

Li₃Al(MoO₄)₃, a lyonsite molybdate

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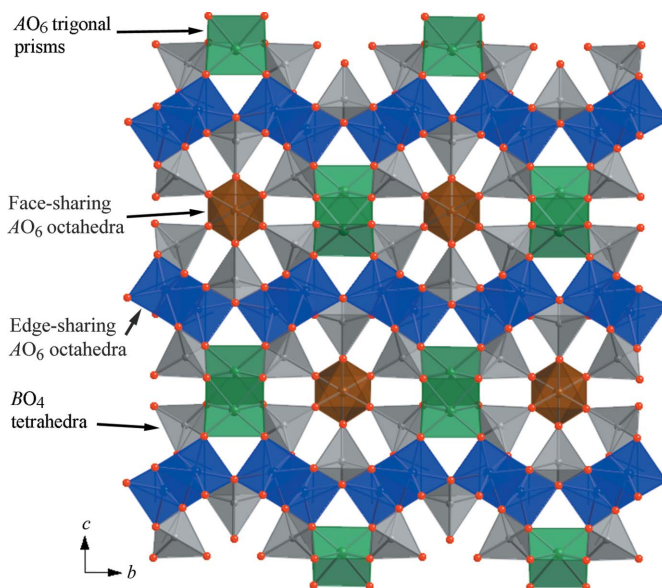
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Trilithium aluminium trimolybdate(VI), Li₃Al(MoO₄)₃, has been grown as single crystals from α -Al₂O₃ and MoO₃ in an Li₂MoO₄ flux at 998 K. This compound is an example of the well known lyonsite structure type, the general formula of which can be written as A₁₆B₁₂O₄₈. Because this structure can accommodate cationic mixing as well as cationic vacancies, a wide range of chemical compositions can adopt this structure type. This has led to instances in the literature where membership in the lyonsite family has been overlooked when assigning the structure type to novel compounds. In the title compound, there are two octahedral sites with substitutional disorder between Li⁺ and Al³⁺, as well as a trigonal prismatic site fully occupied by Li⁺. The (Li,Al)O₆ octahedra and LiO₆ trigonal prisms are linked to form hexagonal tunnels along the [100] axis. These polyhedra are connected by isolated MoO₄ tetrahedra. Infinite chains of face-sharing (Li,Al)O₆ octahedra extend through the centers of the tunnels. A mixed Li/Al site, an Li, an Mo, and two O atoms are located on mirror planes.

Comment

Although its namesake mineral, α -Cu₃Fe₄(VO₄)₆, was not structurally characterized until much later (Hughes *et al.*, 1987), the lyonsite crystal structure was first observed in 1964 in NaCo_{2.31}(MoO₄)₃ (Ibers & Smith, 1964). An excellent review of this structure type was published recently (Smit *et al.*, 2006). The general formula for the lyonsite family of compounds can be written as A₁₆B₁₂O₄₈ [or A₁₆(BO₄)₁₂ or A₄(BO₄)₃]. The A cations, with octahedral and trigonal prismatic coordination environments, most commonly have formal oxidation states of 1+, 2+, or 3+, though some examples have been found with cations in higher oxidation states, such as Ti⁴⁺ (Smit *et al.*, 2008) and Nb⁵⁺ (Smit *et al.*, 2006). The tetrahedral B cations in lyonsite consist exclusively of V³⁺, Mo⁶⁺ and W⁶⁺. Typically, there is a mixture of two cations on the A site, or sometimes cationic vacancies, in order to preserve overall electroneutrality.

The lyonsite crystal structure (Fig. 1) features isolated BO₄ tetrahedra which are interconnected by AO₆ octahedra and

**Figure 1**

Polyhedral representation of the lyonsite crystal structure type. (In the electronic version of the paper, edge-sharing AO₆ octahedra are shown in blue, face-sharing AO₆ octahedra in brown, AO₆ trigonal prisms in green and BO₄ tetrahedra in gray.)

trigonal prisms. The octahedra and trigonal prisms form hexagonal tunnels in the [100] direction. The BO₄ tetrahedra line the interior of these tunnels, and infinite chains of face-sharing AO₆ octahedra extend through the centers of the tunnels. The AO₆ octahedra in the hexagonal tunnels share edges to form columns, while the AO₆ trigonal prisms share edges to form zigzag sheets. When there are multiple A cations, the larger ones tend to be localized on the more geometrically accommodating trigonal prismatic site. Because the face-sharing octahedra in the infinite chains possess the shortest A···A interatomic distances, cationic vacancies, when present, are concentrated on this site to reduce coulombic repulsions.

The title compound crystallizes in the space group *Pnma* of the orthorhombic system with the lyonsite structure type. Previously, only the unit-cell parameters of Li₃Al(MoO₄)₃ had been reported on the basis of indexing of powder X-ray diffraction data (Klevtsov, 1970). Here, we report the first high-quality single-crystal X-ray diffraction structure determination. The crystals were prepared by a high-temperature solution reaction where Li₂MoO₄ served as the flux. Alkali molybdates are commonly used as flux for the growth of single crystals of complex molybdenum-containing oxides (Bugaris & zur Loye, 2012).

In Li₃Al(MoO₄)₃ (Fig. 2), the B sites are occupied by Mo⁶⁺ cations tetrahedrally coordinated by oxide anions. The Mo—O bond lengths in the title compound are in the range 1.7244 (17)–1.7937 (16) Å [average 1.766 (5) Å]. These interatomic distances are consistent with those for the isostructural compound Li₃Ga(MoO₄)₃ (van der Lee *et al.*, 2008), which are in the range 1.734 (2)–1.795 (2) Å. The O—Mo—O angles of 104.01 (12)–116.13 (12)° correspond to a nearly regular MoO₄ tetrahedron.

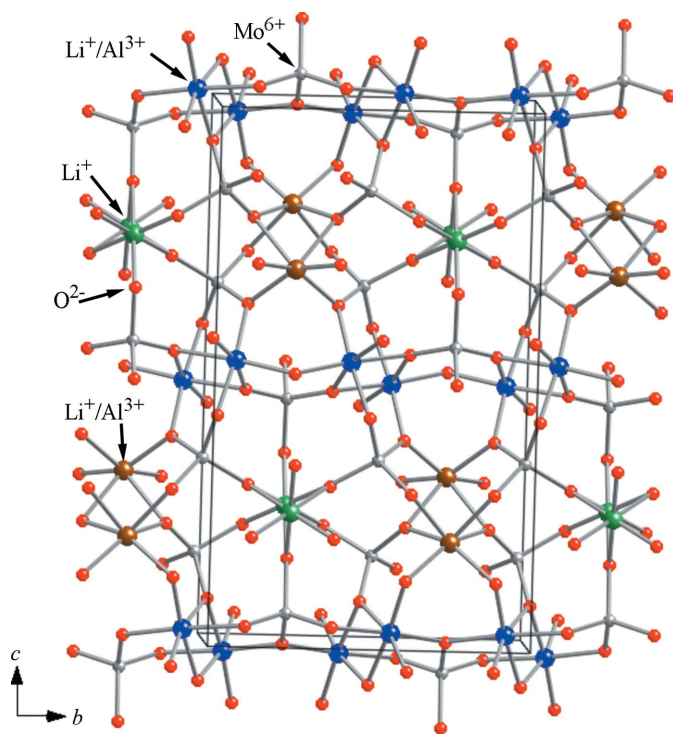


Figure 2 Ball-and-stick representation of the crystal structure of $\text{Li}_3\text{Al}(\text{MoO}_4)_3$, as viewed down $[100]$. [In the electronic version of the paper, the blue spheres are Li^+ and Al^{3+} cations [mixed sites with 72.1 (2):27.9 (2)% occupancy, respectively], the brown spheres are Li^+ and Al^{3+} cations [mixed sites with 55.8 (5):44.2 (4)% occupancy, respectively], the green spheres are Li^+ cations, the gray spheres are Mo^{6+} cations and the red spheres are O^{2-} anions.]

The *A* cationic sites in the title compound are occupied by a mixture of Li^+ and Al^{3+} cations in the 3:1 ratio necessary to preserve charge electroneutrality. The trigonal prismatic sites are occupied completely by Li^+ cations, while the octahedral sites are occupied by a mixture of Li^+ and Al^{3+} cations. The edge-sharing AO_6 octahedra in the hexagonal tunnels contain 72.1 (2)% Li^+ , while the face-sharing AO_6 octahedra in the infinite chains contain 55.8 (5)% Li^+ . As the ionic radius of six-coordinate Al^{3+} is significantly smaller than that of six-coordinate Li^+ (0.535 Å versus 0.76 Å; Shannon, 1976), it is to be expected that a higher percentage of Al^{3+} is found on the face-sharing octahedral site in order to alleviate Coulombic repulsions. No Al^{3+} is found on the trigonal prismatic site, consistent with the fact that this site is more accommodating towards a larger cation, in this case Li^+ . A similar separation of large and small cations into trigonal prismatic and octahedral sites is observed in the 2H-perovskite-related oxide structure type (zur Loye *et al.*, 2012).

Other compounds belonging to the $\text{Li}_3\text{M}^{3+}(\text{MoO}_4)_3$ family of compounds with the lyonsite structure type exhibit disorder of the Li^+ and M^{3+} cations on the *A* sites. The edge-sharing AO_6 octahedral sites contain 70 (1), 69.2 (1), 66.67, 71.91 (17) and 75% of Li^+ , while the face-sharing AO_6 octahedral sites contain 56 (1), 61.7 (1), 66.67, 57.9 (3) and 58% of Li^+ , for $M = \text{V}^{3+}$ (Mikhailova *et al.*, 2010), Cr^{3+} (Sarapulova *et al.*, 2009), Fe^{3+} (Klevtsova & Magarill, 1970), Ga^{3+} (van der Lee *et al.*,

2008) and Sc^{3+} (Kolitsch & Tillmanns, 2003), respectively. With regard to the examples containing V^{3+} , Cr^{3+} , Fe^{3+} and Ga^{3+} , the trigonal prismatic site is occupied entirely by Li^+ . For $\text{Li}_3\text{Sc}(\text{MoO}_4)_3$, the trigonal prismatic site contains 92% Li^+ and 8% Sc^{3+} . The appearance of Sc^{3+} on the trigonal prismatic site can be attributed to the larger ionic radius of six-coordinate Sc^{3+} (0.745 Å), which is approaching the size of six-coordinate Li^+ . The ionic radii of six-coordinate Cr^{3+} (0.615 Å), Ga^{3+} (0.62 Å), V^{3+} (0.64 Å) and Fe^{3+} (0.645 Å) are significantly smaller than that of Li^+ , so as in the title compound, none of these cations is found on the trigonal prismatic site.

In $\text{Li}_3\text{Al}(\text{MoO}_4)_3$, the Li/Al–O bond lengths in the edge-sharing octahedra are in the range 2.003 (2)–2.143 (3) Å. For the face-sharing octahedra, the Li/Al–O interatomic distances are in the range 1.957 (2)–2.023 (3) Å. The bond lengths are shorter for the face-sharing octahedra because a higher concentration of the smaller Al^{3+} cation is found on those sites. Finally, the Li–O interatomic distances in the trigonal prisms are in the range 2.103 (5)–2.222 (6) Å.

The Li-ion conductivity of various Li-containing lyonsite materials has been investigated for their potential application as electrolyte materials in Li-ion batteries (Sebastian *et al.*, 2003). It was determined that, although the lyonsite crystal structure is a three-dimensional framework, the conduction pathway of the Li^+ ions is limited to the zigzag sheets of edge-sharing trigonal prisms. Therefore, it is to be expected that compounds with a greater concentration of Li^+ on the trigonal prismatic sites would exhibit higher ionic conductivities. For example, the ionic conductivities measured for $\text{Li}_3\text{Cr}(\text{MoO}_4)_3$ and $\text{Li}_3\text{Fe}(\text{MoO}_4)_3$ were higher than those of the $\text{Li}_{2-2x}\text{Mg}_{2+x}(\text{MoO}_4)_3$ series of compounds. In the Cr- and Fe-containing materials, the trigonal prismatic sites are fully occupied by Li^+ , whereas in the Mg-containing materials the trigonal prismatic sites are occupied by a mixture of Li^+ and Mg^{2+} . It would be interesting to measure the ionic conductivity of the title compound, $\text{Li}_3\text{Al}(\text{MoO}_4)_3$, which contains only Li^+ on the trigonal prismatic sites, in order to ascertain whether the ionic conductivity is comparable with or higher than the Cr- and Fe-containing materials.

Experimental

Colorless prismatic crystals of $\text{Li}_3\text{Al}(\text{MoO}_4)_3$ were grown from a mixture of Li_2MoO_4 (Alfa Aesar, 99+%), $\alpha\text{-Al}_2\text{O}_3$ (Alfa Aesar, 99.9%) and MoO_3 (Alfa Aesar, 99.95%). The Li_2MoO_4 was dried overnight at 423 K to remove any adsorbed water. The starting reagents $\alpha\text{-Al}_2\text{O}_3$ (0.10196 g, 1 mmol), and MoO_3 (0.14394 g, 1 mmol), with Li_2MoO_4 (0.43455 g, 2.5 mmol) acting as both a source of Li and a flux, were ground together thoroughly using a mortar and pestle. The mixture was transferred to an alumina crucible, covered loosely and placed in a furnace. The mixture was heated at a rate of 200 K h⁻¹ to 998 K, where it was held for 12 h, before being cooled at a rate of 2 K h⁻¹ to 773 K, at which point it was allowed to cool rapidly to room temperature. The excess lithium molybdate flux was removed by washing with hot water, aided by sonication, and colorless prismatic crystals of the title compound were isolated by vacuum filtration.

Table 1
Selected bond lengths (Å).

Li1—O5	2.003 (2)	Li3—O6 ^v	2.103 (5)
Li1—O5 ⁱ	2.025 (2)	Li3—O7 ^{vi}	2.168 (5)
Li1—O6	2.029 (2)	Li3—O7 ⁱ	2.168 (5)
Li1—O2 ⁱⁱ	2.061 (2)	Li3—O7 ^{vii}	2.222 (6)
Li1—O3	2.093 (2)	Li3—O7 ^{viii}	2.222 (6)
Li1—O2 ⁱ	2.143 (3)	Mo1—O2	1.7550 (17)
Li2—O4 ⁱⁱⁱ	1.957 (2)	Mo1—O2 ^v	1.7550 (17)
Li2—O4 ^{iv}	1.957 (2)	Mo1—O3	1.781 (3)
Li2—O4 ^v	1.965 (2)	Mo1—O1	1.781 (2)
Li2—O4	1.965 (2)	Mo1—O7	1.7244 (17)
Li2—O1 ^{iv}	2.018 (3)	Mo2—O6 ^{ix}	1.7595 (17)
Li2—O1	2.023 (3)	Mo2—O5	1.7770 (17)
Li3—O6	2.103 (5)	Mo2—O4 ^x	1.7937 (16)

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

Crystal data

Li ₃ Al(MoO ₄) ₃	$V = 897.8 (3) \text{ \AA}^3$
$M_r = 527.62$	$Z = 4$
Orthorhombic, <i>Pnma</i>	Mo $K\alpha$ radiation
$a = 5.0372 (10) \text{ \AA}$	$\mu = 4.29 \text{ mm}^{-1}$
$b = 10.320 (2) \text{ \AA}$	$T = 298 \text{ K}$
$c = 17.272 (4) \text{ \AA}$	$0.07 \times 0.07 \times 0.05 \text{ mm}$

Data collection

Bruker SMART APEX CCD area-detector diffractometer	14109 measured reflections
Absorption correction: numerical (SADABS; Sheldrick, 2008)	1606 independent reflections
$T_{\min} = 0.661, T_{\max} = 0.746$	1414 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$	99 parameters
$wR(F^2) = 0.048$	4 restraints
$S = 1.12$	$\Delta\rho_{\text{max}} = 0.80 \text{ e \AA}^{-3}$
1606 reflections	$\Delta\rho_{\text{min}} = -0.76 \text{ e \AA}^{-3}$

A model with substitutional disorder between Li and Al was proposed for this compound. Similar disorder was observed in the isostructural compounds Li₃M³⁺(MoO₄)₃ ($M = \text{V, Cr, Fe, Ga, Sc}$). The occupancies of the Li1/Al1 and Li2/Al2 crystallographic sites were constrained to 1.00, whereas restraints with an s.u. value of 0.001 were used for keeping the total number of Li atoms in the structural formula at 3.0 and the total number of Al atoms in the structural formula at 1.0, *i.e.* occupancy(Li1) + 0.5 × occupancy(Li2) = 1.0, and occupancy(Al1) + 0.5 × occupancy(Al2) = 0.5. There is no evidence

in the refinement for the presence of Al on the trigonal prismatic site (100% Li).

The largest positive and negative residual electron densities of 0.804 and $-0.763 \text{ e \AA}^{-3}$ are located 0.76 and 0.58 Å, respectively, from atom Mo1.

Data collection: SMART (Bruker, 2001); cell refinement: SMART; data reduction: SAINT-Plus (Bruker, 2001); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: CrystalMaker (Palmer, 2012); software used to prepare material for publication: SHELXTL97 (Sheldrick, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3069). Services for accessing these data are described at the back of the journal.

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