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A three-dimensional supramolecular vanadium hydroxylamide complex: poly[di-μ_2-aqua-bis(hydroxylamido)-μ_3-malonato-oxidosodiumvanadium(V)]

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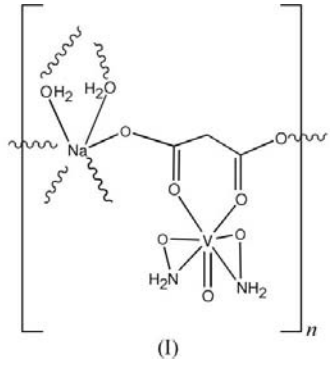
The crystal structure of the title compound, [NaV-$(C_3H_2O_4)(NH_2O)_2O(H_2O)_2$], is built up of NaO_6 and VO_5N_2 polyhedra connected through malonate bridges. The NaO_6 octahedra are linked by edge sharing in the equatorial plane to form one-dimensional infinite chains. These chains are linked together by the malonate bridges to form two-dimensional layers. The distorted VO_5N_2 pentagonal bipyramid is grafted on to the layer by a malonate carboxylate O atom. Adjacent layers are connected through O—H···O and N—H···O hydrogen bonds to build up a three-dimensional supramolecular structure.

Comment

Simple vanadium salts such as $NaVO_3$ and $VOSO_4$ can lower blood glucose levels by activating glucose uptake by cells for metabolism in humans, but numerous studies have shown that organic vanadium complexes are less toxic and several times more effective in lowering blood glucose levels (Thompson *et al.*, 2002). Therefore, much research has gone into exploring the synthesis and structure of insulin-mimetic vanadium complexes. Vanadium hydroxylamide compounds are known to be promising candidates in the study of the insulin-mimetic activity of vanadium compounds (Tracey, 2000). Several vanadium hydroxylamide compounds have been reported, such as $[VO(NH_2O)(dipic)(H_2O)]$ (dpic is dipicolinic acid; Nuber *et al.*, 1981), $[VO(NH_2O)_2L]\cdot H_2O$ (L = glycine, serine and glycylglycine), $[VO(NH_2O)_2(imidazole)]Cl$ (Keramidas *et al.*, 1997), but no vanadium hydroxylamide complexes with carboxylate ligands have been reported to date. Investigation of the preparation and crystal structure of vanadium hydroxylamide complexes with malonic acid provides not only useful information on vanadium chemistry but also promising new candidates for the study of the insulin-mimetic activity of vanadium. Therefore, we report here the preparation and crystal structure of the title vanadium hydroxylamide complex with malonic acid, (I).



(I)

In the structure of (I), the V^V ion is seven-coordinated in a pentagonal bipyramidal geometry by two bidentate hydroxylamide ligands, one oxide ligand and two O atoms from a malonate ligand (Fig. 1). The hydroxylamide ligands coordinate in a side-on manner, as observed in related structures (Paul *et al.*, 1997; Keramidas *et al.*, 1997; Nuber *et al.*, 1981). The malonate behaves as a chelating ligand to the V^V ion. The centroids of the two hydroxylamide ligands and atom O2 of the malonate define the equatorial plane perpendicular to the V═O bond. The other chelating atom, O1, is in an axial position *trans* to the oxide ligand, with an axial O1—V1—O7 angle of 171.06 (5)°. The terminal V1═O7 bond length is 1.6017 (10) Å, leading to the expected *trans* lengthening of the V1—O1 bond to 2.1470 (9) Å, which is longer than the V1—O2 bond (Table 1). The O—N, V—O and V—N distances and O—V—N angles involving the hydroxylamide ligands are comparable, within experimental errors of 0.0004 Å and

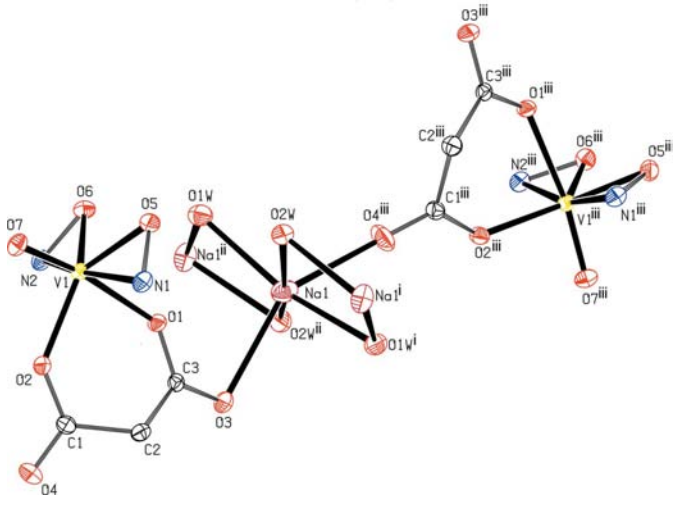


Figure 1
A view of part of the layer structure of (I), showing the asymmetric unit, atom connectivities and coordination environment. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) x, $-y+\frac{1}{2}$, $z-\frac{1}{2}$; (ii) x, $-y+\frac{1}{2}$, $z+\frac{1}{2}$; (iii) $x+1$, $-y+\frac{1}{2}$, $z+\frac{1}{2}$.]

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0.0002°, respectively, with related vanadium hydroxylamide complexes reported in the literature (Table 3).

The coordination environment around the Na^{I} ion can be described as a distorted octahedron. The vertices are occupied by six O atoms, of which four belong to water molecules [Na—O = 2.4132 (13)–2.4305 (13) Å] located in the equatorial plane, with two slightly more distant O atoms from two different malonate ligands at the apices (Table 1 and Fig. 1). In the crystal structure, adjacent Na polyhedra are linked by a shared edge on opposite sides in the equatorial plane to form an infinite one-dimensional chain. These chains are connected by malonate bridges to form two-dimensional layers (Fig. 2). The VO_5N_2 polyhedra are grafted on to this layer *via* carboxylate atoms O1 and O2 of the malonate ligands, which are distributed on both sides of the layers owing to the alternating orientation of the two carboxylate groups (Fig. 2). This arrangement model for VO_5N_2 favours the minimization of steric hindrance and boosts the stability of the crystal structure.

The remarkable organization of the crystal structure of (I) can be recognized in a view along the *c* axis (Fig. 3), which shows the two-dimensional layers parallel to the (010) plane. An extensive hydrogen-bonding network (Table 2) links the different layers through different functional groups, such as hydroxylamide O and water O, or hydroxylamide N and carboxyl O. This leads to the formation of a stable three-dimensional supramolecular structure.

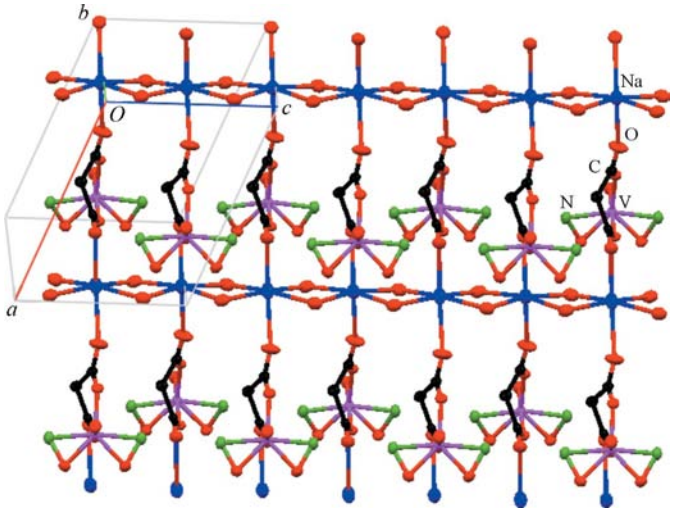

Figure 2
The two-dimensional layer structure of (I), viewed in the *ac* plane. Atom labels represent atoms types and H atoms have been omitted for clarity.

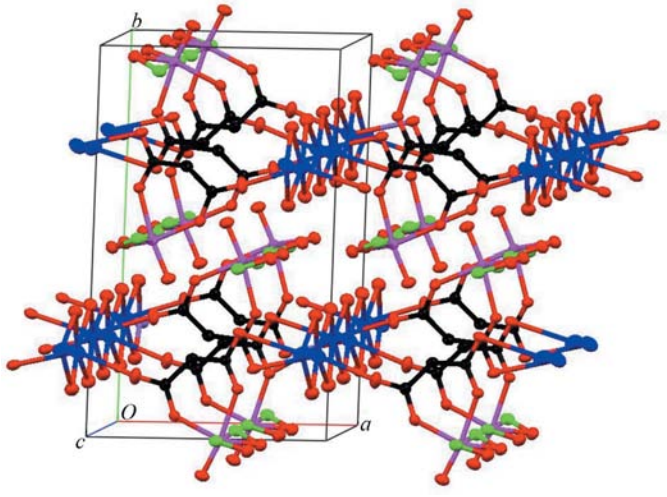

Figure 3
A packing view of (I), showing the two-dimensional layers parallel to the (010) plane. H atoms have been omitted for clarity.

Experimental

NH_4VO_3 (1.375 mmol), malonic acid (2.637 mmol) and NaOH (7.863 mmol) were dissolved in H_2O (10 ml) at room temperature. The resulting light-yellow solution was stirred for approximately 0.5 h in an ice bath. $NH_2OH{\cdot}HCl$ (7.326 mmol) was added gradually with constant stirring for 0.5–1.0 h. The resulting yellow solution (pH = 6.02) was filtered. Colourless crystals of (I) suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a mixture of the filtrate and anhydrous ethanol at 277 K over a period of a few days.

Table 1
Selected geometric parameters (Å, °).

V1—N1	2.0193 (11)	Na1—O1*W*	2.4305 (13)
V1—N2	2.0080 (12)	Na1—O1*W*^{i}	2.4169 (13)
V1—O1	2.1470 (9)	Na1—O2*W*	2.4132 (13)
V1—O2	2.0368 (9)	Na1—O2*W*^{ii}	2.4140 (13)
V1—O5	1.9030 (10)	Na1—O3	2.6027 (13)
V1—O6	1.8969 (10)	Na1—O4^{iii}	2.5303 (14)
V1—O7	1.6017 (10)	N1—O5	1.4000 (15)
Na1—O1	2.9173 (12)	N2—O6	1.3969 (15)
O1—V1—O6	84.60 (4)	N1—V1—O5	41.69 (5)
O1—V1—O7	171.06 (5)	N1—V1—O6	128.15 (5)
O2—V1—O5	136.61 (4)	N1—V1—O7	96.99 (5)
O2—V1—O6	132.05 (4)	N2—V1—O2	90.89 (4)
O2—V1—O7	89.58 (5)	N2—V1—O5	128.56 (5)
O5—V1—O6	87.28 (4)	N2—V1—O6	41.80 (5)
O5—V1—O7	100.38 (5)	N2—V1—O7	97.75 (5)
O6—V1—O7	101.96 (5)	O2*W*—Na1—O3	102.47 (4)
N1—V1—N2	163.98 (5)	O3—Na1—O4^{iii}	145.72 (5)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O1	0.85	2.58	3.1245 (15)	123
O1*W*—H1*WB*···O5^{iv}	0.85	2.24	2.8987 (14)	134
O1*W*—H1*WA*···O6	0.85	2.07	2.8994 (15)	166
O2*W*—H2*WA*···O5	0.85	2.03	2.8633 (15)	167
O2*W*—H2*WB*···O6^{iv}	0.85	2.31	2.9701 (14)	135
N1—H1*A*···O3^{i}	0.84	2.15	2.9717 (15)	163
N1—H2*A*···O2^{v}	0.84	2.13	2.9635 (15)	172
N2—H1*B*···O2^{vi}	0.85	2.10	2.9418 (15)	173
N2—H2*B*···O3^{ii}	0.85	2.07	2.9010 (15)	168

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

Table 3
Selected bond distances (Å) and angles (°) in vanadium(V) hydroxylamide complexes.

Compound	N—O	V—O	V—N	O—V—N	Ref
NH_2OH	1.47				(*a*)
$[VO(H_2NO)(C_7H_3NO_4)(H_2O)]$	1.3710 (4)	1.9030 (3)	2.0070 (3)	40.93 (2)	(*b*)
$[VO(H_2NO)_2(GlyGly)]\cdot H_2O$	1.397 (3)	1.8961 (14)	2.0046 (16)	41.87 (7)	(*c*)
	1.3960 (19)	1.889 (2)	2.0165 (15)	41.72 (7)	
$[VO(H_2NO)_2(GlyGly)]\cdot H_2O$	1.4040 (3)	1.8920 (3)	2.0210 (4)	41.90 (2)	(*d*)
	1.3970 (4)	1.9080 (3)	2.0070 (4)	41.90 (2)	
$[VO(H_2NO)_2(Gly)]\cdot H_2O$	1.4050 (3)	1.8980 (4)	2.0180 (3)	41.89 (3)	(*d*)
	1.4020 (3)	1.9020 (3)	2.0100 (4)	41.91 (4)	
$[VO(H_2NO)_2(Ser)]$	1.3980 (5)	1.8990 (5)	2.0100 (3)	41.08 (5)	(*d*)
	1.3870 (4)	1.8940 (4)	2.0040 (3)	41.56 (15)	
$[VO(H_2NO)_2(imidazole)_2]$	1.4030 (4)	1.9290 (3)	1.9910 (4)	41.90 (14)	(*d*)
	1.3900 (3)	1.9130 (4)	1.9940 (3)	41.63 (9)	
$[VO(H_2NO)_2(Ala)]\cdot 2H_2O$	1.4070 (11)	1.9160 (8)	2.0280 (10)	41.70 (3)	(*e*)
	1.3830 (10)	1.9080 (9)	1.9970 (10)	41.40 (3)	
$[VO(H_2NO)_2(Thr)]$	1.3980 (3)	1.8960 (2)	2.0140 (3)	41.80 (9)	(*e*)
	1.3940 (4)	1.8830 (2)	2.0270 (3)	41.33 (12)	
$Na[VO(NH_2O)_2(C_7H_2O_4)]\cdot H_2O$	1.4002 (15)	1.9031 (10)	2.0193 (11)	41.70 (4)	(*f*)
	1.3972 (15)	1.8970 (10)	2.0080 (12)	41.81 (5)	

References: (*a*) Meyers *et al.* (1955); (*b*) Nuber *et al.* (1981); (*c*) Paul *et al.* (1997); (*d*) Keramidas *et al.* (1997); (*e*) Li *et al.* (2004); (*f*) this work.

Crystal data

$[NaV(C_3H_2O_4)(NH_2O)_2O(H_2O)_2]$
M_r = 292.06
Monoclinic, $P2_1/c$
a = 9.6393 (2) Å
b = 15.4265 (4) Å
c = 7.4346 (2) Å
β = 111.984 (1)°
V = 1025.14 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.05 mm^{-1}
T = 296 K
0.33 × 0.15 × 0.13 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2005)
T_{min} = 0.825, T_{max} = 0.873
13757 measured reflections
2529 independent reflections
2306 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.065
S = 1.02
2529 reflections
145 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

All H atoms are placed in calculated positions and refined using a riding model, with U_{iso}(H) values of $1.2U_{eq}$(carrier) for NH_2 and CH_2 groups or $1.5U_{eq}$(carrier) for water molecules.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3120). Services for accessing these data are described at the back of the journal.

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