The Structure of Tetraethylammonium Vanadyl(IV) (±)-Tartrate(4—) Octahydrate

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Abstract

The crystal structure of tetraethylammonium dioxo-μ-(+)-tartrato(4—)-μ-(—)-tartrato(4—)-divanadate(IV) octahydrate has been determined by single-crystal X-ray diffraction techniques. This compound crystallizes with two $[NEt_4]_4[(VO)_2\{(+)\text{-}C_4H_2O_6\}\{(—)\text{-}C_4H_2O_6\}].8H_2O$ units in a monoclinic unit cell of $P2_1/n$ symmetry and cell dimensions $a = 12{\cdot}058$ (2), $b = 13{\cdot}532$ (4), $c = 17{\cdot}159$ (4) Å and $\beta = 108{\cdot}18$ (2)°. This structure was solved by direct methods and refined by full-matrix least-squares techniques to $R_1 = 0{\cdot}058$ for 4538 independent diffractometer-collected reflections with $I \geq 3\sigma(I)$. The binuclear tetranegative anion exhibits a vanadium–vanadium distance of 3·985 (1) Å.

Introduction

Exchange coupling in binuclear vanadyl(IV) tartrate complexes has been extensively studied by EPR spectroscopy in solutions and glasses (McIlwain, Tapscott & Coleman, 1977, and references therein); however, owing to line-broadening interdimer interactions, acceptable solid-state EPR spectra have not been available. We have now found that crystals of the tetraethylammonium salt of the (±)-tartrate(4—) complex are magnetically dilute and give well resolved triplet-state EPR spectra. In preparation for a single-crystal EPR study, a crystal structure determination has been carried out on $[NEt_4]_4[(VO)_2\{(+)\text{-}C_4H_2O_6\}\{(—)\text{-}C_4H_2O_6\}].8H_2O$. When compared with the results of a previously reported structure determination on the sodium salt (Tapscott, Belford & Paul, 1968), the results of the present study also permit us to determine the effect of environment on the structure of the binuclear anion in order to help evaluate the possible importance of media effects in earlier EPR studies.

The tetraethylammonium salt of vanadyl(IV) (±)-tartrate(4—) was prepared by a previously described method (Tapscott & Belford, 1967) with tetraethylammonium hydroxide used as the base. Crystals were obtained by slow evaporation of the solvent under a nitrogen atmosphere and were used without further recrystallization. A purple crystal with dimensions 0·6 × 0·4 × 0·3 mm was glued to the tip of a glass fiber, covered with a thin film of butyl acetate cement to prevent hydration of the specimen, and mounted on a eucentric goniometer head.

The determination of the Bravais lattice and cell dimensions and the collection of intensity data were carried out using a Syntex *P*3/*F* diffractometer system equipped with a graphite-crystal monochromator and a molybdenum-target X-ray tube ($\lambda K\alpha = 0{\cdot}71069$ Å).

The lattice parameters were determined using 25 independently centered reflections ($9° < 2\theta < 25°$) and an automatic indexing routine from the *P*3 software package. After least-squares refinement of the angle settings, the crystal system and axial lengths were checked using axial photographs.

Crystal data

$[N(C_2H_5)_4]_4[V_2(C_4H_2O_6)_2O_2].8H_2O$, $M_r = 1091{\cdot}30$, monoclinic, $P2_1/n$, $a = 12{\cdot}058$ (2), $b = 13{\cdot}532$ (4), $c = 17{\cdot}159$ (4) Å, $\beta = 108{\cdot}18$ (2)°, $V = 2660$ (1) Å³, λ(Mo $K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}46$ mm⁻¹, $Z = 2$, $D_c = 1{\cdot}36$ Mg m⁻³.

The intensities were measured in the 2θ–θ scan mode with a variable scan rate (3·90 to 29·30° min⁻¹) and a background time to scan time ratio of 1·00. A scan range of 1·00° on each side of the $K\alpha$ doublet was used. A total of 6904 reflections were collected with $4{\cdot}0° \leq 2\theta \leq 55{\cdot}0°$ to yield a unique data set of 6152 non-zero reflections, of which 4538 were considered observed with $I \geq 3\sigma(I)$ based on $\sigma(I) = \{$total scan counts $- [$(sum of background counts)/(background to scan ratio)²$]\}^{1/2} \times$ scan rate. The intensities of two standard reflections, which were measured every 50 reflections, indicated no significant decay during the data-collection period. Atomic scattering factors (Cromer & Mann, 1968) were used for all atoms except H (Stewart, Davidson & Simpson, 1965) and anomalous-dispersion corrections were made for vanadium (Dauben & Templeton, 1955). No absorption or extinction corrections were applied.

Structural determination and refinement

The structural determination and initial refinement calculations were carried out on the Syntex *XTL*

structure determination system. Phases provided by *MULTAN* (Germain, Main & Woolfson, 1971) were used to solve the structure with all nonhydrogen atoms being located in subsequent Fourier syntheses. Block-diagonal refinement of the nonhydrogen atoms with isotropic thermal factors converged to $R_1 = 0.100$. A difference map revealed the locations of all H atoms which were then placed in idealized positions. Full-matrix anisotropic refinement (Stewart, 1976) of all nonhydrogen atoms and positional refinement of the two independent hydrogens in the $[(VO)_2(C_4H_2O_6)_2]^{4-}$

Table 1. *Fractional coordinates of refined atoms with standard deviations and their corresponding B_{eq} values for anisotropically refined atoms*

	x	y	z	B_{eq} (Å^2)
Vanadyl(IV) tartrate(4−) anion				
V	0.03582 (4)	0.05323 (4)	0.61345 (3)	1.690
O(1)	0.2222 (2)	0.2646 (2)	0.5469 (2)	2.462
O(2)	−0.3128 (2)	0.0547 (2)	0.5456 (2)	2.739
O(3)	0.0926 (2)	0.1894 (2)	0.5958 (2)	1.962
O(4)	−0.1295 (2)	0.1064 (2)	0.5761 (2)	2.110
O(5)	0.1844 (2)	0.0170 (2)	0.5979 (1)	1.890
O(6)	−0.0429 (2)	−0.0636 (2)	0.5618 (2)	2.204
O(7)	0.0577 (2)	0.0441 (2)	0.7100 (2)	2.743
C(1)	0.1780 (3)	0.1893 (3)	0.5653 (2)	1.939
C(2)	0.2189 (3)	0.0869 (2)	0.5504 (2)	1.689
C(3)	−0.1638 (3)	−0.0624 (2)	0.5415 (2)	1.637
C(4)	−0.2075 (3)	0.0401 (2)	0.5551 (2)	1.797
H(1)	0.307 (5)	0.089 (5)	0.562 (3)	−
H(2)	−0.199 (4)	−0.019 (4)	0.575 (3)	−
Tetraethylammonium cation*				
N(1)	0.3330 (2)	0.1774 (2)	0.8732 (2)	1.888
C(5)	0.3009 (3)	0.0700 (3)	0.8740 (2)	2.322
C(6)	0.3223 (4)	0.0251 (3)	0.9576 (3)	3.291
C(7)	0.2954 (3)	0.2077 (3)	0.7838 (2)	2.545
C(8)	0.3199 (4)	0.3142 (3)	0.7683 (3)	2.730
C(9)	0.4640 (3)	0.1918 (3)	0.9129 (2)	2.851
C(10)	0.5400 (4)	0.1351 (4)	0.8729 (3)	3.370
C(11)	0.2753 (3)	0.2401 (3)	0.9224 (3)	2.910
C(12)	0.1440 (5)	0.2322 (4)	0.8954 (4)	4.356
Tetraethylammonium cation*				
N(2)	0.1668 (2)	0.1507 (2)	0.1783 (2)	1.997
C(13)	0.0934 (4)	0.2223 (3)	0.2084 (3)	2.995
C(14)	0.0270 (4)	0.2968 (4)	0.1450 (3)	4.184
C(15)	0.2134 (4)	0.0753 (3)	0.2466 (3)	3.295
C(16)	0.2901 (5)	−0.0036 (4)	0.2273 (4)	4.749
C(17)	0.0937 (4)	0.0995 (4)	0.1000 (3)	3.338
C(18)	−0.0115 (5)	0.0443 (4)	0.1080 (4)	4.850
C(19)	0.2657 (3)	0.2033 (3)	0.1586 (2)	2.680
C(20)	0.3537 (4)	0.2509 (4)	0.2304 (3)	3.644
Water molecules				
O(8)	0.3993 (3)	−0.0294 (3)	0.7015 (2)	3.797
O(9)	0.0145 (3)	0.3765 (2)	0.6387 (2)	3.293
O(10)	0.5349 (3)	−0.0865 (3)	0.5777 (2)	4.606
O(11)	0.3553 (4)	0.2883 (3)	0.4364 (3)	5.234

* In the tetraethylammonium cations the odd-numbered carbons designate the methylene carbons and the even-numbered carbons designate methyl carbons.

anion converged at $R_1 = 0.058$ and $R_2 = 0.096$. All least-squares refinements were based upon the minimization of $\sum w_i ||F_o| - |F_c||^2$ using counter weights (Grant, Killean & Lawrence, 1969) where $w_i^{-1} = \sigma_{F_i}^2 + C^2 F_i^2$, with $C = 0.106$. A final difference map revealed no maxima greater than 0.2 e Å^{-3}. The final fractional coordinates of the refined atoms are listed in Table 1.*

Results and discussion

The binuclear tetranegative anion, which lies on an inversion center, has the same site symmetry as that observed for the anions in the related sodium vanadyl-(IV) $(\pm)$-tartrate(4−) (Tapscott, Belford & Paul, 1968) and the sodium vanadyl(IV) $(\pm)$-dimethyltartrate(4−) (Ortega, Campana, Tapscott & Morosin, 1978) compounds. Tables 2 and 3 give the bond lengths and bond angles for the tetranegative anion which is shown in Fig. 1. The bonding parameters found for the tetra-ethylammonium salt do not vary significantly from those found for the sodium salt. The major differences lie in the molecular conformation and the nonbonding distances.

* Lists of structure factors, anisotropic thermal parameters and idealized hydrogen positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35232 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances (Å) with standard deviations*

V−V'	3.985 (1)	C(1)−O(1)	1.235 (5)
V−O(7)	1.599 (3)	C(4)−O(2)	1.244 (4)
V−O(3)	2.021 (3)	C(1)−O(3)	1.292 (5)
V−O(4)	2.026 (2)	C(4)−O(4)	1.298 (4)
V−O(6)	1.913 (2)	C(2)−O(5)	1.394 (4)
V−O(5)	1.955 (3)	C(3)−O(6)	1.389 (4)
C(1)−C(2)	1.519 (5)		
C(3)−C(4)	1.528 (5)	C(2)−H(1)	1.01 (6)
C(2)−C(3)'	1.544 (4)	C(3)−H(2)	1.03 (6)

Table 3. *Bond angles (°) with standard deviations*

| O(7)−V−O(3)	105.7 (1)	O(1)−C(1)−O(3)	124.3 (3)
O(7)−V−O(4)	105.6 (1)	O(2)−C(4)−O(4)	124.1 (3)
O(7)−V−O(5)	105.3 (1)	O(1)−C(1)−C(2)	121.4 (3)
O(7)−V−O(6)	108.3 (1)	O(2)−C(4)−C(3)	120.7 (3)
O(3)−V−O(4)	88.5 (1)	O(3)−C(1)−C(2)	114.3 (3)
O(3)−V−O(5)	80.8 (1)	O(4)−C(4)−C(3)	115.2 (3)
O(5)−V−O(6)	94.1 (1)	C(4)−C(3)−O(6)	110.9 (3)
O(4)−V−O(6)	81.4 (1)	C(1)−C(2)−O(5)	110.5 (3)
O(3)−V−O(6)	145.7 (1)	O(6)−C(3)−C(2)'	109.7 (3)
O(4)−V−O(5)	154.1 (1)	O(5)−C(2)−C(3)'	109.8 (2)
V−O(3)−C(1)	114.2 (2)	C(4)−C(3)−C(2)'	107.0 (2)
V−O(4)−C(4)	114.1 (2)	C(1)−C(2)−C(3)'	107.9 (2)
V−O(5)−C(2)	111.3 (2)	O(6)−C(3)−H(2)	116 (3)
V−O(6)−C(3)	115.9 (2)	O(5)−C(2)−H(1)	113 (3)
O(7)−V−V'	154.1 (1)	C(1)−C(2)−H(1)	109 (3)
		C(4)−C(3)−H(2)	104 (3)
		H(2)−C(3)−C(2)'	109 (3)
		H(1)−C(2)−C(3)'	107 (3)
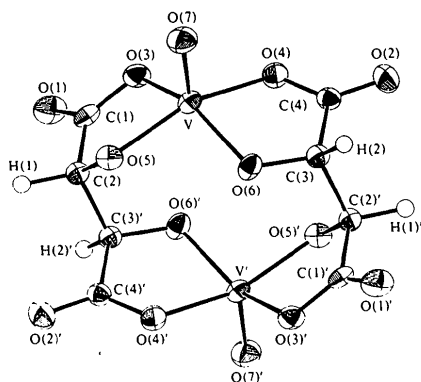
Fig. 1. A view of the [(VO)₂{(+)-C₄H₂O₆}{(−)-C₄H₂O₆}] tetranegative anion. Primed atoms are obtained by the symmetry operation $-x, -y, 1-z$.

Since this study is a prelude to a single-crystal EPR study, the geometry about the V atoms as well as the intra- and intermolecular distances require special attention. The minimum intermolecular V−V distance is 8·906 Å for the tetraethylammonium salt, compared to 7·351 Å for the sodium salt and 7·887 Å for the dimethyltartrate(4−) complex. The observed increase in intermolecular distance apparently minimizes inter-dimer interactions. The intramolecular V−V distance in this structure [3·985 (1) Å] is shorter than that in the sodium salt structure [4·082 (2) Å]. The dihedral angle (Table 4) for O(3)−C(1)−C(2)−O(5) is −20·5 (3)° while the dihedral angle for O(4)−C(4)−C(3)−O(6) is only 4·8 (4)°. The same dihedral angles in the sodium salt structure are −15·0 and 1·0°, while in the dimethyltartrate(4−) structure the corresponding angles are −23·5 (4) and 0·7 (5)°. Thus these dihedral angles show relatively small variation upon changing either the counterion or the substituent on carbons 2 and 3 of the α-hydroxycarboxylate chain.

The four-carbon chain for (+)- or (−)-tartrates is known to be nearly planar (Tapscott, Belford & Paul,

1969). The molecule in the present structure determination is no exception, and, in addition, the four coordinating oxygens [O(4), O(6), O(3)′, O(5)′] are also nearly planar with this plane approximately parallel to the carbon plane.

The two independent tetraethylammonium cations lie in general positions. The tetraethylammonium cations show no obvious distortions, though the methyl C atoms show high thermal motion. The average N−C bond distance is 1·52 ± 0·01 Å and the average C−C bond distance is 1·51 ± 0·01 Å, where eight bond distances were averaged in each case.

The hydrogen-bonding network through the water molecules [O(8), O(9), O(10), and O(11)] is not as extensive as that in the sodium vanadyl(IV) tartrate(4−) structure. The water hydrogens are coordinated to the tartrate hydroxyl and the carbonyl oxygens as well as to other water oxygen atoms. The distances and angles about the water molecules are listed in Table 5.

A comparison of the vanadyl(IV) (±)-tartrate(4−) anionic complexes from this study and the sodium salt study reveals that this complex is fairly rigid and that only slight distortions in geometry occur upon a change in the counterion.

Table 4. Dihedral angles (°)

O(3)−C(1)−C(2)−O(5)	−20·5 (3)
O(4)−C(4)−C(3)−O(6)	4·8 (4)
O(5)−C(2)−C(3)′−O(6)′	−60·3 (3)

Table 5. Water molecule coordination lengths and angles

(A) Coordination distances (Å)		(B) Coordination angles (°)	
O(8) ← O(5)	2·720 (3)	O(10)−O(8)−O(5)	101·8 (1)
O(8) → O(9)	2·907 (4)	O(3)−O(9)−O(8)	125·3 (1)
O(8) ← O(10)	3·152 (6)	O(2)−O(10)−O(2)′	105·5 (1)
O(9) ← O(3)	2·875 (4)	O(2)−O(10)−O(8)	118·1 (1)
O(10) ← O(2)	2·822 (5)	O(2)−O(10)−O(11)	105·2 (2)
O(10) → O(2)′	2·881 (4)	O(2)−O(10)−O(8)	84·3 (1)
O(10) ← O(11)	3·080 (6)	O(2)−O(10)−O(11)	113·5 (1)
O(11) ← O(1)	2·857 (6)	O(8)−O(10)−O(11)	126·7 (2)
		O(10)−O(11)−O(1)	107·3 (2)

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