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A New Decavanadate with Mixed Cations, $[Li(H_2O)_4]_2[N(CH_3)_4]_4[V_{10}O_{28}].4H_2O$

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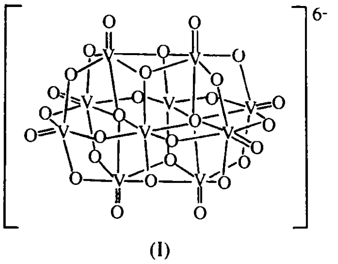
Abstract

The title compound, tetrakis(tetramethylammonium) bis(lithium tetrahydrate) decavanadate tetrahydrate, $(C_4H_{12}N)_4[Li(H_2O)_4]_2[V_{10}O_{28}].4H_2O$, was synthesized and found to crystallize in the triclinic system (space group $P\overline{1}$). The centrosymmetric $[V_{10}O_{28}]^{6-}$ polyanions form layers in the *ac* plane by hydrogen bonding with tetrahedral $[Li(H_2O)_4]^+$ cations and water molecules of crystallization. The tetramethylammonium cations fill the space between the layers.

Comment

We have recently been exploring the syntheses and crystal structures of the metastable oxides $(TMA)V_4O_{10}$ (Zavalij, Whittingham, Boylan, Pecharsky & Jacobson, 1996) (where TMA is tetramethylammonium), $Li_xV_{2-\delta}O_{4-\delta}.H_2O$ (Chirayil, Zavalij & Whittingham, 1996) and K_xMnO_2 (Chen, Zavalij & Whittingham, 1996), which have open frameworks, using mild hydrothermal synthesis (Whittingham *et al.*, 1995). We report here the structure of a new vanadium oxide compound that was prepared using microwave hydrothermal synthesis. Under conditions where regular hydrothermal methods lead to open structures with a reduced oxidation state of the metal, such as in $(TMA)V_4O_{10}$ and $Li_xV_{2-\delta}O_{4-\delta}.H_2O$, the new microwave method yielded a cluster with vanadium in its highest oxidation state of +5. The new compound is built from tetramethylammonium cations, $[N(CH_3)_4]^+$, lithium tetrahydrate cations, $[Li(H_2O)_4]^+$, waters of crystallization and decavanadate anions $[V_{10}O_{28}]^{6-}$, (I).

This vanadium cluster, (I) (Fig. 1), is well known from recent works (Averbuch-Pouchot, 1994; Ninclaus, Riou & Férey, 1996; Kamenar, Cindrić & Strukan, 1996) that report decavanadate structures with organic cations. In the present compound, two kinds of cations, lithium tetrahydrate and TMA, are present and this is unusual for ionic substances. Hydrated lithium cations, water of crystallization and decavanadate clusters are joined by hydrogen bonds forming a layer parallel to the *ac* plane (Fig. 2). The $[V_{10}O_{28}]^{6-}$ clusters are arranged in the layer in a hexagonal network and the smaller tetrahedra of hydrated lithium cations fill the trigonal cavities between them. The role of the TMA cations is to join together these negatively charged layers, $\{[Li(H_2O)_4]_2[V_{10}O_{28}].4H_2O\}^{4-}$. The topology of the centrosymmetric decavanadate cluster is very close to that found in decavanadate structures with other cations.



(I)

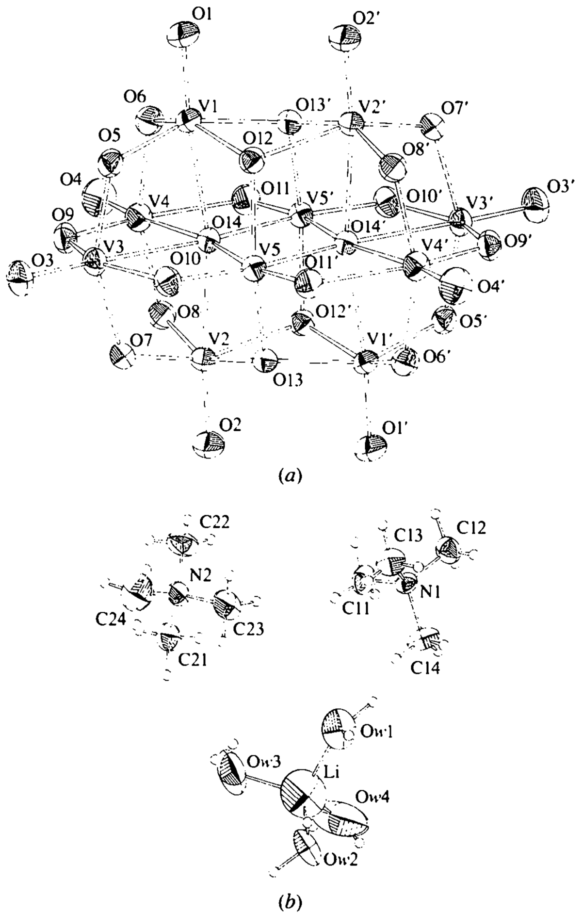


Fig. 1. View of (*a*) the decavanadate cluster, and (*b*) the TMA molecules and lithium tetrahydrate. Primed atoms are centrosymmetric equivalents of the unprimed set. Displacement ellipsoids are shown at 50% probability levels. H atoms are shown as small circles.

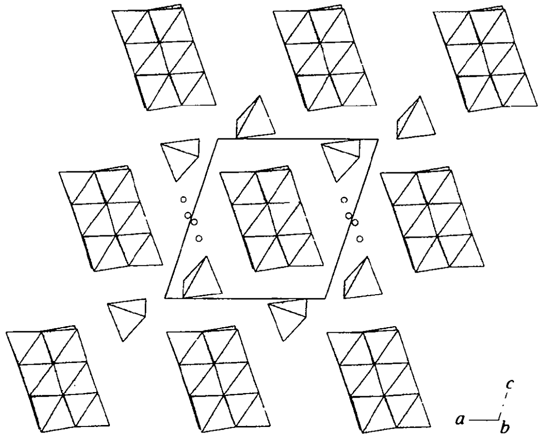


Fig. 2. Packing of the decavanadate clusters, with $[Li(H_2O)_4]^+$ shown as tetrahedra and water molecules shown as circles on the *ac* plane.

Experimental

The title compound was prepared by microwave hydrothermal treatment of V_2O_5, TMA chloride and LiOH (in a 1:2:1 molar ratio) acidified to pH 3.7 with HNO_3. The reaction mixture was heated in a microwave oven for 2 h at 473 K. Orange crystals precipitated out of the solution after 2 d.

Crystal data

$(C_4H_{12}N)_4[Li(H_2O)_4]_2$-$[V_{10}O_{28}].4H_2O$
$M_r = 1484.20$
Triclinic
$P\overline{1}$
$a = 11.187\,(1)$ Å
$b = 11.284\,(1)$ Å
$c = 11.5771\,(8)$ Å
$\alpha = 103.991\,(7)°$
$\beta = 99.233\,(9)°$
$\gamma = 106.523\,(8)°$
$V = 1317.7\,(2)$ Å^3
$Z = 1$
$D_x = 1.870$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 46 reflections
$\theta = 14$–$15°$
$\mu = 1.896$ mm^{-1}
$T = 293$ K
Prism
0.30 × 0.25 × 0.08 mm
Orange

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (Walker & Stuart, 1983)
$T_{min} = 0.65$, $T_{max} = 0.86$
9831 measured reflections
9413 independent reflections
6160 reflections with $I > 2\sigma(I)$

$R_{int} = 0.044$
$\theta_{max} = 32.5°$
$h = 0 \rightarrow 16$
$k = -16 \rightarrow 15$
$l = -17 \rightarrow 17$
3 standard reflections every 97 reflections intensity decay: 2%

Refinement

Refinement on *F*
$R = 0.052$
$wR = 0.058$
$S = 1.24$

$w = 1/[\sigma^2(F) + 0.001F^2]$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.6$ e Å^{-3}

6160 reflections
411 parameters
All H atoms refined except those of water

Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

V1—O1	1.614 (3)	V3—O14	2.335 (3)
V1—O5	1.832 (3)	V4—O4	1.596 (3)
V1—O6	1.778 (3)	V4—O6	1.913 (3)
V1—O12	2.046 (3)	V4—O8	1.851 (3)
V1—O13	1.992 (3)	V4—O9	1.806 (3)
V1—O14	2.250 (2)	V4—O11	2.072 (3)
V2—O2	1.602 (3)	V4—O14	2.319 (3)
V2—O7	1.786 (3)	V5—O10	1.695 (3)
V2—O8	1.848 (3)	V5—O11^{i}	1.672 (3)
V2—O12^{i}	2.036 (3)	V5—O12	1.970 (3)
V2—O13^{i}	1.984 (3)	V5—O13^{i}	1.901 (3)
V2—O14	2.252 (2)	V5—O14	2.127 (3)
V3—O3	1.601 (3)	V5—O14^{i}	2.078 (3)
V3—O5	1.856 (3)	Li—O*w*1	2.03 (2)
V3—O7	1.887 (3)	Li—O*w*2	1.89 (2)
V3—O9	1.836 (3)	Li—O*w*3	2.04 (2)
V3—O10	2.037 (3)	Li—O*w*4	1.82 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

H-atom positions were located from difference maps.

Data collection: Siemens *P*4 software. Cell refinement: Siemens *P*4 software. Data reduction: Siemens *P*4 software. Program(s) used to solve structure: *CSD* (Akselrud *et al.*, 1993). Program(s) used to refine structure: *CSD*. Molecular graphics: *ZORTEP* (Zsolnai, 1995) and *POLIEDRI* (Pilati, 1990).

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Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: TA1131). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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