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A Molybdenophosphate with a Mixed Valence of Molybdenum, Mo(VI)–Mo(V): $NaMo_3P_3O_{16}$

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A new sodium molybdenophosphate, $NaMo_3P_3O_{16}$, has been isolated. It crystallizes in the triclinic system, $P\bar{1}$, $a = 6.4023\ (6)$ Å, $b = 7.6097\ (10)$ Å, $c = 12.7395\ (14)$ Å, $\alpha = 80.031\ (11)^\circ$, $\beta = 79.039\ (9)^\circ$, $\gamma = 83.517\ (11)^\circ$. The originality of this oxide, whose structure was solved from a single crystal by X-ray diffraction, consists of the mixed valency of molybdenum, Mo(V)–Mo(VI) and of the ability of molybdenum to present a trigonal bipyramidal coordination. Two independent molybdenum atoms are octahedrally coordinated and form with PO_4 groups $[MoPO_8]_\infty$ chains running along **a**; the third independent molybdenum atom forms MoO_5 bipyramids which share two corners with PO_4 tetrahedra, leading to $[MoPO_7]_\infty$ chains running along **a**. The octahedral and bipyramidal sites are occupied by Mo(V) and Mo(VI), respectively, according to the formula $NaMo^{V}_{2}Mo^{VI}P_3O_{16}$. The $[Mo_3P_3O_{16}]_\infty$ framework can be described by the association of these chains, connected through PO_4 tetrahedra, forming five-sided tunnels where the sodium ions are located. © 1991 Academic Press, Inc.

Introduction

The previous investigations of molybdenum phosphates have shown the great ability of the phosphate matrix to stabilize pentavalent molybdenum in an octahedral coordination forming molybdenyl cations *(1–10)*, contrary to pure octahedral structures for which such isolated Mo(V) species are very rarely observed. Contrary to tungsten, molybdenum does not often form mixed valent oxides, Mo(V)–Mo(VI), if one excepts the well known molybdenum bronzes A_xMoO_3 *(11)*. Another peculiarity of this element is the coexistence of several coordinations in the same matrix even for a mixed valence of molybdenum as shown for both forms of the oxide Mo_4O_{11} *(12)*, which exhibit the octahedral and tetrahedral coordinations simultaneously. No mixed valence of molybdenum involving the oxidation states V and VI has been observed up to now in molybdenophosphates. The present paper reports on the crystal structure of such a mixed valent molybdenum phosphate, $NaMo_3P_3O_{16}$, in which molybdenum exhibits, besides the usual octahedral coordination, the rare trigonal bipyramidal coordination.

Synthesis

Pure powder of the phosphate $NaMo_3P_3O_{16}$ was prepared in two steps, starting from mixture in adequate molar ratios in order to obtain the above formula. First an adequate mixture of Na_2CO_3, $H(NH_4)_2PO_4$, and MoO_3 was ground and heated up to 673 K in air to eliminate CO_2, H_2O, and NH_3. In the second step the appropriate quantity

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TABLE I

INTERPLANAR DISTANCES (Å)

h	k	l	d_{obs}	d_{calc}	I/I_0	h	k	l	d_{obs}	d_{calc}	I/I_0
1	0	1	6.029	6.0267	53	1	3	0		2.382	
0	1	2	5.145	5.171	7	1	2	−3	2.335	2.339	3
1	1	1	5.086	5.093	13.5	0	3	3	2.293	2.294	4
1	1	0	5.012	5.008	5	2	−2	1	2.284	2.282	5
1	0	2	4.844	4.840	6	−1	3	1	2.246	2.245	14.5
1	1	2	4.453	4.457	52.5	0	2	5	2.225	2.226	12
1	1	−1	4.287	4.291	52.5	1	−1	5	2.210	2.208	5.5
−1	1	1		4.278		2	1	−3	2.187	2.188	8.5
0	0	3	4.122	4.118	60.5	2	−1	4		2.186	
0	1	3	3.869	3.863	2.5	2	2	−2	2.144	2.146	5
0	2	1	3.741	3.739	100	1	−2	4		2.142	
1	1	3	3.645	3.646	4	3	0	1	2.120	2.120	6
−1	1	2		3.641		1	3	4		2.120	
0	2	2	3.440	3.442	39	0	3	4	2.105	2.105	7
0	−2	1		3.4302		1	1	6	2.092	2.092	20
0	−1	3	3.396	3.390	15.5	3	0	2		2.092	
1	2	0	3.321	3.331	18.5	0	0	6	2.061	2.059	12.5
1	2	2	3.273	3.265	2.5	−1	3	3	2.044	2.043	5
2	0	1	3.173	3.170	30	1	1	−5	2.027	2.028	8
1	−1	3	3.127	3.123	17	0	−3	3	1.999	1.998	11.5
−1	2	0	3.091	3.097	29	3	−1	1	1.984	1.983	5
0	0	4		3.089		−2	1	4		1.983	
2	0	2	3.015	3.013	69	−1	2	5	1.974	1.973	8
2	1	0	2.978	2.977	31	−3	1	0	1.968	1.969	8.5
1	−2	1		2.974		1	2	6		1.967	
2	1	2	2.955	2.959	13.5	3	2	2	1.941	1.940	10
−2	0	1	2.919	2.917	9.5	2	2	−3		1.940	
−2	1	0	2.806	2.807	18.5	3	2	1	1.937	1.938	16.5
2	−1	1	2.803	2.797	26	1	3	5		1.937	
0	−1	4	2.710	2.709	4	3	1	4	1.911	1.910	4
1	2	−2	2.683	2.684	4.5	0	−1	6		1.910	
−2	1	1		2.681		1	−2	5	1.892	1.892	8
2	−1	2	2.657	2.650	4.5	1	3	−3		1.893	
0	−2	3	2.576	2.574	2	0	4	2	1.871	1.870	13.5
2	2	0	2.506	2.504	6.5	−1	1	6	1.858	1.858	6
0	3	0	2.490	2.490	5	2	3	−2	1.806	1.806	5
1	1	5	2.467	2.467	9	0	−3	4		1.806	
1	0	5	2.449	2.449	9	0	1	7	1.781	1.781	6.5
0	3	2		2.445		0	0	7	1.766	1.765	5
2	0	4	2.422	2.420	13	−1	4	1	1.757	1.757	6
1	3	2	2.405	2.403	7	−1	4	2	1.729	1.728	12
1	1	−4	2.384	2.382	4	0	3	6	1.724	1.724	12

of molybdenum was added and the finely ground mixture was sealed in an evacuated silica ampoule and heated up to 973 K for 2 days.

Single crystals of this phase were prepared by a similar method, but using an excess of molybdenum oxide and heating at 1073 K instead of 973 K in the second step of synthesis. Purple single crystals for this study were indeed isolated from a mixture of nominal composition $NaMo_6P_3O_{23}$.

The powder X-ray pattern (Table I) of

TABLE II

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS AND STRUCTURE REFINEMENT PARAMETERS

1. Crystal data	
Space group	$P\bar{1}$
Cell dimensions	$a = 6.4023$ (6) Å
	$b = 7.6097$ (10) Å
	$c = 12.7395$ (14) Å
	$\alpha = 80.031$ (11)°
	$\beta = 79.039$ (9)°
	$\gamma = 83.517$ (11)°
Volume	598 (2) Å^3
Z	2
2. Intensity measurements	
λ (Mo$K\alpha$)	0.71073 Å
Scan mode	$\omega - 2/3\ \theta$
Scan width (°)	$1.10 + 0.35 \tan \theta$
Slit aperture (mm)	$1 + \tan \theta$
Max θ (°)	45
Standard reflections	3 measured every 3000 sec (no decay)
Reflections with $I > 3\sigma$	2839
μ (mm^{-1})	3.555
3. Structure solution and refinement	
Parameters refined	208
Agreement factors	$R = 0.032$, $R_w = 0.032$
Weighting scheme	$w = f(\sin \theta/\lambda)$
Δ/σ max	0.005
$d\rho$ max	1.172 e/Å^3

the phase was indexed in a triclinic cell in agreement with the parameters obtained from the single crystal study (Table II).

Structure Determination

A purple crystal with dimensions 0.072 × 0.048 × 0.024 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 atoms 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 $R = 0.032$ and $R_w = 0.032$ and to the atomic parameters of Table III.

Description of the Structure and Discussion

This molybdophosphate exhibits a very original $[Mo_3P_3O_{16}]_\infty$ host lattice built up from corner sharing MoO_6 octahedra, MoO_5 trigonal bipyramids, and PO_4 tetrahedra, forming cages where the sodium ions are located (Fig. 1).

The three independent PO_4 tetrahedra, P(1), P(2), and P(3), share their apices with two MoO_5 bipyramids + two MoO_6 octahedra, four MoO_6 octahedra, and one MoO_5 bipyramid + three MoO_6 octahedra, respec-

TABLE III

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	B (Å^2)
Mo(1)	0.20382(7)	0.21539(6)	0.54109(4)	0.534(6)
Mo(2)	0.40953(8)	0.75135(6)	0.16255(4)	0.620(6)
Mo(3)	0.05866(7)	0.20623(6)	0.14284(4)	0.628(6)
P(1)	0.5726(2)	0.1656(2)	0.1026(1)	0.57(2)
P(2)	0.3077(2)	0.8543(2)	0.4210(1)	0.56(2)
P(3)	0.0645(2)	0.4818(2)	0.3166(1)	0.55(2)
Na	0.5981(5)	0.3333(5)	0.3316(3)	2.71(1)
O(1)	0.1922(8)	0.0498(6)	0.6451(4)	1.71(9)
O(2)	−0.1002(7)	0.2238(6)	0.5216(4)	1.16(7)
O(3)	0.5179(6)	0.2567(5)	0.5220(3)	0.85(6)
O(4)	0.3039(7)	0.0525(5)	0.4278(3)	1.10(7)
O(5)	0.1366(6)	0.4249(5)	0.6224(3)	0.89(7)
O(6)	0.2269(6)	0.4094(5)	0.3892(3)	0.73(6)
O(7)	0.0872(8)	0.3130(7)	0.0163(4)	1.59(8)
O(8)	−0.0206(6)	0.3298(5)	0.2735(3)	0.78(6)
O(9)	−0.2587(6)	0.2028(5)	0.1665(3)	0.82(6)
O(10)	0.1266(7)	−0.0145(6)	0.1344(4)	1.26(7)
O(11)	0.3575(6)	0.2384(5)	0.1630(3)	0.85(6)
O(12)	0.6057(7)	0.5952(6)	0.1821(4)	1.43(8)
O(13)	0.3770(7)	0.7329(5)	0.0120(3)	1.06(7)
O(14)	0.1603(7)	0.6064(6)	0.2160(3)	1.10(7)
O(15)	0.3542(8)	0.8408(6)	0.3012(3)	1.52(8)
O(16)	0.5772(6)	0.9652(5)	0.1015(3)	0.87(6)

Note. The equivalent thermal factor B is deduced from the anisotropic thermal factors β_{ij} as $B = 4/3\ [\beta_{11} a^2 + \beta_{22} b^2 + \beta_{33} c^2 + \beta_{12}\, ab \cos \gamma + \beta_{13}\, ac \cos \beta + \beta_{23}\, bc \cos \alpha]$.

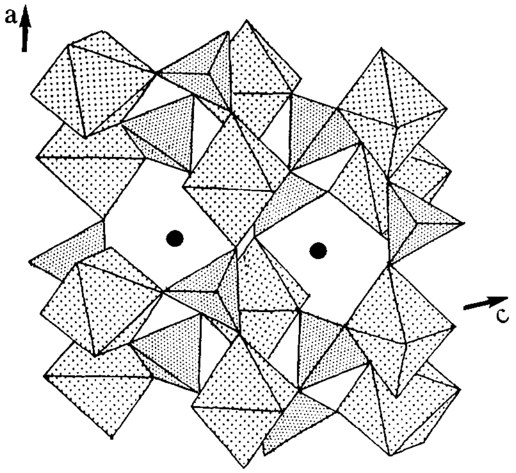

FIG. 1. Projection of $NaMo_3P_3O_{16}$ along **b**.

tively. Their geometry is usual with four nearly equal P–O distances (Table IV).

The two independent MoO_6 octahedra, Mo(1) and Mo(2), exhibit an almost regular "O_6" octahedral configuration. Mo(1) shares its corners with five PO_4 tetrahedra, whereas Mo(2) is linked to four PO_4 tetrahedra and one MoO_5 bipyramid. Both octahedra are characterized by a free apex (O(1) and O(12), respectively), with a short Mo–O distance (1.65–1.66 Å) corresponding to this free oxygen atom, and a long distance (2.21–2.42 Å), the other four bonds being normal (Table IV). This geometry of MoO_6 octahedra, in which molybdenum is off-centered, tending to form molybdenyl ions, is characteristic of Mo(V). The sum of the electrostatic valences calculated with the Zachariasen curves (*13*) confirms that both octahedral sites are occupied by pentavalent molybdenum (calculated valencies of 5.1 and 5.2 for Mo(1) and Mo(2), respectively), whereas an oxidation state close to six (5.9) is obtained for molybdenum in bipyramidal coordination, leading to the formula $Na(Mo^{V}_{2})_{oct}(Mo^{VI})_{bipy}P_3O_{16}$. This phase is the eleventh Mo(V) phosphate that was isolated (*1–10*); it confirms the great ability of phosphate matrix to stabilize pentavalent molybdenum.

The bipyramidal coordination of molybdenum (Mo(3)) is quite unusual. A bipyramidal coordination has however been observed for Mo(VI) in $Bi_2(MoO_4)_3$ (*14*). Nevertheless, in the latter oxide, Mo is off-centered in its bipyramid so that it forms in fact a MoO_4 tetrahedron. This is not the case here as shown from the interatomic Mo–O distances (Table IV). One indeed observes (Fig. 2) three normal and almost equal Mo–O distances which correspond to three oxygen atoms shared with PO_4 tetrahedra (two apical oxygen O(9) and O(11) and one equatorial oxygen O(8)), one short Mo–O bond (1.66 Å) which corresponds to the free O(7) corner, and an intermediate Mo–O distance (1.70 Å) which corresponds to the Mo(3)–O(10)–Mo(2) bond.

The three-dimensional framework $[Mo_3P_3O_{16}]_\infty$ exhibits infinite $[MoPO_8]_\infty$ chains of corner sharing MoO_6 and PO_4 polyhedra running along **a**, in which one MoO_6 octahedron alternates with one PO_4 tetrahedron (Fig. 3a). Such a feature is characteristic of many molybdenum phosphates; it has indeed been observed for $MoPO_5$ (*1*) and $MoAlP_2O_9$ (*10*).

Each of these chains shares the corners of its octahedra and tetrahedra with the tetrahedra and octahedra of another chain,

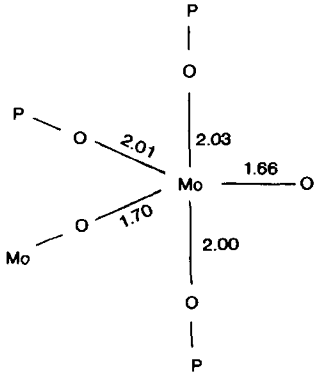

FIG. 2. The bipyramid MoO_5.

TABLE IV

DISTANCES (Å) AND ANGLES (°) IN COORDINATION POLYHEDRA, MoO$_6$ OCTAHEDRA[a]

Mo(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.660(4)	2.752(6)	2.816(6)	2.721(7)	2.808(6)	3.866(6)
O(2)	97.0(2)	2.001(4)	3.994(6)	2.902(6)	2.870(6)	2.780(6)
O(3)	98.9(2)	163.9(2)	2.033(4)	2.736(6)	2.812(6)	2.778(5)
O(4)	94.5(2)	92.1(2)	84.7(2)	2.029(4)	4.008(6)	2.681(6)
O(5)	99.3(2)	91.3(2)	88.1(2)	165.2(2)	2.012(4)	2.938(6)
O(6)	172.7(2)	82.4(2)	81.6(2)	78.3(2)	88.0(2)	2.213(4)

Mo(2)	O(10$^{\mathrm{i}}$)	O(12)	O(13)	O(14)	O(15)	O(16)
O(10$^{\mathrm{i}}$)	2.425(4)	4.077(7)	2.844(6)	2.890(7)	2.803(7)	2.826(6)
O(12)	178.7(2)	1.652(5)	2.830(6)	2.795(7)	2.786(7)	2.823(7)
O(13)	79.4(2)	101.3(2)	1.998(4)	2.769(6)	3.884(7)	2.798(6)
O(14)	81.2(2)	99.9(2)	88.0(2)	1.987(5)	2.754(7)	3.936(7)
O(15)	78.7(2)	100.7(2)	158.1(2)	88.5(2)	1.958(5)	2.739(6)
O(16)	78.5(2)	100.4(2)	88.5(2)	159.7(2)	87.2(2)	2.011(4)

MoO$_5$ bipyramid

Mo(3)	O(7)	O(8)	O(9)	O(10)	O(11)
O(7)	1.662(5)	3.240(6)	2.743(6)	2.691(7)	2.730(6)
O(8)	123.8(2)	2.006(4)	2.588(6)	3.362(6)	2.644(6)
O(9)	96.6(2)	80.5(2)	1.999(4)	2.813(6)	3.976(7)
O(10)	106.2(2)	129.8(2)	98.6(2)	1.703(4)	2.667(6)
O(11)	95.0(2)	82.0(2)	162.3(2)	90.9(2)	2.025(4)

PO$_4$ tetrahedra

P(1)	O(9$^{\mathrm{ii}}$)	O(11)	O(13$^{\mathrm{iii}}$)	O(16$^{\mathrm{iv}}$)
O(9$^{\mathrm{ii}}$)	1.546(4)	2.449(5)	2.484(6)	2.517(6)
O(11)	105.1(2)	1.539(4)	2.526(6)	2.529(6)
O(13$^{\mathrm{iii}}$)	108.0(2)	111.2(2)	1.523(4)	2.509(9)
O(16$^{\mathrm{iv}}$)	110.1(2)	111.3(2)	110.8(2)	1.524(4)

P(2)	O(2$^{\mathrm{v}}$)	O(3$^{\mathrm{vi}}$)	O(4$^{\mathrm{i}}$)	O(15)
O(2$^{\mathrm{v}}$)	1.520(4)	2.429(6)	2.523(6)	2.527(6)
O(3$^{\mathrm{vi}}$)	105.1(2)	1.540(4)	2.530(6)	2.505(6)
O(4$^{\mathrm{i}}$)	112.0(3)	111.4(2)	1.523(4)	2.425(6)
O(15)	112.6(3)	110.1(2)	105.8(3)	1.517(5)

P(3)	O(5$^{\mathrm{v}}$)	O(6)	O(8)	O(14)
O(5$^{\mathrm{v}}$)	1.540(4)	2.536(6)	2.442(6)	2.521(6)
O(6)	112.2(2)	1.516(4)	2.542(6)	2.523(6)
O(8)	104.3(2)	111.8(2)	1.553(4)	2.450(6)
O(14)	110.6(2)	112.0(2)	105.4(2)	1.527(4)

Oxygens atoms surrounding Na$^+$

Na–O(1)	3.058(6)
Na–O(3)	2.365(5)
Na–O(4)	2.956(6)
Na–O(5)	2.841(6)
Na–O(6)	2.386(5)
Na–O(8)	2.411(5)
Na–O(9)	2.457(6)
Na–O(11)	3.091(6)
Na–O(12)	2.752(6)

Note. Symmetry code: i: x, $1 + y$, z; ii: $1 + x$, y, z; iii: $1 - x$, $1 - y$, $-z$; iv: x, $y - 1$, z; v: $-x$, $1 - y$, $1 - z$; vi: $1 - x$, $1 - y$, $1 - z$.

[a] The M–Oi bonds are on the diagonal, above it are the O(i) ··· O(j) distances and below the $O(i)$ ··· M ··· O(j) angles.

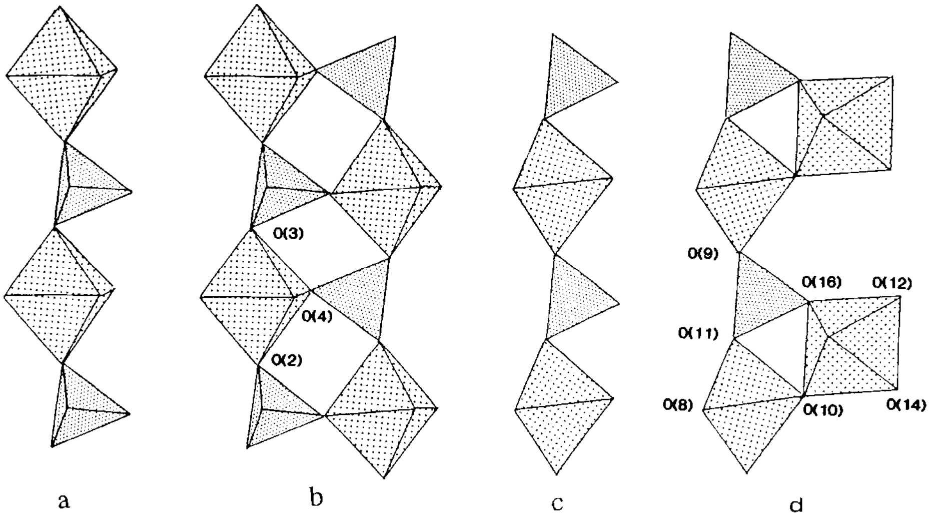

FIG. 3. (a) Infinite chains $[MoPO_8]_2$ along **a**, (b) double chains $[Mo_2P_2O_{14}]_\infty$ along **a**, (c) infinite chains $[MoPO_7]_\infty$ along **a**, (d) infinite chains $[Mo_2PO_{11}]$ along **a**.

respectively, forming double chains $[Mo_2P_2O_{14}]_\infty$ (Fig. 3b). Such double chains are generally observed in molybdenum phosphates as for instance in ε-$NaMo_2P_3O_{13}$ (*7*) and γ-$CsMo_2P_3O_{13}$ (*6*).

In a similar way, the MoO_5 bipyramids and the PO_4 tetrahedra form $[MoPO_7]_\infty$ chains running along **a** (Fig. 3c) in which one PO_4 tetrahedron alternates with one MoO_5 bipyramid. In fact the $[MoPO_7]_\infty$ chains are connected to the Mo(2) octahedra in such a way that each MoO_6 octahedron shares one corner with one MoO_5 bipyramid and one corner with one PO_4 tetrahedron, forming

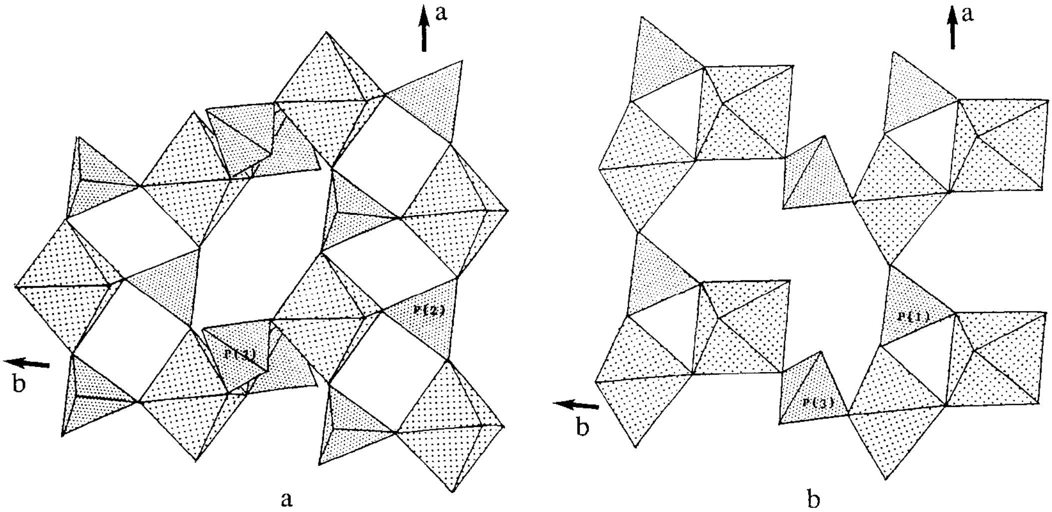

FIG. 4. The $P(3)O_4$ tetrahedra bonding. (a) the $[Mo_2P_2O_{14}]_\infty$ double chains, (b) the $[Mo_2PO_{11}]$ chains.

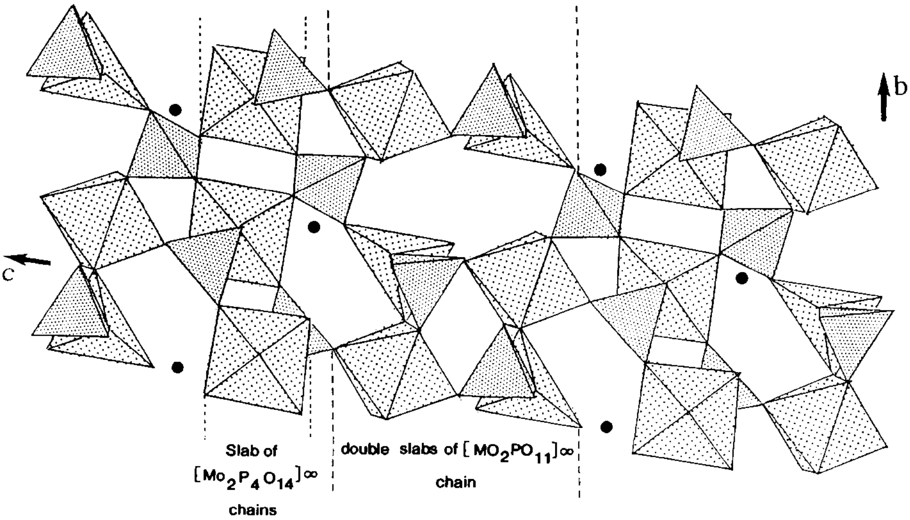

FIG. 5. Projection of $NaMo_3P_3O_{16}$ along a showing the stacking of the chains.

$[Mo_2PO_{11}]_\infty$ chains (Fig. 3d). Note the Mo_2O_{10} units built up from one MoO_6 octahedron and one MoO_5 bipyramid, which represent the only connection between Mo polyhedra in this structure.

Thus the framework $[Mo_3P_3O_{16}]_\infty$ can be described as the assemblage of $[Mo_2P_2O_{14}]_\infty$ double chains and $[Mo_2PO_{11}]_\infty$ chains, which are linked by single PO_4 tetrahedra. Indeed, laterally in the (001) plane, two successive $[Mo_2P_2O_{14}]_\infty$ chains are linked by PO_4 tetrahedra (P(3)) (Fig. 4a), whereas two successive $[Mo_2PO_{11}]_\infty$ chains are also linked by the same P(3) tetrahedra (Fig. 4b). Along **c** the layers of $[Mo_2PO_{11}]_\infty$ and $[Mo_2P_2O_{14}]_\infty$ chains are stacked in such a way that one layer of $[Mo_2P_2O_{14}]_\infty$ chains alternates with a double layer of $[Mo_2PO_{11}]_\infty$ chains as shown from the projection onto the (100) plane (Fig. 5). The P(3) tetrahedra ensure the junction between these two sorts of layers forming five-sided tunnels where the sodium cations are located with Na–O distances ranging from 2.36 Å to 3.09 Å (Table IV). One observes also an empty tunnel principally delimited by the free apices of the $Mo(2)O_6$ octahedra and of the $Mo(3)O_5$ pyramids.

Concluding Remarks

The synthesis of the molybdenum phosphate $NaMo_3P_3O_{16}$ shows the possibility of introducing in a phosphate matrix Mo(V) and Mo(VI) simultaneously. The bond valence calculations suggest an ordered distribution of Mo(V) and Mo(VI) in the octahedral and bipyramidal sites, respectively. This feature should be studied by EPR, if one takes into consideration that one MoO_5 bipyramid and one MoO_6 octahedron share one corner, forming isolated Mo_2O_{10} units within which electronic exchanges should be considered. This structure, and the previous ones we have studied, confirm the great flexibility of such mixed frameworks involving PO_4 tetrahedra and transition metal polyhedra. The existence of MoO_5 bipyramids is a very original feature of this structure, which opens the route to the synthesis of new molybdenophosphates.

References

1. P. Kierkegaard and J. M. Longo, *Acta Chem. Scand* **24,** 427 (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.* **24,** 51 (1979).
3. A. Leclaire, J. C. Monier, and B. Raveau, *J. Solid State Chem.* **48,** 147 (1983).
4. K. H. Lii and R. C. Haushalter, *J. Solid State Chem.* **69,** 320 (1987).
5. K. H. Lii, D. C. Johnston, D. P. Goshorn and R. C. Haushalter, *J. Solid State Chem.* **71,** 131 (1987).
6. J. J. Chen, K. H. Lii, and S. L. Wang, *J. Solid State Chem.* **76,** 204 (1988).
7. A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *J. Solid State Chem.* **89,** 10 (1990).
8. G. Costentin, M. M. Borel, A. Grandin, A. Leclaire, and B. Raveau, *J. Solid State Chem.* **89,** 83 (1990).
9. G. Costentin, M. M. Borel, A. Grandin, A. Leclaire, and B. Raveau, *J. Solid State Chem.* **89,** 31 (1990).
10. A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *Z. Kristallogr.* **190,** 135 (1990).
11. A. Manthiram and J. Gopalakrishnan, *Rev. Inorg. Chem.* **6,** 69 (1984).
12. L. Kihlborg, *Ark. Kemi* **21,** 365 (1963).
13. W. H. Zachariasen, *J. Less-Common Met.* **62,** 1 (1978).
14. A. F. Van Den Elzen and G. D. Rieck, *Acta Crystallogr. Sect. B* **29,** 2433 (1973).