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Tetrasodium Bis(μ-L-tartrato)-1κ^2O^1,O^2:2κ^2O^3,O^4-bis[oxovanadate(IV)] Hexahydrate

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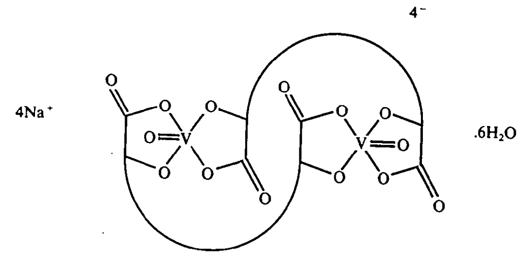
Abstract

The structure of the title compound, Na$_4$[(VO)(L-C$_4$H$_2$O$_6$)]$_2$.6H$_2$O, is described. The crystal structure comprises an arrangement of dimeric tetranegative [(VO)(L-C$_4$H$_2$O$_6$)]$_2^{4-}$ anions, Na cations and water molecules. The vanadyl ions are coordinated by two L-tartrate ligands in a *cis* position. These ions exhibit a V···V′ intradimeric distance of 4.2929 (5) Å and are nearly colinear, showing an O=V···V′ angle of 177.30 (9)°. In the crystal structure, the Na$^+$ cations and the water molecules form layers which alternate with layers of the dimeric anions along the *c* axis.

Comment

There is a growing interest in alkaline earth vanadium oxides because of the proposed relationship between spin $\frac{1}{2}$ antiferromagnets and superconductivity. Heterobimetallic complexes of alkaline earth ions and vanadium(IV) are of potential value in this context because they contain well defined V^{IV}:M^{II} ratios and can result in mixed oxides after adequate thermal treatment (García-Jaca, Insausti, Larramendi, Arriortua, Rojo & Hernandez, 1993; García-Jaca, Insausti, Pizarro, Cortes, Arriortua & Rojo, 1994). The title compound (I) has been used as a precursor for the preparation of alkaline earth vanadyl L-tartrates.



(I)

The crystal structure of the title compound consists of dimeric tetranegative [(VO)(L-C$_4$H$_2$O$_6$)]$_2^{4-}$ anions and a complex arrangement of Na$^+$ ions and water molecules. The dimeric anions are formed by two VO^{2+} ions [V···V^i 4.2929 (5) Å; symmetry code: (i) *y*, *x*, −*z*] bonded by two L-tartrate tetranegative ligands forming a geometry with C_2 but close to D_2 symmetry, as shown in Fig. 1. The vanadyl groups in each dimer are nearly parallel with an O=V···V^i angle of 177.30 (9)°. Each VO^{2+} group is coordinated by the O atoms of two hydroxyl groups [O(3) and O(4)] and by one O atom of each of two carboxyl groups [O(2) and O(5)] from the tartrate ligands; the four coordinating O atoms deviate significantly from coplanarity. The two V—O(hydroxyl) bond lengths [V—O(3) and V—O(4)] are slightly shorter than the two V—O(carboxyl) bond lengths

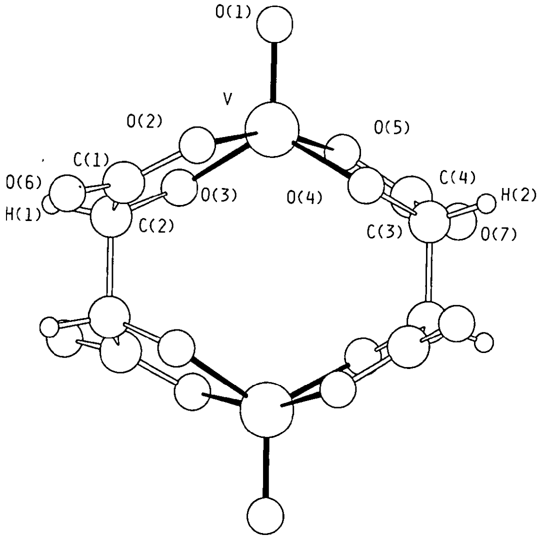


Fig. 1. A view of the [(VO)(L-C$_4$H$_2$O$_6$)]$_2^{4-}$ dimer, showing the atomic numbering.

[V—O(2) and V—O(5)] with average distances of 1.892 (2) and 2.014 (2) Å, respectively. It is of note that both types of O atom around the vanadyl ions are in *cis* positions, while in racemic vanadyl tartrate dimers (Tapscott, Belford & Paul, 1968) they are in *trans* positions.

The distortion of the coordination polyhedron formed by the five O atoms surrounding the V cation, which is between a trigonal bipyramid (TBP, $\Delta = 0$) and a square pyramid (SP, $\Delta = 1$), has been evaluated (Muetterties & Guggenberger, 1974). The value obtained ($\Delta = 0.57$) is in good agreement with an intermediate polyhedron geometry.

The Na cations and the water molecules are located in layers between the tetranegative anionic dimers, as shown in Fig. 2. The Na^+ ions are linked to O atoms with Na—O distances ranging from 2.311 (2) to 2.667 (2) Å. Na(1) is hexacoordinated by two water molecules, three O atoms from the hydroxyl and carboxyl groups of the tartrate ligands, and the O atom of a vanadyl group. The O atoms surrounding Na(1) form a distorted octahedral geometry ($\Delta = 0.17$, calculated between an octahedron, for which $\Delta = 0$, and a trigonal prism, $\Delta = 1$). The Na(2) cations are pentacoordinated by two water molecules and three O atoms from different carboxyl groups from the tartrate ligands. The coordination polyhedron of Na(2) has an intermediate geometry ($\Delta = 0.63$). The presence of an O atom O($W3^{ix}$) with an Na(2)···O($W3^{ix}$) distance of 2.968 (3) Å is of note [symmetry code: (ix) $\frac{3}{2} - x, y + \frac{1}{2}, \frac{1}{4} - z$]. Although this O atom could be considered as a sixth atom coordinated to Na(2), the Na(2)···O($W3^{ix}$) distance is too long to be a bonding distance.

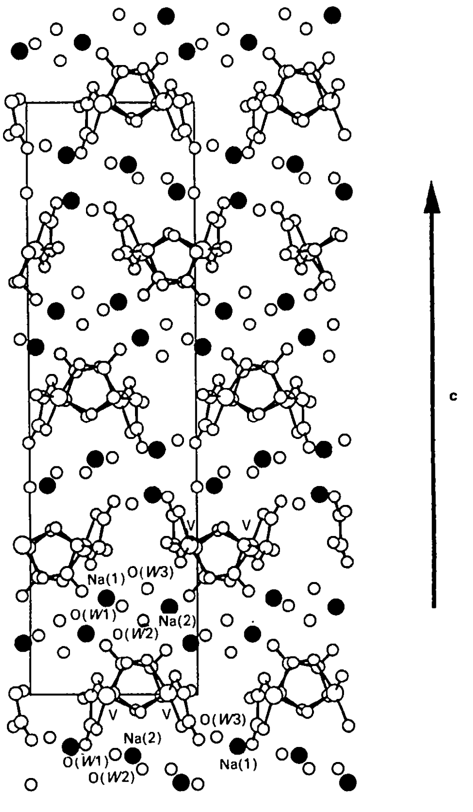


Fig. 2. A view along the [100] direction of the unit-cell contents in $Na_4[(VO)(L\text{-}C_4H_2O_6)]_2.6H_2O$. Na^+ cations are drawn as filled circles and Na—O bonds are omitted for clarity.

Each water molecule coordinates at least one Na cation and it is inferred that each is involved in hydrogen bonds with another water molecule or the tartrate ligand.

Experimental

The title complex may be obtained in polycrystalline form as described in the literature (Tapscott & Belford, 1967). Single crystals suitable for the structure determination were prepared for this work using a diffusion technique in which a solution of $Na_4[(VO)(L\text{-}C_4H_2O_6)]_2.6H_2O$ was left to mix with a 1/1 mixture of water/propanone in a diffusion device. Violet crystals with a tetragonal bipyramidal form were obtained.

Crystal data

$Na_2[(VO)(C_4H_2O_6)].3H_2O$
$M_r = 313.022$
Tetragonal
$P4_12_12$
$a = 8.2973$ (8) Å
$c = 29.4350$ (3) Å
$V = 2026.5$ (3) Å^3
$Z = 8$
$D_x = 2.052$ Mg m^{-3}
$D_m = 2.04$ (1) Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 8$–$12°$
$\mu = 1.071$ mm^{-1}
$T = 293$ K
Bipyramidal
0.31 × 0.25 × 0.25 mm
Violet

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3392 measured reflections
1807 independent reflections
1617 observed reflections [$I \geq 2.5\sigma(I)$]

$\theta_{max} = 30°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 41$
2 standard reflections
frequency: 60 min
intensity variation: 3.4%

Refinement

Refinement on F
$R = 0.0255$
$wR = 0.0269$
$S = 1.47$
1617 reflections
180 parameters
Only coordinates and two common isotropic displacement parameters for H atoms refined

$w = 1/[\sigma^2|F_o| + 0.0047|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.008$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
V	0.45478 (4)	0.82048 (4)	0.00206 (1)	1.42 (1)
Na(1)	0.2366 (1)	0.9581 (1)	0.08695 (3)	2.18 (2)
Na(2)	0.6052 (1)	0.3312 (1)	0.10246 (3)	3.22 (2)
O(1)	0.3162 (2)	0.9576 (2)	0.00619 (6)	2.23 (3)
O(2)	0.5736 (2)	0.9000 (2)	−0.05316 (5)	1.97 (3)
O(3)	0.6554 (2)	0.8628 (2)	0.03040 (5)	1.76 (3)
O(4)	0.3982 (2)	0.6244 (2)	−0.02644 (5)	1.82 (3)
O(5)	0.3914 (2)	0.6958 (2)	0.05807 (5)	1.90 (3)
O(6)	0.8084 (2)	1.0047 (2)	−0.07515 (5)	2.21 (3)
O(7)	0.3248 (2)	0.4516 (2)	0.08305 (5)	2.10 (3)
O(*W*1)	0.5022 (2)	1.0482 (2)	0.09996 (6)	2.76 (4)
O(*W*2)	0.1121 (2)	1.2009 (2)	0.07096 (7)	2.65 (4)
O(*W*3)	0.8371 (2)	0.1750 (4)	0.12499 (8)	4.08 (5)
C(1)	0.7203 (2)	0.9449 (2)	−0.04578 (7)	1.67 (3)
C(2)	0.7825 (2)	0.9141 (2)	0.00190 (7)	1.59 (4)
C(3)	0.3610 (2)	0.4924 (2)	0.00197 (7)	1.49 (3)
C(4)	0.3557 (2)	0.5475 (2)	0.05158 (6)	1.63 (4)

Table 2. *Selected geometric parameters* (Å, °)

V and Na coordination spheres			
V—O(1)	1.622 (2)	V—O(4)	1.890 (1)
V—O(2)	2.012 (1)	V—O(5)	2.016 (1)
V—O(3)	1.894 (1)	V···V^{i}	4.2929 (5)
O(4)—V—O(5)	81.74 (6)	O(3)—V—O(5)	87.94 (6)
O(3)—V—O(4)	124.98 (6)	O(2)—V—O(5)	163.04 (6)
O(2)—V—O(4)	92.61 (6)	O(2)—V—O(3)	82.21 (6)
O(1)—V—O(5)	96.53 (7)	O(1)—V—O(4)	117.44 (7)
O(1)—V—O(3)	117.38 (7)	O(1)—V—O(2)	100.25 (7)
V—O(2)—C(1)	114.9 (1)	V—O(3)—C(2)	116.8 (1)
V—O(4)—C(3)	117.3 (1)	V—O(5)—C(4)	115.6 (1)
O(1)—V···V^{i}	177.30 (9)		
Na(1)—O(1)	2.467 (2)	Na(2)—O(7)	2.596 (2)
Na(1)—O(5)	2.667 (2)	Na(2)—O(*W*3)	2.413 (2)
Na(1)—O(*W*1)	2.359 (2)	Na(2)—O(*W*1^{iv})	2.500 (2)
Na(1)—O(*W*2)	2.312 (2)	Na(2)—O(4^{i})	2.311 (2)
Na(1)—O(6^{ii})	2.316 (2)	Na(2)—O(6^{v})	2.325 (2)
Na(1)—O(7^{iii})	2.410 (2)		
Average values for the tartrate ligands			
C—C	1.53 (1)	C—O(carboxyl)	1.285 (8)
C—O(hydroxyl)	1.413 (1)	C═O	1.242 (8)
C—H	0.980 (8)		
C—C—C	106.7 (4)	C—C—O(carboxyl)	120.7 (4)
C—C—O(hydroxyl)	108.3 (3)	C—C═O	115.4 (6)
Hydrogen bonds			
O(*W*1)···O(3)	2.859 (2)	O(*W*1)···O(*W*3^{vi})	3.062 (3)
O(*W*2)···O(7^{vi})	2.751 (2)	O(*W*2)···O(1^{viii})	2.778 (3)
O(*W*3)···O(*W*2^{vii})	2.789 (3)		

Symmetry codes: (i) $y, x, -z$; (ii) $y-1, x, -z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z$; (iv) $x, y-1, z$; (v) $\frac{3}{2}-y, x-\frac{1}{2}, \frac{1}{4}+z$; (vi) $x, 1+y, z$; (vii) $1+x, y-1, z$; (viii) $y-1, x+1, -z$.

The data were corrected for Lorentz and polarization effects. The structure was determined by Patterson methods using the program *SHELXS*86 (Sheldrick, 1990) and refined by a full-matrix least-squares method using *SHELX*76 (Sheldrick, 1976). The H atoms were located from difference Fourier maps and were refined isotropically. Figures were produced using *SCHAKAL*88 (Keller, 1988) and molecular geometry calculations were performed using *BONDLA* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1114). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Second Triclinic Form of Pyridinium μ-oxo-μ-sulfato-bis[oxotris(isothiocyanato)-molybdate(V)]

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Abstract

Crystals of the new triclinic form of the title compound, $(C_5H_6N)_4[Mo_2O_3(SO_4)(NCS)_6]$, space group $P\bar{1}$, have been prepared and structurally characterized. There are two crystallographically independent complex