

Crystal structure of $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ studied by synchrotron X-ray diffraction

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Abstract

The crystal structure of sodium pentamolybdbl tetradiphosphate $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ has been determined from synchrotron diffraction data collected at 293 K on two microcrystals. The compound crystallizes in a monoclinic space group $I 1 1 2/a$ (no. 15, setting 11), with unit cell parameters $a = 22.905(3)$, $b = 23.069(2)$, $c = 4.8537(2)$ Å, $\gamma = 90.641(9)^\circ$ and $a = 22.898(3)$, $b = 23.056(2)$, $c = 4.8551(2)$ Å, $\gamma = 90.82(1)^\circ$, for crystals **I** and **II**, respectively. The structure is pseudo-tetragonal, and the crystals are pseudo-merohedrally twinned by 90° rotation around the c -axis. The structure closely resembles the previously reported Li-deintercalated $\text{Mo}_{1.3}\text{OP}_2\text{O}_7$ [V.V. Lisnyak, N.V. Stus, P. Popovich, D.A. Stratiichuk, Ya. Filinchuk, V.M. Davydov, J. Alloys Compd. 360 (2003) 81–84]. Comparison of the two structures led us to conclude that the Mo_2 and Mo_3 clusters were erroneously identified in $\text{Mo}_{1.3}\text{OP}_2\text{O}_7$. A revised structure of $\text{Mo}_{1.3}\text{OP}_2\text{O}_7$ contains a fully occupied oxygen site instead of the 16% occupied Mo(2) site, thus the revised formulae for the Li-deintercalated compound is $(\text{MoO})_5(\text{P}_2\text{O}_7)_4$. In both structures, the $(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ framework strongly resembles the one in the earlier reported $\text{Ag}(\text{MoO})_5(\text{P}_2\text{O}_7)_4$, while the location of Na and Ag atoms differ.

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1. Introduction

Ionic rechargeable batteries are the preferred energy storage devices for modern portable electronics. Their application was limited by the choice of suitable lithium- or sodium-liberating cathode materials and knowledge of the cell chemistry of the corresponding batteries. Recent use of chemically stable phosphate-based cathode materials instead of oxide-based ones enabled production of safe large-format Li^+ and Na^+ ionic batteries *via* the Saphion technology [1]. The diversity of molybdenum phosphate's frameworks [2] along with the ability of Mo to change its oxidation state makes this class of compounds capable of cycling reversibly lithium or sodium ions. Exploring the potential of lithium molybdenum phosphates, we

had reported earlier the synthesis and crystal structure of a novel molybdenum diphosphate “ $\text{Mo}_{1.3}\text{OP}_2\text{O}_7$ ” [3]. The structure of $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$, presented in this communication, closely resembles the previously reported $\text{Mo}_{1.3}\text{OP}_2\text{O}_7$ [3]. On the basis of their comparison we show that the Mo_2 and Mo_3 clusters were erroneously identified in $\text{Mo}_{1.3}\text{OP}_2\text{O}_7$ and suggest for it a revised $(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ composition. The pentamolybdbl tetradiphosphate framework in $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ and $(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ structures resembles closely the one in $\text{Ag}(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ [4].

2. Experimental part

2.1. Synthesis

Needle-like crystals of $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ colored bluish- or grayish-green have been grown from a melt in the $(\text{Li},\text{Na})_2\text{O}-\text{MoO}_3-\text{Mo}-\text{P}_2\text{O}_5$ system. The composition of the melt and the synthetic route were similar to the ones used for crystallization of the lithium-containing precursor of $\text{Mo}_{1.3}\text{OP}_2\text{O}_7$ [3]. X-ray powder diffraction (Dron-3 diffractometer, Ni-filtered $\text{Cu K}\alpha$ radiation) showed that the unit cell parameters of the phase of interest are similar to

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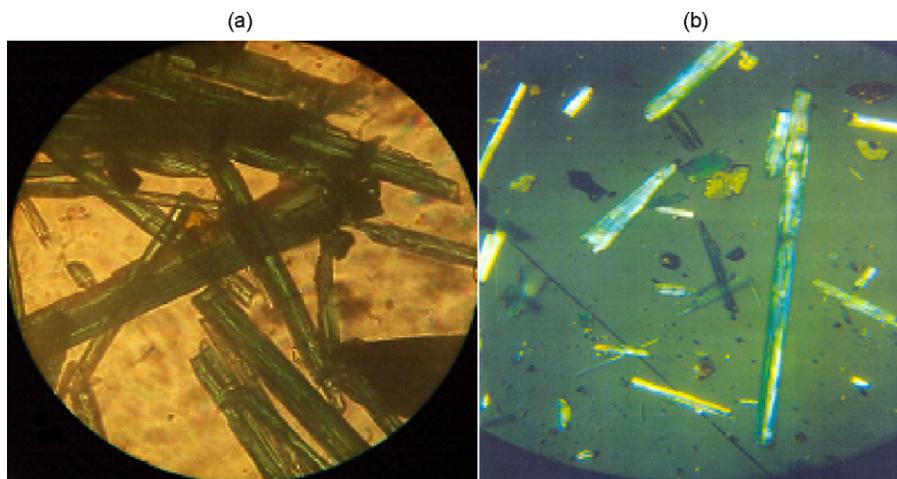


Fig. 1. Microphotographs of $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ crystals, magnification $140\times$ (a) and $80\times$ (b).

those of the Li-deintercalated phase, “ $\text{Mo}_{1.3}\text{OP}_2\text{O}_7$ ” [3]. The crystals were studied by an energy dispersive X-ray microanalysis (Linx EDX superprobe mounted on a JEOL 200CX microscope): analysis showed a Mo/P ratio of $\sim 5/8$, well in agreement with the formula deduced from the diffraction studies (below). Although the crystals were very thin (see microphotographs in Fig. 1), they were sufficiently large for single-crystal synchrotron diffraction experiment.

2.2. Single-crystal synchrotron diffraction study

Two crystals have been selected from the polycrystalline powder sample and measured at the Swiss-Norwegian Beam Lines (SNBL) at European Synchrotron Radiation Facility (ESRF). Diffraction data were collected at 293 K using the Oxford Diffraction KM6 kappa diffractometer equipped with an Onyx CCD area detector. The wavelength was 0.71000 \AA , crystal-to-detector distance 62.9 mm . 444 frames with 1 s exposure per frame (first crystal) and 328 frames with 4 s exposure (second crystal) were collected at different angular positions of the detector. Diffraction images were treated with CrysAlis software [5]. For each crystal, most of the diffraction spots were indexed in a monoclinic unit cell, which appeared to be remarkably pseudo-tetragonal. Integrated diffraction intensities were scaled with ABSPACK to correct for the decay of the incoming beam and the absorption anisotropy.

Analysis of the reciprocal space sections revealed that the crystals are pseudo-merohedrally twinned by a 90° rotation around the c -axis. Due to a severe overlap of low-angle reflections, the pseudo-merohedral twinning impaired the quality of the integrated intensities. This explains the somewhat higher R -factors for both crystals (see Table 1), without raising doubts about structure’s validity. A twin fraction has been refined to partially compensate for twinning; however this can handle the problem only in case of a complete overlap of peaks from different twins (merohedral twinning). As can be seen from diffraction and optical examination, all of the $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ crystals are liable to twinning by pseudo-merohedry.

The structure was solved and refined using SHELX97 [6] in the space group $I112/a$. Since the title structure closely resembles the previously reported one [3], the same atomic numbering scheme was used to facilitate a comparison. Mo, P and O positions were refined anisotropically. A disordered Mo atom position has been modeled by two partially occupied Mo(1) and Mo(3) positions with anisotropic displacement parameters constrained to be equal. Atomic displacement for P and O atoms were restrained to be similar along the P–O bond direction. A single Na position has been clearly identified from the difference Fourier maps and refined isotropically, the other residual electron density peaks are located in the close vicinity of the other atoms, mostly Mo.

Details of data collection and structure refinement are given in Table 1, the list of atomic parameters in Table 2 and selected distances in Table 3.

3. Results and discussion

The $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ appears to be a molybdophosphate framework structure containing intercalated sodium atoms. The framework contains infinite $(\text{MoO})_4(\text{P}_2\text{O}_7)_4$ channels running along the $[010]$ direction. The channels are filled by sodium atoms (Fig. 2), and connected *via* bridging (MoO) chains into a three-dimensional structure.

The $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ structure closely resembles the previously reported Li-deintercalated $\text{Mo}_{1.3}\text{OP}_2\text{O}_7$ [3]. Both structures have the same symmetry and very similar unit cell parameters. Their comparison led us to conclude that the molybdophosphate frameworks in $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ and “ $\text{Mo}_{1.3}\text{OP}_2\text{O}_7$ ” are identical. This implies that the Mo_2 and Mo_3 clusters were erroneously identified in “ $\text{Mo}_{1.3}\text{OP}_2\text{O}_7$ ”. A revised structure of $\text{Mo}_{1.3}\text{OP}_2\text{O}_7$ contains a fully occupied oxygen site instead of the 16% occupied Mo(2) site [3], thus the revised formulae of the Li-deintercalated compound is $(\text{MoO})_5(\text{P}_2\text{O}_7)_4$. The structure of the Na-containing compound, reported here, has been characterized with nearly 5 times higher precision than the one for $(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ [3]. This was possible owing to a much larger number of reflections measured using synchrotron radiation: ~ 4300 independent reflections were measured for each Na-containing crystal, compared to 942 reflections in [3]. Atomic parameters for the crystals **I** and **II** are practically identical, however the two crystals slightly differ in the refined sodium content.

$\text{Ag}(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ [4] is another structure closely related to $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$. The $(\text{MoO})_4(\text{P}_2\text{O}_7)_4$ channels in $\text{Ag}(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ are identical to those found in $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ and $(\text{MoO})_5(\text{P}_2\text{O}_7)_4$. If one neglects the differences in the location of Na^+ and Ag^+ cations inside the channels, and the detailed structure of the (MoO) chains, the two compounds can be considered as isostructural. Therefore, we will comment here on the features which differ between the structures, and refer the reader to [4] for their general description.

It is noteworthy that the $(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ framework is able to accommodate different cations. A series of $\text{A}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$

Table 1
Single crystal data and details of data collection and structure refinement for crystals **I** and **II**

	Crystal I	Crystal II
Empirical formula, $Z = 4$	$\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$	
x	0.74(8)	0.52(6)
Crystal system, space group	Monoclinic, $I112/a$ (no. 15, setting 11)	
Unit cell parameters (\AA , $^\circ$)	$a = 22.905(2)$ $b = 23.069(3)$ $c = 4.8537(2)$ $\gamma = 90.641(9)$	$a = 22.898(3)$ $b = 23.056(2)$ $c = 4.8551(2)$ $\gamma = 90.817(10)$
Cell volume (\AA^3)	2564.5(4)	2563.0(4)
Density (g cm^{-3})	3.371	3.373
$2\theta_{\text{max}}$ ($^\circ$)	65	65
Index ranges	$-34 \leq h \leq 24$, $-25 \leq k \leq 34$, $-6 \leq l \leq 5$	$-34 \leq h \leq 34$, $-34 \leq k \leq 25$, $-6 \leq l \leq 5$
Absorption coefficient (mm^{-1})	3.055	3.056
Refl. collected/unique	9648/4277	10,925/4369
Data/restraints/parameters	4277/24/219	4639/24/219
R indices [$I > 2\sigma(I)$] R_1 , wR_2	0.0996/0.2646	0.1055/0.2584
R indices (all data) R_1 , wR_2	0.1377/0.2839	0.1209/0.2676
Good	1.148	1.138
Highest diff. peak and hole (e \AA^{-3})	4.61/−3.33	4.63/−4.34

compounds has been obtained for $A = \text{Li}, \text{Na}, \text{Ag}, \text{Ba}$ [4]. The unit cell parameters for the $\text{A}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ series (Table 4) correlate with a size of the intercalated cations. The unit cell volume for $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ ($x = 0.74(8)$ in crystal **I** and 0.52(6) in **II**) is by $\sim 0.3\%$ smaller than for the presumably stoichiometric

$\text{Na}(\text{MoO})_5(\text{P}_2\text{O}_7)_4$. The crystal structure was reported only for the compounds with $A = \text{Ag}$ [4], a vacancy [3], and Na (this work). Sodium atoms occupy a single crystallographic position. However, a short $\text{Na} \cdots \text{Na}$ contact of 2.47 \AA prevents this position from being fully occupied. The largest possible

Table 2
Atomic coordinates and displacement parameters in the crystal structure of $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$

Atom	Crystal I				Crystal II			
	x/a	y/b	z/c	$U_{\text{eq/iso}}$ (\AA^2)	x/a	y/b	z/c	$U_{\text{eq/iso}}$ (\AA^2)
Mo(1) ^a	1/4	0	0.7517(5)	0.0131(5)	1/4	0	0.7521(5)	0.0116(4)
Mo(3) ^a	3/4	0	0.4945(13)	0.0131(11)	3/4	0	0.4934(16)	0.0116(10)
Mo(4)	0.15694(5)	0.80426(5)	0.1089(2)	0.0120(3)	0.15690(5)	0.80421(5)	0.1094(2)	0.0087(3)
Mo(5)	0.44536(5)	0.90761(5)	0.1468(2)	0.0117(3)	0.44532(4)	0.90764(5)	0.1471(2)	0.0085(3)
P(1)	0.34814(16)	0.89800(15)	0.6463(7)	0.0123(6)	0.34803(13)	0.89794(14)	0.6462(7)	0.0083(5)
P(2)	0.37759(16)	0.78754(14)	0.8840(8)	0.0138(7)	0.37757(14)	0.78769(14)	0.8835(7)	0.0105(6)
P(3)	0.14736(16)	0.90144(14)	0.6013(7)	0.0118(6)	0.14739(14)	0.90164(14)	0.6018(7)	0.0090(6)
P(4)	0.53738(16)	0.87295(15)	0.6438(8)	0.0138(7)	0.53725(14)	0.87297(15)	0.6456(7)	0.0100(6)
O(1)	0.1764(5)	0.9607(4)	0.621(2)	0.0175(19)	0.1766(4)	0.9611(4)	0.626(2)	0.0134(17)
O(2)	0.5121(6)	0.9073(5)	0.887(3)	0.026(2)	0.5130(5)	0.9071(5)	0.889(2)	0.0182(19)
O(3)	0.1791(5)	0.8621(5)	0.410(2)	0.020(2)	0.1787(4)	0.8626(5)	0.407(2)	0.0156(18)
O(4)	0.0679(5)	0.6826(4)	0.514(2)	0.016(2)	0.0683(4)	0.6824(4)	0.518(2)	0.0152(19)
O(5)	0.2888(5)	0.9269(4)	0.642(2)	0.0156(18)	0.2887(4)	0.9267(4)	0.642(2)	0.0136(17)
O(6)	0.4569(6)	0.9731(4)	0.271(2)	0.019(2)	0.4575(5)	0.9732(5)	0.269(2)	0.017(2)
O(7)	0.6086(6)	0.2541(6)	0.345(3)	0.034(3)	0.6083(5)	0.2533(6)	0.347(3)	0.033(3)
O(8)	0.8624(5)	0.1254(6)	0.116(2)	0.030(3)	0.8628(5)	0.1251(6)	0.116(2)	0.024(3)
O(9)	0.1293(5)	0.1104(5)	0.362(2)	0.022(2)	0.1296(4)	0.1104(5)	0.356(2)	0.0162(19)
O(10)	0.0076(5)	0.1391(5)	0.418(2)	0.025(2)	0.0086(4)	0.1391(5)	0.423(2)	0.019(2)
O(11)	0.4336(4)	0.1834(4)	0.271(2)	0.0128(18)	0.4330(4)	0.1830(4)	0.274(2)	0.0096(16)
O(12)	0.7773(5)	0.2091(5)	0.019(2)	0.021(2)	0.7772(5)	0.2088(5)	0.023(2)	0.018(2)
O(13)	0.6089(5)	0.0714(4)	0.173(2)	0.019(2)	0.6087(5)	0.0713(4)	0.172(2)	0.0143(18)
O(14)	0.1580(5)	0.2417(6)	0.111(3)	0.035(3)	0.1577(5)	0.2412(6)	0.109(3)	0.031(3)
O(15)	0.6666(5)	0.1645(4)	0.2302(19)	0.0115(18)	0.6661(4)	0.1648(4)	0.232(2)	0.0102(16)
O(16)	0.4142(5)	0.0834(4)	0.483(2)	0.015(2)	0.4148(4)	0.0836(4)	0.481(2)	0.0125(17)
O(17)	1/4	0	0.163(5)	0.035(5)	1/4	0	0.160(6)	0.037(5)
Na(1) ^b	0.4935(15)	0.2567(14)	0.201(7)	0.063(13)	0.4947(12)	0.2580(12)	0.177(6)	0.027(9)

^a Mo(1) and Mo(3) site occupancies: 0.722(5) and 0.275(7) for **I**; 0.815(5) and 0.237(7) for **II**.

^b Na(1) site occupancy: 0.37(4) and 0.26(3) for **I** and **II**, respectively.

Table 3
Selected interatomic distances (Å) in the crystal structure of $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$

	Crystal I	Crystal II		Crystal I	Crystal II
Mo(1)–O(5)	$2 \times 1.987(9)$	$2 \times 1.994(9)$	P(1)–O(9)	1.488(12)	1.515(11)
Mo(1)–O(17)	1.99(2)	1.98(3)	P(1)–O(13)	1.490(12)	1.496(11)
Mo(1)–O(1)	$2 \times 2.007(11)$	$2 \times 1.991(9)$	P(1)–O(5)	1.521(10)	1.519(10)
Mo(3)–O(17)	1.66(3)	1.68(3)	P(1)–O(15)	1.595(10)	1.592(10)
Mo(3)–O(1)	$2 \times 1.987(11)$	$2 \times 1.980(10)$	P(2)–O(4)	1.504(12)	1.490(10)
Mo(3)–O(5)	$2 \times 2.026(9)$	$2 \times 2.030(10)$	P(2)–O(7)	1.507(12)	1.504(13)
Mo(4)–O(12)	1.661(10)	1.671(10)	P(2)–O(14)	1.523(13)	1.510(11)
Mo(4)–O(8)	2.011(11)	2.019(11)	P(2)–O(15)	1.606(9)	1.595(10)
Mo(4)–O(3)	2.039(11)	2.032(10)	P(3)–O(3)	1.493(11)	1.496(11)
Mo(4)–O(7)	2.043(12)	2.049(12)	P(3)–O(1)	1.517(11)	1.521(9)
Mo(4)–O(11)	2.240(10)	2.231(9)	P(3)–O(8)	1.520(11)	1.521(9)
Mo(4)–O(14)	1.982(11)	1.995(10)	P(3)–O(16)	1.567(11)	1.582(10)
Mo(5)–O(6)	1.645(10)	1.644(10)	P(4)–O(11)	1.524(10)	1.518(10)
Mo(5)–O(2)	1.983(13)	1.992(11)	P(4)–O(10)	1.526(12)	1.530(11)
Mo(5)–O(10)	2.021(11)	2.025(10)	P(4)–O(2)	1.538(13)	1.529(12)
Mo(5)–O(9)	2.042(12)	2.030(10)	P(4)–O(16)	1.611(11)	1.598(10)
Mo(5)–O(13)	2.051(11)	2.047(10)	Na(1)–O(11)	2.19(4)	2.27(3)
Mo(5)–O(4)	2.240(10)	2.243(10)	Na(1)–O(10)	2.47(3)	2.42(3)
			Na(1)–O(4)	2.51(3)	2.56(3)
			Na(1)–O(4)'	2.59(3)	2.60(3)

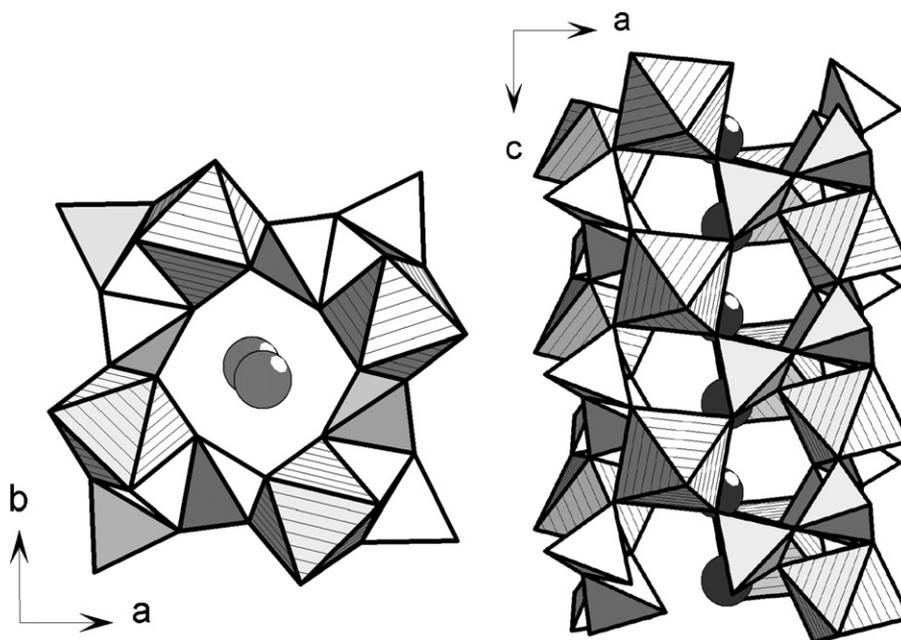


Fig. 2. The framework-forming $(\text{MoO})_4(\text{P}_2\text{O}_7)_4$ channel filled by Na atoms in the structure of $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$.

Table 4
The unit cell parameters for the $\text{A}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ (A—a vacancy, Li, Na, Ag, Ba) series

A atom	x	a (Å)	b (Å)	c (Å)	γ (°)	V (Å ³)	References
Na	0.74(8)	22.905(3)	23.069(2)	4.8537(2)	90.641(9)	2564.5(4)	This work
Na	0.52(6)	22.898(3)	23.056(2)	4.8551(2)	90.82(1)	2563.0(4)	This work
Na	1(–)	22.95(1)	23.08(1)	4.853(1)	90.39(3)	2571(3)	[4]
–		22.88(1)	22.94(2)	4.83(1)	90.36(5)	2533(7)	[3]
Li	1(–)	22.765(7)	22.951(8)	4.853(2)	91.17(3)	2535(2)	[4]
Ba	1(–)	23.034(8)	23.218(10)	4.830(2)	90.90(3)	2583(2)	[4]
Ag	1(–)	23.050(8)	22.935(9)	4.831(4)	90.42(5)	2554(3)	[4]

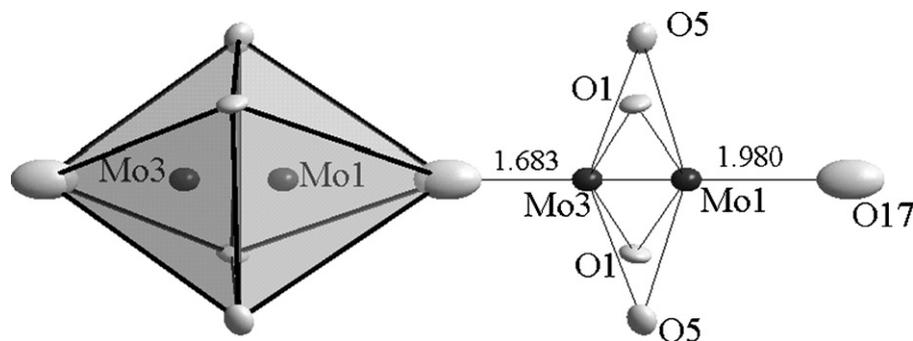


Fig. 3. The coordination environment for Mo(1) and Mo(3) atoms in the structure of $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$.

occupancy of 0.5 corresponds to $x=1$. Na atom forms four shorter Na–O bonds at 2.2–2.6 Å (see Table 3) and three longer Na–O contacts at 2.7–3.0 Å. Ag atoms are located differently within the columns. They take two partially occupied positions, each of Ag atoms forms five Ag–O bonds of 2.34–2.82 Å [4] and two longer ones. The ability of the framework to accommodate different cations and to be fully deintercalated [3] demonstrates the rigidity of the framework, while a different location of the partially occupied A-sites suggests that the cations are relatively mobile. A larger K atom occupies a center of a very similar channel in the $\text{K}_{0.17}\text{Mo}(\text{P}_2\text{O}_7)$ structure, forming six K–O bonds at 2.66–3.10 Å [7]. Coordination numbers and interatomic distances for cations A, located in channels of different open frameworks of molybdenyl diphosphate family, correlate with their size [8–11]. Thus, these parameters are influenced by peculiarities of the framework structure and its rigidity.

The (MoO) chain, bridging the channels in the $\text{Na}_x(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ structure, show a disorder on the molybdenum site. Two partially occupied positions show a Mo(1)–Mo(3) distance of 1.195(7) Å and 1.192(8) Å (for crystal I and II, respectively) and the total occupancy close to 1. The occupancy of the Mo(1) site is notably larger than for the Mo(3) site. Each of the two molybdenum sites has a tetragonal-pyramidal coordination by five oxygen atoms. Mo–O distances are almost identical and equal to 2.0 Å in the equatorial plane (see Table 3), while they differ significantly with respect to the apical oxygen atom: Mo(1)–O(17) 1.99 Å and Mo(3)–O(17) 1.67 Å. The disorder on the Mo sites induces a disorder on the O(17) position. The latter has been modeled by a displacement ellipsoid elongated along the direction of the disordered (MoO) chain (Fig. 3). Each (MoO) chain is oriented along the [010] direction and isolated from other chains. An ordering of Mo atoms within an isolated chain is possible (either Mo(1) or Mo(3) site would be occupied there), while a correlation between the chains is unlikely. In the revised cation-free $(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ framework, a similar disorder occurs, revealing 0.58(3) and 0.39(4) occupancies for the Mo(1) and Mo(3) sites. In the stoichiometric $\text{Ag}(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ [4], the

Mo(1)-type site is fully occupied, while the Mo(2)-type site is empty. An effect of the cation concentration on the occupancy of the molybdenum sites suggests a different oxidation state for molybdenum atoms in the Mo(1) and Mo(3) sites, as well as their participation in redox processes involving intercalated cations.

Soon after submission of this work a recent paper describing crystal structure of the compounds in the $\text{A}(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ (A = Ag, Li, Na, K) and $\text{A}(\text{MoO})_{10}(\text{P}_2\text{O}_7)_8$ (A = Ba, Sr, Ca, Cd, Pb) series became available [12], where conclusions drawn are highly consistent with those presented in this work.

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