

The molybdenum diphosphate $\text{Mo}_{1.3}\text{O}(\text{P}_2\text{O}_7)$, containing Mo_2 and Mo_3 clusters

V.V. Lisnyak^{a,*}, N.V. Stus^{a,*}, P. Popovich^b, D.A. Stratiychuk^{a,c}, Ya. Filinchuk^d, V.M. Davydov^d

^aChemical Department, National Taras Shevchenko University, Volodymyrska Str. 64, UA-01033 Kyiv, Ukraine

^bInstitute of Physics and Chemistry of Solids, Voloshina Str. 51, UA-88000 Uzhgorod, Ukraine

^cInstitute for Superhard Materials, National Academy of Science, Avtozavodska Str. 2, UA-254074 Kyiv, Ukraine

^dDepartment of Inorganic Chemistry, Ivan Franko Lviv National University, Kyrilla i Mefodiya Str. 6, UA-79005 Lviv, Ukraine

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Abstract

A novel molybdenum diphosphate, $\text{Mo}_{1.3}\text{O}(\text{P}_2\text{O}_7)$, was obtained by electrochemical lithium deintercalation. The diphosphate crystallises in space group $I2/a$ with the lattice parameters $a=22.88(1)$, $b=22.94(2)$, $c=4.832(1)$ Å, $\gamma=90.36^\circ$, $Z=8$. Its original framework is built up from MoO_6 octahedra, P_2O_7 groups and also from MoO_4 , Mo_2O_4 and Mo_3O_8 units containing Mo_2 and Mo_3 clusters. These polyhedra delimit large octagonal and z-shaped tunnels running along c , in which the inserted cations may be located. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

Numerous complex oxides containing low-valent molybdenum have been synthesised by solid state reactions and molten-salt electrolysis during the last decades [1–4]. The presence of metal–metal bonded molybdenum atoms is a characteristic feature of most of these compounds. Clusters of different size Mo_n ($n=2–8$) may be isolated or condensed to form larger units, infinite chains or sheets. The unusual topology and the specific electrophysical properties have led to a significant interest in molybdenum oxo-cluster compounds.

Our study on molybdenum complex oxides was focused on the design of phosphate material with controllable cluster dimensions. Most of the molybdenum phosphates with Mo–Mo bonded atoms contain larger inserted cations: Cs or rarely Rb [5–8]. But, as is known, the largest variety of unique molybdenum clusters has been observed in lithium containing oxides [9–12]. Therefore we suppose that alkaline phosphate systems containing light metals,

especially lithium, are prospective materials for the synthesis of compounds with molybdenum clusters.

2. Experimental

The starting materials Mo (purity, 99.99%), Li_2MoO_4 (purity, 99.99%), MoO_3 (purity, 99.95%), Li_2CO_3 (purity, 99%), and $\text{NH}_4\text{H}_2\text{PO}_4$ (purity, 99%) were commercial products of AG quality, used without further purification. The lithium–molybdenum bronze LiMoO_2 was synthesised according to Ref. [12]. The methaphosphate glass with molar ratio $\text{Li}_2\text{O}:\text{P}_2\text{O}_5$ 0.5–0.7 was obtained by a technique reported elsewhere [13]. Powders of metallic molybdenum and LiMoO_2 , in a molar ratio of 9:1 were sintered in a vacuum induction-arc furnace for 7 h at 2010 K. The obtained sintered bar with the composition $\text{LiMo}_{10}\text{O}_2$ was crushed first in a vibratory mill and subsequently in a high-energy planetary ball mill (5-mm WC balls, argon atmosphere, milling intensity of 590 m s^{-2}). In order to avoid the formation of hydrocarbon compounds, no lubricating agents were employed during the ball milling.

The initial mixture of lithium methaphosphate glass (70 mass%), MoO_3 (15–20 mass%) and crushed $\text{LiMo}_{10}\text{O}_2$

*Corresponding authors. Fax: +380-44-276-7542.

E-mail addresses: lisnyak@chem.univ.kiev.ua (V.V. Lisnyak), stus@chem.univ.kiev.ua (N.V. Stus).

(7–10 mass%) was progressively heated up to 1000 K for 1 h first in argon at ambient pressure. The melt was homogenised for 24 h at 1110 K. Then coarse-dispersed molybdenum ($\mu = 30 \mu\text{m}$) was brought into the melt through alundum pipe. The resulting viscous melt was heated up to 1273 K over 4 h while applying mechanical stirring. Then the furnace was cooled automatically (2 K h^{-1}). Small needle-like green crystals were grown.

The lithium electrochemical deintercalation was performed using a Li/liquid electrolyte/LiMo_{0.3}(MoO)(P₂O₇) cell. The cathode material was a slurry of the desired viscosity prepared by mixing the Merck cathode materials ‘super P’ carbon black, and a polyvinylidene fluoride binder in a weight ratio of 90:4:4 in *N*-methyl-2-pyrrolidene. The coin-type half cell contained a test cathode, a lithium metal counter-and-reference electrode, a 15- μm -thick microporous polyethylene separator, and an electrolyte solution of 1 M LiPF₆ in 1:1 vol.% mixture of ethylene carbonate with dimethyl carbonate. The cells

assembled in an argon-filled dry box were charged at very low current density ($C/600$, i.e. 600 h are needed to remove one Li from the formula). Before recovering the positive electrode, the cells were allowed to relax until their open-circuit voltage varied by no more than 1 mV h^{-1} .

The elemental content of the synthesised compounds was determined by energy dispersive X-ray spectroscopy (EDXS). The lithium content in the samples was analysed using both ICP-AES (Perkin-Elmer ICP/6000) and AAS (Varian AASin-10) spectrometers.

The X-ray crystallography study was performed on an DARCH diffractometer. The cell parameters and the orientation matrix for data collection were obtained by a least-squares refinement of 24 reflections in the range $15.0 < 2\theta < 21.0^\circ$. The structure was solved by the heavy atom method and refined by full-matrix least-squares techniques using SHELXL-93 [14]. Details of the X-ray experiment and the structure refinement are listed in Table

Table 1
Summary of crystal data, intensity measurements and structure refinement parameters

<i>A. Crystal data</i>	
Formula	Mo _{1.3} O(P ₂ O ₇)
Formula weight	314.7
Crystal system	Monoclinic
Space group	<i>I</i> 2/a
Cell dimensions	$a = 22.88(1)$, $b = 22.94(1)$, $c = 4.83(1)$ Å, $\gamma = 90.36(5)^\circ$
Volume	2896 Å ³
Z	8
Calculated and observed density	$d_{\text{calc}} = 4.08(1)$ g/cm ³ , $d_{\text{obs}} = 3.95$ g/cm ³
<i>B. Intensity measurement</i>	
Diffractometer	Enraf-Nonius CAD-3
Single crystal dimension, mm	0.06 × 0.22 × 0.70
λ (Mo K α)	0.71073 Å
Scan mode	$\omega - 2\theta$
Omega scan width (degrees)	$0.6 + 0.34 \times \text{tg}\theta$
Horizontal aperture (mm)	$2.50 + 1.00 \times \text{tg}\theta$
Maximum scan speed	6.7 (degrees/min)
Index ranges	$-16 \leq h \leq 16$, $0 \leq k \leq 16$, $0 \leq l \leq 8$
Theta ranges	0–21.03°
Reflection measured	1178 total, 942 independent
<i>C. Structure solution and refinement</i>	
Reflection included	1038 with $F > 4\sigma(F_o)$
Number of refined parameters	108
Mode of refinement	$F(hkl)$
Weighing scheme	$1/[\sigma(F)^2 + 0.025 * F(\text{obs})^2]$
Number of atom sites	25
Number of free parameters	108
$F(000)$ (electrons)	2896
Number of atoms in cell	208.0
Absorption coefficient (1/cm)	43.93
Agreement factors	$R_w = 0.1482$, $R_F = 0.1315$, $R_\sigma = 0.0535$, $R_{\text{eq}} = 0.0923$ $w = 1/\sigma(F_{o(2)}) + 0.025F^2$
Goodness of fit (GOF)	1.120

Table 2
Atomic parameters

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U(is/eq)</i>
Mo(1) ^a	1/4	0	0.753(2)	0.001(2)
Mo(2) ^a	1/4	0	0.230(13)	0.05(3)
Mo(3) ^a	3/4	0	0.475(6)	0.05(1)
Mo(4)	0.1570(2)	−0.1961(2)	1.1107(7)	0.016(2)
Mo(5)	0.4459(2)	−0.0929(2)	0.1525(7)	0.015(2)
P(1)	0.3479(7)	−0.1004(7)	0.639(3)	0.022(4)
P(2)	0.3771(6)	−0.2123(7)	0.878(3)	0.018(4)
P(3)	0.1489(6)	−0.0981(7)	0.599(3)	0.016(4)
P(4)	0.5389(6)	−0.1259(7)	−0.364(3)	0.016(4)
O(1)	0.178(2)	−0.038(2)	0.619(6)	0.02(1)
O(2)	0.508(2)	−0.091(2)	−0.147(6)	0.02(1)
O(3)	0.1784(15)	−0.139(2)	0.408(6)	0.015(1)
O(4)	0.0671(13)	−0.3159(15)	0.522(6)	0.008(7)
O(5)	0.2900(15)	−0.072(2)	0.612(6)	0.012(8)
O(6)	0.4567(14)	−0.023(2)	0.267(7)	0.013(9)
O(7)	0.604(2)	0.256(2)	0.372(9)	0.06(1)
O(8)	0.859(2)	0.124(2)	0.122(7)	0.03(1)
O(9)	0.128(2)	0.110(2)	0.371(6)	0.02(1)
O(10)	0.007(2)	0.139(2)	0.395(7)	0.03(1)
O(11)	0.429(2)	0.187(2)	0.268(7)	0.03(1)
O(12)	0.7758(14)	0.2107(15)	0.011(6)	0.013(7)
O(13)	0.605(2)	0.072(2)	0.171(6)	0.019(8)
O(14)	0.160(2)	0.243(2)	0.105(6)	0.020(8)
O(15)	0.6599(12)	0.1642(13)	0.231(5)	0.007(7)
O(16)	0.4125(13)	0.082(2)	0.490(7)	0.021(7)

$$U_{eq} = \frac{1}{3} [U_{11}a^*a^2 + \dots + 2U_{23}b^*c^*bc \cos \alpha].$$

^a Occupations: Mo(1) −0.58(3), Mo(2) −0.16(3), Mo(3) −0.39(4).

Table 3
Selected interatomic distances (Å) in Mo_{1.3}O(P₂O₇) with esds in parentheses

Interatomic distances	<i>d</i> , Å	Interatomic distances	<i>d</i> , Å
<i>MoO₄, Mo₂O₄, Mo₃O₈ units</i>			
Mo(1)–O(1)	1.97(4)	Mo(3)–O(1a)	1.92(4)
Mo(1)–O(1a)	1.97(4)	Mo(3)–O(1b)	1.92(4)
Mo(1)–O(5)	2.01(4)	Mo(3)–O(5a)	1.93(4)
Mo(1)–O(5a)	2.01(4)	Mo(3)–O(5b)	1.93(4)
Mo(2)–Mo(1a)	2.30(6)	Mo(2)–Mo(1b)	2.52(6)
<i>MoO₆ octahedra</i>			
Mo(4)–O(3)	1.99(4)	Mo(6)–O(2)	2.02(4)
Mo(4)–O(7)	2.01(5)	Mo(6)–O(4)	2.27(4)
Mo(4)–O(8)	2.04(4)	Mo(6)–O(6)	1.71(4)
Mo(4)–O(11)	2.11(4)	Mo(6)–O(9)	2.03(4)
Mo(4)–O(12)	1.68(3)	Mo(6)–O(10)	1.92(4)
Mo(4)–O(14)	1.96(4)	Mo(6)–O(13)	2.02(4)
<i>PO₄ tetrahedra</i>			
P(1)–O(5)	1.49(4)	P(2)–O(4)	1.51(4)
P(1)–O(9a)	1.42(4)	P(2)–O(7a)	1.55(5)
P(1)–O(13a)	1.55(4)	P(2)–O(14a)	1.55(4)
P(1)–O(15a)	1.60(4)	P(2)–O(15a)	1.62(3)
P(3)–O(1)	1.53(4)	P(4)–O(2)	1.49(4)
P(3)–O(3)	1.49(4)	P(4)–O(10a)	1.59(4)
P(3)–O(8a)	1.48(4)	P(4)–O(11a)	1.60(5)
P(3)–O(16a)	1.55(4)	P(4)–O(16a)	1.62(4)

1. The final atomic parameters are given in Table 2. The principal interatomic distances in the molybdenum diphosphate are listed in Table 3.

3. Results and discussion

The original framework of the novel molybdenum diphosphate Mo_{1.3}O(P₂O₇) is built up from MoO₆ octahedra, P₂O₇ groups and also from MoO₄, Mo₂O₄ and Mo₃O₈ units. Large octagonal and z-shaped tunnels, where the Li⁺ cations may be located, run along the *c* direction (Fig. 1). The Mo(4) and Mo(5) atoms in the Mo_{0.3}(MoO)(P₂O₇) framework are sixth-fold coordinated by oxygen atoms; each MoO₆ octahedron contains one terminal vertex, the Mo–O_(t) distances are noticeably shorter than the Mo–O(P) ones. The Mo(1) and Mo(3) atoms occupy two close positions with a total occupancy of ~1 (interpositional distance Mo(1)–Mo(3) is 1.1 Å, occupancy of Mo(1) is 0.58, while that of Mo(3) is 0.39). These atoms are coordinated by four oxygen atoms, forming a square pyramid. The distances from the molybdenum atoms to the base of the pyramid are 0.58(1) and 0.59(1) Å for Mo(3) and Mo(1), respectively. The Mo(2) atom is twofold coordinated by molybdenum atoms, and the occupancy of the Mo(2) position is 0.16(3). Considering the Mo–Mo distances and the molybdenum site occupancies leads to the conclusion that two kinds of clusters are possible: Mo₂ (Mo–Mo distance 2.52 Å), and linear Mo₃ (Mo–Mo distances 2.52 and 2.3 Å) (Fig. 2). The framework of Cs₃Mo₅P₆O₂₅ [8] also contains MoO₆ octahedra and P₂O₇ groups, but the cluster type is differ-

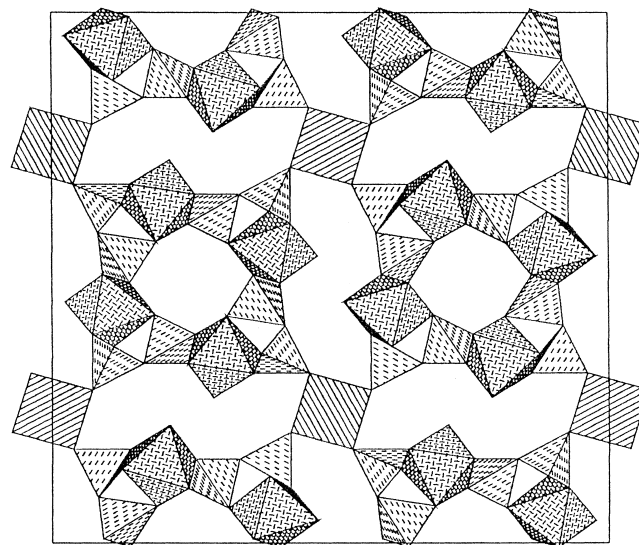


Fig. 1. Projection of the Mo_{1.3}O(P₂O₇) framework on [001].

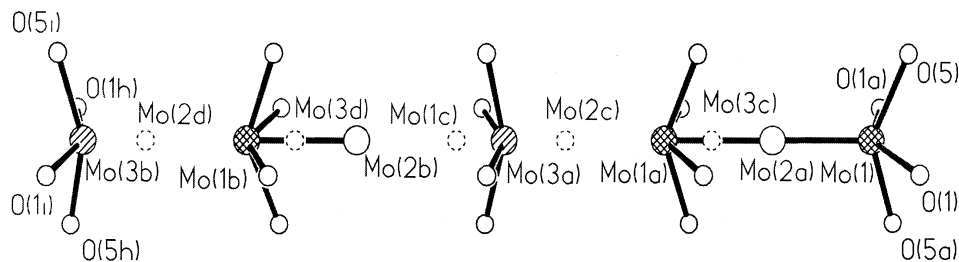


Fig. 2. Mo_2O_4 , Mo_3O_8 clusters and MoO_4 units, projection on [010]. Unoccupied positions are shown as reduced dotted circles.

ent: Mo_4 tetrahedra ($\text{Mo}-\text{Mo}$ distances 2.558 and 2.697 Å) in Mo_4O_4 cubane-like units. Similar cubane-like clusters have been observed in the structures of $\text{Cs}_3\text{Mo}_3\text{P}_7\text{O}_{24}$ [6] and $\text{Rb}_4\text{Mo}_8\text{P}_{12}\text{O}_{52}$ [7].

The synthesised molybdenum diphosphate $\text{Mo}_{1.3}\text{O}(\text{P}_2\text{O}_7)$ is a rare example of a compound containing small clusters with zero-valent molybdenum. Its synthesis is the first stage in the formation of a material with controllable cluster dimensions, from discrete Mo_2 units up to metallic chains. This is possible due to the variable $\text{Mo}(2)$ occupancy. Moreover, the molybdenum oxidation level and the electrophysical properties of the compound can be modified by insertion of light cations.

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