

Hexalithium hexadecahydrate decavanadate, $[\text{Li}_6(\text{H}_2\text{O})_{16}\text{V}_{10}\text{O}_{28}]_n$

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The novel title compound, poly[octa- μ -aqua-octaaqua- μ -decavanadato-hexalithium], contains $[\text{V}_{10}\text{O}_{28}]^{6-}$ polyanions with $2/m$ symmetry linked by centrosymmetric $[\text{Li}_6(\text{H}_2\text{O})_{16}]^{6+}$ cation chains. The $[\text{V}_{10}\text{O}_{28}]^{6-}$ polyanions form a two-dimensional network with $[\text{Li}_6(\text{H}_2\text{O})_{16}]^{6+}$ chains *via* O-polyanion-Li-chain coordination, with Li–O bond lengths in the range 2.007 (5)–2.016 (5) Å. The hexalithium hexadecahydrate chain is composed of a centrosymmetric pair of LiO_6 octahedra and four distorted LiO_4 tetrahedra. Hydrogen bonds occur between the polyanion and the Li-based chains, and within the Li-based chains.

Comment

Recently, polyoxometalates have received increased attention because of their varied applications in many fields, such as clinical chemistry, catalysis, medicine, solid-state devices and

materials science (Kozhevnikov, 1998; Müller, 1998; Rhule *et al.*, 1998; Toshihiro, 1998). Polyoxovanadate clusters, an important class of polyoxometalates, have been studied extensively because of their fascinating structure and potential applications (Zhang & Chen, 2003). In this work, orange single crystals of hexalithium hexadecahydrate decavanadate, $[\text{Li}_6(\text{H}_2\text{O})_{16}\text{V}_{10}\text{O}_{28}]_n$, (I), have been synthesized and their structure determined.

Compound (I) contains $[\text{V}_{10}\text{O}_{28}]^{6-}$ polyanions with $2/m$ symmetry and centrosymmetric $[\text{Li}_6(\text{H}_2\text{O})_{16}]^{6+}$ cation chains (Fig. 1). The decavanadate anion, presenting a cage-like structure, is composed of ten VO_6 octahedra combined *via* shared edges and shared corners. Six octahedra are arranged in a 2×3 equatorial plane sharing edges with one another; the other four octahedra are distributed above and below the equatorial plane, connected by shared sloping edges with the central six octahedra. According to the coordinative conditions, the O atoms in the polyanion can be classified into four types, *viz.* eight terminal O atoms (O3, O9, O6 and symmetry-related atoms) lying on the outer corners, with V–O distances of 1.595 (2)–1.607 (2) Å; 14 double-bridging O atoms (O4, O8, O2 and O1), with V–O distances of 1.694 (1)–1.882 (1) Å; four triply bridging O atoms (O7) lying on the surface of the $[\text{V}_{10}\text{O}_{28}]^{6-}$ cluster, with V–O distances of 1.898 (1)–2.019 (1) Å; and two six-coordinate O atoms (O5) in the centers of the VO_6 octahedra, with V–O distances of 2.126 (1)–2.308 (1) Å. The bond lengths and angles of the $[\text{V}_{10}\text{O}_{28}]^{6-}$ anion show a similar trend to those found in the literature (Kamenar *et al.*, 1996; Choi & Chang, 2003).

The hexalithium hexadecahydrate chain is composed of a centrosymmetric pair of edge-shared octahedra (Li3) extended from the symmetry center by an edge-shared tetrahedron (Li2) linked to a corner-shared tetrahedron (Li1). In the octahedra, the lengths of the Li–O bonds are in the range 2.072 (6)–2.195 (4) Å, the *cis*-O–Li–O angles are in the

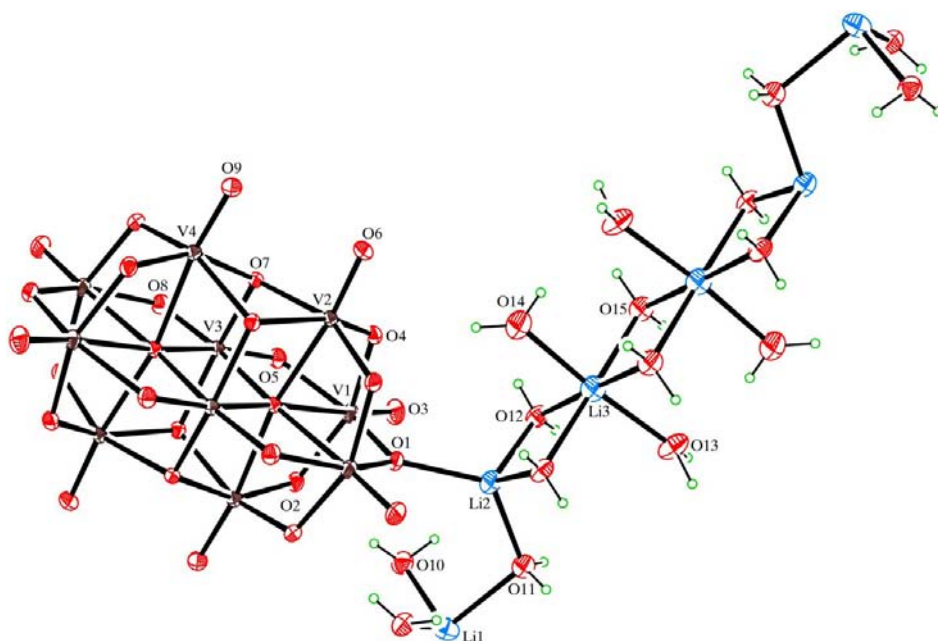


Figure 1

The structure of $[\text{Li}_6(\text{H}_2\text{O})_{16}\text{V}_{10}\text{O}_{28}]_n$, showing 40% probability displacement ellipsoids and the labeling of the atoms.

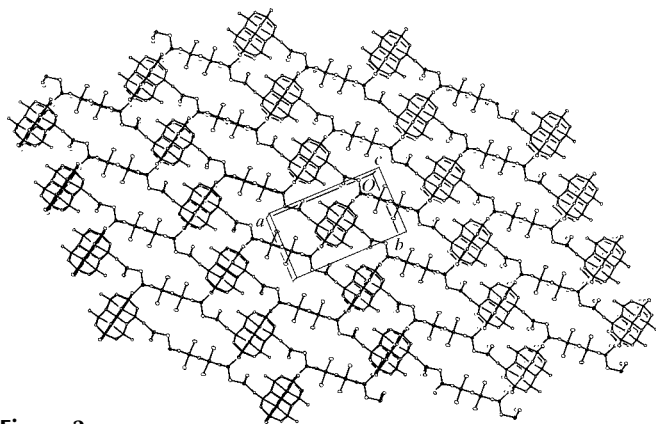


Figure 2
A two-dimensional layered structure packing diagram for $[\text{Li}_6(\text{H}_2\text{O})_{16}\text{V}_{10}\text{O}_{28}]_n^-$.

range $83.9(2)–93.33(5)^\circ$ and the *trans*-O–Li–O angles are in the range $175.4(3)–177.2(2)^\circ$. In the tetrahedra, one O atom is from the $[\text{V}_{10}\text{O}_{28}]^{6-}$ ion, with Li–O lengths of $2.007(5)–2.016(5) \text{ \AA}$, and three O atoms are from water molecules, with Li–O lengths of $1.954(4)–2.144(6) \text{ \AA}$; the O–Li–O angles are $94.0(2)–149.8(5)^\circ$.

In the *ab* plane, $[\text{V}_{10}\text{O}_{28}]^{6-}$ clusters are linked through $[\text{Li}_6(\text{H}_2\text{O})_{16}]^{6+}$ chains to form an extended two-dimensional array (Fig. 2). Atom Li2 in the $[\text{Li}_6(\text{H}_2\text{O})_{16}]^{6+}$ chain is bonded to an axial terminal O atom (O1) of a neighboring $[\text{V}_{10}\text{O}_{28}]^{6-}$ anion, and atom Li1 is bonded to atom O6 of another $[\text{V}_{10}\text{O}_{28}]^{6-}$ anion.

Hydrogen bonds occur between the polyanion and Li-based chain, and within the Li-based chain in the compound. The water molecules, except the two water molecules containing O15, form hydrogen bonds with O atoms of the decavanadate group; there are also OW–H...OW hydrogen-bond interactions. All of the O atoms on the surface of the decavanadate anion form hydrogen bonds with water molecules, except for atoms O1, O3, O6 and O9. Atom O3 participates in no hydrogen-bond interactions. Hydrogen bonds with an O...O distance of less than 2.95 \AA are listed in Table 1.

TGA results show that the weight loss of the crystal is around 22.0% in the range 343–583 K. This is compatible with the content of water (22.4 wt%) resulting from the theoretical calculation in the molecular formula.

Experimental

The title compound was prepared by hydrothermal treatment of NH_4VO_3 and LiOH (1:0.6 molar ratio) acidified to pH 4.5. The reaction mixture was heated for 10 h at 393 K. The filtrate was kept at room temperature and orange single crystals formed after 15 d.

Crystal data

$\text{Li}_6(\text{H}_2\text{O})_{16}\text{V}_{10}\text{O}_{28}$	Mo $K\alpha$ radiation
$M_r = 1287.29$	Cell parameters from 16 609 reflections
Orthorhombic, $Pnmm$	$\theta = 2.3–27.5^\circ$
$a = 17.6164(2) \text{ \AA}$	$\mu = 2.79 \text{ mm}^{-1}$
$b = 10.3189(1) \text{ \AA}$	$T = 273(1) \text{ K}$
$c = 9.2348(3) \text{ \AA}$	Block, orange
$V = 1678.72(6) \text{ \AA}^3$	$0.39 \times 0.31 \times 0.26 \text{ mm}$
$Z = 2$	
$D_x = 2.546 \text{ Mg m}^{-3}$	

Table 1
Hydrogen-bonding geometry ($\text{ \AA}, ^\circ$).

$D–H \cdots A$	$D–H$	$H \cdots A$	$D \cdots A$	$D–H \cdots A$
O10–H2...O4 ⁱ	0.90	1.94	2.804 (2)	159
O11–H3...O8 ⁱⁱ	0.85	2.01	2.851 (2)	163
O12–H4...O10 ⁱⁱⁱ	0.83	1.98	2.815 (2)	174
O12–H5...O7 ⁱ	0.82	1.97	2.777 (2)	167
O13–H6...O8 ⁱ	0.95	1.92	2.872 (2)	171
O14–H8...O13 ^{iv}	0.82	2.14	2.952 (3)	167
O10–H1...O2	0.79	2.18	2.969 (2)	170
O14–H7...O4	0.86	2.56	3.312 (3)	146
O15–H9...O2 ⁱⁱ	0.94	2.10	3.034 (2)	175

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

Data collection

Rigaku R-AXIS RAPID diffractometer	2044 independent reflections
ω scans	1611 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.021$
$T_{\text{min}} = 0.391, T_{\text{max}} = 0.484$	$\theta_{\text{max}} = 27.5^\circ$
16 609 measured reflections	$h = -22 \rightarrow 22$
	$k = -13 \rightarrow 13$
	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	H-atom parameters constrained
$R(F) = 0.021$	$w = 1/[0.001F_o^2 + \sigma(F_o^2)]/(4F_o^2)$
$wR(F^2) = 0.072$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
1611 reflections	$\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$
160 parameters	

The coordinates of all H atoms were determined from a difference Fourier map. H atoms were included in the final cycles of refinement in a riding model, with O–H = $0.80–0.95 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$.

Data collection: *PROCESS-AUTO* (Rigaku, 2002); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1996); molecular graphics: *WinGX* (Farrugia, 1999); software used to prepare material for publication: *CrystalStructure*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1489). Services for accessing these data are described at the back of the journal.

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