- μ -oxo-1:3 κ^2 O:1:6 κ^2 O:2:4 κ^2 O:-2:5 κ^2 O-di- μ -sulfato-3:4 κ^2 O:O':5:6 κ^2 O:O'-tetrasulfato-3 κ^2 O:4 κ^2 -O,O':5 κ O:6 κ^2 O,O'-tetrairon(II)diosmium(VI)]-di- μ -sulfato-2 κ O:-3' κ O':3 κ O:2' κ O'] dodecahydrate].