

**Bis(ethylenediammonium) deca-
 aquadisodium decavanadate,
 (C₂H₁₀N₂)₂[Na₂(H₂O)₁₀][V₁₀O₂₈]**

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In the title compound, the decavanadate anion, [V₁₀O₂₈]⁶⁻, and the bridged [Na₂(H₂O)₁₀]²⁺ dication lie across inversion centers. The charge balance is achieved by ethylenediammonium cations, H₃NCH₂CH₂NH₃²⁺, which are disordered. The decavanadate anions are surrounded by the [Na₂(H₂O)₁₀]²⁺ dications, thus forming layers, and the ethylenediammonium cations are located between these layers.

Comment

Polyoxometalate chemistry has a long history and still attracts much attention owing to the various applications of poly-

oxometalates in catalysis, biology, medicine, geochemistry and materials science (Pope & Muller, 1991, 1994; Rhule *et al.*, 1998). The polyoxovanadates compose an important part of the polyoxometalate group, the decavanadate anion being particularly well studied. Many compounds containing decavanadate polyanions of the types [V₁₀O₂₈]⁶⁻, [HV₁₀O₂₈]⁵⁻, [H₂V₁₀O₂₈]⁴⁻, [H₃V₁₀O₂₈]³⁻ and [H₄V₁₀O₂₈]²⁻ have been reported (Arrieta, 1992; Durif *et al.*, 1980; Evans, 1966; Zhang *et al.*, 2004; Lee & Joo, 2004; Iida & Ozeki, 2004). The present work is part of a series of studies aimed at synthesizing new polyoxovanadates. The experimental powder pattern, IR spectrum and ICP-AES (inductively coupled plasma atomic emission spectrometry) of this compound are in good agreement with the results of the single-crystal X-ray diffraction analysis.

The asymmetric unit in the title compound contains one-half of a [V₁₀O₂₈]⁶⁻ anion, one-half of an [Na₂(H₂O)₁₀]²⁺ cation and a disordered H₃NCH₂CH₂NH₃²⁺ cation (Fig. 1). The structure of the decavanadate anion can be described as comprising six VO₆ octahedra (involving atoms V1, V4, V5, V1ⁱ, V4ⁱ and V5ⁱ) forming a plane, with four VO₆ octahedra (those centered on atoms V2, V3, V2ⁱ and V3ⁱ) linked *via* edge-sharing, as reported by Evans (1966) [symmetry code: (i) 1 - x, 1 - y, -z]. The [Na₂(H₂O)₁₀]²⁺ dication comprises a pair of edge-sharing NaO₆ octahedra, each Na atom being surrounded by six water molecules, two of which act as bridges between the octahedra (Fig. 1 and Table 1). Such a structural unit has also been reported in Na₂CO₃·10H₂O (Taga, 1969) and Cs₄[Na₂(H₂O)₁₀]V₁₀O₂₈ (Piro *et al.*, 2003).

The decavanadate anion and the bridged [Na₂(H₂O)₁₀]²⁺ cation are linked by hydrogen bonds to form an [Na₂(H₂O)₁₀V₁₀O₂₈]⁴⁻ layer (Fig. 2). Hydrogen bonds within the layers involve the H atoms of water molecules and the O atoms from the decavanadate anion (Table 2), and the

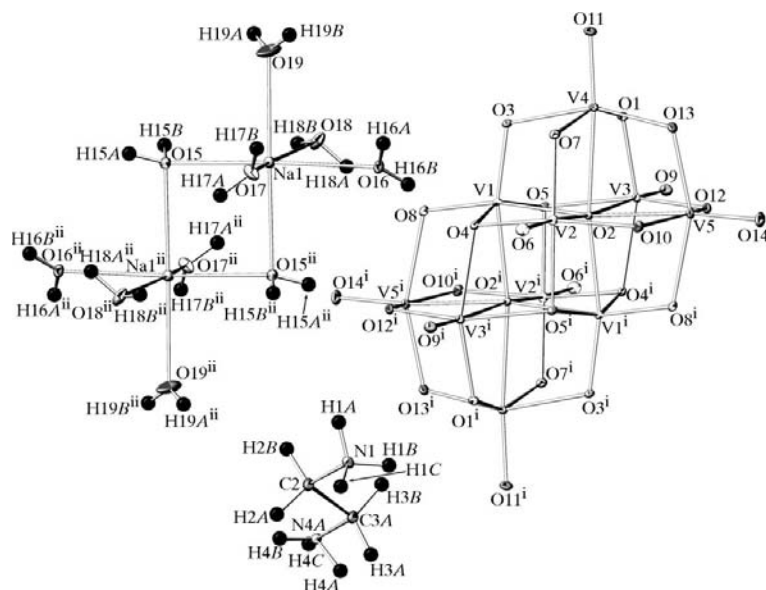


Figure 1

A perspective view of an asymmetric unit and selected neighbors of the title compound. Displacement ellipsoids are drawn at the 20% probability level and H atoms are drawn as small spheres of arbitrary radii. [Symmetry codes: (i) 1 - x, 1 - y, -z; (ii) -x, -y, -z.]

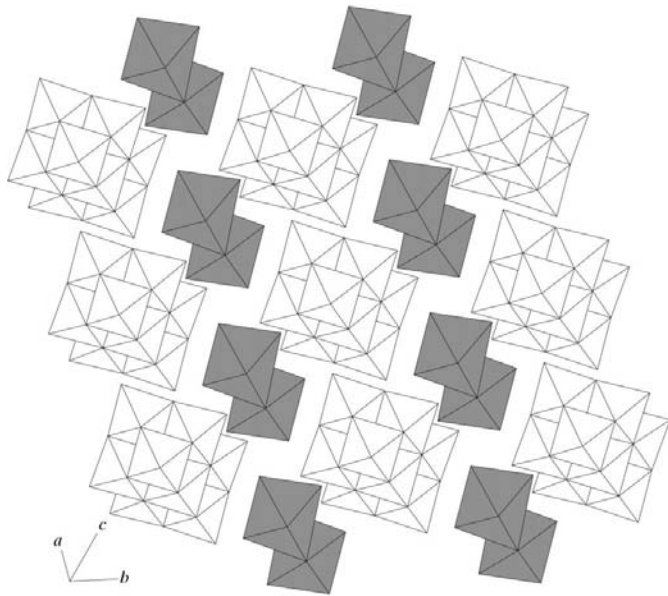


Figure 2
A packing diagram of the $[\text{Na}_2(\text{H}_2\text{O})_{10}\text{V}_{10}\text{O}_{28}]^{4-}$ layer of the title compound, viewed along the c axis. White and dark-gray octahedra represent VO_6 and $\text{Na}(\text{H}_2\text{O})_6$ groups, respectively.

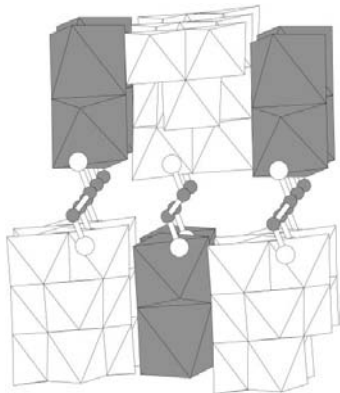


Figure 3
A packing diagram of the title compound, viewed along the b axis. White octahedra, dark-gray octahedra, white circles and dark-gray circles represent VO_6 groups, $\text{Na}(\text{H}_2\text{O})_6$ groups, C atoms and N atoms, respectively.

$\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3^{2+}$ cations are located between the $[\text{Na}_2(\text{H}_2\text{O})_{10}\text{V}_{10}\text{O}_{28}]^{4-}$ layers (Fig. 3).

Experimental

The title compound was obtained by hydrothermal synthesis. All reagents were of analytical grade. A 50 ml Teflon-lined autoclave was loaded with a mixture of NaVO_3 (5.00 g), H_2O (30 ml), BPO_4 (5.00 g) and $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (1.0 ml) and heated at 423 K for 5 d. After hydrothermal treatment, the solution was filtered and allowed to stand in a glass beaker, whereupon single crystals of the title compound grew in less than 2 d. These crystals were isolated in ca

30% initial yield (based on vanadium) but continued to be produced over time as the solution was allowed to stand in the beaker.

Crystal data

$(\text{C}_2\text{H}_{10}\text{N}_2)_2[\text{Na}_2(\text{H}_2\text{O})_{10}][\text{V}_{10}\text{O}_{28}]$
 $M_r = 1307.78$
 Monoclinic, $P2_1/n$
 $a = 8.8919$ (18) Å
 $b = 11.080$ (2) Å
 $c = 18.579$ (4) Å
 $\beta = 92.40$ (3)°
 $V = 1828.8$ (6) Å³
 $Z = 2$

$D_x = 2.375$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5659 reflections
 $\theta = 2.1\text{--}33.5^\circ$
 $\mu = 2.58$ mm⁻¹
 $T = 293$ (2) K
 Tablet, orange
 0.2 × 0.2 × 0.2 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 ω scans
 17 284 measured reflections
 6815 independent reflections
 5660 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 33.5^\circ$
 $h = -13 \rightarrow 13$
 $k = -17 \rightarrow 16$
 $l = -17 \rightarrow 28$

Table 1

Selected interatomic distances (Å).

V1—O2	2.1046 (15)	V4—O3	2.0374 (16)
V1—O3	1.6904 (14)	V4—O7	1.8594 (16)
V1—O4	1.9247 (14)	V4—O11	1.6063 (16)
V1—O5	1.8972 (14)	V4—O13	1.8215 (17)
V1—O8	1.6923 (15)	V5—O2	2.3278 (15)
V2—O2	2.2439 (13)	V5—O8 ⁱ	2.0264 (16)
V2—O4	1.9920 (15)	V5—O10	1.8799 (17)
V2—O5 ⁱ	2.0025 (15)	V5—O12	1.8705 (17)
V2—O6	1.6006 (16)	V5—O13	1.8477 (17)
V2—O7	1.8148 (15)	V5—O14	1.5924 (18)
V2—O10	1.8270 (16)	N1—C2	1.477 (3)
V3—O1	1.8055 (15)	C2—C3A	1.554 (5)
V3—O2	2.2219 (13)	C3A—N4A	1.483 (5)
V3—O4 ⁱ	2.0013 (14)	Na1—O15 ⁱⁱ	2.420 (2)
V3—O5	2.0065 (15)	Na1—O15	2.476 (2)
V3—O9	1.6195 (16)	Na1—O16	2.432 (2)
V3—O12	1.8135 (17)	Na1—O17	2.354 (2)
V4—O1	1.8896 (16)	Na1—O18	2.363 (2)
V4—O2	2.3038 (15)	Na1—O19	2.367 (2)

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—H}\cdots A$	$D\text{—H}$	$\text{H}\cdots A$	$D\cdots A$	$D\text{—H}\cdots A$
N1—H1A \cdots O9 ⁱⁱⁱ	0.89	2.33	2.840 (3)	116
N1—H1B \cdots O1 ⁱ	0.89	2.29	2.953 (3)	131
N1—H1C \cdots O16 ^{iv}	0.89	2.19	3.055 (3)	164
N4A—H4A \cdots O3 ^v	0.89	2.18	2.828 (3)	129
N4A—H4B \cdots O18 ^v	0.89	2.21	2.963 (4)	142
N4A—H4C \cdots O10 ^{vi}	0.89	2.19	2.716 (3)	118
O15—H15A \cdots O12 ^{vii}	0.82	2.03	2.835 (2)	166
O15—H15B \cdots O9 ^{viii}	0.82	2.41	2.969 (2)	126
O16—H16A \cdots O11 ^{ix}	0.82	2.12	2.922 (3)	168
O16—H16B \cdots O4	0.82	1.95	2.769 (2)	177
O17—H17A \cdots O11 ⁱⁱⁱ	0.82	2.45	2.993 (3)	124
O17—H17B \cdots O7 ^{ix}	0.82	2.04	2.814 (2)	157
O18—H18A \cdots O8	0.82	2.09	2.871 (2)	160
O18—H18B \cdots O1 ^{viii}	0.82	2.49	3.225 (3)	150
O19—H19A \cdots O6 ^x	0.82	2.27	2.899 (3)	134
O19—H19B \cdots O13 ^{ix}	0.82	2.19	3.009 (3)	175

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

Refinement

Refinement on F^2

$$R[F^2 > 2\sigma(F^2)] = 0.039$$

$$wR(F^2) = 0.119$$

$$S = 1.00$$

6815 reflections

273 parameters

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.077P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.97 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.76 \text{ e } \text{\AA}^{-3}$$

H atoms were located from a difference electron-density map. The positional parameters of the H atoms were fixed, with the X–H distances applied as constraints and $U_{\text{iso}}(\text{H})$ set at 1.5 (for C and N atoms) or 1.2 (for O atoms) times U_{eq} of the parent atom. In the region of the $\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3^{2+}$ cation, the difference electron-density map showed two electron-density features separated by a short distance (about 1 Å), and two H atoms are located nearby. As a result, we found one disordered C atom (C3) with a *ca* 4:1 occupancy ratio for its C3A and C3B components; similarly, we identified one disordered N atom (N4), with a similar occupancy ratio for components N4A and N4B. No superstructural diffraction spots were observed in any direction on the frames of data collected.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2001) and *ViewerLite* (Accelrys, 2001); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1587). Services for accessing these data are described at the back of the journal.

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