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La_2LiMoO_6

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Abstract

Dilanthanum lithium molybdenum(V) oxide has a monoclinically distorted perovskite-type structure with an ordered distribution of the Mo^{5+} and Li^+ ions over the octahedral sites. The Mo—O distances within the slightly distorted MoO_6 octahedra range between 1.959 (2) and 1.970 (2) Å with an average value of 1.965 Å. The LiO_6 octahedra are more distorted with Li—O distances in the range 2.099 (2)–2.155 (2) Å (average distance 2.132 Å). The La^{3+} ions are surrounded by eight O atoms at distances ranging from 2.409 (3) to 2.776 (2) Å with the four nearest O atoms forming a distorted tetrahedron and the remaining O atoms roughly capping two faces or bridging two edges of this tetrahedron.

Comment

The $AMoO_3$ (A = Ca, Sr and Ba) (Scholder & Brixner, 1955) compounds are the only ternary reduced molybdenum oxides which crystallize with the perovskite structure. Replacement of half of the Mo^{4+} ions by a 3d element (Sc, Cr, Fe) (Patterson, Moeller & Ward, 1963) or a rare earth element (La → Lu) (Brandle & Steinfink, 1971) leads to reduced Mo compounds with general formula A_2BMoO_6. The differences in radius and valence between the B^{3+} and Mo^{5+} ions lead to the ordering of the latter. As a consequence, these quaternary oxides crystallize in cubic, tetragonal or orthorhombic perovskite supercells, closely related to the cryolite structure, depending upon the sizes of the A and B ions. More complex quadruple oxides containing Mo^{5+} ions and having perovskite-related structures are also known, such as $ALaMnMoO_6$ (A = Ca, Sr and Ba) (Nakamura & Choy, 1977) and $La_2M_{4/3}Mo_{2/3}O_6$ (M = Mg and Mn) (Bazuev, Makarova & Shveikin, 1987). However, with the exception of Ba_2NdMoO_6, the structure of which was determined at 473 K (Brandle & Steinfink, 1971), none of the above compounds has been the subject of accurate single-crystal or powder structure determinations.

We present here the crystal structure of a new ordered A_2BMoO_6 compound containing Mo^{5+} ions: La_2LiMoO_6. This compound belongs to the large family of analogous phases La_2LiMO_6 (M = V, Fe, Nb, Ru, Ta, Re, Os and Ir) and was mentioned by Demazeau, Oh-Kim, Choy & Hagenmuller in 1987, though no details of the synthesis or the structural parameters were given. La_2LiMoO_6 crystallizes in a monoclinically distorted variant (space group $P2_1/n$) of the perovskite structure with unit-cell parameters of ca $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$ where a_p is the unit-cell parameter of an ideal cubic

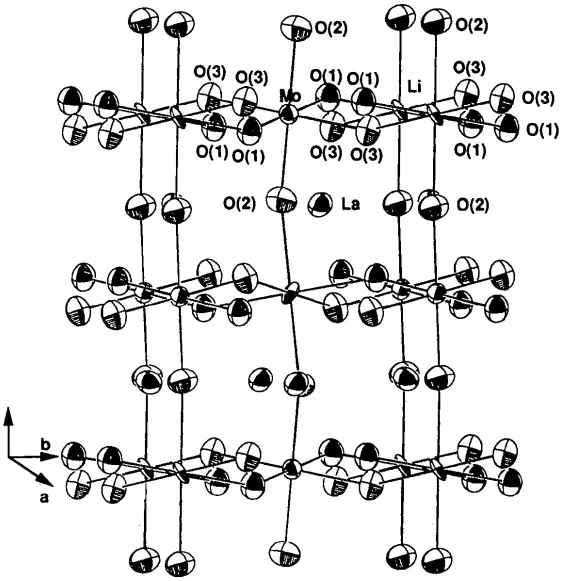

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the structure of La_2LiMoO_6. Displacement ellipsoids are drawn at the 95% probability level.

perovskite. Consequently, the structure consists of a framework of ordered corner-sharing MoO_6 and LiO_6 octahedra which are tilted and rotated to optimize the La—O bond lengths (Fig. 1).

Although they are of low symmetry (point group $\bar{1}$), the MoO_6 octahedra are only slightly distorted with Mo—O distances ranging from 1.959 (2) to 1.970 (2) Å and O—Mo—O angles varying between 88.9 (1) and 89.8 (1)°. The average Mo—O distance is 1.965 Å and is close to that calculated for La_3MoO_7 (1.987 Å) (Tortelier & Gougeon, 1995) in which Mo^{5+} ions are also present. On the other hand, this value is smaller than the distance expected from the sum of the ionic radii of O^{2-} and Mo^{5+} (2.03 Å) according to Shannon & Prewitt (1969) and larger than the value of 1.86 (2) Å observed for Ba_2NdMoO_6. [The short Mo—O distance in Ba_2NdMoO_6 was attributed to a large overlap of the oxygen orbitals and the 4*d* orbitals of molybdenum by the authors. However, it could be due to the inaccuracy in the position of the unique crystallographically independent O atom, which shows a large isotropic displacement parameter of 4.1 (4) Å².]

The LiO_6 octahedra are more distorted with Li—O distances ranging between 2.099 (2) and 2.155 (2) Å and O—Li—O angles between 88.7 (1) and 89.92 (9)°. The average Li—O distance is 2.132 Å, which lies between the distances calculated from the sum of the ionic radii of Li^+ and O^{2-} with coordination number IV (2.12 Å) and VI (2.14 Å).

The deformation from the ideal perovskite structure is mainly due to the small radius of the La^{3+} ion. This is reflected by its environment, which consists of eight O atoms instead of twelve in the ideal cubic perovskite structure. Of these eight O atoms, the nearest four [at distances ranging from 2.409 (3) to 2.496 (3) Å] form a distorted tetrahedron and the remaining four [2.660 (2)–2.776 (2) Å] roughly cap two faces or bridge two edges of this tetrahedron.

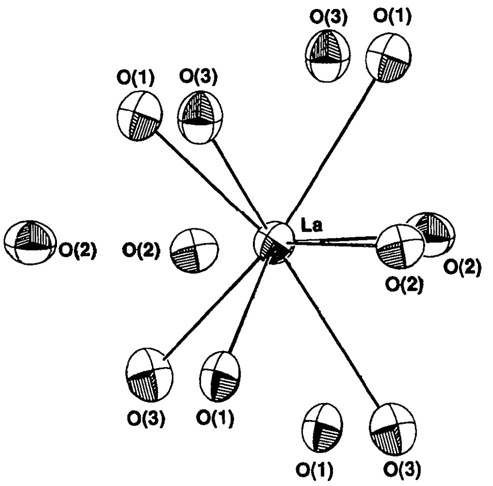

Fig. 2. Environment of the La^{3+} cation. The unconnected ellipsoids represent the remaining four O atoms forming the *A* site in the ideal cubic perovskite structure.

Experimental

Single crystals were obtained by mixing La_2O_3, Li_2MoO_4, MoO_3 and Mo, all in powder form, in the ratio 6:3:2:1. The mixture was pressed into a pellet and placed in a molybdenum crucible which was then sealed under a low argon pressure using an arc welding system. The mixture was heated at a rate of 100 K h^{-1} to about 2020 K, held at this temperature for 48 h, and then cooled at a rate of 100 K h^{-1} to 1400 K, at which temperature the power was turned off.

Crystal data

La_2LiMoO_6
$M_r = 476.70$
Monoclinic
$P2_1/n$
$a = 5.590\ (1)$ Å
$b = 5.6932\ (8)$ Å
$c = 7.878\ (2)$ Å
$\beta = 90.260\ (9)°$
$V = 250.72\ (8)$ Å^3
$Z = 2$
$D_x = 6.314$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5.2$–$18.6°$
$\mu = 19.178$ mm^{-1}
$T = 295$ K
Irregular
0.12 × 0.10 × 0.10 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
θ–2θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.678$, $T_{\max} = 0.997$
1792 measured reflections
1519 independent reflections
1519 observed reflections

$R_{\rm int} = 0.033$
$\theta_{\max} = 40°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 10$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 90 min
intensity decay: <1%

Refinement

Refinement on F
$R = 0.026$
$wR = 0.033$
$S = 0.764$
1519 reflections
50 parameters
$w = 1/[\sigma^2(F_o) + 0.0004F_o^2 + 1]$ (Killean & Lawrence, 1969)
$(\Delta/\sigma)_{\max} < 0.01$

$\Delta\rho_{\max} = 2.50$ e Å^{-3}
$\Delta\rho_{\min} = -3.11$ e Å^{-3}
Extinction correction: Stout & Jensen (1968)
Extinction coefficient: $9.6\ (2) \times 10^{-7}$
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Li	0	0	0	0.36 (8)
Mo	1/2	1/2	0	0.422 (4)
La	0.99084 (3)	0.55103 (3)	0.75150 (2)	0.660 (2)
O(1)	0.7139 (4)	0.8069 (4)	0.5420 (3)	0.69 (3)
O(2)	0.9154 (5)	0.0205 (5)	0.2589 (3)	0.82 (3)
O(3)	0.6917 (4)	0.7817 (4)	0.9534 (3)	0.77 (3)

Table 2. *Selected geometric parameters (Å, °)*

Mo—O(1)	1.970 (2)	O(1)—Mo—O(2)	89.8 (1)
Mo—O(2)	1.959 (2)	O(1)—Mo—O(3)	88.9 (1)
Mo—O(3)	1.965 (2)	O(2)—Mo—O(3)	89.8 (1)
Li—O(1)	2.142 (2)	O(1)—Li—O(2)	88.7 (1)
Li—O(2)	2.099 (2)	O(1)—Li—O(3)	89.92 (9)
Li—O(3)	2.155 (2)	O(2)—Li—O(3)	89.2 (1)
		Mo—O(1)—Li	151.9 (1)
		Mo—O(2)—Li	152.2 (1)
		Mo—O(3)—Li	151.1 (1)
La—O(1)	2.430 (2)	La—O(1)	2.687 (2)
La—O(2)	2.409 (3)	La—O(1)	2.724 (2)
La—O(2)	2.496 (3)	La—O(3)	2.660 (2)
La—O(3)	2.446 (2)	La—O(3)	2.776 (2)

For ease of comparison with the perovskite structure, the non-conventional $P2_1/n$ setting was retained. Data were corrected for Lorentz and polarization effects. The structure was solved with the aid of *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and subsequent difference Fourier syntheses. Refinements of the occupancy factors for the Li and Mo sites confirmed that they are fully occupied. All calculations were performed on a Digital MicroVAX 3100.

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1142). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cadmium Hexacyanoiridate(III) Dodecahydrate

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Abstract

Single crystals of tricadmium bis[hexacyanoiridate(III)] dodecahydrate, $Cd_3[Ir(CN)_6]_2.12H_2O$, were synthesized by the 'slow-diffusion U-tube' method. The disordered structure crystallizes in the cubic space group $Fm\bar{3}m$ (No. 225) with a lattice constant of 10.848 (1) Å and one-and-a-third molecules in the unit cell. Divalent Cd atoms are linked to the Ir atoms by linear cyanide bridges. When disorder occurs cavities are formed, a water molecule, O2, replaces an Ir atom and a cyanide bridge is replaced with a coordinated water molecule, O1. A hydrogen-bonding network is set up between O1, O2, and O3 within the cavities of the crystal lattice. Dehydration and IR studies were conducted on single crystals of the title compound. The compound is isostructural with the dodecahydrates of $Cd_3[Co(CN)_6]_2$ and $Mn_3[Co(CN)_6]_2$.

Comment

IR, dehydration, electron diffraction and powder and single-crystal X-ray diffraction methods have been employed to investigate the structural and morphological relationships of the transition metal ferro-, ferri- and cobalticyanides (Milligan *et al.*, 1970; Beall, Milligan, Korp & Bernal, 1977; Mullica, Oliver, Milligan & Hills, 1979). However, in spite of the structural investigations of the hydrated Prussian blue analogs, there are still questions concerning the zeolitic water structure in these materials. A clear understanding of the water network is essential in order to model the H_2O transport in the semi-permeable membranes. Several structural investigations of the transition metal hexacyanides have led to proposals of various models for the face-centered cubic lattice (Keggin & Miles, 1936; Ludi & Güdel,

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