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Lithium potassium tungstate monohydrate, $LiKWO_4{\cdot}H_2O$

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The crystal structure of lithium potassium tungstate monohydrate, $LiKWO_4{\cdot}H_2O$, has been refined at room temperature. It is isomorphous with its molybdate analogue. The structure can be viewed as consisting of undulating sheets formed by corner sharing of WO_4 and LiO_4 tetrahedra, held together by hydrogen bonding.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(W–O) = 0.005 Å
R factor = 0.020
wR factor = 0.020
Data-to-parameter ratio = 10.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

A number of phases of the general formula $LiA^{+}B^{6+}O_4$ (A = large monovalent cation; B = hexavalent Mo, W) have been reported (Choudhary & Choudhary, 1998, and references therein). They exhibit polymorphism in a wide temperature range, sometimes accompanied by the onset of interesting physical properties, such as ferroelectricity and pyroelectricity (Aleksandrov *et al.*, 1981; Choudhary *et al.*, 1997). While most of the sulfate and chromate members of this general formula can readily be grown as single crystals from aqueous solutions, in the case of tungstates and molybdates, this method yields the corresponding monohydrates. Moreover, when prepared as polycrystalline samples, these materials are very hygroscopic and gradually convert into the hydrated forms (Okada & Ossaka, 1981).

The crystal structure of $LiKWO_4{\cdot}H_2O$ can be viewed as a layered structure formed by tetrahedral building blocks and held together by hydrogen bonding. It is isomorphous with its molybdate analogue (Makitova *et al.*, 1989). W atoms bond to four O atoms, with an average W—O distance of 1.771 (4) Å. They form fairly regular WO_4 tetrahedra, with the O—W—O

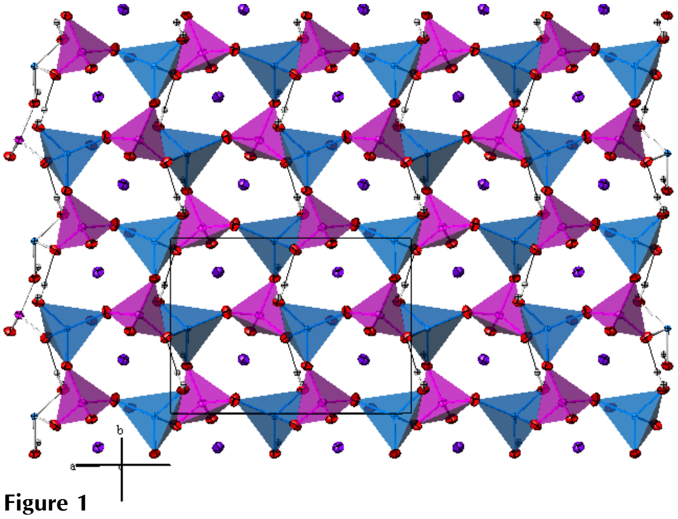

Figure 1
Polyhedral view of $LiKWO_4{\cdot}H_2O$ along the [001] direction. WO_4 (pink) and and LiO_4 (blue) tetrahedra share corners forming six-membered puckered rings. K atoms (purple) are located in the interstices. O atoms are shown in red and H atoms in gray.

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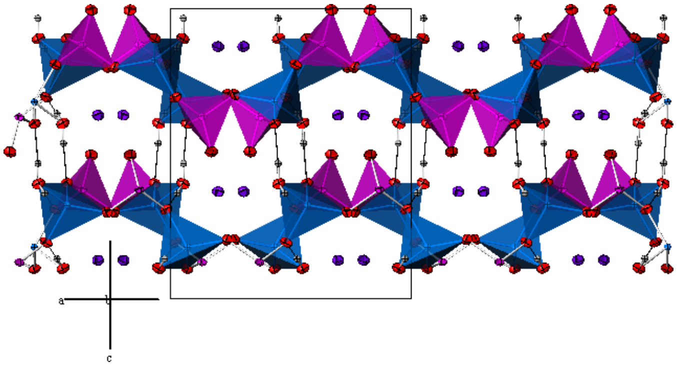

Figure 2
Polyhedral view of $LiKWO_4{\cdot}H_2O$ along the [010] direction. Six-membered rings of tetrahedra form undulating sheets held together by hydrogen bonding (black lines).

angles ranging between 107.9 (2) and 111.0 (2)°. The bond-valence sum (Brown & Altermatt, 1985) for W in this environment is 6.00. Li atoms are found in a tetrahedral coordination geometry as well, with one of the apical O atoms being that of the water molecule. The average Li—O bond length is 1.94 (1) Å and the O—Li—O angles range between 102.6 (2) and 116.2 (2)°. The bond-valence sum for Li in this environment is 1.10. WO_4 and LiO_4 tetrahedral groups alternately share corners to form an undulating two-dimensional network (Fig. 1). The mid-plane of the puckered sheets is parallel to the crystallographic *ab* plane (Fig. 2). K atoms are located at the interstices in the middle of the six-membered rings formed by the WO_4 and LiO_4 tetrahedra. The coordination environment of each K atom includes a total of eight O atoms, six of them belonging to the WO_4 groups and the remaining two to water molecules. The average K—O bond length is 2.943 Å, resulting in a bond-valence sum of 0.94 for this cation. Hydrogen bonding provides the connectivity along the crystallographic *c* axis between the sheets, as depicted in Fig. 2. The two unique O···H contacts are 1.78 (1) and 1.84 (1) Å, resulting in a separation at the points of closest contact between the puckered sheets of about 2.75 Å. Differential scanning calorimetry measurements show that, above 373 K, $LiKWO_4{\cdot}H_2O$ undergoes dehydration followed by a reconstructive phase transition into the beryllonite-type monoclinic $LiKWO_4$.

Experimental

The title compound was prepared by slow evaporation from an aqueous solution of stoichiometric quantities of Li_2WO_4 and K_2WO_4. White crystals up to a few mm in size were formed.

Crystal data

$LiKWO_4{\cdot}H_2O$
M_r = 311.90
Orthorhombic, *Pbca*
a = 10.671 (2) Å
b = 7.767 (2) Å
c = 12.876 (3) Å
V = 1067.1 (7) Å^3
Z = 8
D_x = 3.883 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 911 reflections
θ = 5.3–26.7°
μ = 22.35 mm^{-1}
T = 293 (2) K
Prism, white
0.22 × 0.08 × 0.06 mm

Data collection

SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: integration (Coppens *et al.*, 1965)
T_{min} = 0.045, T_{max} = 0.301
11 020 measured reflections

1219 independent reflections
836 reflections with $I > 2\sigma(I)$
R_{int} = 0.07
θ_{max} = 27.5°
$h = -13 \rightarrow 13$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 16$

Refinement

Refinement on F
R = 0.020
wR = 0.020
S = 1.01
836 reflections
81 parameters
H-atom parameters constrained

Weighting scheme: Chebychev polynomial with 3 parameters (Carruthers & Watkin, 1979), 0.268, 0.125 and 0.184
$(\Delta/\sigma)_{max}$ = 0.007
$\Delta\rho_{max}$ = 0.87 e Å^{-3}
$\Delta\rho_{min}$ = −0.91 e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 12.3 (10)

Table 1
Selected geometric parameters (Å, °).

W1—O2	1.766 (4)	K1—O2^{i}	2.801 (5)
W1—O3	1.746 (4)	K1—O2	3.090 (6)
W1—O4	1.784 (4)	K1—O3^{iv}	2.792 (5)
W1—O5	1.786 (4)	K1—O3^{v}	2.865 (5)
Li1—O2	1.93 (1)	K1—O4^{vi}	2.853 (5)
Li1—O4^{i}	1.92 (1)	K1—O5	3.104 (5)
Li1—O5^{ii}	1.95 (1)	K1—O1^{vii}	3.011 (5)
Li1—O1^{iii}	1.98 (1)	K1—O1^{viii}	3.026 (5)
O3—W1—O2	109.6 (2)	O4^{i}—Li1—O2	114.9 (5)
O3—W1—O4	108.9 (2)	O4^{i}—Li1—O5^{ii}	104.7 (5)
O2—W1—O4	110.1 (2)	O2—Li1—O5^{ii}	111.7 (5)
O3—W1—O5	111.0 (2)	O4^{i}—Li1—O1^{iii}	105.3 (5)
O2—W1—O5	107.9 (2)	O2—Li1—O1^{iii}	116.2 (5)
O4—W1—O5	109.3 (2)	O5^{ii}—Li1—O1^{iii}	102.6 (5)

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

H atoms were found in a difference Fourier map and refined with restraints. O—H bond lengths in the water molecules were restrained to 0.92 (1) Å and the H—O—H angle to 104.5 (1)°. A single atomic displacement parameter was used for both H atoms.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2001); molecular graphics: *ATOMS* (Shape Software, 2000).

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