

# A Sodium Mo(V) Monophosphate with a Tunnel Structure: $\text{Na}_3(\text{MoO})_4(\text{PO}_4)_5$

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A new molybdenum monophosphate  $\text{Na}_3(\text{MoO})_4(\text{PO}_4)_5$  has been synthesized. It crystallizes in the space group  $C2/c$  with  $a = 16.789(1)$ ,  $b = 8.500(1)$ ,  $c = 16.361(1)$  Å,  $\beta = 126.34(1)^\circ$ . Its tridimensional framework can be described by the stacking along  $b$  from  $[\text{Mo}_4\text{P}_5\text{O}_{24}]_\infty$  layers sharing the apices of their polyhedra and forming cross-shaped tunnels running along that direction. The sodium ions are located on the walls of the tunnels, near large windows that allow a communication between two adjacent tunnels. Molybdenum exhibits an octahedral coordination, characteristic of Mo(V), i.e., with an abnormally short Mo-O bond corresponding to one free apex for each  $\text{MoO}_6$  octahedron. © 1995 Academic Press, Inc.

## INTRODUCTION

The crystal chemistry of pentavalent molybdenum phosphates has been considerably developed these past years. Association with the  $\text{PO}_4$  tetrahedra, the  $\text{MoO}_6$  octahedra can indeed offer various possibilities to create original host lattices where cations such as  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Tl}^+$ , or  $\text{Cs}^+$  can be accommodated (for a review see Ref. [1]). This property is due to the ability of Mo(V) to form a molybdenyl ion, so that the  $\text{MoO}_6$  octahedra exhibit one free apex leading to the formation of cages or tunnels. Nevertheless, very few sodium Mo(V) phosphates have been isolated until now, despite the great flexibility of Mo(V) and the possible isotypism between sodium and potassium. If one excludes hydroxyphosphates such as  $\text{Na}_3\text{Mo}_2\text{P}_2\text{O}_{11}(\text{OH}) \cdot 2\text{H}_2\text{O}$  [2] or  $(\text{Et}_4\text{N})_6\text{Na}_{14}\text{Mo}_{24}\text{P}_{17}\text{O}_{97}(\text{OH})_{31} \cdot x\text{H}_2\text{O}$  [3], only two anhydrous sodium Mo(V) phosphates have been synthesized so far that exhibit the same formulation  $\text{Na}(\text{MoO})_2(\text{P}_2\text{O}_7)(\text{PO}_4)$  [4, 5]. The recent synthesis of the Mo(V) monophosphate  $\text{K}_3(\text{MoO})_4(\text{PO}_4)_5$  [6], which exhibits an original tunnel structure, encouraged us to explore the sodium homologous compound. We report here on the synthesis and crystal structure of the new sodium Mo(V) monophosphate  $\text{Na}_3(\text{MoO})_4(\text{PO}_4)_5$  whose tunnel structure is different from that of the potassium phase.

## SYNTHESIS AND CRYSTAL GROWTH

Single crystals of the title compound were grown from a mixture of nominal composition  $\text{Na}_3\text{Mo}_4\text{P}_4\text{O}_{22}$ . This compound has been synthesized in two steps: first  $\text{H}(\text{NH}_4)_2\text{PO}_4$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{MoO}_3$  were mixed in an agate mortar in adequate ratios according to the composition  $\text{Na}_3\text{Mo}_{3.5}\text{P}_4\text{O}_{22}$  and heated at 600 K in a platinum crucible to decompose the ammonium phosphate and carbonate. In a second step the resulting mixture was then added to the required amount of molybdenum (0.5 mol), sealed in an evacuated silica ampoule, heated for 1 day at 963 K, and cooled at 9 K per hour down to 823 K. The sample was finally quenched to room temperature.

Two sorts of crystals were extracted from the resulting product: brown crystals identified as  $\text{NaMo}_3\text{P}_3\text{O}_{16}$  [7] and green crystals; the microprobe analysis of these latter confirmed the composition  $\text{Na}_3\text{Mo}_4\text{P}_5\text{O}_{24}$  deduced from the structure determination.

Several attempts to prepare this phase in the form of powder always led to a mixture of crystals: the  $\text{Na}_3(\text{MoO})_4(\text{PO}_4)_5$  green crystals and the yellow crystals identified as  $\xi\text{NaMoP}_3\text{O}_{13}$  [5]. The green crystals were picked out with tweezers using a binocular. These crystals were crushed leading to a green powder which was studied by X ray powder diffraction.

The powder X ray diffraction pattern was indexed in a monoclinic cell in agreement with the parameters obtained from the single crystal X ray study (Table 1).

## STRUCTURE DETERMINATION

A green crystal with dimensions  $0.180 \times 0.103 \times 0.103$  mm was selected for the structure determination. The cell parameters reported in Table 2 were determined and refined by diffractometer techniques at 294 K with a least-squares refinement based upon 25 reflections with  $18^\circ < \theta < 22^\circ$ . The systematic absences  $h + k = 2n + 1$  for all the  $hkl$  and  $l = 2n + 1$  for  $h0l$  are consistent with the space group  $Cc(n^9)$  and  $C2/c(n^{15})$ . The data were collected on a CAD4 Enraf Nonius diffractometer with the data

TABLE 1  
Interreticular Distances for  $\text{Na}_3(\text{MoO})_4(\text{PO}_4)_5$

<i>h k l</i>	<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	<i>I</i> / <i>I</i> <sub>0</sub>	<i>h k l</i>	<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	<i>I</i> / <i>I</i> <sub>0</sub>
2 0 -2	7.394	7.381	1.5	1 3 -2	2.675	2.674	2.0
1 1 -1	7.369			6 0 -2	2.672		
1 1 0	7.197	7.213	2.5	1 3 1	2.650	2.649	11.5
2 0 0	6.764	6.763	41.0	4 2 0	2.646		
0 0 2	6.593	6.588	4.5	5 1 0	2.578	2.580	16.0
1 1 -2	5.870	5.866	29.5	3 1 -6	2.578		
1 1 1	5.617	5.617	6.0	4 2 -5	2.551	2.553	1.0
3 1 -2	4.654	4.652	64.0	3 3 -1	2.503	2.505	2.5
1 1 -3	4.422	4.415	13.0	2 0 4	2.447	2.447	3.5
0 2 0	4.250	4.255	18.0	3 1 3	2.393	2.392	1.0
4 0 -2	4.177	4.175	1.0	4 2 1	2.390		
2 0 -4	4.057	4.051	3.5	7 1 -4	2.309	2.310	2.5
0 2 -1	4.045			5 1 1	2.298	2.296	3.5
2 2 -2	3.685	3.683	6.0	6 2 -5	2.255	2.253	5.0
1 1 -4	3.435	3.437	100.0	6 0 0	2.255		
4 0 0	3.382	3.381	66.0	1 3 3	2.226	2.218	24.5
3 1 1	3.358	3.351	52.0	2 2 -6	2.211		
2 2 -3	3.350			7 1 -6	2.184	2.187	1.5
1 1 3	3.315	3.316	10.0	7 1 -2	2.174	2.172	34.0
5 1 -2	3.057	3.055	10.0	5 3 -3	2.165	2.167	15.0
0 2 3	3.055			6 2 1	2.142	2.140	7.5
3 1 -5	3.055			4 2 2	2.137	2.137	3.0
5 1 -4	3.020	3.023	1.5	8 0 -4	2.089	2.088	6.0
4 2 -2	2.979	2.978	1.5	3 1 4	2.064	2.062	3.5
2 2 -4	2.935	2.938	39.0	3 3 2	2.056	2.057	10.0
4 2 -1	2.863	2.864	3.0	1 3 -5	2.039	2.038	1.0
5 1 -1	2.852	2.853	10.0	7 1 -1	2.038		
6 0 -4	2.781	2.779	4.5	6 0 -8	2.016	2.017	3.5
1 1 -5	2.775			2 4 -3	1.979	1.979	1.5

TABLE 2  
Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters for  $\text{Na}_3(\text{MoO})_4(\text{PO}_4)_5$

1. Crystal data	
Space group	<i>C</i> <sub>2/c</sub>
Cell dimensions	<i>a</i> = 16.789(1) Å <i>b</i> = 8.500(1) Å <i>β</i> = 126.34(1) <i>c</i> = 16.361(1) Å
Volume	1880 Å <sup>3</sup>
<i>Z</i>	4
<i>d</i> <sub>calc</sub>	3.50
2. Intensity measurements	
<i>λ</i> (MoK $\alpha$ )	0.71073 Å
Scan mode	$\omega - \theta$
Scan width (°)	1 + 0.35 tan $\theta$
Slit aperture (mm)	1.1 + tan $\theta$
Max $\theta$ (°)	45
Standard reflections	3 measured every hour
Reflections measured	8276
Reflections with <i>I</i> > 3 $\sigma$	4967
$\mu$ (mm <sup>-1</sup> )	3.16
3. Structure solution and refinement	
Parameters refined	169
Agreement factors	<i>R</i> = 0.020 <i>R</i> <sub>w</sub> = 0.022
Weighting scheme	<i>w</i> = <i>f</i> (sin $\theta$ / $\lambda$ )
$\Delta/\sigma$ max	<0.004
$\Delta\rho$ (eÅ <sup>-3</sup> )	0.46

collection parameters of Table 2. The reflections were corrected for Lorentz, polarization, absorption, and secondary effects. The Harker peaks present in the Patterson function are characteristic of the centrosymmetric space group *C*<sub>2/c</sub>.

TABLE 3  
Positional Parameters and Their Estimated Standard Deviations

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )	Site	Occupation
Mo(1)	0.13119(1)	0.05912(1)	-0.01603(1)	0.445(1)	8 <i>f</i>	1
Mo(2)	0.09579(1)	0.43449(2)	0.18077(1)	0.449(1)	8 <i>f</i>	1
P(1)	0.54982(2)	0.25494(5)	0.04157(2)	0.457(5)	8 <i>f</i>	1
P(2)	0.36614(2)	0.07679(5)	0.10400(2)	0.466(5)	8 <i>f</i>	1
P(3)	0.	0.14788(6)	0.25	0.515(7)	4 <i>e</i>	1
Na(1)	0.35650(8)	0.3447(2)	0.23134(8)	2.34(2)	8 <i>f</i>	1
Na(2)	0.2308(2)	0.2242(3)	0.4257(3)	3.32(7)	8 <i>f</i>	0.5
O(1)	0.1795(1)	0.1308(2)	0.0984(1)	1.56(2)	8 <i>f</i>	1
O(2)	0.14381(9)	0.2459(2)	-0.08273(9)	1.07(2)	8 <i>f</i>	1
O(3)	0.11417(7)	-0.1645(2)	0.01562(8)	0.89(2)	8 <i>f</i>	1
O(4)	-0.01239(7)	0.1188(2)	-0.08003(8)	0.77(2)	8 <i>f</i>	1
O(5)	0.26786(7)	-0.0080(2)	0.02360(9)	0.87(2)	8 <i>f</i>	1
O(6)	0.07523(9)	-0.0426(2)	-0.16088(8)	1.15(2)	8 <i>f</i>	1
O(7)	0.21406(8)	0.3844(2)	0.2363(1)	1.14(2)	8 <i>f</i>	1
O(8)	0.03872(8)	0.3285(2)	0.04909(8)	0.87(2)	8 <i>f</i>	1
O(9)	0.0604(1)	0.2482(2)	0.2279(1)	1.68(2)	8 <i>f</i>	1
O(10)	0.11531(8)	0.5700(2)	0.29214(8)	1.12(2)	8 <i>f</i>	1
O(11)	0.11499(8)	0.6401(2)	0.12883(8)	0.86(2)	8 <i>f</i>	1
O(12)	-0.05306(8)	0.5027(2)	0.10368(9)	1.07(2)	8 <i>f</i>	1

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

$$B = \sum_i \sum_j \beta_{ij} a_i \cdot a_j.$$

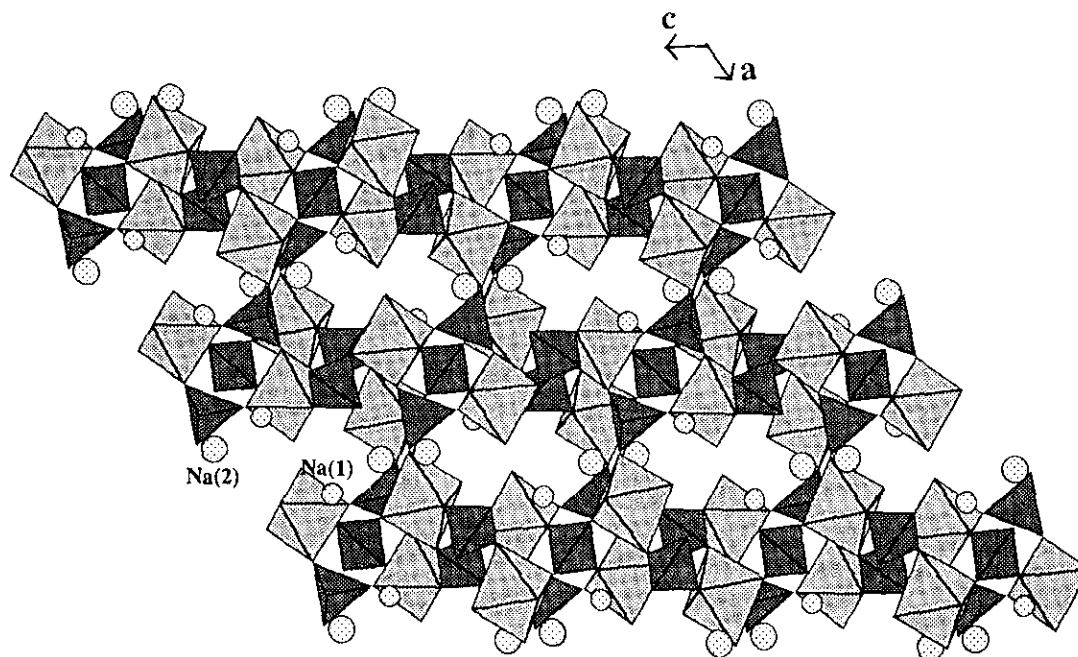


FIG. 1. Projection of the  $\text{Na}_3\text{Mo}_4\text{P}_5\text{O}_{24}$  structure along **b** showing the cross-shaped tunnels.

The structure was solved with the heavy atom method. The refinement of the atomic coordinates and the anisotropic thermal factors led to  $R = 0.020$  and  $R_w = 0.022$  and to the atomic parameters of Table 3. Note that the Na(2) sites are half occupied leading to four Na atoms spread randomly over eight sites. This is consistent with

the fact that two sites related by a center of symmetry are separated by only 2.15 Å.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The projection of the structure of  $\text{Na}_3\text{Mo}_4\text{P}_5\text{O}_{24}$  onto the (010) plane (Fig. 1) shows that the  $[\text{Mo}_4\text{P}_5\text{O}_{24}]_\infty$  host

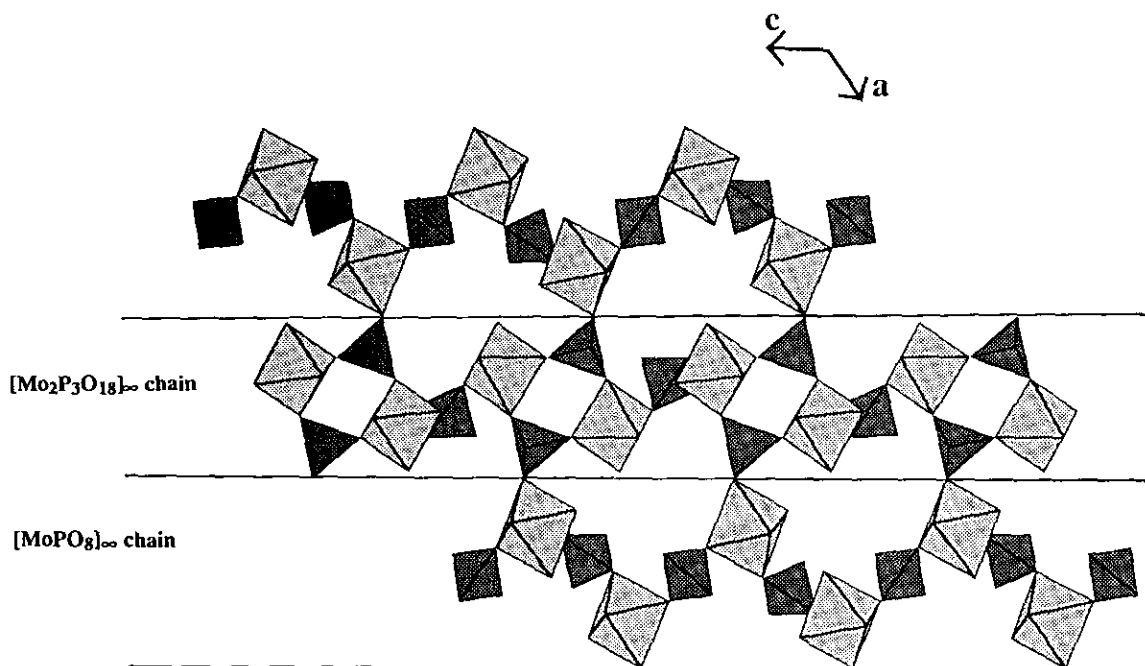


FIG. 2.  $[\text{Mo}_4\text{P}_5\text{O}_{24}]_\infty$  layer containing  $[\text{Mo}_2\text{P}_3\text{O}_{18}]_\infty$  and  $[\text{MoPO}_8]_\infty$  chains which delimit large windows made of five octahedra and five tetrahedra.

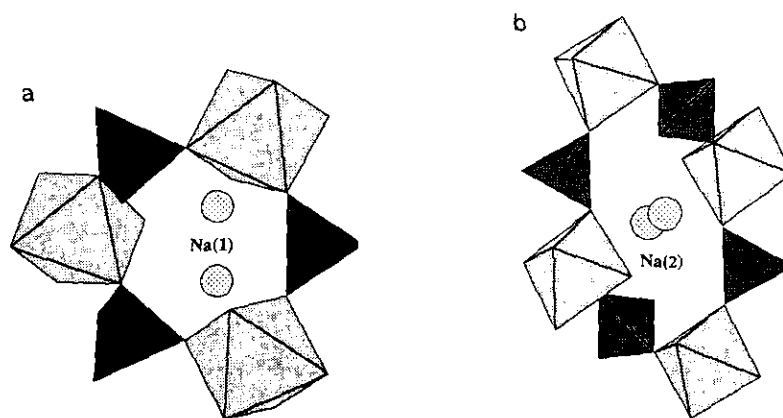


FIG. 3. (a) The six-sided windows connecting the cross-shaped tunnels along the **a** axis. (b) The eight-sided windows connecting the cross-shaped tunnels along the **c** axis.

lattice is built up from monophosphate groups  $\text{PO}_4$  sharing their four apices with the  $\text{MoO}_6$  octahedra so that each octahedron is linked to five  $\text{PO}_4$  tetrahedra and exhibits one free apex.

This framework  $[\text{Mo}_4\text{P}_5\text{O}_{24}]_\infty$  can easily be described by the stacking along **b** of two identical  $[\text{Mo}_4\text{P}_5\text{O}_{32}]_\infty$  layers. Each layer consists of two kinds of chains running along **a**.

(i)  $[\text{MoPO}_8]_\infty$  chains waving along **a**, in which one  $\text{MO}_6$  octahedron alternates with one  $\text{PO}_4$  tetrahedron (Fig.

2). Note that the geometry of these chains is very different from that generally observed for  $[\text{MoPO}_8]_\infty$  chains in molybdenum phosphates.

(ii)  $[\text{Mo}_2\text{P}_3\text{O}_{18}]_\infty$  chains in which each  $\text{MoO}_6$  octahedron is linked to three  $\text{PO}_4$  tetrahedra (Fig. 2).

These  $[\text{Mo}_4\text{P}_5\text{O}_{32}]_\infty$  layers (Fig. 2) delimit large windows built up from 10 corner-sharing polyhedra (five octahedra and five tetrahedra), the free apex of each octahedron being oriented toward the center of the window.

Two successive  $[\text{Mo}_4\text{P}_5\text{O}_{32}]_\infty$  (010) layers are shifted

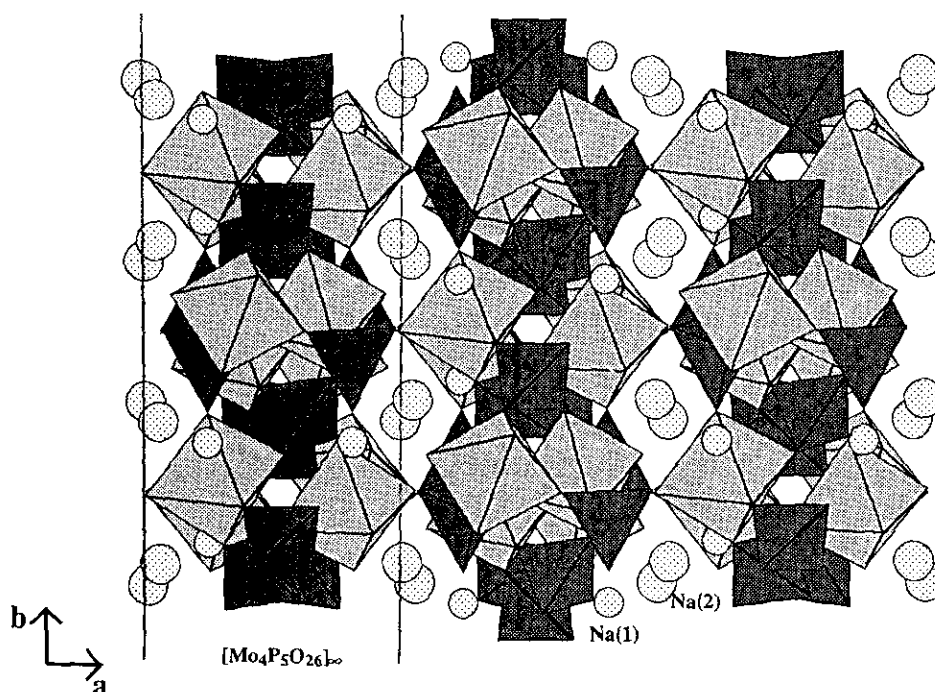


FIG. 4. Projection of the  $\text{Na}_3\text{Mo}_4\text{P}_5\text{O}_{24}$  structure along **c** showing the stacking of the  $[\text{Mo}_4\text{P}_5\text{O}_{26}]_\infty$  layers.

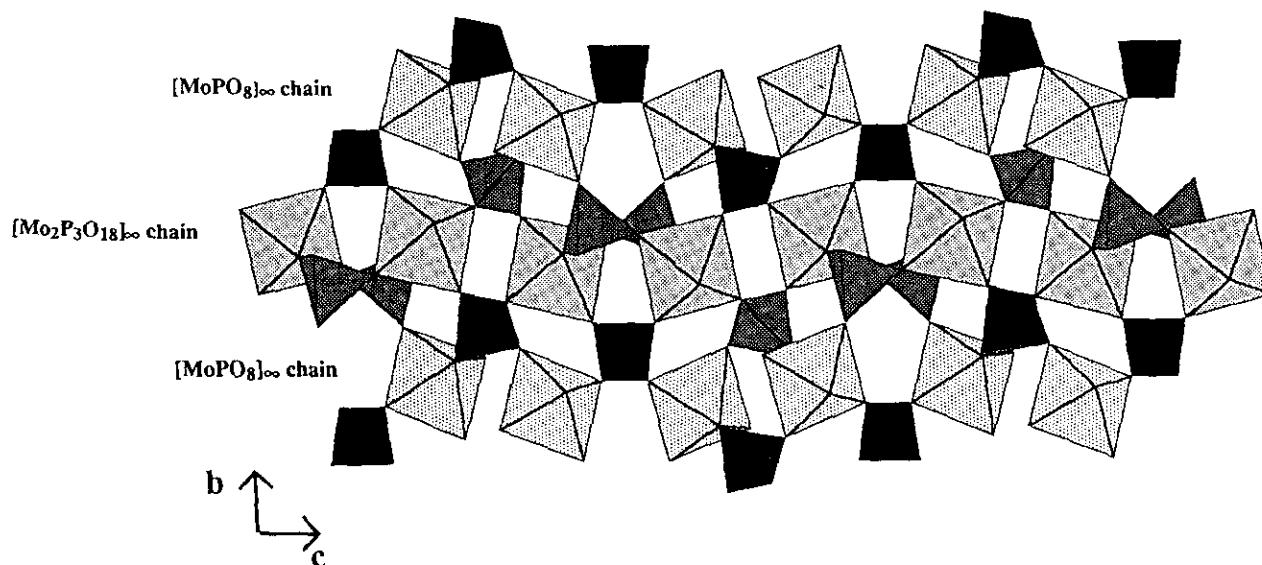


FIG. 5. The  $[\text{Mo}_4\text{P}_5\text{O}_{26}]_\infty$  layer built of  $[\text{MoPO}_8]_\infty$  chains alternating with  $[\text{Mo}_2\text{P}_3\text{O}_{18}]_\infty$  chains.

$a/2$  with respect to each other and share the apices of their polyhedra in such a way that one  $\text{MoO}_6$  octahedron of one layer is linked to one  $\text{PO}_4$  tetrahedron of the next layer and vice versa.

The so-formed tridimensional framework  $[\text{Mo}_4\text{P}_5\text{O}_{24}]_\infty$  exhibits cross-shaped tunnels running along **b** (Fig. 1), which are partly obstructed by the oxygen atoms corresponding to the free apices of the  $\text{MoO}_6$  octahedra. One interesting characteristic of this structure deals with the fact that two adjacent tunnels communicate through rather large windows. Two  $[010]$  tunnels communicate along **b** through six-sided windows built up from three octahedra and three tetrahedra (Fig. 3a), and along **c** through eight-sided windows built up from four octahedra and four tetrahedra (Fig. 3b). The sodium cations are located in these tunnels, close to the six-sided windows and to the eight-sided windows for Na(1) and Na(2), respectively, i.e., at the boundary between two adjacent tunnels. Note that the center of the eight-sided windows is also a symmetry center so that it implies a splitting of the Na(2) site on both sides of the window.

The projection of this structure along **c** (Fig. 4) is more complex. Nevertheless, it shows that the structure can also be described from the stacking along **a** of identical  $[\text{Mo}_4\text{P}_5\text{O}_{26}]_\infty$  layers sharing the apices of their polyhedra, two successive layers being shifted  $(\mathbf{a} + \mathbf{b})/2$  with respect to each other. One also recognizes small four-sided tunnels running along **c** where the sodium cations are located. From the projection of one  $[\text{Mo}_4\text{P}_5\text{O}_{26}]_\infty$  layer onto the (100) plane (Fig. 5) one also observes  $[\text{MoPO}_8]_\infty$  chains and  $[\text{Mo}_2\text{P}_3\text{O}_{18}]_\infty$  chains running along **c**, which share the apices of their polyhedra along **b**. Note that one  $[\text{MoPO}_8]_\infty$  chain alternates with one  $[\text{Mo}_2\text{P}_3\text{O}_{18}]_\infty$  chain along **b**. It

results in each  $[\text{Mo}_2\text{P}_3\text{O}_{18}]_\infty$  chain being connected to four  $[\text{MoPO}_8]_\infty$  chains and reciprocally, to form the  $[\text{Mo}_4\text{P}_5\text{O}_{24}]_\infty$  framework.

Another remarkable characteristic of this structure deals with the existence of “ $\text{Mo}_2\text{P}_3\text{O}_{18}$ ” units (Fig. 6) built up from two  $\text{MoO}_6$  octahedra connected through three monophosphate groups. Such units, clearly visible on the (010) and (100) projections (Figs. 1 and 5), form the basis of the nasicon-type structure of the phosphates  $\text{NaMo}_2\text{P}_3\text{O}_{12}$  [8] and  $\text{AMo}_2\text{P}_3\text{O}_{12}$  with  $A = \text{Ca}, \text{Sr}, \text{Ba}$  [9] in which molybdenum is tetravalent or mixed valent Mo(III)–Mo(IV). In the present monophosphate, the “ $\text{Mo}_2\text{P}_3\text{O}_{18}$ ” units cannot be directly linked one to the

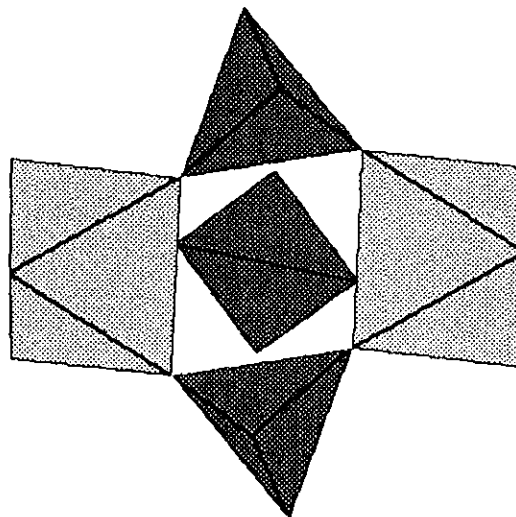


FIG. 6. The  $\text{Mo}_2\text{P}_3\text{O}_{18}$  unit.

TABLE 4  
Distances (Å) and Angles (°) in Polyhedra

Mo(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.653(1)	2.827(2)	2.753(2)	2.787(2)	2.690(2)	3.798(2)
O(2)	100.66(9)	2.008(1)	3.995(2)	2.861(2)	2.780(2)	2.689(2)
O(3)	96.02(8)	162.42(6)	2.034(1)	2.971(2)	2.837(2)	2.758(2)
O(4)	97.32(7)	89.85(6)	93.53(5)	2.043(1)	4.089(2)	2.846(2)
O(5)	92.16(7)	86.18(6)	87.68(5)	170.26(5)	2.061(1)	2.844(2)
O(6)	176.84(7)	80.58(6)	82.48(6)	85.56(5)	85.02(6)	2.147(1)
Mo(2)	O(7)	O(8)	O(9)	O(10)	O(11)	O(12)
O(7)	1.677(1)	2.755(2)	2.756(2)	2.805(2)	2.667(2)	3.781(3)
O(8)	97.35(7)	1.981(1)	2.809(2)	3.952(2)	2.894(2)	2.645(2)
O(9)	96.72(8)	89.78(8)	1.999(2)	2.879(3)	4.040(3)	2.802(2)
O(10)	98.60(7)	163.67(6)	91.76(8)	2.012(1)	2.734(2)	2.738(2)
O(11)	90.81(7)	91.74(6)	172.06(7)	84.61(6)	2.051(1)	2.849(2)
O(12)	176.57(7)	80.58(6)	86.04(7)	83.31(6)	86.52(6)	2.106(1)
	P(1)	O(3 <sup>i</sup> )	O(4 <sup>ii</sup> )	O(8 <sup>ii</sup> )	O(11 <sup>iii</sup> )	
	O(3 <sup>i</sup> )	1.536(1)	2.513(2)	2.536(2)	2.482(2)	
	O(4 <sup>ii</sup> )	108.90(8)	1.553(1)	2.495(2)	2.485(2)	
	O(8 <sup>ii</sup> )	112.35(8)	108.79(7)	1.516(1)	2.510(2)	
	O(11 <sup>iii</sup> )	108.13(7)	107.49(8)	111.05(8)	1.529(1)	
	P(2)	O(2 <sup>ii</sup> )	O(5)	O(10 <sup>iv</sup> )	O(12 <sup>iii</sup> )	
	O(2 <sup>ii</sup> )	1.533(1)	2.529(2)	2.389(2)	2.527(2)	
	O(5)	110.281(8)	1.549(1)	2.523(2)	2.469(2)	
	O(10 <sup>iv</sup> )	102.19(9)	109.75(8)	1.537(1)	2.537(2)	
	O(12 <sup>iii</sup> )	112.91(9)	108.21(8)	113.42(8)	1.498(1)	
	P(3)	O(6 <sup>v</sup> )	O(6 <sup>vi</sup> )	O(9)	O(9 <sup>vii</sup> )	
	O(6 <sup>v</sup> )	1.530(1)	2.481(3)	2.546(2)	2.428(2)	
	O(6 <sup>vi</sup> )	108.4(1)	1.530(1)	2.428(2)	2.546(2)	
	O(9)	113.0(1)	105.31(9)	1.524(2)	2.526(4)	
	O(9 <sup>vii</sup> )	105.31(9)	113.0(1)	112.0(2)	1.524(2)	

Note. The Mo–O or P–O bond lengths are on the diagonal. Above it are the O–O distances and below it are the O–M–O or O–P–O angles.

other to form a tridimensional framework, due to the fact that the pentavalent character of molybdenum imposes one free apex for each MoO<sub>6</sub> octahedron. As a result, only one kind of molybdenum atom Mo(2) belongs to the "Mo<sub>2</sub>P<sub>3</sub>O<sub>18</sub>" units; the second one, Mo(1), and PO<sub>4</sub> tetrahedra ensure the connection between these units.

The geometry of the MoO<sub>6</sub> octahedra (Table 4) is characteristic of Mo(V), with one abnormally short Mo–O bond (1.653–1.677 Å) corresponding to the free apex and the opposite Mo–O distance being the longest bond (2.106–2.147 Å), whereas the four basal Mo–O bonds are intermediate (1.981 to 2.061 Å). Taking into consideration the crystallographic results previously obtained for all the Mo(V) phosphates, a valence calculation can be carried out with the Brese and O'Keeffe expression [10]; the bond valence parameter can be refined to  $R_{ij} = 1.879$ , on the basis of the data obtained from 59 Mo(V) octahedra in the

literature. With this new  $R_{ij}$  value one obtains calculated valences of 4.95 and 5.07 for Mo(1) and Mo(2), respectively, that confirm the pentavalent character of molybdenum.

The PO<sub>4</sub> tetrahedra exhibit P–O bond lengths ranging from 1.498 to 1.553 Å, characteristic of the monophosphate groups (Table 4).

Both sodium cations are surrounded by seven oxygen atoms with Na–O distances smaller than 3.25 Å. In fact the oxygen atoms are not uniformly distributed around the cations so that the nearest neighbors of sodium belong to the wall of the large cavities. Consequently, the coordination of Na(1) can be better described (Fig. 7a) as a distorted pentagonal pyramid NaO<sub>7</sub>, characterized by six Na–O distances ranging from 2.458 to 2.682 Å (Table 4), the seventh oxygen atom, which caps one triangular face, sitting much further apart at 3.03 Å. In the same way,

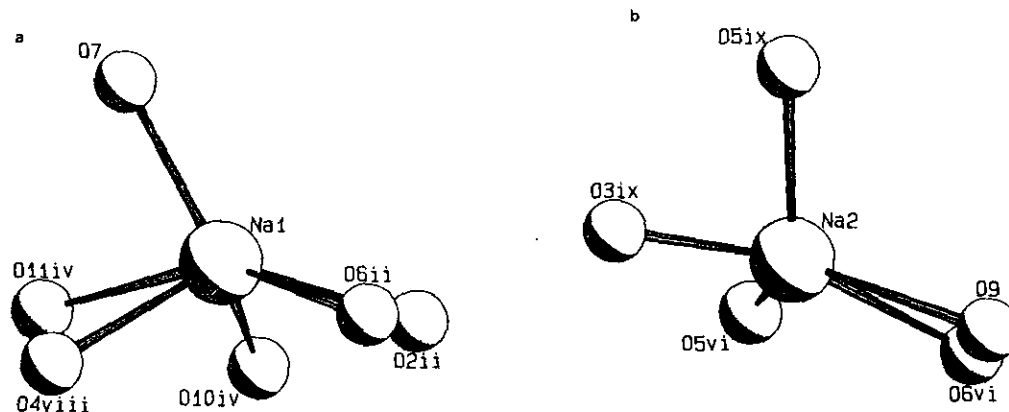


FIG. 7. (a) The pentagonal pyramid of oxygen atoms around Na(1). (b) The square pyramid of oxygen atoms around Na(2).

Na(2) forms a distorted square pyramid NaO<sub>5</sub> (Fig. 7b), with five Na–O distances ranging from 2.269 to 2.779 Å (Table 4), the two other additional oxygen atoms sitting far away at 3.11 and 3.24 Å.

#### CONCLUDING REMARKS

Na<sub>3</sub>(MoO)<sub>4</sub>(PO<sub>4</sub>)<sub>5</sub> represents the first sodium Mo(V) monophosphate and the third sodium Mo(V) phosphate that has been synthesized until now. The originality of this structure deals with its large tunnels running along **b**, which communicate laterally one with the other, through large windows, so that a certain mobility of the sodium cation can be expected in agreement with the rather high thermal factors observed for the latter. Ion exchange and ionic conduction properties of this new phase will be investigated.

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