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Key indicators

Single-crystal X-ray study

T = 298 K

Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$

R factor = 0.067

wR factor = 0.151

Data-to-parameter ratio = 10.7

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Disodium μ -triethylenetetraaminehexa-
acetato-bis[oxovanadate(IV)] hexahydrate

The crystals structure of the title heterometallic coordination compound, $\text{Na}_2[(\text{C}_{18}\text{H}_{24}\text{N}_4\text{O}_{12})(\text{VO})_2] \cdot 6\text{H}_2\text{O}$, is built of Na^+ cations, binuclear $[\text{C}_{18}\text{H}_{24}\text{N}_4\text{O}_{12}(\text{VO})_2]^{2-}$ dianions and water molecules. The cations and anion occupy special positions at inversion centers. The V atom has an octahedral coordination environment formed by the vanadyl oxo atom [$\text{V}=\text{O}$ 1.618 (3) Å], two N [$\text{V}-\text{N}$ 2.174 (4) and 2.289 (4) Å] and three O atoms [$\text{V}-\text{O}$ 1.993 (3), 1.998 (3) and 2.001 (3) Å] of the amino-carboxylato group.

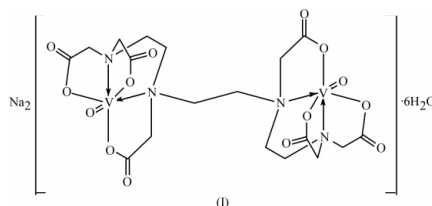
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Comment

We have recently reported several heterometallic coordination compounds in which main-group metal atoms are linked to transition metals through carboxylate groups (Long *et al.*, 2002; Ren *et al.*, 2002). Sodium μ -triethylenetetraaminehexaacetato-bis(oxovanadate) was reported earlier as a decahydrate (Fallon & Gatehouse, 1976). In this paper, we report the structure of the hexahydrate form, (I), of this complex.



The dinuclear anion and both Na^+ cations occupy special positions at inversion centers (one of the Na^+ cations is disordered in the vicinity of the inversion center). The V(IV) atom has an octahedral coordination environment defined by the vanadyl oxo atom, two N and three O atoms of the aminoacetato anion (Fig. 1). The $\text{V}=\text{O}$ double-bond distance [$\text{V1}=\text{O7}$ 1.618 (3) Å] is significantly shorter than the other three $\text{V}-\text{O}$ bond lengths [1.993 (3), 1.998 (3), 2.001 (3) Å]. The $\text{V}-\text{N}$ bond *trans* to the $\text{V}=\text{O}$ bond [$\text{V1}-\text{N2}$ 2.289 (4) Å] is somewhat longer than the other $\text{V}-\text{N}$ bond [$\text{V1}-\text{N1}$ 2.174 (4) Å]. The distances are similar to those found in the decahydrate, and the coordination geometry of the V atom is also the same. In the decahydrate, the $\text{V}=\text{O}$ double-bond length is 1.605 (8) Å; the $\text{V}-\text{N}$ bond length *trans* to the vanadyl bond is 2.294 (7) Å (Fallon & Gatehouse, 1976).

One of the Na^+ cations (Na2) is coordinated by six water molecules whereas the other (Na1) is only penta-coordinate. Four of the neighbors of Na1 are water O atoms bridging it to Na2 , the fifth being a carbonyl O atom belonging to the aminoacid ligand (Fig. 2). The bridging pattern gives rise to a tightly held network structure. The packing of the hexahydrate

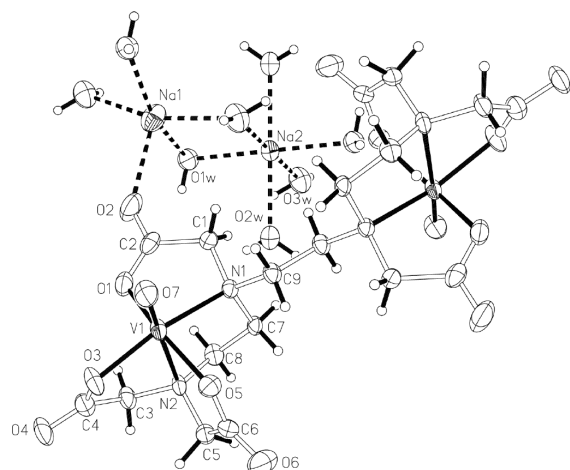


Figure 1
ORTEP (Johnson, 1976) plot of a fragment of the structure of sodium μ -triethylenetetraaminehexaacetato[oxovanadate(IV)] hexahydrate, with displacement ellipsoids drawn at the 50% probability level. Only one component of the disordered atom Na1 is shown.

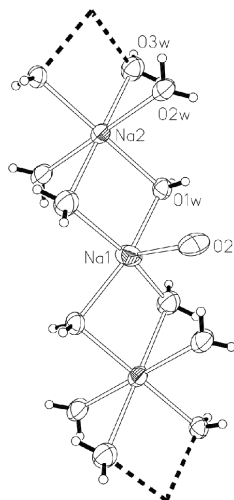


Figure 2
ORTEP (Johnson, 1976) plot of the water- and carbonyl O-linked cationic chain. H atoms are drawn as spheres of arbitrary radii.

is more compact than that of the decahydrate, as noted from the higher density.

The blue color of the title complex leaves no doubt that the V atom oxidation state is 4+. It is not clear, however, what the exact nature of the reducing agent in the process of its synthesis from metavanadate is, whose V has an oxidation state of 5. One may guess, though, that under hydrothermal conditions, the carboxylate group or even water may exhibit redox activity.

Experimental

The compound was synthesized hydrothermally from the reaction of ammonium metavanadate (0.12 g, 1 mmol), triethylenetetraaminehexaacetic acid (0.15 g, 0.5 mmol) and sodium hydroxide (0.12 g, 3 mmol); the pH of the solution was approximately 7. The solution was heated in a steel bomb to 453 K and was kept at this temperature for 72 h. The bomb was then cooled to room temperature at the rate

of 5 K per hour. Blue polyhedral crystals separated from the solution in about 50% yield.

Crystal data

$[\text{Na}_2(\text{C}_{18}\text{H}_{24}\text{N}_4\text{O}_{14}\text{V}_2)]6\text{H}_2\text{O}$
 $M_r = 776.37$
 Monoclinic, $P2_1/n$
 $a = 6.7086$ (2) Å
 $b = 10.5746$ (3) Å
 $c = 20.9333$ (5) Å
 $\beta = 98.678$ (1)°
 $V = 1468.02$ (7) Å³
 $Z = 2$

$D_x = 1.756$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2808 reflections
 $\theta = 2.0$ – 27.0 °
 $\mu = 0.76$ mm⁻¹
 $T = 298$ (2) K
 Block, blue
 0.31 × 0.21 × 0.14 mm

Data collection

Bruker APEX area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.390$, $T_{\max} = 0.862$
 7204 measured reflections

2485 independent reflections
 2162 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.054$
 $\theta_{\max} = 25.0$ °
 $h = -5 \rightarrow 7$
 $k = -12 \rightarrow 11$
 $l = -13 \rightarrow 24$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.067$
 $wR(F^2) = 0.151$
 $S = 1.21$
 2485 reflections
 232 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0674P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.58$ e Å⁻³
 $\Delta\rho_{\min} = -0.35$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

V1—O1	1.998 (3)	Na1—O1w	2.264 (8)
V1—O3	1.993 (3)	Na1—O1w ⁱ	2.344 (8)
V1—O5	2.001 (3)	Na1—O3w ⁱⁱ	2.475 (9)
V1—O7	1.618 (3)	Na1—O3w ⁱⁱⁱ	2.433 (9)
V1—N1	2.174 (4)	Na2—O1w	2.324 (3)
V1—N2	2.289 (4)	Na2—O2w	2.366 (4)
Na1—O2	2.561 (6)	Na2—O3w	2.593 (4)
O1—V1—O3	88.7 (1)	N1—V1—N2	80.4 (1)
O1—V1—O5	160.8 (1)	O2—Na1—O1w	86.7 (2)
O1—V1—O7	102.0 (2)	O2—Na1—O1w ⁱ	112.7 (3)
O1—V1—N1	80.8 (1)	O2—Na1—O3w ⁱⁱ	107.2 (3)
O1—V1—N2	85.9 (1)	O2—Na1—O3w ⁱⁱⁱ	91.0 (2)
O3—V1—O5	94.6 (1)	O1w—Na1—O1w ⁱ	160.5 (2)
O3—V1—O7	104.2 (2)	O1w—Na1—O3w ⁱⁱⁱ	90.2 (3)
O3—V1—N1	154.0 (1)	O1w—Na1—O3w ⁱⁱ	88.5 (3)
O3—V1—N2	75.1 (1)	O1w ⁱ —Na1—O3w ⁱⁱ	87.4 (3)
O5—V1—O7	95.5 (2)	O1w ⁱ —Na1—O3w ⁱⁱⁱ	87.7 (3)
O5—V1—N1	88.1 (1)	O3w ⁱⁱ —Na1—O3w ⁱⁱⁱ	161.6 (2)
O5—V1—N2	76.8 (1)	O1w—Na2—O2w	84.9 (1)
O7—V1—N1	101.2 (1)	O1w—Na2—O3w	95.0 (1)
O7—V1—N2	172.1 (2)	O2w—Na2—O3w	74.4 (1)

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $x - 1, y, z$; (iii) $2 - x, -y, 1 - z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1w—H1w2 \cdots O4 ^{iv}	0.86 (1)	1.98 (2)	2.811 (5)	164 (4)
O1w—H1w1 \cdots O5 ^v	0.85 (1)	1.94 (1)	2.782 (4)	170 (4)
O2w—H2w1 \cdots O2 ^{vi}	0.85 (1)	1.87 (1)	2.716 (5)	176 (5)
O2w—H2w2 \cdots O4 ^{iv}	0.84 (1)	2.03 (3)	2.760 (5)	145 (5)
O3w—H3w1 \cdots O7 ^{vii}	0.85 (1)	2.12 (2)	2.971 (5)	172 (5)
O3w—H3w2 \cdots O6 ^v	0.85 (1)	2.04 (2)	2.836 (5)	156 (4)

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

One of the two independent Na atoms (Na1) is disordered over an inversion center at $(\frac{1}{2}, 0, \frac{1}{2})$. The water H atoms were located and refined subject to the restraint $O-H = 0.85(1)$ and $H \cdots H = 1.39(1)$ Å; their displacement parameters were set to 1.2 times U_{eq} of the parent O atoms. The C-bound H atoms were positioned geometrically ($C-H = 0.97$ Å) and were included in the refinement in the riding model approximation; their displacement parameters were treated as those of the water H atoms.

Although the diffraction data were collected up to a 2θ of 55° , the use of the reflections with $2\theta > 50^\circ$ led to an R index higher than 0.070. The 2θ limit was therefore set to 50° in the final refinement.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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