ζ-NaMo$_2$P$_3$O$_{13}$, a Second Form of Pentavalent Molybdenum Sodium Phosphate

G. COSTENTIN, M. M. BOREL, A. GRANDIN, A. LECLAIRE,[1] AND B. RAVEAU

Laboratoire de Cristallographie et Sciences des Matériaux, CRISMAT, CNRS, ISMRa, University of Caen, Boulevard du Maréchal Juin, 14032 Caen Cedex, France

A second form of sodium molybdenum (V) phosphate ζ-NaMo$_2$P$_3$O$_{13}$ has been synthesized. It crystallizes in the system $P2_1/c$, $a = 6.3682(5)$ Å, $b = 22.2546(11)$ Å, $c = 8.6172(8)$ Å, $\beta = 126.139(7)°$. The determination of the structure was performed from a single crystal. The ζ-NaMo$_2$P$_3$O$_{13}$ phase represents the sixth original structure of the AMo$_2$P$_3$O$_{13}$ series. [Mo$_2$P$_3$O$_{13}$]$_\infty$ frameworks exhibit similar MoO$_6$ octahedra characterized by a short Mo–O distance, signature of Mo(V), and similar [MoP$_2$O$_{11}$] units formed of one P$_2$O$_7$ group sharing two of its corners with the same MoO$_6$ octahedron. Like in the β, γ, and ε forms one can recognize in ζ-NaMo$_2$P$_3$O$_{13}$ [MoP$_2$O$_{10}$]$_\infty$ chains built up from corner-sharing [MoP$_2$O$_{11}$] units. Another interesting feature concerns the existence of [MoPO$_8$]$_\infty$ chains in which one tetrahedron alternates with one octahedron, often observed in other molybdenum phosphates. A comparison is made with the α-MoPO$_5$ structure. © 1990 Academic Press, Inc.

Introduction

Among the great number of molybdenum phosphates which were synthesized these last years, those involving pentavalent molybdenum represent an interesting family. Until 1983, Mo(V) could be considered an unusual valency for molybdenum in oxides and especially in phosphates since only two molybdenum phosphates were known, MoPO$_5$ (*1*) and Mo$_2$P$_4$O$_{15}$ (*2*). Since that time five new Mo(V) phosphates have been synthesized and their structure has been determined from single crystals (*3–9*). Moreover they all exhibit the same formulation AMo$_2$P$_3$O$_{13}$, but each of them is characterized by a fundamentally different

[Mo$_2$P$_3$O$_{13}$]$_\infty$ framework depending on the nature of the A univalent cation. This great flexibility of the [Mo$_2$P$_3$O$_{13}$]$_\infty$ framework may be related to the particular electronic configuration of Mo(V), which forms an abnormally short Mo–O bond and makes each Mo^{V}O$_6$ octahedron always exhibit one free apex, i.e., which is connected neither to a PO$_4$ tetrahedron nor to another MoO$_6$ octahedron. This suggests that various mixed frameworks involving Mo(V), built up from MoO$_6$ and PO$_4$ tetrahedra, might be synthesized and that polymorphism can be expected, according to the experimental conditions. During the synthesis of the oxide ε-NaMo$_2$P$_3$O$_{13}$ (*10*), single crystals of this compound were isolated but a pure phase could never be obtained, another phase being preferentially formed, which could be

[1] To whom correspondence should be addressed.

31

prepared as a single phase material by increasing temperature. We report here on this latter phase ζ-NaMo$_2$P$_3$O$_{13}$ which corresponds to a second form of the sodium phosphate.

Synthesis

The synthesis of single crystals of the molybdenum phosphate NaMo$_2$P$_3$O$_{13}$ was performed in two steps. First, H(NH$_4$)$_2$PO$_4$, Na$_2$CO$_3$, and MoO$_3$ were mixed in an agate mortar in the appropriate molecular ratio to obtain the composition "NaMo$_{1.666}$P$_3$O$_{13}$." The mixture was heated at 600 K in air in order to decompose the carbonate and the ammonium phosphate. The resulting product was then added to the required amount of molybdenum and placed in an evacuated silica ampoule. This mixture was heated for 5 days at 1073 K.

As previously pointed out (10), under these experimental conditions a pure phase could not be obtained. However, two sorts of single crystals were isolated which were shown to both have the same formula Na-Mo$_2$P$_3$O$_{13}$. Their composition was determined both by chemical analysis and from structure determination.

Contrary to the ε-NaMo$_2$P$_3$O$_{13}$ form which could not be isolated as a pure phase in the form of bulk samples, the quantitative synthesis of the ζ-NaMo$_2$P$_3$O$_{13}$ form was performed in two steps. The first step was identical to that described above for the single crystal synthesis, whereas in the second step the silica ampoule was heated up to 1173 K for 3 days. The powder X-ray diffraction pattern of this phase was indexed in a monoclinic cell (Table I) in agreement with the parameters obtained from the single crystal study.

Structure Determination

A yellowish crystal with dimensions 0.120 × 0.096 × 0.060 mm was selected for the structure determination. The cell parameters reported in Table II were determined and refined by diffractometric techniques at 294 K with a least-squares refinement based upon 25 reflections with $18 < \theta < 22°$.

The data were collected on a CAD-4 Enraf–Nonius diffractometer with the data collection parameters reported in Table II. The reflections were corrected for Lorentz and polarization effects; no absorption corrections were performed.

Atomic coordinates of the molybdenum atom were deduced from the Patterson function and the other atoms were located by subsequent Fourier series. Refinement of the atomic coordinates and their anisotropic thermal parameters led to $R = 0.062$ and $R_w = 0.077$ and to atomic parameters of Table III.[2]

TABLE I

ζ-NaMo$_2$P$_3$O$_{13}$: INTERETICULAR DISTANCES

h k l	d_{obsd}	d_{calcd}	I	h k l	d_{obsd}	d_{calcd}	I
0 2 1	5.909	5.900	54	1 7 0	2.706	2.704	6
1 0 0	5.133	5.143	37	−2 4 1	2.690	2.689	6
0 3 1	5.075	5.075	49	−1 8 1	2.542	2.542	4.5
0 4 1	4.354	4.356	74	2 2 0	2.505	2.505	7
1 3 0	4.231	4.226	18	1 8 0	2.449	2.447	12
−1 4 1	4.164	4.159	29	0 2 3	2.270	2.271	12
0 5 1	3.754	3.750	65	2 5 0	2.226	2.227	9
−1 3 2	3.711	3.710	83	0 10 1	2.119	2.220	22.5
0 6 0		3.709					
0 2 2	3.321	3.321	100	−3 2 3	2.053	2.052	9
				1 5 2		2.055	
0 6 1	3.273	3.273	12	−1 2 4	2.024	2.023	13
−2 0 2	3.131	3.131	22	−2 4 4	1.998	1.999	13.5
−2 1 1	3.039	3.043	7	−3 1 4	1.900	1.899	7
1 6 0	3.011	3.008	33	0 7 3	1.874	1.874	13
0 4 2	2.951	2.950	13	2 6 1	1.794	1.795	13.5
0 7 1	2.891	2.892	13	−1 12 1	1.779	1.778	7
				1 8 2		1.780	
−1 7 1	2.834	2.835	4.5	−3 7 3	1.746	1.745	6
−1 6 2	2.805	2.804	6	1 2 3	1.740	1.739	5
0 8 0	2.779	2.782	65	0 1 4	1.736	1.734	4.5

[2] Lists of structure factors and anisotropic thermal motion parameters are available on request to the authors.

TABLE II

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR ζ-NaMo$_2$P$_3$O$_{13}$

1. Crystal data

Space group	$P2_1/c$
Cell dimensions	$a = 6.3682(5)$ Å
	$b = 22.2546(11)$ Å $\beta = 126.139(7)°$
	$c = 8.6172(8)$ Å
Volume	$V = 986(6)$ Å^3
Z	4

2. Intensity measurement

λ (Mo$K\alpha$)	0.71073 Å
Scan mode	$\omega - 4/3\theta$
Scan width (°)	$0.85 + 0.35 \tan \theta$
Slit aperture (mm)	$1. + \tan \theta$
Max θ (°)	43°
Standard reflections	3 measured every 4000 sec (no decay)
Reflections with $I > 2.5\sigma$	2693
μ (mm^{-1})	3.078

3. Structure solution and refinement

Parameters refined	172
Agreement factors	$R = 0.062$, $R_w = 0.077$
Weighting scheme	$W = f(\sin \theta/\lambda)$
Δ/σ_{max}	0.01

TABLE III

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	B(Å^2)
Mo(1)	0.2559(1)	0.20833(4)	0.04173(9)	0.329(9)
Mo(2)	0.5520(1)	0.43650(4)	0.2793(1)	0.368(9)
P(1)	0.6439(4)	0.2964(1)	0.4170(3)	0.40(3)
P(2)	0.5319(4)	0.5827(1)	0.1516(3)	0.40(3)
P(3)	0.0208(4)	0.5995(1)	−0.2024(3)	0.44(3)
Na	0.9661(9)	0.1306(3)	0.3016(7)	1.5(1)
O(1)	0.189(2)	0.2764(4)	−0.057(1)	1.0(1)
O(2)	0.578(1)	0.1876(4)	0.0600(9)	0.7(1)
O(3)	−0.060(1)	0.2076(5)	0.046(1)	1.0(1)
O(4)	0.059(1)	0.1608(4)	−0.2047(9)	0.8(1)
O(5)	0.510(1)	0.2376(3)	0.314(1)	0.8(1)
O(6)	0.309(1)	0.1243(4)	0.180(1)	1.0(1)
O(7)	0.716(2)	0.4408(5)	0.519(1)	1.4(2)
O(8)	0.482(1)	0.5225(4)	0.209(1)	1.1(1)
O(9)	0.553(1)	0.3475(3)	0.2691(9)	0.8(1)
O(10)	0.186(1)	0.4327(4)	0.200(1)	1.0(1)
O(11)	0.868(1)	0.4418(4)	0.2770(9)	0.7(1)
O(12)	0.366(1)	0.4229(4)	−0.0332(8)	0.7(1)
O(13)	0.247(1)	0.6130(4)	0.0188(9)	0.7(1)

Description of the Structure and Discussion

The projection of the structure of this new molybdenum phosphate onto the (100) plane shows that the host lattice of ζ-NaMo$_2$P$_3$O$_{13}$ is built up from corner-sharing MoO$_6$ octahedra, single PO$_4$ tetrahedra, and diphosphate P$_2$O$_7$ groups, like the [Mo$_2$P$_3$O$_{13}$]$_\infty$ frameworks of the five other AMo$_2$P$_3$O$_{13}$ phosphates.

The geometry of the PO$_4$ tetrahedra is similar to that commonly observed in other phosphates. The P–O distances in the monophosphate groups are almost equal, whereas the diphosphate groups which exhibit an almost eclipsed configuration are characterized by one long P–O bond corresponding to the bridging oxygen and three shorter P–O distances (Table IV).

The geometry of the MoO$_6$ octahedra is characteristic of Mo(V) as observed in all

TABLE IV

DISTANCES (Å) AND ANGLES (°) IN THE PO$_4$ TETRAHEDRA P(1) CORRESPONDS TO THE MONOPHOSPHATE GROUP AND P(2) AND P(3) TO THE DIPHOSPHATE GROUP

P(1)	O(2^i)	O(3^{ii})	O(5)	O(9)
O(2^i)	1.56(1)	2.42(1)	2.53(1)	2.54(1)
O(3^{ii})	103.4(4)	1.526(6)	2.557(9)	2.517(9)
O(5)	109.7(5)	113.7(5)	1.528(7)	2.51(1)
O(9)	109.8(5)	110.2(5)	109.9(4)	1.544(8)

P(2)	O(6^{iii})	O(8)	O(12^{iv})	O(13)
O(6^{iii})	1.500(8)	2.51(1)	2.50(1)	2.477(8)
O(8)	112.4(5)	1.525(9)	2.54(1)	2.47(1)
O(12^{iv})	112.9(5)	113.9(5)	1.506(9)	2.53(1)
O(13)	105.3(4)	103.5(4)	108.0(4)	1.616(7)

P(3)	O(4^v)	O(10^{vi})	O(11^{iv})	O(13)
O(4^v)	1.510(8)	2.54(1)	2.55(1)	2.457(9)
O(10^{vi})	114.3(5)	1.51(1)	2.48(1)	2.460(9)
O(11^{iv})	114.8(5)	110.2(5)	1.52(1)	2.51(1)
O(13)	104.3(4)	104.7(5)	107.6(4)	1.599(6)

Note. Symmetry codes. (i): x, $1/2 - y$, $1/2 + z$. (ii): $1 + x$; $1/2 - y$; $1/2 + z$. (iii): $1 - x$, $1/2 + y$, $1/2 - z$. (iv): $1 - x$, $1 - y$, $-z$. (v): $-x$, $1/2 + y$, $-1/2 - z$. (vi): $-x$, $1 - y - z$. (vii): $1 + x$, y, z. (viii): x, $1/2 - y$, $z - 1/2$. (ix): $1 - x$; $y - 1/2$; $1/2 - z$.

TABLE V

DISTANCES (Å) AND ANGLES (°) IN THE MoO$_6$ OCTAHEDRA

Mo(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.666(8)	2.85(1)	2.70(1)	2.77(1)	2.726(9)	3.79(1)
O(2)	100.9(4)	2.013(9)	4.01(1)	2.752(9)	2.71(1)	2.84(1)
O(3)	93.5(5)	165.6(4)	2.032(9)	2.87(1)	3.009(9)	2.66(1)
O(4)	97.2(3)	86.2(3)	90.5(4)	2.015(7)	4.00(1)	2.82(1)
O(5)	95.1(3)	84.4(3)	96.1(4)	165.7(3)	2.015(6)	2.75(1)
O(6)	172.3(5)	86.4(4)	79.4(4)	85.7(3)	83.1(3)	2.136(9)

Mo(2)	O(7)	O(8)	O(9)	O(10)	O(11)	O(12)
O(7)	1.678(8)	2.82(1)	2.72(1)	2.834(9)	2.77(2)	3.90(1)
O(8)	100.8(4)	1.977(8)	3.92(1)	2.72(1)	2.81(1)	2.83(1)
O(9)	95.5(4)	163.5(3)	1.983(8)	2.79(1)	2.88(1)	2.71(1)
O(10)	100.0(4)	85.9(4)	88.6(4)	2.010(8)	4.00(1)	2.85(1)
O(11)	96.2(4)	89.3(4)	91.7(4)	163.7(3)	2.027(9)	2.734(7)
O(12)	173.6(4)	84.1(3)	79.9(3)	84.3(3)	79.7(3)	2.232(7)

Note. The M–O distance are on the diagonal; above it are the O . . . O distances and below it are the O–M–O angles.

the other Mo(V) phosphates (*1–10*). One observes (Table V) one very short Mo–O bond (1.666–1.678 Å) and one abnormally long Mo–O distance (2.136–2.232 Å) whereas the four other Mo–O distances are normal (1.977–2.032 Å). It is worth pointing out that in all these Mo(V) phosphates, the Mo^{V}O$_6$ octahedron shares only five corners with other polyhedra of the host lattice, whereas the free one corresponds to the abnormally short Mo–O distance. This particular feature of Mo(V) which imposes one oxygen atom to be "free" with respect to the PO$_4$ tetrahedra allows a great flexibility
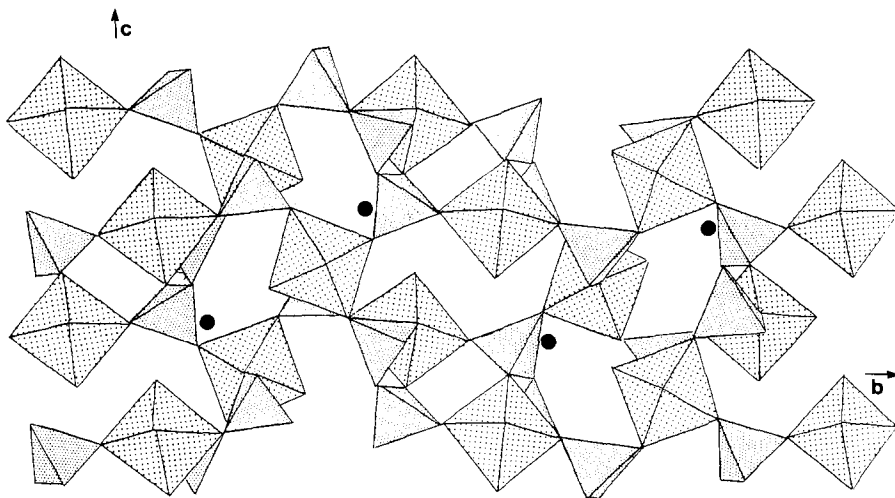

FIG. 1. Projection of ζ-NaMo$_2$P$_3$O$_{13}$ onto *bc* plane.

of the structure and is certainly at the origin of the various [Mo$_2$P$_3$O$_{13}$]$_\infty$ frameworks observed. Although they are different from each other, the [Mo$_2$P$_3$O$_{13}$]$_\infty$ frameworks have a common feature which is reflected in the existence of MoP$_2$O$_{11}$ units built up from one P$_2$O$_7$ group sharing two of its corners with the same MoO$_6$ octahedron (Fig. 2; see also Fig. 1). In ζ-NaMo$_2$P$_3$O$_{13}$ these MoP$_2$O$_{11}$ units share their corners along a exactly in the same way as in β (4, 5)-, γ (6)-, and ε-[Mo$_2$P$_3$O$_{13}$] frameworks forming infinite [MoP$_2$O$_{10}$]$_\infty$ chains (Fig. 3A). Two single [MoP$_2$O$_{10}$]$_\infty$ chains share the corners of their polyhedra in such a way that one tetrahedron of one chain is linked to one MoO$_6$ octahedron of the other chain. It results in double infinite ribbons [Mo$_2$P$_4$O$_{18}$]$_\infty$ running along a (Fig. 3B) which are similar to those observed for γ-CsMo$_2$P$_3$O$_{13}$ (6) and ε-NaMo$_2$P$_3$O$_{13}$ (10).

Another interesting feature concerns the existence of infinite [MoPO$_8$]$_\infty$ chains running along a (Fig. 4A) in which one single PO$_4$ tetrahedron alternates with one MoO$_6$ octahedron. Such infinite chains are often encountered in molybdenum phosphates and especially in the β-, γ-, and ε-[Mo$_2$P$_3$O$_{13}$]$_\infty$ frameworks. But contrary to the latter AMo$_2$P$_3$O$_{13}$ oxides, one does not observe double ribbons [Mo$_2$P$_2$O$_{14}$]$_\infty$ formed of two single [MoPO$_8$]$_\infty$ chains sharing the corners of their polyhedra (Fig. 4B). In the (010) plane those [MoPO$_8$]$_\infty$ chains share only some of the corners of their polyhedra-forming [MoPO$_7$]$_\infty$ layers (Fig.
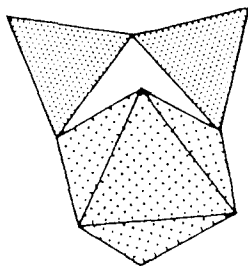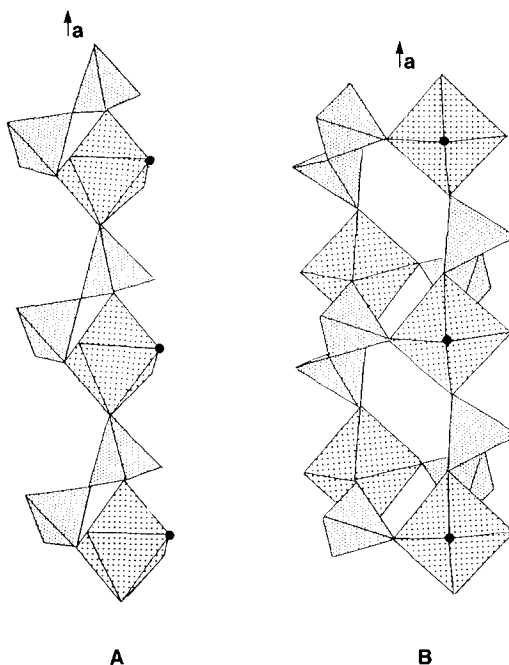

FIG. 3. (a) [MoP$_2$O$_{10}$]$_\infty$ chains running along a. (b) [Mo$_2$P$_4$O$_{18}$]$_\infty$ ribbons running along a.

FIG. 2. MoP$_2$O$_{11}$ units.

4C) which exhibit some similarity with the layers observed for MoPO$_5$ (Fig. 4D). In both layers only one type of polyhedra in each chain is connected to the next chain. However, the nature of those polyhedra differs in the two structures; the MoO$_6$ octahedra of one chain share their corners with the PO$_4$ tetrahedra of the next [MoPO$_8$]$_\infty$ chain in ζ-NaMo$_2$P$_3$O$_{13}$ (Fig. 4C), whereas two successive [MoPO$_8$]$_\infty$ chains share always the corners of their MoO$_6$ octahedra in α-MoPO$_5$ (Fig. 4D)-forming octahedral [MoO$_3$]$_\infty$ perovskite-type chains. Thus the [MoPO$_7$]$_\infty$ layer of α-MoPO$_5$ can be deduced from that of ζ-NaMo$_2$P$_3$O$_{13}$ by a translation of one [MoPO$_8$]$_\infty$ chain out of two along a, i.e., along the chain of about $a/2$. MoPO$_5$ also differs from ζ-NaMo$_2$P$_3$O$_{13}$ in that its [MoPO$_5$]$_\infty$ framework is only built up from [MoPO$_7$]$_\infty$ layers sharing the corners of their polyhedra, whereas the ξ-[Mo$_2$P$_3$O$_{13}$]$_\infty$ framework results from the as-

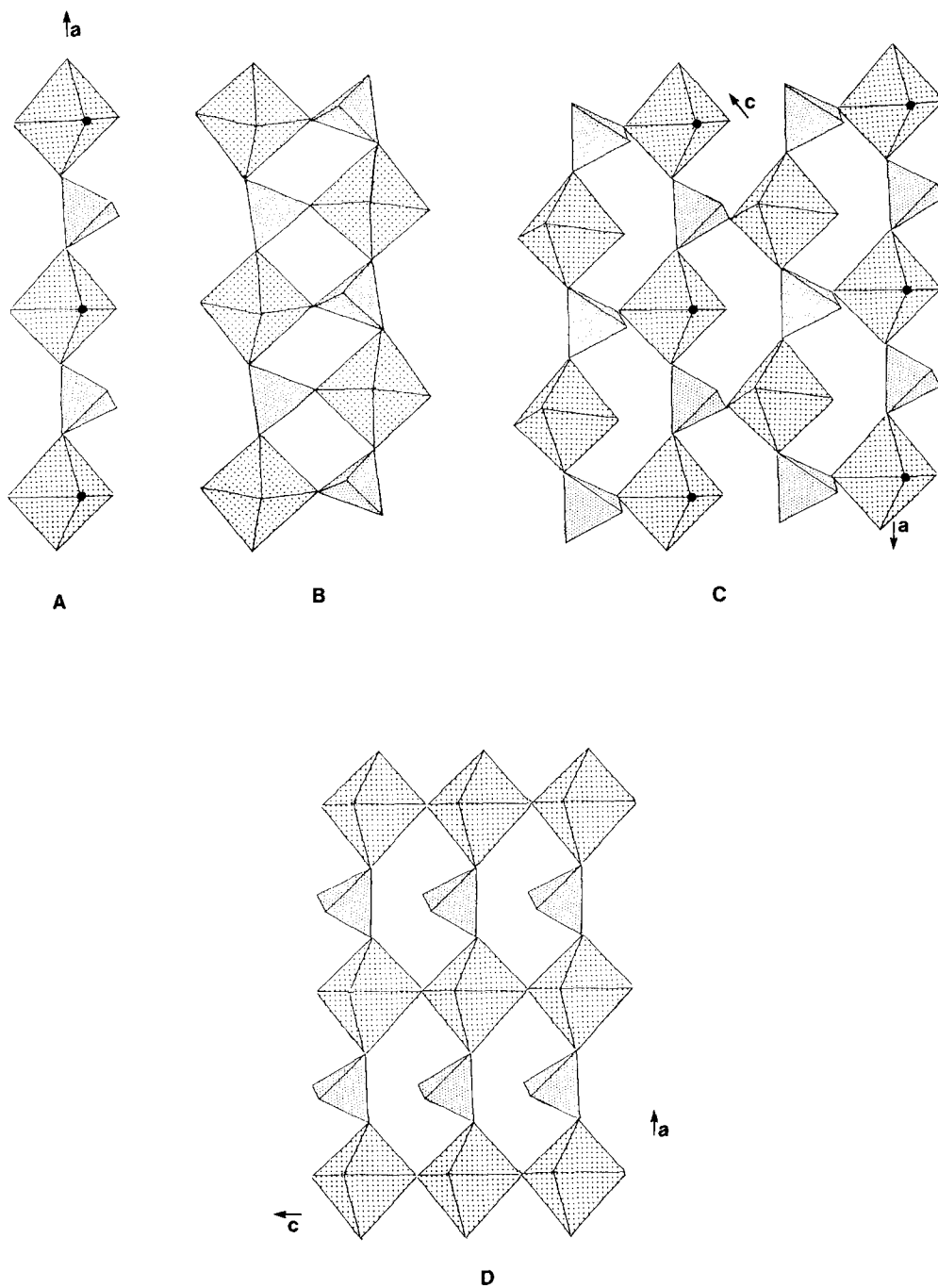FIG. 4. (a) $[MoPO_8]_\infty$ chains running along a. (b) $[Mo_2P_2O_{14}]_\infty$ ribbons. (c) $[MoP_2O_7]_\infty$ layers perpendicular to b axis. (d) $[MoP_4O_7]_\infty$ layers in α-$MoPO_5$.

TABLE VI

SURROUNDING OF Na$^+$ WITH
Na–O < 3.20 Å

Na–O(12$^{\text{iii}}$)	2.376(9) Å
Na–O(1$^{\text{ii}}$)	2.395(9) Å
Na–O(2)	2.447(8) Å
Na–O(7$^{\text{viii}}$)	2.54(1) Å
Na–O(13$^{\text{ix}}$)	2.62(1) Å
Na–O(3$^{\text{vii}}$)	2.72(1) Å
Na–O(6$^{\text{vii}}$)	2.93(1) Å
Na–O(10$^{\text{ii}}$)	3.18(1) Å

Note. Symmetry codes are given in the footnote to Table IV.

semblage along b of [MoPO$_7$]$_\infty$ layers with [Mo$_2$P$_4$O$_{18}$]$_\infty$ ribbons (Fig. 1).

The ζ-[Mo$_2$P$_3$O$_{13}$]$_\infty$ lost lattice delimits large cavities which are completely occupied by the sodium cations. The Na–O distances, ranging from 2.376 to 3.18 Å (Table VI), are in agreement with the sum of ionic radii. The rather great size of the windows which border these cavities leads us to consider possible ionic conduction properties of this structure. Nevertheless the smaller B factor of Na$^+$ (1.5 Å^2) compared to that of the ε-form (4.5 Å^2) suggests a much smaller mobility of Na$^+$.

Appendix

Table of Refined Displacement Parameter Expressions—Betas

Name	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	0.00242(9)	0.00022(1)	0.00132(5)	−0.00009(7)	0.0018(1)	−0.00008(5)
Mo(2)	0.0040(1)	0.00016(1)	0.00227(6)	−0.00006(7)	0.0042(1)	0.00011(5)
P(1)	0.0035(4)	0.00021(3)	0.0020(2)	−0.0002(2)	0.0029(4)	0.0000(2)
P(2)	0.0046(4)	0.00018(3)	0.0020(2)	0.0003(2)	0.0036(4)	0.0003(2)
P(3)	0.0028(4)	0.00032(3)	0.0023(2)	0.0003(2)	0.0036(4)	0.0001(2)
Na	0.009(1)	0.0010(1)	0.0059(6)	0.0010(6)	0.004(1)	0.0004(5)
O(1)	0.015(2)	0.0003(1)	0.0006(7)	0.0003(8)	0.001(2)	−0.0000(5)
O(2)	0.007(1)	0.0004(1)	0.0041(7)	0.0011(6)	0.009(1)	0.0012(5)
O(3)	0.002(1)	0.0009(1)	0.0042(7)	−0.0010(8)	0.003(1)	−0.0005(7)
O(4)	0.009(1)	0.0005(1)	0.0031(7)	−0.0014(7)	0.006(1)	−0.0013(5)
O(5)	0.010(2)	0.00016(9)	0.0015(7)	−0.0004(7)	0.000(2)	−0.0003(5)
O(6)	0.010(2)	0.0005(1)	0.0023(8)	−0.0005(8)	0.002(2)	0.0006(5)
O(7)	0.013(2)	0.0008(2)	0.0029(8)	0.0015(9)	0.005(2)	0.0002(7)
O(8)	0.012(1)	0.00014(9)	0.010(1)	0.0001(6)	0.015(2)	0.0003(5)
O(9)	0.015(1)	0.00027(9)	0.0028(6)	0.0012(7)	0.010(1)	0.0010(5)
O(10)	0.007(1)	0.0006(1)	0.0073(8)	−0.0002(7)	0.0011(1)	0.0003(6)
O(11)	0.004(1)	0.0005(1)	0.0045(7)	−0.0003(6)	0.005(1)	−0.0004(5)
O(12)	0.006(1)	0.0006(1)	0.0020(6)	−0.0003(6)	0.006(1)	−0.0004(5)
O(13)	0.006(1)	0.0005(1)	0.0020(7)	0.0021(7)	0.002(1)	0.0004(5)

Note. The form of the anisotropic displacement is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

References

1. P. KIERKEGAARD AND J. M. LONGO, *Acta Chem. Scand.* **427,** 24 (1970).

2. L. KH. MINACHEVA, A. S. ANTSYSHKINA, A. V. LAVROV, V. G. SAKHAROVA, V. P. NIKOLAEV, AND M. A. PORAI-KOSHITS, *Russ. J. Inorg. Chem.* **51,** 24 (1979).

3. A. LECLAIRE, J. C. MONIER, AND B. RAVEAU, *J. Solid State Chem.* **147,** 48 (1983).

4. K. H. LII AND R. C. HAUSHALTER, *J. Solid State Chem.* **320,** 69 (1987).

5. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *Acta Crystallogr.* in press (1990).
6. J. J. CHEN, K. H. LII, AND S. L. WANG, *J. Solid State Chem.* **204,** 76 (1988).
7. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *Z. Kristallogr.* **77,** 188 (1989).
8. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *J. Solid State Chem.* **250,** 80 (1989).
9. K. H. LII, D. C. JOHNSTON, D. P. GOSHORN, AND R. C. HAUSHALTER, *J. Solid State Chem.* **31,** 71 (1987).
10. A LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *J. Solid State Chem.* **89,** 10 (1990).