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Key indicators

Single-crystal X-ray study

$T = 210\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$

R factor = 0.025

wR factor = 0.066

Data-to-parameter ratio = 13.1

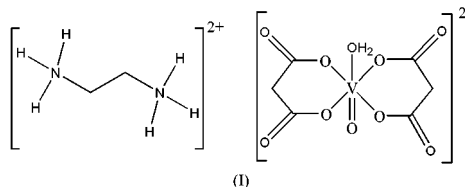
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Ethylenediamonium aquabis(malonato)-oxovanadate(IV)

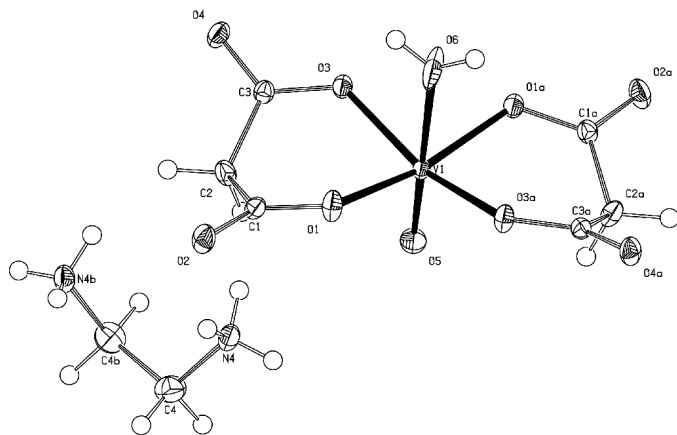
In the anion of the title compound, $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{VO}(\text{H}_2\text{O})(\text{C}_3\text{H}_2\text{O}_4)_2]$ or $\text{H}_2\text{en}[\text{VO}(\text{mal})_2\text{H}_2\text{O}]$, vanadium(IV) is distorted-octahedrally coordinated by six donor O atoms. The two malonate ligands are situated in the equatorial plane, whereas the oxo and the water ligand occupy axial positions. The apical $\text{V}=\text{O}$ bond exhibits a strong *trans* influence. The anion possesses crystallographically imposed C_2 symmetry, with the central V atom, the oxo and the water ligand lying on the twofold axis.

Comment

There are only a few crystal structures of bis(dicarboxylato)-oxovanadate(IV) complexes described in the literature, namely disodium bis(oxalato)fluorooxovanadate(IV) hexahydrate (Rieskamp & Mattes, 1976), diammonium aquabis(oxalato)oxovanadate(IV) monohydrate (Hazell, 1968; Oughtred *et al.*, 1976), dipotassium aquabis(malonato)-oxovanadate(IV) trihydrate (Fillipova & Kiosse, 2000), diammonium aquabis(malonato)oxovanadate(IV) monohydrate (Piro & Baran, 1997) and N,N,N',N' -tetramethylethylenediamonium aquabis(malonato)oxovanadate(IV) dihydrate (Pajunen & Pajunen, 1980).



For this type of complex, two different coordination modes are observed for the dicarboxylate ligands, which can be arranged either *cis* or *trans* to each other. It was noted that the oxovanadate(IV) complexes containing oxalate ligands prefer a *cis* configuration, while the corresponding malonate complexes prefer a *trans* configuration. This suggests that the size of the chelate ring has a profound effect on the distribution of geometric isomers. The chelate ring is in a boat conformation. As expected, in the ethylenediamonium aquabis(malonato)oxovanadate(IV) complex, (I), the malonate ligands are *trans* (Fig. 1), as in N,N,N',N' -tetramethylethylenediamonium aquabis(malonato)oxovanadate(IV) dihydrate, (II) (Pajunen & Pajunen, 1980). Comparing the apical $\text{V}=\text{O}$ bond distances in these two complexes, we note that they are equivalent. However, for complex (I) the $\text{V}-\text{O}$ bond distances in the equatorial plane [$\text{V}-\text{O}1 = 2.012$ (1) and $\text{V}-\text{O}3 = 2.000$ (1) \AA] are longer than in complex (II) [$\text{V}-\text{O}1 = 1.981$ (2) and $\text{V}-\text{O}3 = 1.995$ (2) \AA]. Atoms V1, O5 and O6 lie on a twofold symmetry axis.


Figure 1

A view of the molecular structure of $\text{H}_2\text{en}[\text{VO}(\text{mal})_2\text{H}_2\text{O}]$, showing the atom labeling. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (a) $1-x, y, \frac{1}{2}-z$; (b) $-x, y, \frac{1}{2}-z$.]

The ethylenediammonium ion participates in five strong intermolecular hydrogen bonds with five O atoms (Table 1). In addition, water atom O6 acts as a hydrogen-bond donor to atom O2. Structural units are exclusively connected through hydrogen bonds, which extend in three dimensions. Cyclic hydrogen bonds are formed between atoms N4 and O4 around the inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Comparing the same intermolecular hydrogen bond in complexes (I) (Table 1) and (II) $[\text{N}(\text{H}) \cdots \text{O} = 1.89(1) \text{ \AA}]$, we found an unexpected result. The bulkier cation of (II) has a shorter hydrogen-bond distance. The conformation of the cation in (I) is closer to eclipsed, with an $\text{N4}-\text{C4}-\text{C4b}-\text{N4b}$ torsion angle of $-54.8(2)^\circ$. The intermolecular interactions probably stabilize the conformation of the cation.

Experimental

The title complex was obtained by the reaction of an aqueous solution of ammonium metavanadate(V), malonate acid and ethylenediamine-*N*-acetic acid in a 1:1:1 molar ratio at pH 4.5. The reaction solution was filtered in order to remove the yellow solid which precipitated during the reaction. After a few days, a blue compound crystallized from the mother liquor. Some reduction occurred and a vanadium(IV) complex was obtained.

Crystal data

$(\text{C}_2\text{H}_{10}\text{N}_2)[\text{VO}(\text{C}_3\text{H}_2\text{O}_4)_2(\text{H}_2\text{O})]$
 $M_r = 351.17$
 Monoclinic, $C2/c$
 $a = 14.579(2) \text{ \AA}$
 $b = 11.866(1) \text{ \AA}$
 $c = 8.758(2) \text{ \AA}$
 $\beta = 123.13(1)^\circ$
 $V = 1268.8(4) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.838 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 48 reflections
 $\theta = 4.4\text{--}13.6^\circ$
 $\mu = 0.84 \text{ mm}^{-1}$
 $T = 210(2) \text{ K}$
 Prism, blue
 $0.52 \times 0.34 \times 0.26 \text{ mm}$

Data collection

Siemens P4 diffractometer
 Profile data from ω scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.717, T_{\max} = 0.804$
 3486 measured reflections
 1689 independent reflections
 1568 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$
 $\theta_{\text{max}} = 29.0^\circ$
 $h = -19 \rightarrow 19$
 $k = -16 \rightarrow 16$
 $l = -11 \rightarrow 11$
 3 standard reflections
 every 100 reflections
 intensity decay: 5.4%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.066$
 $S = 1.06$
 1689 reflections
 129 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 1.3358P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.53 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bonding geometry ($\text{\AA}, ^\circ$).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N4}-\text{H4A} \cdots \text{O4}^{\text{i}}$	0.88 (3)	1.91 (3)	2.7859 (15)	171 (2)
$\text{N4}-\text{H4B} \cdots \text{O4}^{\text{ii}}$	0.81 (2)	2.12 (2)	2.8067 (15)	142 (2)
$\text{N4}-\text{H4B} \cdots \text{O1}^{\text{iii}}$	0.81 (2)	2.58 (2)	3.0080 (16)	115 (2)
$\text{N4}-\text{H4C} \cdots \text{O3}^{\text{iv}}$	0.84 (2)	2.05 (2)	2.8312 (15)	154 (2)
$\text{N4}-\text{H4C} \cdots \text{O5}^{\text{v}}$	0.84 (2)	2.46 (2)	2.9829 (17)	122 (2)
$\text{O6}-\text{H6} \cdots \text{O2}^{\text{i}}$	0.79 (2)	1.91 (2)	2.6902 (12)	168 (2)

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

All H atoms were located in a difference Fourier synthesis and were refined with individual isotropic displacement parameters.

Data collection: *XSCANS* (Bruker, 1999); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

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