

INORGANIC COMPOUNDS

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LiMoP₂O₇

S. LEDAIN, A. LECLAIRE, M. M. BOREL AND B. RAVEAU

Laboratoire CRISMAT, CNRS URA 1318, ISMRA et
Université de Caen, Bd du Maréchal Juin, 14050 Caen
CEDEX, France

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Abstract

The structure of lithium molybdenum(III) diphosphate has been determined for the first time from single-crystal X-ray diffraction data. LiMoP₂O₇, which crystallizes in the space group *P*2₁, is isotypic with LiVP₂O₇ and LiFeP₂O₇; it has a tunnel structure consisting of corner-sharing MoO₆ octahedra and diphosphate groups which form chains running along *b*. The Li⁺ ions have tetrahedral coordination geometry. The geometry of the different polyhedra can be compared with those in LiVP₂O₇.

Comment

The structure of LiMoP₂O₇ was previously studied from a polycrystalline, tetraphasic mixture using pattern decomposition in conjunction with the Rietveld method (Wang, Wang & Nieh, 1990). It was found to be isotypic with LiVP₂O₇ (Lii, Wang, Chen & Wang, 1990) and, therefore, with LiFeP₂O₇ (Genkina, Maksimov, Timofeeva, Bykov & Mel'nikov, 1985). Though the isotypism of this compound with LiFeP₂O₇ is unquestionable, some problem with the powder diffraction study remains; the final *R* factors and standard deviations are higher than expected, and positive differences appear in the powder patterns. This suggests that the atomic coordinates deduced from this difficult powder study may not be accurate enough to provide an exact comparison of the geometry of the polyhedra with those in LiVP₂O₇.

The projection of the structure along *a* (Fig. 1) confirms the isotypism of this phase with LiVP₂O₇. The structure contains MoP₂O₁₁ units in which one MoO₆ octahedron shares two apices with the same P₂O₇ group. Each MoO₆ octahedron is linked to five P₂O₇ groups, whereas each PO₄ tetrahedron is linked to three MoO₆ octahedra and to one PO₄ tetrahedron. This results in large seven-sided tunnels running along *a*.

The atomic coordinates (Table 1) and consequently the interatomic distances (Table 2) are significantly different from those deduced from the powder data obtained previously. The MoO₆ octahedra exhibit six rather long Mo—O bonds, ranging from 2.068 (5)

to 2.131 (4) Å, characteristic of Mo^{III}, which can be compared with the V—O distances ranging from 1.952 to 2.027 Å for V^{III} in LiVP₂O₇. It should be noted that the abnormally short Mo—O bond of 1.91 Å previously observed in the powder study is no longer present.

The P₂O₇ groups exhibit a semi-eclipsed configuration and are very similar to those observed in LiVP₂O₇. Each PO₄ tetrahedron is characterized by three shorter P—O distances [1.493 (5)–1.521 (4) Å], corresponding to the P—O—Mo bonds, and one longer P—O distance [1.602 (3), 1.606 (4) Å] to the bridging O atom of the P₂O₇ group. These values are close to the values of 1.503–1.520 Å and 1.602 Å, respectively, observed in LiVP₂O₇.

The Li⁺ ions, located near the walls of the tunnels, also exhibit similar Li—O distances [1.96 (1)–2.15 (1) Å] to those observed in LiVP₂O₇ (1.96–2.12 Å).

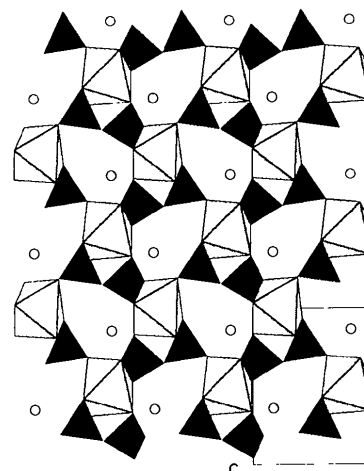


Fig. 1. Projection of the structure of LiMoP₂O₇ along [100].

Experimental

Single crystals of LiMoP₂O₇ were grown from a batch of nominal composition Li₂MoP₃O₁₀ heated at 973 K for 24 h and cooled by 9 K h⁻¹ to 298 K.

Crystal data

LiMoP₂O₇
M_r = 277
Monoclinic
*P*2₁
a = 4.8984 (4) Å
b = 8.3919 (8) Å
c = 7.034 (1) Å
β = 109.33 (1)°
V = 272.83 (7) Å³
Z = 2
D_x = 3.36 Mg m⁻³

Mo *Kα* radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 18–22°
μ = 2.896 mm⁻¹
T = 294 K
Parallelepiped
0.077 × 0.051 × 0.025 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer	$\theta_{\max} = 45^\circ$
Bisect scans	$h = -9 \rightarrow 9$
Absorption correction: none	$k = 0 \rightarrow 16$
2457 measured reflections	$l = 0 \rightarrow 14$
2457 independent reflections	3 standard reflections
1339 observed reflections	frequency: 60 min
$[I > 3\sigma(I)]$	intensity decay: <1%

Refinement

Refinement on F^2	$\Delta\rho_{\max} = 0.95 \text{ e } \text{\AA}^{-3}$
$R = 0.029$	$\Delta\rho_{\min} = -0.95 \text{ e } \text{\AA}^{-3}$
$wR = 0.027$	Extinction correction: none
$S = 0.997$	Atomic scattering factors
1339 reflections	from <i>International Tables</i>
94 parameters	for <i>X-ray Crystallography</i>
$w = 1/\sigma(F)$	(1974, Vol. IV)
$(\Delta/\sigma)_{\max} < 0.001$	

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$B_{\text{iso}}/B_{\text{eq}}$
Mo	0.21270 (8)	0.5	0.22578 (6)	0.339 (6)
P(1)	0.4030 (3)	0.1806 (2)	0.0289 (2)	0.42 (2)
P(2)	0.7937 (3)	0.2851 (2)	0.4194 (2)	0.47 (2)
Li	0.797 (2)	0.364 (1)	0.821 (2)	1.8 (2)
O(1)	0.0539 (9)	0.3200 (6)	0.3608 (7)	0.96 (8)
O(2)	0.3985 (8)	0.6822 (5)	0.0963 (6)	0.80 (8)
O(3)	0.1328 (8)	0.7007 (5)	0.3807 (6)	0.72 (8)
O(4)	0.6172 (7)	0.4331 (5)	0.4226 (6)	0.96 (8)
O(5)	0.2403 (8)	0.3376 (4)	0.0069 (5)	0.56 (8)
O(6)	0.5967 (8)	0.1593 (4)	0.2607 (5)	0.80 (8)
O(7)	-0.2025 (7)	0.5375 (4)	0.0077 (5)	0.62 (7)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Mo—O(1)	2.068 (5)	P(1)—P(2)	2.915 (2)
Mo—O(2)	2.131 (4)	P(2)—O(4)	1.518 (4)
Mo—O(3)	2.112 (5)	P(2)—O(6)	1.606 (4)
Mo—O(4)	2.084 (3)	P(2)—O(1 ^{iv})	1.493 (5)
Mo—O(5)	2.093 (4)	P(2)—O(3 ^{iv})	1.508 (4)
Mo—O(7)	2.126 (3)	Li—O(5 ^v)	2.15 (1)
P(1)—O(5)	1.521 (4)	Li—O(7 ^v)	1.96 (1)
P(1)—O(6)	1.602 (3)	Li—O(2 ^{iv})	1.99 (1)
P(1)—O(7 ^v)	1.518 (4)	Li—O(3 ^{iv})	2.08 (1)
P(1)—O(2 ⁱⁱ)	1.513 (5)		
O(1)—Mo—O(2)	177.0 (1)	O(5)—P(1)—O(2 ⁱⁱ)	110.4 (2)
O(1)—Mo—O(3)	100.5 (2)	O(6)—P(1)—O(7 ^v)	102.5 (2)
O(1)—Mo—O(4)	85.3 (2)	O(6)—P(1)—O(2 ⁱⁱ)	108.4 (2)
O(1)—Mo—O(5)	89.3 (2)	P(1)—O(6)—P(2)	130.6 (3)
O(1)—Mo—O(7)	91.4 (1)	O(4)—P(2)—O(6)	109.5 (2)
O(2)—Mo—O(3)	80.0 (2)	O(4)—P(2)—O(1 ^{iv})	112.7 (3)
O(2)—Mo—O(4)	91.8 (1)	O(4)—P(2)—O(3 ^{iv})	109.4 (3)
O(2)—Mo—O(5)	90.7 (2)	O(5 ^v)—Li—O(7 ^v)	83.8 (4)
O(2)—Mo—O(7)	91.6 (1)	O(5 ^v)—Li—O(2 ^{iv})	103.2 (5)
O(3)—Mo—O(4)	99.8 (1)	O(5 ^v)—Li—O(3 ^{iv})	89.0 (5)
O(3)—Mo—O(5)	165.2 (1)	O(6)—P(2)—O(1 ^{iv})	108.0 (3)
O(3)—Mo—O(7)	87.6 (1)	O(6)—P(2)—O(3 ^{iv})	104.0 (2)
O(4)—Mo—O(5)	92.0 (1)	O(7 ^v)—Li—O(2 ^{iv})	105.6 (7)
O(4)—Mo—O(7)	172.4 (1)	O(7 ^v)—Li—O(3 ^{iv})	169.1 (7)
O(5)—Mo—O(7)	81.1 (1)	O(1 ^{iv})—P(2)—O(3 ^{iv})	112.8 (2)
O(5)—P(1)—O(6)	108.3 (2)	O(2 ⁱⁱ)—Li—O(3 ^{iv})	84.0 (5)
O(5)—P(1)—O(7 ^v)	112.3 (2)		

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

Calculations were performed using a SPARC station with the *Xtal3.2* system (Hall, Flack & Stewart, 1992). The figure was obtained with *MOLVIEW* (Cense, 1993).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1147). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Lead(II) Diiron(III) Pyrophosphate and Barium Diiron(III) Pyrophosphate

AICHA BOUTFESSI,^a ALI BOUKHARI^a AND ELIZABETH M. HOLT^{b*}

^aLaboratoire de Chimie du Solide Appliquée, Département de Chimie, Faculté des Sciences, Université Mohammed V, Avenue Ibn Batouta, Rabat, Morocco, and ^bDepartment of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA. E-mail: chememh@osucc.bitnet

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Abstract

$\text{PbFe}_2^{\text{II}}(\text{P}_2\text{O}_7)_2$ [diiron(III) lead(II) bis(diphosphate)] crystallizes to form two types of metallic column, one containing uniquely Fe^{III} [$\text{Fe} \cdots \text{Fe}$ 7.851 (3) \AA] and the other with alternating Pb and Fe atoms [$\text{Pb} \cdots \text{Fe}$ 3.925 (3) \AA]. The crystalline structure of $\text{BaFe}_2^{\text{II}}(\text{P}_2\text{O}_7)_2$ [barium diiron(III) bis(diphosphate)] is characterized by chains of Fe–O octahedra sharing faces with Ba–O decahedra and linked by corner-sharing Fe–O octahedra.

Comment

While there are numerous structural studies of $A^{\text{II}}B^{\text{III}}\text{P}_2\text{O}_7$ compounds, pyrophosphates of the form $A^{\text{II}}B^{\text{II}}(\text{P}_2\text{O}_7)_2$ are relatively unknown.

$\text{SrFe}_2^{\text{II}}(\text{P}_2\text{O}_7)_2$ (Boutfessi, Boukhari & Holt, 1995) crystallizes in space group $P\bar{1}$, with metal atoms