

Na₆(H₂O)₂₀(V₁₀O₂₈)·4H₂O, a novel polyvanadate(V) with a three-dimensional framework

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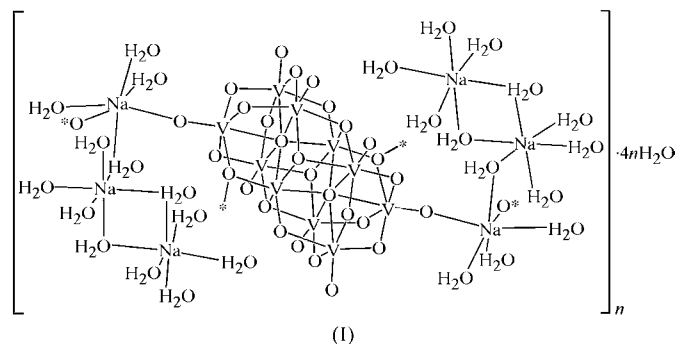
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The novel title polyvanadate(V), poly[[octa- μ -aqua-dodeca-aqua- μ_4 -octacosaoxidodecavanadato-hexasodium] tetrahydrate], [Na₆(H₂O)₂₀(V₁₀O₂₈)·4H₂O]_n, contains [V₁₀O₂₈]⁶⁻ anions which lie about inversion centres and have approximate 2/m symmetry and which are linked to [Na₃(H₂O)₁₀]³⁺ cations through two terminal and two μ_2 -bridging O atoms. The structure contains three inequivalent Na⁺ cations, two of which form [Na₂(H₂O)₈]_n chains, which are linked *via* NaO₆ octahedra involving the third Na⁺ ion, thus forming a three-dimensional framework.

Comment

Owing to their unusual topological properties and economically important applications in fields such as analytical chem-

istry, materials science and catalysis, nanotechnology, chemical sensing, luminescence, and medicine, polyoxometalates have



aroused more and more attention in the past decade (Tanielian, 1998; Ouahab, 1998; Sadakane *et al.*, 2000). Of the large polyoxometalate family, the most interesting class is polyoxovanadates, which are known to exhibit interesting physical and chemical properties with relevance to catalysis, biochemical processes and materials science (Zheng *et al.*, 2005; Yang *et al.*, 2003; Law *et al.*, 2000). In recent years, a number of polyoxovanadate clusters exhibiting diverse topologies and interesting structural and electronic properties have been reported (Chen *et al.*, 2005; Laye & McInnes, 2004). Although many compounds constructed from the [V₁₀O₂₈]⁶⁻ polyoxoanion have been extensively studied, only a few complexes with three-dimensional frameworks have been reported (Zhang *et al.*, 2004; Lee & Joo, 2003). We describe here a novel framework compound, Na₆(H₂O)₂₀(V₁₀O₂₈)·4H₂O, (I), prepared from V₂O₅, NaOH and HCl in solution.

The basic unit of (I) contains one [V₁₀O₂₈]⁶⁻ polyanion with 2/m symmetry and two noncentrosymmetric [Na₃(H₂O)₁₀]³⁺ cations (Fig. 1 and Table 1). The decavanadate anion is composed of ten VO₆ octahedra combined *via* shared edges and shared corners. The bond lengths and angles of the

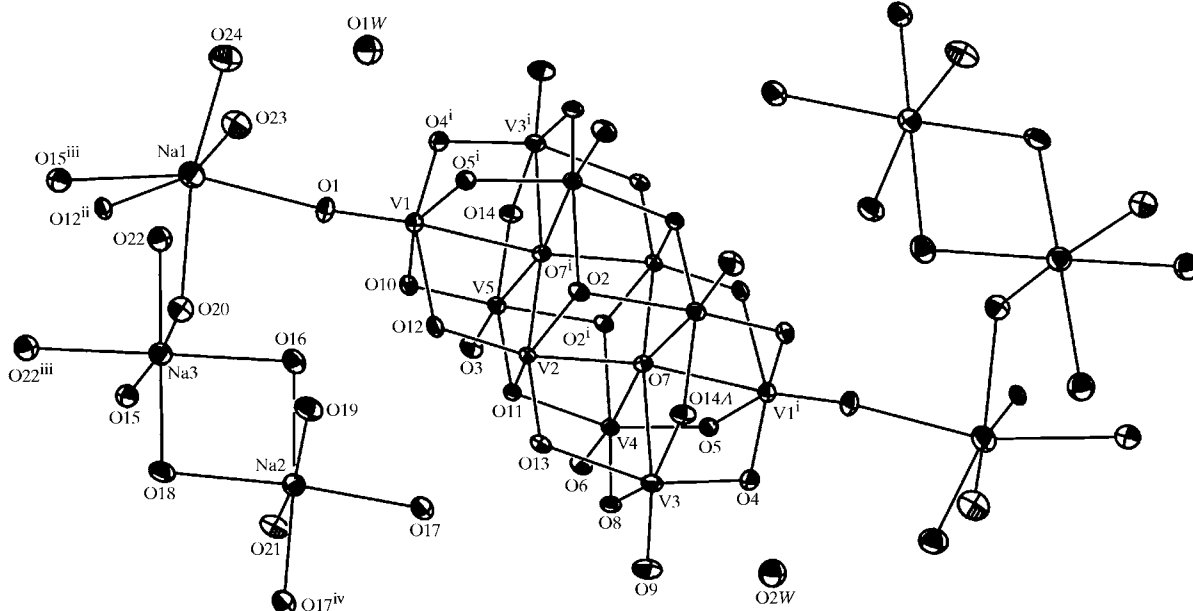


Figure 1

The crystal structure of (I), showing 35% probability displacement ellipsoids. H atoms have been omitted for clarity. See Table 1 for symmetry codes.

$[\text{V}_{10}\text{O}_{28}]^{6-}$ anion are similar to those in the analogous compound $\text{Li}_6(\text{H}_2\text{O})_{16}\text{V}_{10}\text{O}_{28}$ (Xie & Ma, 2005). Bond-valence-sum calculations (Brown & Altermatt, 1985; O'Keeffe & Navrotsky, 1981) confirm that all the V atoms are in the +5 oxidation state (with bond valence sums in the 5.00–5.06 range).

There are three independent Na^+ cations in (I). Atom Na1 is in a distorted octahedral coordination involving four O atoms (O20, O23, O24 and O15B) from coordinated water molecules, one O atom (O1) from the $[\text{V}_{10}\text{O}_{28}]^{6-}$ anion and one μ_2 -O atom (O12B). Atoms Na2 and Na3 are both coordinated by six O atoms from water molecules that form distorted octahedral environments. Atoms Na2 and Na3 are linked by two μ_2 -O atoms (O16 and O18) to form dinuclear cations that are further linked to form $[\text{Na}_2(\text{H}_2\text{O})_8]_n$ chains in which the $\text{Na3}\cdots\text{Na3A}$, $\text{Na2}\cdots\text{Na2A}$ and $\text{Na2}\cdots\text{Na3}$ distances are 3.368 (3), 3.563 (3) and 3.448 (2) Å, respectively.

In the packing of (I), each $[\text{V}_{10}\text{O}_{28}]^{6-}$ anion acts as a μ_4 -bridge, linking four Na1 cations through two terminal and two μ_2 -O atoms (Fig. 2). The decavanadate anions and the $[\text{Na}_2(\text{H}_2\text{O})_8]_n$ chains are linked to each other through Na1O_6 octahedra to form a three-dimensional framework. To the best of our knowledge, a similar three-dimensional structure has

not been described previously. In $\text{Na}_6\text{V}_{10}\text{O}_{28}\cdot 18\text{H}_2\text{O}$ (Durif *et al.*, 1980), decavanadate anions and trinuclear cations, $[\text{Na}_3(\text{H}_2\text{O})_9]^{3+}$, link together to form a two-dimensional layer structure. In the related compound, $\text{K}_2\text{Na}_4[\text{V}_{10}\text{O}_{28}]\cdot 18\text{H}_2\text{O}$ (Lee, 2006), chains of edge- and face-sharing KO_9 and NaO_6 polyhedra are interconnected by decavanadate anions to form a different three-dimensional network.

Experimental

The title compound was prepared by hydrothermal treatment of V_2O_5 (0.3861 g, 2.1 mmol) and NaOH (0.0672 g, 1.7 mmol) acidified to pH 5.8 with aqueous HCl. The reaction mixture was heated for 20 h at 393 K. The filtrate was kept at room temperature and block-shaped orange–yellow single crystals formed after one week. Compound (I) is air-stable both in the solid state and in solution at room temperature. The FT-IR spectrum of (I) shows two strong bands at 957 and 989 cm^{-1} that can be assigned to the stretching of the terminal V–O bonds. The antisymmetric modes of the V–O–V bridges possibly correspond to the bands at 750 and 848 cm^{-1} , while the symmetric modes are probably at 558 and 605 cm^{-1} . The broad band at 3467 cm^{-1} is due to the coordinated and solvent water molecules. Thermogravimetric analysis shows that the crystals lose 28.15 wt% in the temperature range 358–595 K. This is consistent with the number of coordinated and solvent water molecules in the molecular formula (28.28 wt%).

Crystal data

$\text{Na}_6(\text{H}_2\text{O})_{20}(\text{V}_{10}\text{O}_{28})\cdot 4\text{H}_2\text{O}$
 $M_r = 1527.72$
 Triclinic, $P\bar{1}$
 $a = 10.5834$ (3) Å
 $b = 11.3803$ (3) Å
 $c = 11.6367$ (3) Å
 $\alpha = 108.682$ (4)°
 $\beta = 103.775$ (2)°

$\gamma = 111.674$ (3)°
 $V = 1128.19$ (5) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 2.16$ mm^{-1}
 $T = 223$ (2) K
 $0.30 \times 0.24 \times 0.20$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.542$, $T_{\max} = 0.649$

11109 measured reflections
 4088 independent reflections
 3529 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.104$
 $S = 1.01$
 4088 reflections
 379 parameters
 36 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.48$ e Å⁻³
 $\Delta\rho_{\min} = -0.46$ e Å⁻³

The coordinates of all H atoms were determined from a difference Fourier map. The H atoms were included in the final cycles of refinement, with O–H and H \cdots H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively; $U_{\text{iso}}(\text{H})$ values were set at $1.5U_{\text{eq}}(\text{O})$ for the coordinated water molecules and refined freely for the solvent molecules.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1994); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXL97.

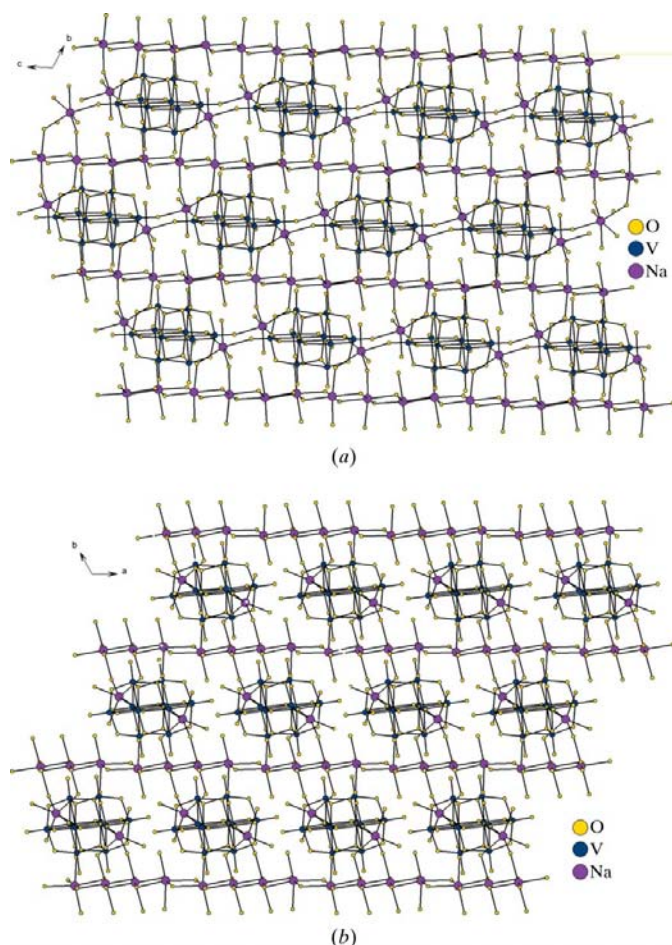


Figure 2

Two-dimensional packing diagrams of (I), viewed along (a) the a axis and (b) the c axis.

Table 1

Selected geometric parameters (Å, °).

V1—O1	1.594 (2)	Na1—O23	2.393 (3)
V1—O4 ⁱ	1.822 (2)	Na1—O1	2.455 (3)
V1—O5 ⁱ	1.886 (2)	Na1—O15 ⁱⁱ	2.508 (3)
V2—O12	1.689 (2)	Na1—O12 ⁱⁱⁱ	2.948 (3)
V2—O7 ⁱ	2.112 (2)	Na2—O21	2.320 (3)
V3—O9	1.606 (2)	Na2—O19	2.352 (3)
V4—O5	1.816 (2)	Na2—O16	2.420 (3)
V5—O14	1.820 (2)	Na3—O18	2.334 (3)
Na1—O24	2.328 (3)	Na3—O22 ⁱⁱ	2.397 (3)
Na1—O20	2.348 (3)	Na3—O16	2.445 (3)
O1—V1—O4 ⁱ	104.20 (12)	O24—Na1—O12 ⁱⁱⁱ	81.98 (10)
O1—V1—O10	102.55 (12)	O23—Na1—O12 ⁱⁱⁱ	166.07 (11)
O4 ⁱ —V1—O5 ⁱ	91.57 (10)	O15 ⁱⁱ —Na1—O12 ⁱⁱⁱ	82.62 (8)
O4 ⁱ —V1—O12	155.93 (10)	O19—Na2—O18	84.58 (10)
O5 ⁱ —V1—O12	81.88 (9)	O21—Na2—O16	89.89 (10)
O5 ⁱ —V1—O7 ⁱ	77.13 (8)	O17—Na2—O16	100.36 (10)
O24—Na1—O20	151.00 (12)	O19—Na2—O17 ^{iv}	92.11 (10)
O20—Na1—O23	111.43 (11)	O16—Na2—O17 ^{iv}	166.64 (11)
O20—Na1—O1	81.30 (9)	O22 ⁱⁱ —Na3—O20	91.32 (9)
O23—Na1—O1	91.56 (11)	O22 ⁱⁱ —Na3—O16	178.15 (10)
O20—Na1—O15 ⁱⁱ	82.00 (9)	O18—Na3—O15	95.80 (10)
O23—Na1—O15 ⁱⁱ	89.50 (11)		

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3048). Services for accessing these data are described at the back of the journal.

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