A Molybdenum V Diphosphate with the KMoOP$_2$O$_7$ Structure: NaMoOP$_2$O$_7$

S. Ledain, A. Leclaire, M. M. Borel, J. Provost, and B. Raveau

Laboratoire CRISMAT, URA 1318 associé au CNRS-ISMRA, Université de Caen Boulevard du Maréchal Juin, 14050 Caen Cedex, France

A new molybdenum (V) diphosphate, NaMoOP$_2$O$_7$, with the KMoOP$_2$O$_7$ structure has been synthesized. This phase differs from KMoOP$_2$O$_7$ by its $P2_12_12_1$ space group ($a = 11.387$ Å, $b = 5.146$ Å, $c = 10.070$Å). In comparison to KMoOP$_2$O$_7$, the MoO$_6$ octahedra of NaMoOP$_2$O$_7$ are dramatically distorted, and the P$_2$O$_7$ groups exhibit a staggered configuration with a different distribution of the P-O distances.　© 1996 Academic Press, Inc.

INTRODUCTION

The investigation of the pentavalent molybdenum phosphates has allowed four diphosphates with the general formulation AMoOP$_2$O$_7$ (1–4) to be isolated for A = Cs, Rb, K, Li. All these diphosphates have in common the existence of P$_2$O$_7$ groups and MoO$_6$ octahedra with a free apex involving an abnormally short Mo–O bond, sharing their apices. However, the four compounds present fundamentally different structures. CsMoOP$_2$O$_7$ (1) has a tunnel structure closely related to that of NaTiP$_2$O$_7$ (5), whereas RbMoOP$_2$O$_7$ (2) is characterized by a layer structure also observed for CsNbOP$_2$O$_7$ (6). The tunnel structure of KMoOP$_2$O$_7$ (3) also encountered for KNbOP$_2$O$_7$ (7), exhibits similarities with CsMoOP$_2$O$_7$ (1); nevertheless the two structures differ by the conformation of their P$_2$O$_7$ groups, and by the size, the shape and orientations of their tunnels. The tridimensional framework of LiMoOP$_2$O$_7$ (4) is still very different from the three others structures since it can be described as an assemblage of P$_2$O$_7$ groups and MoO$_6$ octahedra forming intersecting tunnels occupied by lithium in tetrahedral coordination.

Clearly, the size of the interpolated cation influences dramatically the nature of the host lattice of these diphosphates due to the fact that the free apex of the MoO$_6$ octahedron allows a great flexibility of the [MoP$_2$O$_8$]$_\infty$ host lattice. The behavior of sodium, due to its size intermediate between that of potassium and lithium, is of interest. We report here on the new Mo(V) diphosphate NaMoOP$_2$O$_7$, whose structure is closely related to that of KMoOP$_2$O$_7$ (3).

EXPERIMENTAL

Single crystal of the title compound were grown from a nominal composition Na$_3$Mo$_3$P$_6$O$_{23}$. This compound has been synthesized in two steps: first, (NH$_4$)$_2$HPO$_4$, Na$_2$CO$_3$, and MoO$_3$ were mixed in an agate mortar in adequate ratios according to the composition Na$_3$Mo$_{2.16}$P$_6$O$_{23}$ and heated at 673 K in a platinum crucible to decompose the ammonium phosphate and the sodium carbonate. In a second step, the resulting mixture was then added to the required amount of molybdenum (0.84 mole) sealed in an evacuated silica ampoule then heated for 24 hr at 853 K and cooled at 5.5 K per hour down to 573 K. The sample was finally quenched to room temperature. In the resulting product some pale green crystals were extracted. The microprobe analysis of the latter confirmed the composition NaMoP$_2$O$_8$ deduced from the structure determination.

The compound NaMoOP$_2$O$_7$ could be prepared as a major phase in the form of well crystallized powder starting from the stoichiometric molar ratios Na : Mo : P = 1 : 1 : 2. Nevertheless, the powder X-ray diffractogram always evidenced some weak extra peaks, indicating the presence of impurity.

A pale green crystal with dimensions 0.064 × 0.051 × 0.051 mm^3 was selected for the structure determination.

The cell parameters were determined and refined by diffractometric techniques at 294 K with a least-squares refinement based upon 25 reflections with $18° \leq \theta \leq 22°$. The single crystal data were collected on a Enraf–Nonius diffractometer with the data collection of Table 1. The reflections were corrected for Lorentz, polarization, and absorption effects.

The magnetic measurements were performed on a powder sample from 4.5 K to 300 K with a SQUID magnetometer. After zero field cooling of the sample a field $B = 3000$ G was applied at 4.5 K. The magnetic moment was then measured in increasing temperature up to 300 K. The sample holder and core diamagnetism contribution have been subtracted.

TABLE 1
Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters for NaMoOP$_2$O$_7$

Crystal data	
Space group	$P2_12_12_1$
Cell dimensions	$a = 11.387(2)$, $b = 5.146(1)$, $c = 10.701(2)$ Å
Volume	627.3(2) Å^3
Z	4
ρ_{calc} (gcm^{-3})	3.27
Intensity measurements	
λ (Mo$K\alpha$)	0.7107 Å
Scan mode	$\omega-2/3\theta$
Scan width (°)	$1.3 + 0.35 \tan \theta$
Slit aperture (mm)	$1.10 + \tan \theta$
Max θ (°)	45
Standard reflections	3 per hour
Reflections measured	2932
Reflections with $I > 3\sigma$	550
μ (mm^{-1})	2.68
Structure solution and refinement	
Parameters refined	61
Agreement factors	$R = 0.041$, $R_w = 0.034$
Weighting scheme	$w = 1/\sigma$
Δ/σ max	< 0.005

RESULTS AND DISCUSSION

The systematic absences $h = 2n + 1$ for $h00$, $k = 2n + 1$ for $0k0$ and $l = 2n + 1$ for $00l$ are characteristic of the space group $P2_12_12_1$. One observes also a drastic weakening for $h = 2n + 1$ for $hk0$ and $k + l = 2n + 1$ for $0kl$ similar to the *Pnma* absences. Note also that the orthorhombic cell parameters of NaMoOP$_2$O$_7$ (Table 1) are close to those observed for the diphosphates KMoOP$_2$O$_7$ (3) and

TABLE 2
Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(Å^2)
Mo	0.1386(1)	0.248(1)	0.4110(1)	0.82(2)*
P(1)	0.4543(3)	0.756(4)	0.5941(3)	0.89(9)*
P(2)	0.3180(3)	0.755(3)	0.3665(3)	0.84(7)*
Na	0.3795(5)	0.269(8)	0.1876(5)	4.5(3)*
O(1)	0.1920(8)	0.215(4)	0.5528(7)	2.3(3)
O(2)	0.222(1)	−0.062(2)	0.3394(9)	1.6(3)
O(3)	0.2756(9)	0.466(2)	0.3412(9)	1.3(3)
O(4)	0.0448(8)	−0.068(2)	0.4571(8)	1.3(3)
O(5)	−0.0091(9)	0.462(2)	0.4350(8)	1.6(3)
O(6)	0.0770(8)	0.288(3)	0.2271(7)	1.6(3)
O(7)	0.3353(6)	0.774(4)	0.5153(7)	1.0(2)
O(8)	0.4282(8)	0.807(2)	0.2988(8)	1.3(2)

Note. The starred atoms have been refined anisotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $B = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i \cdot \mathbf{a}_j\beta_{ij}$.

TABLE 3
Distances (Å) and Angles (°) in Polyhedra

Mo	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	**1.645(8)**	2.72(2)	2.77(2)	2.45(2)	3.52(2)	3.74(2)
O(2)	95.4(7)	**2.01(1)**	2.78(2)	2.38(2)	3.90(2)	2.72(2)
O(3)	96.4(7)	86.3(5)	**2.06(1)**	4.00(2)	3.39(2)	2.73(2)
O(4)	83.4(7)	72.6(5)	158.8(5)	**2.01(1)**	2.80(2)	3.09(2)
O(5)	104.3(5)	150.7(5)	112.3(6)	88.1(4)	**2.02(1)**	2.58(2)
O(6)	177.7(4)	83.0(5)	82.0(4)	97.6(5)	77.8(4)	**2.099(8)**

P(1)	O(7)	O(6^i)	O(4^{ii})	O(5^{iii})
O(7)	**1.597(8)**	2.49(1)	2.63(1)	2.30(1)
O(6^i)	108(1)	**1.486(9)**	2.52(1)	2.54(1)
O(4^{ii})	115(1)	114(1)	**1.52(2)**	2.51(1)
O(5^{iii})	94(1)	114(1)	110(1)	**1.54(2)**

P(2)	O(3)	O(7)	O(8)	O(2^{iv})
O(3)	**1.59(2)**	2.54(2)	2.52(1)	2.50(2)
O(7)	105(1)	**1.611(8)**	2.56(1)	2.44(1)
O(8)	110(1)	112(1)	**1.47(1)**	2.48(1)
O(2^{iv})	110(1)	104(1)	115(1)	**1.47(2)**

Na–O(8^v) = 2.20(1)		Na–O(1^{vii}) = 2.99(4)	
Na–O(3) = 2.28(3)		Na–O(8) = 3.06(1)	
Na–O(8^{vi}) = 2.70(4)		Na–O(7^{vii}) = 3.07(4)	
Na–O(4^{vii}) = 2.81(2)		Na–O(1^{viii}) = 3.13(2)	
Na–O(2) = 2.96(3)			

symmetry codes

i: $1/2 - x$; $1 - y$; $1/2 + z$	v: $1 - x$; $y - 1/2$; $1/2 - z$
ii: $1/2 + x$; $1/2 - y$; $1 - z$	vi: x; $y - 1$; z
iii: $1/2 + x$; $3/2 - y$; $1 - z$	vii: $1/2 - x$; $-y$; $z - 1/2$
iv: x; $1 + y$; z	viii: $1/2 - x$; $1 - y$; $z - 1/2$

CsMoOP$_2$O$_7$ (1), which exhibit a monoclinic cell. Due to the weakening of the above reflections the resolution was first started in the *Pnma* space group. Atomic coordinates of the molybdenum atom were deduced from the Patterson function and the other atoms were located by subsequent Fourier series. After the refinements the R factor was lowered to 0.075, with B values ranging from 3 to 10 eÅ^2. These very high B values suggested that some symmetry elements of the *Pnma* space group do not exist in the crystal, and consequently the structure was refined in the noncentrosymmetric space group $Pn2_1a$ in a second step. In this group an R factor of 0.063 and acceptable B values were obtained, but O–P–O angles smaller than 90°, O–Mo–O angles smaller than 70°, and O–O distances smaller than 2.20 Å were obtained. This suggested that some symmetry elements of this group also do not exist in the crystal. The $P2_12_12_1$ space group was finally used. The limited number of reflections did not allow all the atoms to be refined with anisotropic thermal factors. Mo, P, and Na were refined anisotropically, and O was refined with isotropic factors. The two enanthiomorphs led to the same R factor, but one of them gives a better
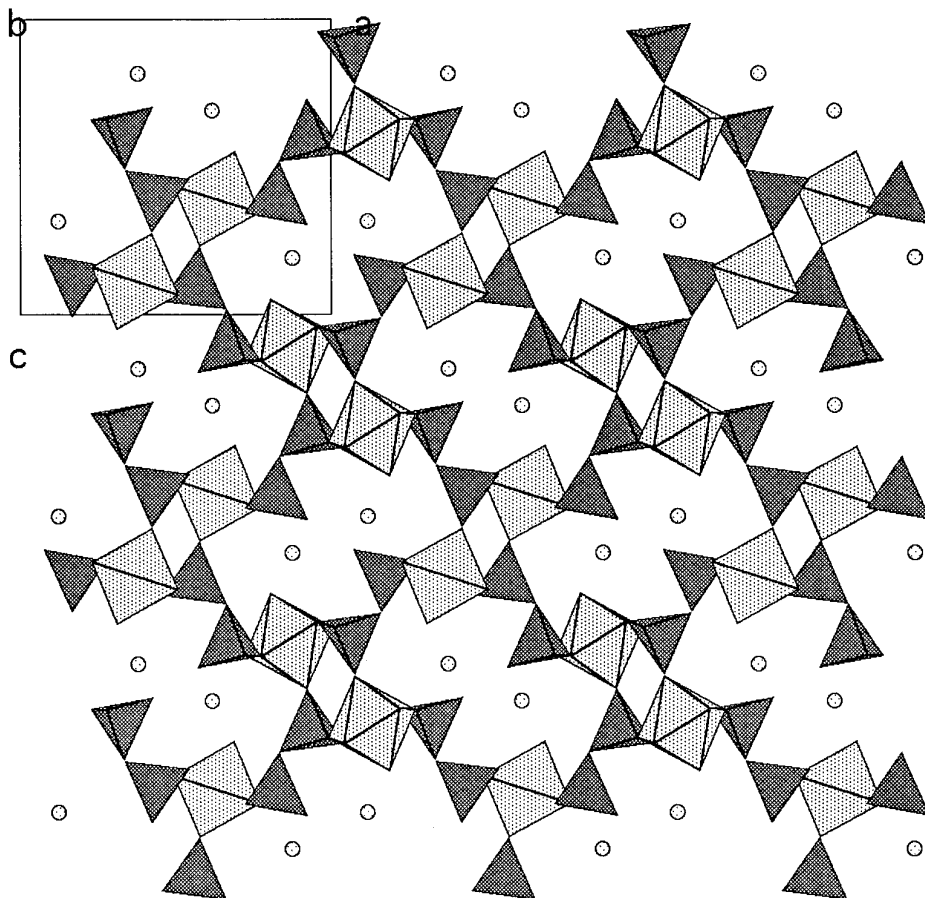
FIG. 1. Projection of the structure of NaMoOP$_2$O$_7$ along **b**.

geometry of the PO$_4$ tetrahedra. The last refinement cycle led to $R = 0.041$ and $R_w = 0.034$ and to the atomic parameters of Table 2 which give acceptable geometry for the polyhedra and acceptable contact distances between the polyhedra. The resulting distances and angles appear in Table 3.

The projection of the structure of NaMoOP$_2$O$_7$ along **b** (Fig. 1) shows that it is very similar with KMoOP$_2$O$_7$ (3) in spite of the different space groups of the two compounds. One observed the same [MoPO$_8$]$_\infty$ host lattice built up from corner-sharing MoO$_6$ octahedra and P$_2$O$_7$ groups forming tunnels along **b**.
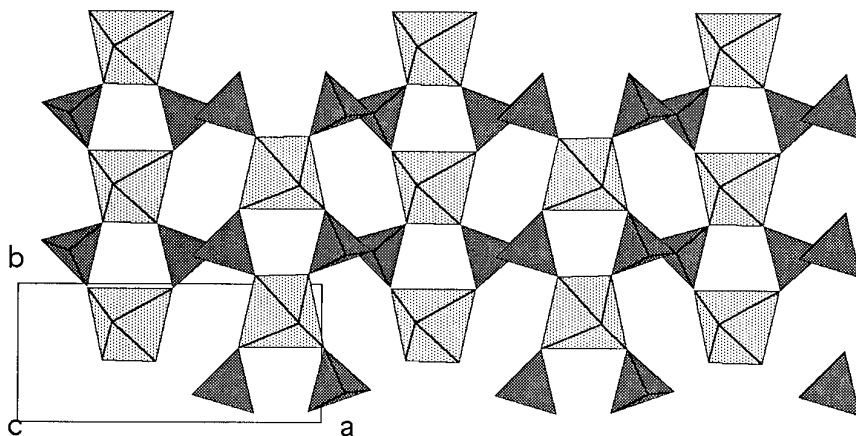

FIG. 2. The [MoP$_2$O$_9$]$_\infty$ layer showing the deformation of the MoO$_6$ octahedra.
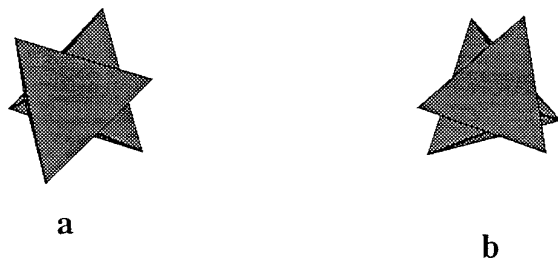
FIG. 3. The staggered diphosphate groups in NaMoOP$_2$O$_7$ (a) and in KMoOP$_2$O$_7$ (b).

FIG. 5. The magnetic susceptibility χ and $1/\chi$ versus T.

Nevertheless the structure of NaMoOP$_2$O$_7$ differs from that of KMoOP$_2$O$_7$ by the geometry of its MoO$_6$ octahedra and PO$_4$ tetrahedra. The MoO$_6$ octahedra are dramatically distorted as shown in Fig. 2. The O–O distances forming the basal plane of the octahedron vary indeed in a large range from 2.38 to 3.39 Å for two opposite edges, whereas they range from 2.69 to 2.89Å in KMoOP$_2$O$_7$ (3). In the same way, the O–Mo–O angles range from 72.6° to 112.3°, as in the Keggin molybdenum oxides (8); however, the Mo–O distances remain characteristic of the Mo(V) species, with one abnormally short Mo–O bond (1.65 Å) corresponding to the free apex opposed to a very long Mo–O bond (2.099 Å), the four equatorial Mo–O bonds of the octahedron being intermediate (2.01–2.06 Å). The sum of the electrostatic valence calculated with a modified Brese and O'Keeffe expression (9) for Mo(V) ($R_1 = 1.8797$) confirms the pentavalent character of molybdenum (5.14).

The second important difference deals with the conformation of the diphosphate group P$_2$O$_7$. One observes a staggered configuration for NaMoOP$_2$O$_7$ (Fig. 3a), whereas a less staggered configuration is obtained for KMoOP$_2$O$_7$ (Fig. 3b). This is to be compared to CsMoOP$_2$O$_7$ (1) which exhibits an eclipsed conformation of the P$_2$O$_7$ groups. Clearly, the tendancy to form a staggered configuration increases as the size of the interpolated cation decreases.
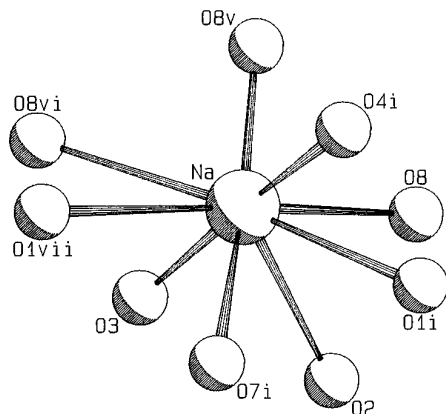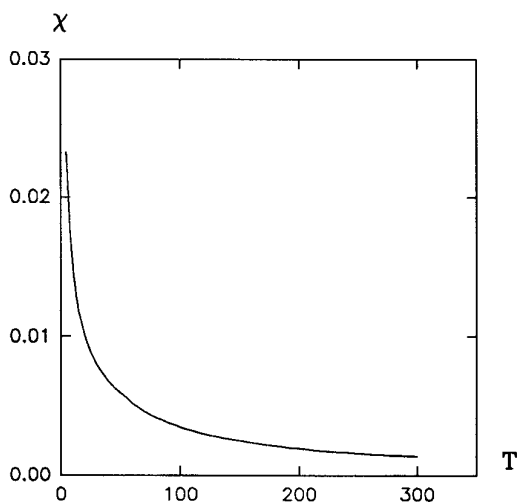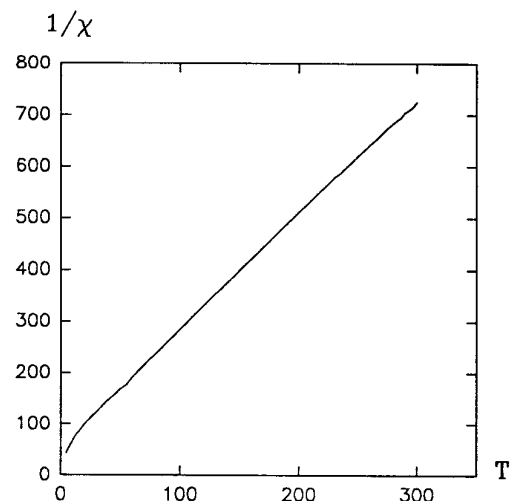
The geometry of the diphosphate groups is also different. In fact the two tetrahedra of the P$_2$O$_7$ groups are characterized by a different distribution of the P–O distances. The P(1) tetrahedra have the general geometry observed in diphosphate groups, i.e., one long P–O bond (1.61 Å) corresponding to a bridging oxygen and three almost equal P–O bonds ranging from 1.49 to 1.54Å similar to those observed in KMoOP$_2$O$_7$ (1.60 Å and 1.49 to 1.52 Å). The P(2) tetrahedra are different: they exhibit two long P–O bonds (1.60 Å) and two shorter ones (1.47 Å). One of the two long P–O distances corresponds to the oxygen bridging the two phosphorus atoms and one of the shorter bonds corresponds to a free apex. The latter tetrahedra also differ from those of KMoOP$_2$O$_7$ which exhibit one long P–O bond (1.61 Å) a shorter one (1.42 Å) corresponding to the free apex and two intermediate ones (1.52–1.53 Å).

The third difference between the two structures deals

FIG. 4. The coordination of Na$^+$.

with the size of the tunnels running along **b**, which are narrower than for $KMoOP_2O_7$ (3); nevertheless, Na^+ exhibits the same ninefold coordination (Fig. 4), but with Na–O distances ranging from 2.20 to 3.14 Å instead of 2.59 to 3.14 Å for K–O distances.

The inverse molar susceptibility χ_M^{-1} plotted versus temperature (Fig. 5) can be fitted with the Curie–Weiss law $\chi_M^{-1} = T/C - \theta/C$ with $\theta = -23.9K$ and $C = 0.44$ cm^{3}K/mol. Nevertheless the value of the Curie constant C leads to the rather high effective magnetic moment for Mo(v), $\mu = 1.87$ μB per molybdenum instead of 1.55 for pure Mo(V). This may be due either to the presence of the impurity in the polycrystalline sample that could contain Mo(IV) or to a slight disproportionation of Mo(V) into Mo(IV) and Mo(VI). Though the sample is not absolutely pure, this result is significant and of interest since it shows that there is no magnetic ordering in the phase $NaMoOP_2O_7$.

The investigation of ''mixed'' Mo(V) diphosphates involving two alkaline cations in various ratios, with a similar formula $(A, A')_1MoOP_2O_7$ should allow a better understanding of the relative stability of these various structures.

REFERENCES

1. A. Guesdon, M. M. Borel, A. Leclaire, A. Grandin, and B. Raveau, *J. Solid State Chem.* **108,** 46 (1994).
2. A Leclaire, M. M. Borel, and B. Raveau, to be published.
3. C. Gueho, M. M. Borel, A. Leclaire, A. Grandin, and B. Raveau, *Z. Anorg. Allg. Chem.* **615,** 104 (1992).
4. S. Ledain, M. M. Borel, A. Leclaire, J. Provost, and B. Raveau, *J. Solid State Chem.* **120,** 260 (1995).
5. A. Leclaire, A. Benmoussa, M. M. Borel, A. Grandin, and B. Raveau. *J. Solid State Chem.* **77,** 299 (1988).
6. V. P. Nikolaev, G. G. Sadikov, A. V. Lavrov, and M. A. Porai-Koshits, *Dokl. Akad. Nauk. SSSR* **264,** 859 (1982).
7. S. A. Linde, Yu. E. Gorbunova, A. V. Lavrov, and I. V. Tananaev. *Dokl. Akad. Nauk SSSR* **250,** 96 (1980).
8. A. Leclaire, M. M. Borel, J. Chardon, and B. Raveau, *Mater. Res. Bull.,* **30,** 1075 (1995).
9. A. Leclaire, T. Hoareau, M. M. Borel, A. Grandin, and B. Raveau, *J. Solid State Chem.* **114,** 543 (1995).