A Mo(V) Monophosphate with an Original Tridimensional Framework: Li₂Na(MoO)₂(PO₄)₃

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

A new molybdenum monophosphate $Li_2Na(MoO)_2(PO_4)_3$ has been synthesized. It crystallizes in the space group $C2/c$ with $a = 15.668(1)$ Å, $b = 8.135(1)$ Å, $c = 17.747(2)$ Å, and $\beta = 107.99(1)°$. Its original tridimensional framework can be described by the stacking along b from two kinds of $[Mo_4P_6O_{38}]_\infty$ layers that are enantiomorphic. It results in elliptic tunnels running along b where the lithium (Li(1) and Li(2)) and sodium (Na(2)) cations are located; in these tunnels the lithium atoms exhibit two kinds of coordination, pyramidal and tetrahedral, respectively, whereas Na(2) is eightfold coordinated. One also observes four-sided tunnels occupied by Na(1) in sixfold coordination. © 1997 Academic Press

INTRODUCTION

A considerable number of pentavalent molybdenum phosphates with an original structure have been isolated these past 15 years (e.g. see Ref. 1). Most of them correspond to the introduction of large univalent cations in a molybdenophosphate matrix, whose high flexibility is certainly related to the specific behavior of the Mo(V) octahedra that systematically exhibit one free apex.

This ability to generate new structures seems to decrease as the size of the univalent cation decreases. In the case of sodium, four phosphates have been isolated, but only three of them are anhydra: the monophosphates ε-NaMo₂O(PO₄)₃ (2) and ζ-NaMo₂O(PO₄)₃ (3) and the diphosphate NaMoOP₂O₇ (4). Only one Mo(V) phosphate containing lithium has been synthesized to date, the diphosphate LiMoOP₂O₇ (5). Moreover, the structures of the two diphosphates NaMoOP₂O₇ and LiMoOP₂O₇ are very different, which emphasizes the prominent role of the size of the univalent cation upon the arrangement of the MoO₆ and PO₄ polyhedra, though in all cases the MoO₆ octahedra have a free apex. This suggests that the association of lithium and sodium in the same matrix should allow other original frameworks to be generated. For this reason, we have investigated the Li–Na–Mo(V)–P–O system. We now report on a new Mo(V) monophosphate Li₂Na(MoO)₂(PO₄)₃ with an original tridimensional framework.

EXPERIMENTAL

Single crystals of this new phosphate were grown from a mixture of the composition Li₂NaMo₂P₃O₁₄. This synthesis was performed in two steps: first an adequate mixture of MoO₃, H(NH₄)₂PO₄, Na₂CO₃, and Li₂CO₃ was ground in an agate mortar and heated in air up to 673 K in a platinum crucible to liberate CO₂, NH₃, and H₂O. In a second step the appropriate amount of molybdenum was added and the finely ground mixture was sealed in a silica ampoule and then heated for 10 h at 823 K, cooled to 3.3 K per hour down to 773 K, and finally quenched to room temperature. The result was a very well crystallized green compound. Several single crystals were extracted from this sample. The microprobe analysis of different crystals leads to a Mo/P ratio (2/3) in agreement with the formula Li₂NaMo₂P₃O₁₄ deduced from the structure determination.

Attempts to prepare this phase in the form of a powder yielded a green compound. The powder X-ray pattern of the latter was indexed in a monoclinic cell in agreement with the parameters obtained from the single crystal X-ray study. Only two weak extra-lines, due to the presence of an impurity, could not be indexed (Table 1).

STRUCTURE DETERMINATION

A green single crystal with dimensions $0.077 \times 0.077 \times 0.025$ mm was selected for the structure determination. The cell parameters were determined by diffractometric techniques at 294 K with a least square refinement based on 25 reflections with $18° < \theta < 22°$. The data were collected on a CAD4 ENRAF NONIUS diffractometer with the parameters reported in Table 2. The systematic extinctions $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$ are consistent with the space groups $C2/c$ and Cc. The reflections were corrected for Lorentz and polarization effects, absorption,

TABLE 1
X-Ray Powder Diffraction Data of Li₂NaMo₂P₃O₁₄

h	k	l	d_{obs} (Å)	d_{calc} (Å)	I
0	0	2	8.440	8.439	11
1	−1	−1	6.960	6.956	91
2	0	−2	6.710	6.707	25
1	1	1	6.256	6.252	17
1	1	−2	5.901	5.898	6
				5.383	7[a]
1	1	2	5.094	5.092	2
2	0	2	4.881	4.886	26
3	1	−1	4.396	4.394	64
2	0	−4	4.277	4.283	47
1	1	3	4.133	4.132	100
0	2	0	4.066	4.067	57
0	2	−1	3.959	3.954	7
1	1	−4	3.896	3.894	60
4	0	0	3.732	3.725	2
0	2	−2	3.667	3.664	9
2	2	−1	3.607	3.603	49
2	2	0	3.565	3.570	2
2	2	−2	3.476	3.478	9
3	1	2	3.443	3.442	38
2	2	1	3.388	3.392	4
0	2	−3	3.294	3.296	8
2	0	4	3.265	3.265	27
1	1	−5	3.240	3.243	14
				3.179	6[a]
2	2	2	3.127	3.126	4
4	2	0	3.076	3.075	44
3	1	−5	3.063	3.064	90
3	1	3	3.024	3.024	5
2	2	−4	2.949	2.949	93
5	1	−1	2.903	2.900	30
4	2	−2	2.809	2.808	51
4	2	0	2.750	2.747	8
5	1	−4	2.725	2.726	10
4	2	−3			
1	3	0	2.668	2.668	10
1	3	−1	2.659	2.658	11
5	1	1	2.642	2.640	30
1	3	1	2.614	2.613	5
4	2	−4	2.589	2.588	12
5	1	−5	2.548	2.548	15
1	1	6	2.495	2.494	3
4	2	2	2.455	2.453	12
4	0	4	2.447	2.443	8
3	3	−1	2.408	2.407	10
1	1	−7	2.395	2.395	19
1	3	3	2.361	2.361	44
3	1	5	2.354	2.355	22
5	1	−6			
3	3	−3	2.318	2.318	9
1	3	4	2.200	2.200	6
7	1	−3	2.153	2.153	15
4	0	−8	2.141	2.141	7
6	2	−4	2.135	2.133	3
6	2	0	2.120	2.120	2
3	3	−5	2.097	2.097	11

[a] Nonindexed extra lines.

TABLE 2
Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters for Li₂NaMo₂P₃O₁₄

1. Crystal data

Space group	$C\,2/c$
Cell dimensions	$a = 15.668(1)$ Å $\quad \alpha = 90°$
	$b = 8.135(1)$ Å $\quad \beta = 107.994(7)°$
	$c = 17.747(2)$ Å $\quad \gamma = 90°$
Volume (Å)³	2151.4(5) Å³
Z	8
ρ_{calc} (g cm⁻³)	3.369

2. Intensity measurements

λ(MoKα)	0.71073
Scan mode	ω–θ
Scan width (°)	$1.0 + 0.35 \tan \theta$
Slit aperture (mm)	$1.0 + \tan \theta$
max θ(°)	45
Standard reflections	3 measured every 3600 s
Measured reflections	9452
Reflections with $I > 3\sigma$	2108
μ (mm⁻¹)	2.9

3. Structure solution and refinement

Parameters refined	192
Agreement factors	$R = 0.034 \quad R_w = 0.030$
Weighting scheme	$w = 1/\sigma^2$
Δ/σ max	< 0.005

and extinction. The structure was solved with the heavy atom method. The Harker peaks of the Patterson function allowed us to choose the centrosymmetrical space group $C2/c$.

The refinement of the atomic coordinates and their anisotropic thermal parameters for Mo, P, O, and Na and isotropic thermal factor for the lithium led to $R = 0.034$ and $R_W = 0.030$ and to the atomic parameters in Table 3.

DESCRIPTION OF THE STRUCTURE

This molybdenum(V) monophoshate exhibits a unique tridimensional $[Mo_2P_3O_{14}]_\infty$ framework that has never been observed to date. The projection of the latter along **b** (Fig. 1) shows that it consists of MoO_6 octahedra, sharing their apices with monophosphate groups. It results in "elliptic" tunnels running along **b**, where the lithium (Li(1) and Li(2)) and sodium (Na(2)) cations are located. One also observes four sided tunnels, involving diamond shaped windows, built up of two PO_4 tetrahedra and two MoO_6 octahedra, where the Na(1) cations are sitting.

Although it is rather complicated, this framework can be described in a rather simple way by considering projection along **c** (Fig. 2). It consists of the stacking along **b** of two kinds of $[Mo_4P_6O_{38}]_\infty$ layers (labeled L₁ and L₂) that are enantiomorphic. The projection of such a layer (L₁) along **b**

TABLE 3
Positional Parameters and Their Estimated Standard Deviations in Li$_2$NaMo$_2$P$_3$O$_{14}$

Atom	x	y	z	B (Å^2)
Mo(1)	0.16963(3)	0.26173(7)	−0.15954(3)	0.416(8)
Mo(2)	−0.07185(3)	0.22894(7)	−0.06058(3)	0.47(2)
P(1)	0.1394(1)	0.1133(2)	0.01185(9)	0.47(3)
P(2)	−0.0395(1)	0.4492(2)	0.1108(1)	0.50(3)
P(3)	0.2461(1)	0.6024(2)	0.19354(9)	0.52(3)
Li(1)	0.108(1)	0.185(2)	0.1452(9)	2.5(3)[a]
Li(2)	0.1201(8)	0.397(2)	0.2583(7)	1.1(2)[a]
Na(1)	0.25	0.25	0.5	2.3(2)
Na(2)	0.0	0.0981(5)	0.25	2.2(2)
O(1)	0.0812(3)	0.1485(6)	−0.2056(3)	1.3(2)
O(2)	0.2954(3)	0.3655(5)	−0.0948(2)	0.72(8)
O(3)	0.1720(3)	0.1899(6)	−0.0517(3)	1.12(8)
O(4)	0.1079(3)	0.4770(5)	−0.1491(3)	0.72(8)
O(5)	0.2555(3)	0.0809(6)	−0.1709(3)	1.04(8)
O(6)	0.1852(3)	0.3896(6)	−0.2518(2)	0.88(8)
O(7)	−0.0648(3)	0.0783(5)	−0.1231(3)	1.0(2)
O(8)	−0.0902(3)	0.3849(5)	0.0289(3)	0.88(8)
O(9)	−0.1247(3)	0.0727(5)	0.0055(3)	0.80(8)
O(10)	−0.0268(3)	0.4153(6)	−0.1060(3)	1.1(2)
O(11)	−0.2012(3)	0.2963(5)	−0.1174(2)	0.72(8)
O(12)	0.0524(3)	0.1949(5)	0.0165(3)	0.80(8)
O(13)	0.0133(3)	0.3189(5)	0.1665(2)	0.80(8)
O(14)	0.3385(3)	0.6700(5)	0.2340(3)	0.80(8)

Note. Anisotropically refined atom are given in the form of the isotropic equivalent displacement parameter defined as

$$B = \tfrac{4}{3} \sum_i \sum_j \mathbf{a}_i \cdot \mathbf{a}_j \cdot \beta_{ij}.$$

[a] Atom isotropically refined.

(Fig. 3) shows that it is built up from disconnected [Mo$_4$P$_6$O$_{38}$]$_\infty$ ribbons running along [101]. Within these ribbons the MoO$_6$ octahedra—Mo(1) and Mo(2)—and the PO$_4$ tetrahedra—P(1) and P(3)—form eight-sided Mo$_4$P$_4$O$_{34}$ rings that delimit cross-shaped windows. Two successive rings along [101] are enantiomorphic and are linked to each other by sharing the apices of their Mo(1) octahedra and P(1) tetrahedra. In these ribbons the P(2) tetrahedra, that are located on the border, share only one apex with the other polyhedra of the ribbon, i.e., with the Mo(2) octahedra. The connection between two successive layers L$_1$ and L$_2$ is ensured in the following way: the P(1) and P(3) tetrahedra of one layer share one apex with the MoO$_6$ octahedra of the next layer, i.e., with Mo(2) and Mo(1), respectively, whereas each P(2) tetrahedron of this same layer is connected to two MoO$_6$ octahedra of the next one, i.e., with Mo(1) and Mo(2). As a result two successive L$_1$ and L$_2$ layers are slightly shifted with respect to each other, so that the stacking of these layers along **b** does not lead to cross-shaped tunnels, but to "elliptic" tunnels that are partially obstructed by this shifting. In fact, the MoO$_6$ octahedra form layers that are connected through layers of
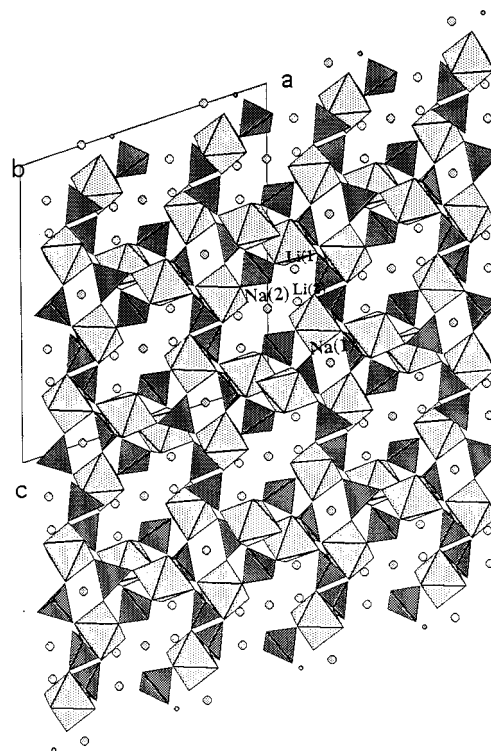

FIG. 1. Projection along **b** of the structure of Li$_2$Na(MoO)$_2$(PO$_4$)$_3$.

PO$_4$ tetrahedra, but in each of these layers the polyhedra are disconnected (Fig. 2).

The MoO$_6$ octahedra exhibit one free apex directed toward the center of the elliptic tunnel. Their geometry is characteristic of pentavelent molybdenum (Table 4), with a very short Mo–O bond (1.654 and 1.680 Å for Mo(1) and Mo(2), respectively) corresponding to the free apex opposite to a longer one (2.125 and 2.121 Å for Mo(1) and Mo(2), respectively). The other Mo–O bonds are rather homogeneous and range from 1.949 to 2.045 Å. The bond valence calculations, performed for these atoms, using the Brese and O'Keefe expression (6), confirm the pentavalent character of molybdenum. The bond valence parameters have been refined to $R_{ij} = 1.879$ on the basis of the data obtained from
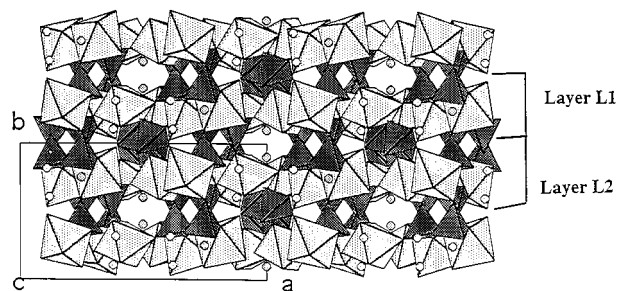

FIG. 2. Projection along **c** of the structure of Li$_2$Na(MoO)$_2$(PO$_4$)$_3$.
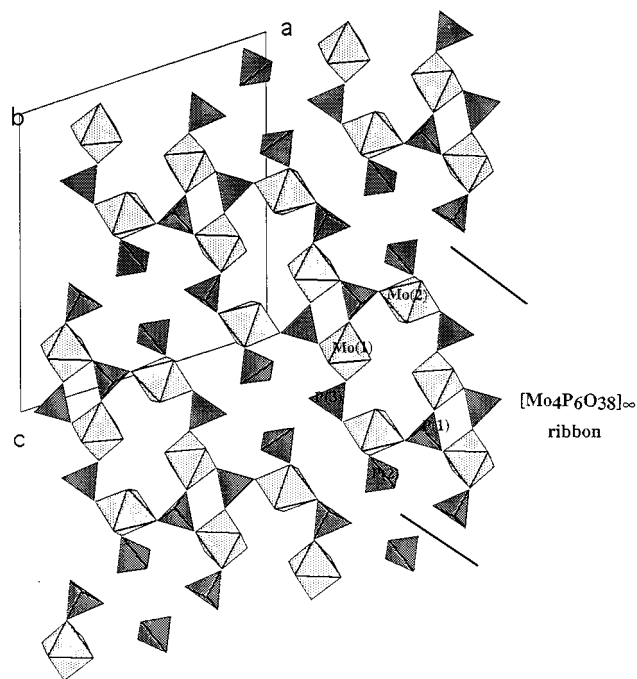
FIG. 3. Projection of the $[Mo_4P_4O_{38}]_\infty$ L1 layer showing the $[Mo_4P_4O_{38}]_\infty$ ribbons running along [101].

68 Mo(V) octahedra of various structures. The calculated valences of Mo(1) and Mo(2) are 5.017 and 4.957, respectively, whereas the valences of the other atoms are in perfect agreement with their expected charges (Table 5).

The PO_4 tetrahedra exhibit almost regular P–O distances (1.507 to 1.559 Å) in agreement with the valence calculation (Table 5). The longest P–O bonds (1.547 to 1.559 Å) correspond to the oxygen atoms that are linked to a MoO_6 octahedron and to an alkaline cation.

The Na(1) cation, located in the four-sided type tunnels, exhibits a distorted antiprismatic coordination (Fig. 4a), with Na–O distances ranging from 2.414 to 2.634 Å, whereas the Na(2) cation in the "elliptic" tunnels has a less regular eightfold coordination (Fig. 4b) with distances ranging from 2.376 to 3.094 Å.

TABLE 4
Distances (Å) and Angles (°) in the Polyhedra in $Li_2NaMo_2P_3O_{14}$

Mo(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	**1.654(4)**	3.764(6)	2.683(6)	2.839(6)	2.664(7)	2.828(7)
O(2)	169.6(2)	**2.125(4)**	2.698(7)	2.938(6)	2.656(6)	2.795(5)
O(3)	94.3(2)	81.8(2)	**1.991(5)**	2.895(6)	2.947(8)	3.969(7)
O(4)	100.1(2)	89.8(2)	91.9(2)	**2.037(5)**	4.054(6)	2.581(7)
O(5)	91.6(2)	79.1(2)	93.8(2)	166.7(2)	**2.045(5)**	2.934(6)
O(6)	100.3(2)	84.8(2)	163.9(2)	79.1(2)	92.5(2)	**2.017(5)**

TABLE 4—*Continued*

Mo(2)	O(7)	O(8)	O(9)	O(10)	O(11)	O(12)
O(7)	**1.680(5)**	3.785(7)	2.723(7)	2.802(6)	2.803(7)	2.757(6)
O(8)	169.5(2)	**2.121(5)**	2.602(6)	2.872(8)	2.739(5)	2.781(5)
O(9)	92.6(2)	76.8(2)	**2.067(5)**	3.988(7)	2.808(6)	2.896(6)
O(10)	100.9(2)	89.7(2)	166.5(2)	**1.949(5)**	2.847(7)	2.796(6)
O(11)	97.3(2)	82.3(2)	86.3(2)	91.03(2)	**2.040(4)**	4.036(6)
O(12)	95.8(2)	84.3(2)	90.1(2)	89.5(2)	166.6(2)	**2.023(4)**

P(1)	O(2)[i]	O(3)	O(9)[ii]	O(12)
O(2)[i]	**1.520(4)**	2.530(6)	2.490(6)	2.411(6)
O(3)	113.3(3)	**1.508(5)**	2.482(7)	2.526(7)
O(9)[ii]	108.5(2)	108.7(3)	**1.547(5)**	2.539(6)
O(12)	103.9(3)	111.8(3)	110.6(3)	**1.542(5)**

P(2)	O(8)	O(13)	O(4)[iii]	O(10)[iii]
O(8)	**1.518(4)**	2.536(6)	2.500(7)	2.515(6)
O(13)	113.8(3)	**1.509(4)**	2.469(6)	2.452(7)
O(4)[iii]	108.9(3)	107.4(3)	**1.555(5)**	2.507(7)
O(10)[iii]	110.9(3)	107.3(3)	108.5(3)	**1.535(5)**

P(3)	O(14)	O(11)[iii]	O(6)[iv]	O(5)[i]
O(14)	**1.507(4)**	2.496(5)	2.539(7)	2.563(6)
O(11)[iii]	109.3(3)	**1.553(4)**	2.527(7)	2.514(6)
O(6)[iv]	111.8(3)	108.6(3)	**1.559(6)**	2.441(7)
O(5)[i]	114.4(3)	108.7(3)	103.8(3)	**1.542(5)**

Na(1)–O(8)[v]: 2.634(5) Na(2)–O(1)[ii]: 2.376(6)
Na(1)–O(8)[vi]: 2.634(5) Na(2)–O(1)[viii]: 2.376(6)
Na(1)–O(9)[v]: 2.414(5) Na(2)–O(7)[ii]: 3.094(6)
Na(1)–O(9)[vi]: 2.414(5) Na(2)–O(7)[vii]: 3.094(6)
Na(1)–O(11)[v]: 2.460(5) Na(2)–O(13): 2.379(6)
Na(1)–O(11)[vi]: 2.460(5) Na(2)–O(13)[v]: 2.379(6)
                          Na(2)–O(14)[viii]: 2.526(6)
                          Na(2)–O(14)[ix]: 2.526(6)

Li(1)–O(2)[x]: 2.03(2) Li(2)–O(4)[iv]: 2.00(1)
Li(1)–O(12): 2.18(1) Li(2)–O(6)[iv]: 2.05(1)
Li(1)–O(13): 1.97(2) Li(2)–O(13): 2.04(1)
Li(1)–O(14)[ix]: 2.05(1) Li(2)–O(14)[ix]: 1.95(1)
Li(1)–O(7)[ii]: 2.24(2)

Symmetry codes

i:	$1/2 - x; 1/2 - y; -z$
ii:	$-x; -y; -z$
iii:	$-x; -y + 1; -z$
iv:	$x; 1 - y; 1/2 + z$
v:	$-x; y; 1/2 - z$
vi:	$x + 1/2; 1/2 - y; z + 1/2$
vii:	$x; -y; z + 1/2$
viii:	$x - 1/2; y - 1/2; z$
ix:	$1/2 - x; y - 1/2; 1/2 - z$
x:	$1/2 - x; 1/2 - y; -z$

Note. The Mo–O or P–O distances are on the diagonal, above it are the O···O distances and below are the O–Mo–O or O–P–O angles.

TABLE 5
Electrostatic Valence Distribution for $Li_2NaMo_2P_3O_{14}$

|	Mo(1)	Mo(2)	P(1)	P(2)	P(3)	Li(1)	Li(2)	Na(1)	Na(2)	$\sum v_i^-$
O(1)	1.795								0.218×2	2.013
O(2)	0.515		1.248			0.223				1.985
O(3)	0.723		1.332							2.055
O(4)	0.652			1.139			0.269			2.060
O(5)	0.640				1.196					1.836
O(6)	0.692				1.127		0.207			2.026
O(7)		1.685				0.123			0.03×2	1.961
O(8)		0.519		1.241				0.105×2		1.865
O(9)		0.597	1.189					0.187×2		1.973
O(10)		0.823		1.219						2.041
O(11)		0.655			1.152			0.161×2		1.968
O(12)		0.680	1.178			0.144				2.002
O(13)				1.297		0.254	0.216		0.205×2	1.972
O(14)					1.308	0.208	0.256		0.14×2	1.912
$\sum v_i^+$	5.017	4.957	4.946	4.896	4.783	0.952	0.949	0.906	1.186	
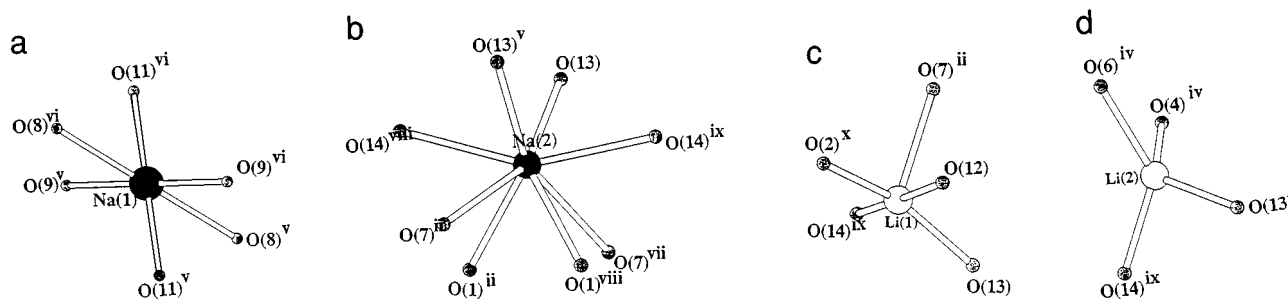
FIG. 4. (a) Distorted antiprismatic coordination of the Na(1) cation. (b) Coordination of the Na(2) cation. (c) Pyramidal coordination of the Li(1) cation. (d) Tetrahedral coordination of the Li(2) cation.

Two kinds of coordination are observed for the lithium ions. The distorted pyramidal coordination observed for Li(1) (Fig. 4c) is rare, though it has been observed in several compounds such as γLiO_3 (7) and $LiBO_2$ (8). The apical Li–O distance of 2.24 Å is significantly longer than the four equatorial distances that range from 1.97 to 2.18 Å (Table 4). The Li(2) cation exhibits an almost regular tetrahedral coordination (Fig. 4d), as observed in other lithium phosphates, with Li–O distances ranging from 1.95 to 2.05 Å (Table 4).

In conclusion, a new molybdenum(V) monophosphate with an original tunnel structure has been synthesized by associating two different cations, lithium and sodium, in the same structure. Such a framework is unique by the fact that it can be considered as a "racemic" structure, formed by the stacking of two sorts of enantiomorphic $[Mo_4P_6O_{38}]_\infty$ layers. Lithium exhibits two kinds of coordination, pyramidal and tetrahedral, which is remarkable. These results emphasize the flexibility of Mo(V), suggesting that it should be possible to prepare lithium-based molybdenophosphate with an original structure.

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