

Structure of Lithium Yttrium Bismolybdate(VI)*

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Abstract. $\text{LiY}(\text{MoO}_4)_2$, triclinic, $P\bar{1}$, $a = 6.7296$ (6), $b = 10.2792$ (7), $c = 5.1916$ (5) Å, $\alpha = 100.26$ (1), $\beta = 113.73$ (1), $\gamma = 71.94$ (1)° at 298 K with $Z = 2$; $D_{\text{meas}} = 4.35$, $D_{\text{calc}} = 4.43$ Mg m⁻³. Transparent colorless crystals elongated along c were grown by slow cooling from a melt of composition $12\text{Li}_2\text{MoO}_4$, 5MoO_3 , $3\text{Y}_2\text{O}_3$. The structure refined to $R_F = 6.0\%$ for 1335 observed reflections. Six-coordinated Li atoms and eight-coordinated Y atoms link the corners of isolated molybdate tetrahedra.

Introduction. Double molybdates with the scheelite structure $\text{LiLn}(\text{MoO}_4)_2$, where $\text{Ln} = \text{Y}$ or lanthanide, are reviewed in *Gmelins Handbuch der Anorganischen Chemie* (1975). Two anomalies are mentioned concerning $\text{LiY}(\text{MoO}_4)_2$: the discrepancy between calculated (4.61) and observed (4.13 Mg m⁻³) densities, and the poor agreement of this structure with an IR study which points to a structure of lower symmetry. A single-crystal structural study therefore seemed appropriate.

Crystals of $\text{LiY}(\text{MoO}_4)_2$ were grown from a melt containing 60.6 mol% Li_2MoO_4 , 24.7 mol% MoO_3 and 14.7 mol% Y_2O_3 , by cooling at 2 K h⁻¹ from 1473 to 1203 K in a dry nitrogen atmosphere. Transparent needle-like crystals up to 3 mm long were recovered by dissolving the matrix in hot dilute hydrochloric acid. The density was measured at 296 K by pycnometry in toluene after calibration with quartz.

The diffraction intensities of a $0.07 \times 0.15 \times 0.37$ mm crystal were measured. Graphite-monochromatized Mo $K\alpha$ radiation generated at 50 kV, 10 mA was used in a $\theta/2\theta$ scan with line-profile analysis (Grant & Gabe, 1978). One unique set was collected up to 55° in 2θ giving 1445 unique measurements, leading to 1335 observed [$I_{\text{net}} > 3\sigma(I_{\text{net}})$] and 110 unobserved reflections. An absorption correction was performed ($\mu = 13.16$ mm⁻¹).

The presence of a center of symmetry was inferred from the statistics for the normalized structure factors. The positions of the Mo and Y atoms were obtained with *MULTAN* (Germain, Main & Woolfson, 1971). The O and Li atoms were found on difference maps.

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Table 1. Atomic fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters

	x	y	z	B_{iso} (Å ²)
Mo(1)	2999 (2)	6796 (1)	4633 (2)	0.67 (4)
Mo(2)	1541 (2)	1998 (1)	2368 (2)	0.81 (4)
Y	2274 (2)	4402 (2)	-1513 (3)	1.78 (6)
Li	3865 (43)	8852 (28)	590 (51)	2.00 (43)
O(1)	4347 (14)	5714 (9)	2375 (17)	1.24 (38)
O(2)	1164 (14)	5930 (9)	4996 (16)	1.00 (36)
O(3)	3122 (17)	686 (10)	850 (20)	1.97 (43)
O(4)	4985 (15)	7068 (9)	8004 (17)	1.15 (37)
O(5)	1762 (15)	8369 (9)	3191 (17)	1.25 (39)
O(6)	422 (15)	3595 (9)	570 (17)	1.32 (38)
O(7)	3244 (15)	2280 (10)	-4041 (18)	1.57 (44)
O(8)	-559 (16)	1378 (10)	2462 (18)	1.58 (43)

The atomic parameters (Table 1)† were refined by block-diagonal least squares on $\sum w(F_o - F_c)^2$ using counting-statistics weights. All the atoms except Li were refined anisotropically. The final residuals are $R_F = 0.060$ and $wR_F = 0.071$. The scattering curves for free atoms were taken from *International Tables for X-ray Crystallography* (1974). The structure factors were corrected for secondary extinction following Larson (1970). Five reflections lose over half their kinematical intensities and $22\bar{1}$ loses 62% of its intensity in the extinction process. The simultaneous existence of high absorption and high extinction in this crystal is probably responsible for the relatively high values of the residuals. The average Δ/σ value after the last cycle was 0.02 while the largest was 0.07.

Single crystals were ground and their powder pattern† recorded on a powder diffractometer with filtered Cu $K\alpha$ radiation, in the 2θ range 11–70°. The agreement with the powder pattern calculated for the same radiation was good although minor intensity differences, possibly due to preferred orientation in the sample, were observed. No extra lines were observed.

† Lists of structure factors, thermal parameters, and powder data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35218 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

All the calculations were performed using the NRC system of programs for the PDP8-E computer (Larson & Gabe, 1978).

Discussion. Fig. 1 is an orthogonal projection of the structure on to the plane perpendicular to *c*. The interatomic distances and angles are listed in Table 2. The structure is made up of eight-coordinated Y polyhedra sharing corners with eight molybdate tetrahedra and edges with three similar Y polyhedra. The Li atoms are in very distorted tetrahedral sites with one O at 1.79 (3) Å and three other neighbors at about 2.2 Å. Their environment can also be described as 4 + 2 with two additional neighbors at 2.5–2.6 Å. These Li polyhedra share one edge with another Li polyhedron, one edge with a Y polyhedron and corners with six molybdate tetrahedra. The molybdate tetrahedra are moderately distorted with Mo–O distances ranging from 1.72 (1) to 1.83 (1) Å.

The structure as a whole can be described as (010) slabs of isolated molybdate tetrahedra sharing corners with inner Y polyhedra and outer Li polyhedra. These slabs are bonded by only two short (1.79 Å) Li–O bonds through the (010) cell face.

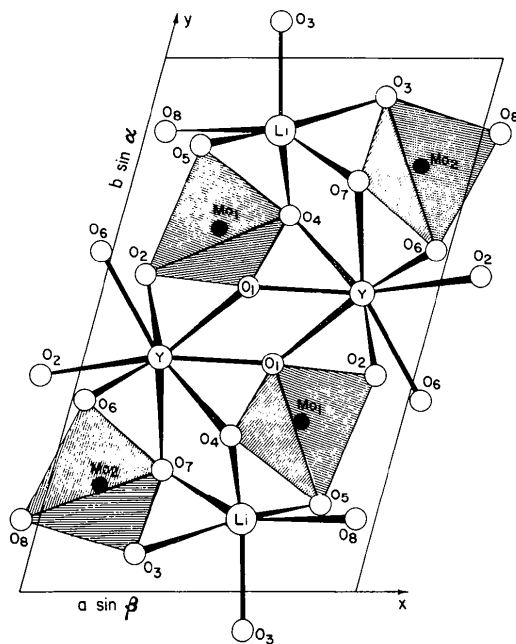


Fig. 1. Orthogonal projection of the structure on to the plane perpendicular to *c*. The Li–O(3) bond through the cell face is the short one.

Table 2. Distances (Å) and selected angles (°)

Mo(1)–O(1)	1.789 (9)	Li–O(3)	1.79 (3)
Mo(1)–O(2)	1.811 (8)	Li–O(3')	2.62 (3)
Mo(1)–O(4)	1.761 (8)	Li–O(4)	2.19 (3)
Mo(1)–O(5)	1.722 (9)	Li–O(5)	2.51 (3)
		Li–O(7)	2.21 (3)
		Li–O(8)	2.21 (3)
Mo(2)–O(3)	1.726 (10)	O(1)–Mo(1)–O(2)	107.5 (4)
Mo(2)–O(6)	1.829 (9)	O(1)–Mo(1)–O(4)	111.2 (4)
Mo(2)–O(7)	1.779 (9)	O(1)–Mo(1)–O(5)	106.3 (4)
Mo(2)–O(8)	1.740 (9)	O(2)–Mo(1)–O(4)	108.4 (4)
		O(2)–Mo(1)–O(5)	117.2 (4)
Y–O(1)	2.402 (8)	O(4)–Mo(1)–O(5)	106.3 (4)
Y–O(1')	2.454 (9)		
Y–O(2)	2.347 (8)	O(3)–Mo(2)–O(6)	113.4 (4)
Y–O(2')	2.375 (8)	O(3)–Mo(2)–O(7)	108.4 (5)
Y–O(4)	2.357 (9)	O(3)–Mo(2)–O(8)	106.4 (5)
Y–O(6)	2.336 (9)	O(6)–Mo(2)–O(7)	110.0 (4)
Y–O(6')	2.410 (9)	O(6)–Mo(2)–O(8)	112.8 (4)
Y–O(7)	2.386 (10)	O(7)–Mo(2)–O(8)	105.4 (4)

This arrangement seems to be new, especially in view of its low symmetry. Similar coordinations are found in other more symmetrical double molybdates, such as $KY(MoO_4)_2$ where eight-coordinated Y and molybdate tetrahedra form layers connected by K–O bonds (Klevtsova & Borisov, 1968).

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