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A Mo(III) Phosphate with a Cage Structure: $NaMoP_2O_7$

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A new Mo(III) phosphate, $NaMoP_2O_7$, was synthesized and its structure determined from single-crystal X-ray data. This phosphate is isotypic with $NaFeP_2O_7$ and has the following parameters: a = 7.4195(3) Å, b = 8.1084(4) Å, c = 9.7598(4) Å, β = 111.868(3)°, space group $P2_1/c$. The behavior of Mo(III) in this oxide is compared to that of Fe(III) in $NaFeP_2O_7$. The structure, described in terms of corner-sharing PO_4 tetrahedra and MoO_6 octahedra, is compared to other molybdenum phosphates which exhibit a mixed framework: MoP_3SiO_{11}, $Mo_4P_6Si_2O_{25}$, and $AMo_3P_6Si_2O_{25}$. © 1988 Academic Press, Inc.

Introduction

Microporous solids are involved in various applications as catalyst or as molecular sieves. Thus, the research of open frameworks, and especially of tunnel and cage structures, is interesting for the generation of such properties. Oxides characterized by a mixed framework built up from octahedra and tetrahedra are inclined to form such tunnel structures due to the rigid character of their polyhedra which oppose the formation of close-packed structures. In this respect, the molybdenum phosphates and silicophosphates (*1–6*) recently studied are interesting candidates due to the great adaptability of the MoO_6 octahedra to the SiO_4 and PO_4 tetrahedra, and also to the various oxidation states of molybdenum—six, five, four, three—which can be involved in different redox reactions. Moreover, the valency III, which seems to be unusual for molybdenum in oxides, appears rather frequently when associated with silicophosphate groups as shown for $Mo_4P_6Si_2O_{25}$ (*7*) and MoP_3SiO_{11} (*8*). However, those oxides do not exhibit an open structure, although they are characterized by a three-dimensional framework. The only tunnel structure is represented by $KMo_3P_6Si_2O_{25}$ (*5*) in which molybdenum takes on two oxidation states, III and IV, simultaneously. The present work is concerned with the structural study of a novel phosphate of Mo(III), $NaMoP_2O_7$, which is characterized by a cage structure.

Experimental

Synthesis and Crystal Growth

The synthesis of phosphate $NaMoP_2O_7$ was performed in two stages. First an adequate mixture of Na_2CO_3, $H(NH_4)_2PO_4$, and MoO_3 was heated to 873 K in order to eliminate CO_2, NH_3, and H_2O. In the second step, the resulting finely ground product was mixed with an appropriate amount

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of molybdenum and sealed in an evacuated silica tube. This sample was heated to 1373 K for 2 days. Thus, dark-grey hexagonal platelets are obtained.

Determination of the Structure

A dark-grey crystal with dimensions 0.31 × 0.34 × 0.14 mm was selected for the structure determination. The Laue patterns showed monoclinic symmetry ($2/m$). The cell parameters, initially measured on precession films and later refined by diffractometric techniques at 294 K, with a least-squares refinement based on 25 reflections, are $a = 7.4195(3)$ Å, $b = 8.1084(4)$ Å, $c = 9.7598(4)$ Å, $\beta = 111.868(3)°$, with $Z = 4$ formula units of $NaMoP_2O_7$.

The systematic absences led to the $P2_1/c$ space group. The data were collected on a CAD-4 Enraf–Nonius diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The intensities were measured up to $\theta = 45°$ with an ω–θ scan of $(1.1 + 0.35 \tan \theta)°$ and a counter slit apperture of $(1.03 + \tan \theta)$ mm, all determined after a study of some reflections in the ω–θ plane. The background intensity was measured on both sides of each reflection. A periodic measurement of three reflections verified the stability of the sample. The 3868 reflections with $I \geq 3\sigma(I)$ were corrected for Lorentz and polarization effect; no absorption corrections were performed.

TABLE I

ATOMIC PARAMETERS OF $NaMoP_2O_7$

Atom	X	Y	Z	B_{eq}
Mo(1)	0.25843(2)	0.00547(2)	0.24845(1)	0.30(0)
P(1)	0.07446(6)	0.25293(6)	0.45857(5)	0.37(0)
P(2)	−0.32763(6)	0.21689(6)	0.45738(5)	0.41(0)
Na	0.28421(23)	0.48235(22)	0.28787(19)	1.78(2)
O(1)	0.53989(21)	0.08981(20)	0.35713(17)	0.81(2)
O(2)	0.30868(25)	−0.20968(18)	0.38279(15)	0.78(2)
O(3)	0.17033(27)	0.12870(21)	0.39527(19)	1.00(2)
O(4)	−0.02348(20)	−0.08760(17)	0.13034(16)	0.67(2)
O(5)	0.19160(26)	0.22060(18)	0.12102(16)	0.88(2)
O(6)	0.37151(22)	−0.10667(18)	0.09997(16)	0.71(2)
O(7)	−0.12504(21)	0.16453(19)	0.44471(19)	0.83(2)

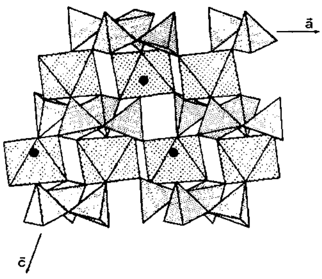

FIG. 1. Projection of the structure of $NaMoP_2O_7$ onto the (010) plane.

Atomic coordinates of the molybdenum atom and of the corresponding coordinating oxygen 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 by full-matrix least squares and a linear weighting scheme $w = f(\sin \theta/\lambda)$ led to $R = 0.035$, $R_w = 0.036$, and to the atomic parameters of Table I.[1]

Scattering factors for Mo, Na, P, and O and their anomalous dispersion were taken from the "International Tables for X-Ray Crystallography" (*9*).

Description of the Structure and Discussion

From the atomic coordinates it is clear that $NaMoP_2O_7$ is isostructural with NaFe P_2O_7 (*10*). This structure confirms the ability of molybdenum to take the oxidation state +III and shows the similar behavior of Mo(III) and Fe(III). Thus both three-dimensional frameworks (Figs. 1 and 2) are built up from corner-sharing MO_6 octahedra (M = Mo, Fe). The $Mo^{III}O_6$ octahedra (Table II) are characterized, as are the FeO_6 octahedra in $NaFeP_2O_7$, by three short Mo–

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

TABLE II

DISTANCES (Å) AND ANGLES (°) IN THE MoO_6 OCTAHEDRON

Mo	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	2.075(2)	3.037(2)	2.918(3)	4.918(3)	2.946(2)	2.839(2)
O(2)	92.48(6)	2.130(2)	2.948(3)	2.933(2)	4.219(3)	3.081(3)
O(3)	90.24(7)	89.84(7)	2.044(2)	3.010(2)	2.839(3)	4.169(3)
O(4)	177.06(7)	87.37(6)	92.69(7)	2.116(2)	2.985(2)	3.057(3)
O(5)	89.98(6)	175.76(8)	86.69(7)	90.36(6)	2.092(6)	3.012(2)
O(6)	84.95(6)	92.65(6)	174.68(7)	92.12(6)	91.01(6)	2.130(2)

Note. The Mo–O distances are on the diagonal of the table. The values above this diagonal are the O–O lengths and the values below it are the O–Mo–O angles.

O distances (2.044 to 2.092 Å to be compared to three short Fe–O distances, 1.938 to 1.994 Å) and three longer distances (2.116 to 2.130 Å to be compared to long Fe–O distances, 2.014 to 2.053 Å). For the PO_4 tetrahedra (Table III) one observes the classical features when they are involved in diphosphate groups:

a long P–O distance (1.604 to 1.610 Å) corresponding to the oxygen atom common to two phosphorus atoms;

three shorter P–O distances (1.493 to 1.527 Å) corresponding to the oxygen atom common to one phosphorus and one molybdenum (or iron) atom.

This mixed framework delimits cages elongated along [101] where the Na^+ ions are located (Fig. 2).

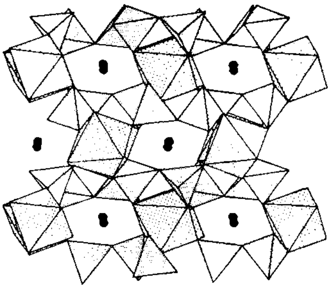

FIG. 2. Projection of the structure of $NaMoP_2O_7$ along [101].

The coordination of the Na^+ ions was determined from the calculated maximum bond length Na–O using the Donnay and Alleman (*12*) procedure with the revised "ionic radii" of Shannon (*13*) leading to (Na–O) max = 3.20 Å.

According to this value the Na^+ ions (Table IV) can be considered as surrounded by seven oxygen atoms with Na–O distances ranging from 2.417 to 3.040 Å. Those distances can be divided into three groups:

—three short Na–O distances ranging from 2.417 to 2.482 Å,

—three medium distances ranging from 2.595 to 2.646 Å, and

—a long distance (3.040 Å).

TABLE III

DISTANCES (Å) AND ANGLES (°) IN THE PO_4 TETRAHEDRA

P(1)	O(3)	$O(4^{i})$	$O(5^{ii})$	O(7)
O(3)	1.493(2)	2.518(2)	2.473(3)	2.431(3)
$O(4^{i})$	113.09(10)	1.524(2)	2.541(2)	2.528(2)
$O(5^{ii})$	110.68(9)	113.58(8)	1.513(2)	2.517(2)
O(7)	103.32(10)	107.79(8)	107.67(10)	1.604(2)
P(2)	$O(1^{iii})$	$O(2^{iv})$	$O(6^{i})$	O(7)
$O(1^{iii})$	1.506(2)	2.555(2)	2.541(2)	2.386(2)
$O(2^{iv})$	115.50(9)	1.514(2)	2.488(2)	2.556(2)
$O(6^{i})$	113.86(7)	109.83(9)	1.527(2)	2.526(2)
O(7)	99.88(9)	109.74(9)	107.25(10)	1.610(2)

Note. Same convention as in Table II. For symmetry code, see Table IV.

TABLE IV

DISTANCES (Å) AND ANGLES (°) IN THE NaO_7 POLYHEDRON

Na	O(1^{v})	O(2^{vi})	O(4^{i})	O(5)	O(6^{ii})	O(6^{v})	O(7^{i})
O(1^{v})	2.417(3)	3.369(3)	4.775(3)	3.558(3)	4.747(3)	2.839(2)	2.386(2)
O(2^{vi})	83.29(8)	2.646(2)	3.699(3)	5.193(3)	2.488(2)	3.965(3)	3.142(2)
O(4^{i})	161.11(7)	93.71(8)	2.419(3)	3.481(3)	3.143(2)	4.390(3)	3.985(3)
O(5)	90.88(7)	162.72(6)	87.60(8)	2.607(2)	5.365(3)	3.648(3)	3.657(3)
O(6^{ii})	120.47(8)	51.33(7)	69.22(6)	143.52(8)	3.040(3)	3.634(3)	4.958(3)
O(6^{v})	70.83(8)	101.24(7)	127.18(7)	91.56(8)	81.62(6)	2.482(2)	4.555(3)
O(7^{i})	56.74(7)	73.65(7)	105.24(8)	89.36(5)	123.05(8)	127.56(9)	2.595(2)

Note. Symmetry code: i = $-x, \frac{1}{2}+y, \frac{1}{2}-z$; ii = $x, \frac{1}{2}-y, \frac{1}{2}+z$; iii = $x-1, y, z$; iv = $-x, -y, 1-z$; v = $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; vi = $x, 1+y, z$.

The gap between the sixth bond (2.646 Å) and the seventh bond (3.040 Å) suggested that one can, as a first approximation, consider the coordination of Na^+ as six instead of seven; however, the sum of the bond strengths (*14*) in this case is only 0.91 instead of 0.98 for seven neighbors. Thus, the polyhedron formed by the seven oxygen atoms surrounding the Na^+ ion can be described as a distorted monocapped triangular prism (Fig. 3).

The coordination of Na^+ in $NaMoP_2O_7$ is different from that in $NaFeP_2O_7$ where it is surrounded by eight oxygen atoms with Na–O distances ranging from 2.83 to 3.064 Å. Clearly, the structure of $NaMoP_2O_7$ is less dense than that of $NaFeP_2O_7$ in which the $[FeP_2O_7]$ framework forms smaller cages owing to the smaller Fe–O distances compared to the Mo^{III}–O distances.

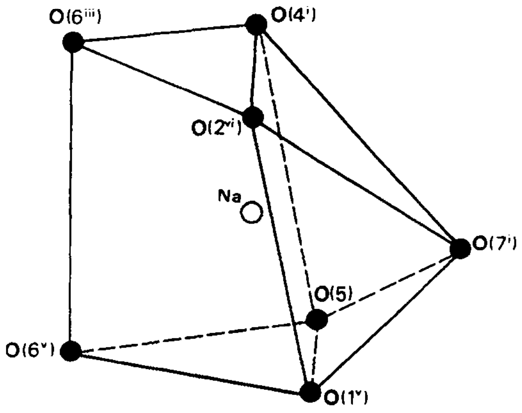

FIG. 3. The NaO_7 polyhedron.

The low valency of molybdenum appears as a remarkable feature since Mo(III) is rarely observed in oxides. The sum of the bond strengths for molybdenum deduced from the Zachariasen curves (*11*), equal to +3.1, confirms this oxidation state. The existence of the oxide $Mo^{III}P_3SiO_{11}$ (*8*), in which the $Mo^{III}O_6$ octahedra exhibit similar Mo–O distances, suggests that the existence of a mixed framework of octahedra and tetrahedra, in which each $Mo^{III}O_6$ octahedron is isolated, is more favorable to the stabilization of Mo(III) than that in pure octahedral structures built up of MoO_6 octahedra which could exhibit a mixed valence.

The fact that each MoO_6 octahedron shares its corners with six PO_4 tetrahedra is a feature which is also observed in MoP_3SiO_{11} (*8*), $Mo_4P_6SiO_{25}$ (*7*), $AMo_3P_6Si_2O_{25}$ (*4–6*), and also in several mixed frameworks such as that of Nasicon (*15*). In this phosphate, and in $NaFeP_2O_7$, all the PO_4 tetrahedra appear in the form of diphosphate groups like those in MoP_3SiO_{11} (*8*), whereas only a part of the PO_4 tetrahedra are in the form of diphosphate groups in $AMo_2P_3O_{12}$ (*3*) and $K_4Mo_8P_{12}O_{52}$ (*1*). Each P_2O_7 group

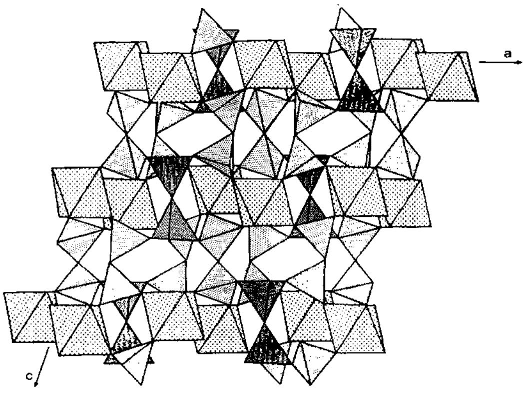

FIG. 4. The MoP_3SiO_{11} structure projected onto the (010) plane.

shares two of its corners with the same MoO_6 (or FeO_6) octahedron as in $K_4Mo_8P_{12}O_{52}$. Therefore, the relative position of the PO_4 tetrahedra forming the diphosphate group is indeed intermediate between the staggered configuration observed for MoP_3SiO_{11} and the eclipsed configuration obtained for $AMo_2P_3O_{12}$.

The view of this structure along *b* (Fig. 1) shows its similarity with that of MoP_3SiO_{11} (*8*). It can indeed be described as an alternating stacking of "diphosphate layers" and octahedral "MoO_6" layers parallel to the (001) plane, whereas $MoPSi_3O_{11}$ can be described by the stacking of diphosphate layers and mixed layers containing MoO_6 octahedra and Si_2O_7 groups (Fig. 4). Moreover, the disposition of the octahedra in the layers is rather similar in both oxides; i.e., one observes a hexagonal arrangement of the MoO_6 octahedra in the (001) layer of MoP_3SiO_{11} (Fig. 5) as well as in the (001) layer of $NaMoP_2O_7$. However the orientation of the octahedra are different in the two structures: the ternary axis of the MoO_6 octahedra is perpendicular to the plane of the layers in MoP_3SiO_{11}, whereas it is slightly tilted in $NaMoP_2O_7$.

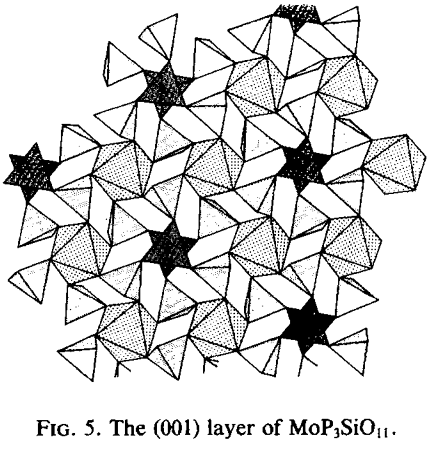

FIG. 5. The (001) layer of MoP_3SiO_{11}.

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