

Table 1. Selected geometric parameters (Å, °)

W—Se4	2.441 (2)	Se2—Se3	2.325 (3)
W—Se8	2.444 (2)	Se3—Se4	2.447 (3)
W—Se5	2.529 (2)	Se3—K	3.527 (5)
W—Se1	2.570 (2)	Se5—Se6	2.386 (4)
Se1—Se2	2.378 (3)	Se6—Se7	2.300 (4)
Se1—K	3.457 (5)	Se7—Se8	2.442 (3)
Se4—W—Se8	124.74 (8)	Se3—Se2—Se1	96.16 (10)
Se4—W—Se5	74.33 (8)	Se2—Se3—Se4	99.45 (11)
Se8—W—Se5	90.09 (8)	Se2—Se3—K	91.32 (10)
Se4—W—Se1	87.29 (8)	Se4—Se3—K	80.92 (11)
Se8—W—Se1	71.67 (8)	W—Se4—Se3	114.03 (9)
Se5—W—Se1	140.21 (8)	Se6—Se5—W	103.89 (10)
Se2—Se1—W	101.82 (9)	Se7—Se6—Se5	96.95 (13)
Se2—Se1—K	92.16 (11)	Se6—Se7—Se8	97.73 (12)
W—Se1—K	103.66 (9)	Se7—Se8—W	114.46 (11)
Se4—W—Se1—Se2	-53.46 (10)	Se8—W—Se5—Se6	-43.48 (12)
W—Se1—Se2—Se3	65.60 (12)	W—Se5—Se6—Se7	63.12 (12)
Se1—Se2—Se3—Se4	-43.10 (13)	Se5—Se6—Se7—Se8	-48.51 (12)
Se1—W—Se4—Se3	25.73 (11)	Se6—Se7—Se8—W	23.19 (15)
Se2—Se3—Se4—W	9.73 (14)	Se5—W—Se8—Se7	12.28 (12)

H atoms were included using a riding model. The residual electron density of $2.15 \text{ e } \text{Å}^{-3}$ is 1.0 Å from the W atom, and that of $-1.25 \text{ e } \text{Å}^{-3}$ is 1.45 Å from W. This may be attributed to residual absorption errors associated with an extremely thin plate.

Data collection: XSCANS (Fait, 1991). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP (Siemens, 1994b). Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1451). Services for accessing these data are described at the back of the journal.

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Bis(tetra-*n*-butylammonium) Bis[(methyl-lactato)dioxovanadate(V)] Dihydrate†

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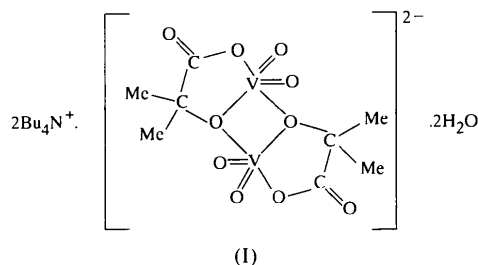
(Received 9 December 1997; accepted 25 February 1998)

Abstract

The crystal structure of $(\text{Bu}_4\text{N})_2[\text{VO}_2(\text{C}_4\text{H}_6\text{O}_3)]_2 \cdot 2\text{H}_2\text{O}$ consists of the dimeric $[\{\text{VO}_2(\text{C}_4\text{H}_6\text{O}_3)\}_2]^{2-}$ anion with C_i symmetry, two Bu_4N^+ cations and two water molecules. The V atom is pentacoordinated by O atoms in a tetragonal-pyramidal arrangement.

Comment

Knowledge of the properties of vanadate complexes is essential to vanadium biochemistry. Information about the interactions of vanadate with biogenic ligands will be needed so that the most potent and biologically significant interactions can be identified (Sigel & Sigel, 1995). In the course of our work on model oxygen-vanadium compounds (Sabirov *et al.*, 1984; Angus-Dunne *et al.*, 1994), we isolated the title compound, (I).



† Systematic name: bis(tetra-*n*-butylammonium) bis[μ -2-hydroxy-2-methylpropanoato(2-)]- $1\kappa^2 O^1, O^2:2\kappa O^2; 1\kappa O^2:2\kappa^2 O^1, O^2$ -bis[dioxovanadate(V)] dihydrate.

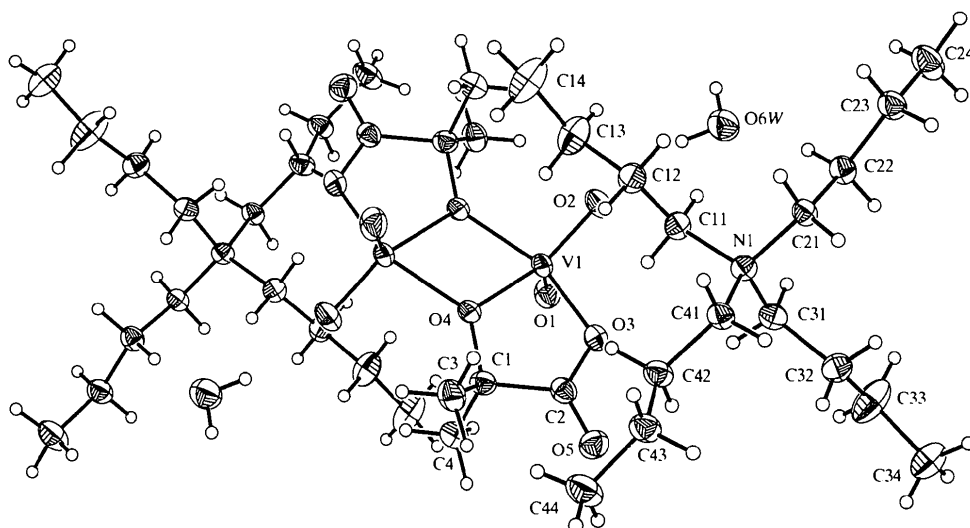


Fig. 1. ORTEP plot (Burnett & Johnson, 1996) of (I) with the non-H atoms drawn as 50% probability displacement ellipsoids.

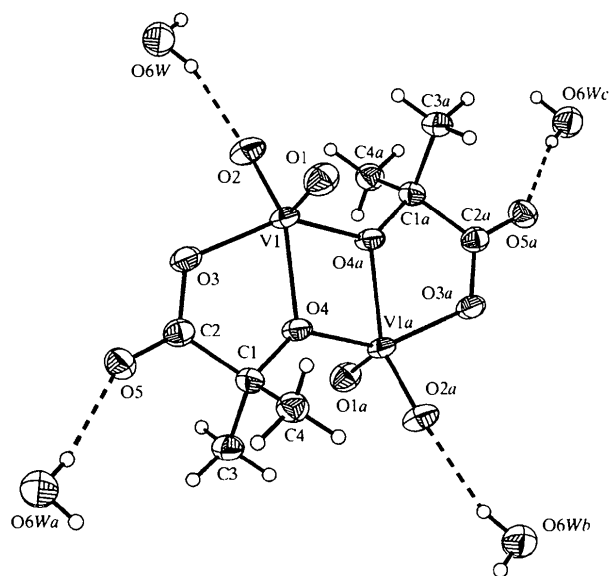


Fig. 2. View of the structure of the dimeric $\{[VO_2(C_4H_6O_3)]_2\}^{2-}$ anion with the adjacent water molecules. The non-H atoms are drawn as 50% probability displacement ellipsoids.

The crystal structure of (I) consists of the dimeric $\{[VO_2(C_4H_6O_3)]_2\}^{2-}$ anion, two Bu_4N^+ cations and two water molecules. All the ions and molecules in the monoclinic unit cell are involved in a hydrogen-bonding network.

The two V atoms are bridged by hydroxyl O atoms resulting in a four-membered V_2O_2 planar heterocycle. In the anionic complex, having C_i symmetry, the methyllactate ions coordinate the metal, producing five-membered chelate rings. The V atoms are each five-coordinated in a tetragonal-pyramidal arrangement involving two hydroxyl O, one methyllactate carboxyl

O and two oxo O atoms. One oxo (O2) and three methyllactate O atoms [O3, O4 and O4(1-x, 1-y, -z)] occupy the equatorial positions within the distorted tetragonal plane (maximum deviation 0.16 Å). The axial position is occupied by the O1 atom [V—O1 1.6073 (19) Å], and the V and O1 atoms are 0.53 (2) and 2.13 (2) Å, respectively, out of the equatorial plane.

Experimental

The synthesis of (I) was carried out by sequential reaction of Bu_4NOH (2.5 mmol) with NH_4VO_3 (2.5 mmol), $Me_2C(OH)COOH$ (2.5 mmol) and H_2O_2 (30%). Red crystals were obtained from the reaction mixture after a few days at 278 K.

Crystal data

$(C_{16}H_{36}N)_2[V_2O_4(C_4H_6O_3)_2] \cdot 2H_2O$
 $M_r = 445.50$
 Monoclinic
 $P2_1/c$
 $a = 9.378$ (2) Å
 $b = 20.241$ (4) Å
 $c = 12.848$ (3) Å
 $\beta = 99.31$ (3)°
 $V = 2406.7$ (9) Å³
 $Z = 4$
 $D_x = 1.230$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 32 reflections

$\theta = 8.5$ – 13.0 °

$\mu = 0.444$ mm⁻¹

$T = 150.0$ (1) K

Prism

$0.80 \times 0.70 \times 0.70$ mm

Red

Data collection

Kuma KM-4 four-circle
 κ -axis diffractometer with
 an Oxford Cryosystems
 Cryostream cooler (Cosier
 & Glazer, 1986)

ω - 2θ scans

Absorption correction: none

3412 reflections with

$I > 2\sigma(I)$

$R_{int} = 0.046$

$\theta_{max} = 25.08$ °

$h = -11 \rightarrow 0$

$k = -24 \rightarrow 0$

$l = -15 \rightarrow 15$

4484 measured reflections
4217 independent reflections

3 standard reflections
every 300 reflections
intensity decay: <2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.133$
 $S = 1.000$
4217 reflections
429 parameters
All H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + 2P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.506 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.921 \text{ e } \text{Å}^{-3}$
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

V1—O1	1.6073 (19)	O4—C1	1.426 (3)
V1—O2	1.6215 (18)	O5—C2	1.215 (3)
V1—O4'	1.9596 (17)	C1—C3	1.518 (3)
V1—O3	1.9749 (18)	C1—C4	1.519 (4)
V1—O4	1.9983 (17)	C1—C2	1.522 (3)
O3—C2	1.297 (3)		
O1—V1—O2	108.57 (10)	O2—V1—O4	136.21 (9)
O1—V1—O4'	103.96 (9)	O4'—V1—O4	70.62 (8)
O2—V1—O4'	99.32 (9)	O3—V1—O4	76.58 (7)
O1—V1—O3	100.99 (9)	C2—O3—V1	120.24 (16)
O2—V1—O3	95.65 (9)	C1—O4—V1'	132.01 (14)
O4'—V1—O3	144.90 (7)	C1—O4—V1	117.84 (14)
O1—V1—O4	115.22 (9)	V1'—O4—V1	109.38 (8)

Symmetry code: (i) $1 - x, 1 - y, -z$.

The phase problem was solved by direct methods using *SHELX97* (Sheldrick, 1997), which was also used to refine the structure.

Data collection: Kuma KM-4 software. Cell refinement: Kuma KM-4 software. Data reduction: Kuma KM-4 software. Molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELX97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1343). Services for accessing these data are described at the back of the journal.

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Tetraethylammonium (1-Pyrrolidinecarbodithioato-*S,S'*)(tetrathiotungstenio-*S,S'*)-nickelate(1-)

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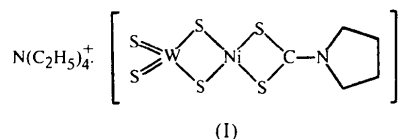
(Received 5 December 1997; accepted 20 March 1998)

Abstract

In the title nickel–tungsten sulfido mixed-metal complex {tetraethylammonium (1-pyrrolidinecarbodithioato- $2\kappa^2S,S'$)-di- μ -thio-1:2 κ^4S -dithio-1 κ^2S -nickeltungsten(*Ni*—*W*), [N(C₂H₅)₄][NiWS₄(S₂CNC₄H₉)]}, the Ni atom is fourfold coordinated by a pyrrolidine-derived dithiocarbamate and a tetrathiotungstate moiety. Dithiocarbamate and tetrathiotungstate act as bidentate ligands, each chelating *via* two S atoms to the Ni atom, thus producing an approximately square-planar geometry. The Ni—W distance is 2.761 (1) Å and the Ni—S_{bridge}—W angles are 77.13 (8) and 77.08 (9)°. The four Ni—S distances are identical within s.u.'s and average 2.205 (3) Å. The WS₄ moiety is a distorted tetrahedron, with S—W—S angles ranging from 102.3 (1) to 111.8 (1)°. The two terminal W—S distances are 2.149 (3) and 2.151 (3) Å, while the bridging W—S distances are 2.221 (2) and 2.226 (3) Å.

Comment

Recently, interesting non-linear optical (NLO) properties have been discovered for Group 6–Group 11 sulfido clusters (Hou *et al.*, 1996). To find compounds of Group 6 with superior NLO properties, we have synthesized a series of Group 6–Group 10 sulfido compounds (Long *et al.*, 1996, 1997). We report here the structure of a nickel–tungsten sulfido mixed-metal complex, (I).



The structure of (I) consists of isolated cations and bimetallic anions (Fig. 1). The Ni atom is four-coordinate: a dithiocarbamate and a tetrathiotungstate each acts as a bidentate ligand, coordinating *via* two S atoms. The geometry of the 1-pyrrolidinecarbodithioate ligand is similar to that found in the complex [Ni(S₂CN-