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# $NaMo_2P_3O_{12}$: A New Phosphate of Mo(IV)

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A new Mo(IV) phosphate, $NaMo_2P_3O_{12}$, has been discovered and characterized by means of single crystal X-ray diffraction. It crystallizes in the trigonal space group $R\bar{3}c$ with $a$ = 8.6160(7), $c$ = 22.075(3) Å, $Z = 6$, $R = 0.015$, $R_w = 0.018$, GOF = 1.613 for 406 unique reflections with $I > 2.5\ \sigma(I)$. The framework of $NaMo_2P_3O_{12}$ is built of $MoO_6$ octahedra, $NaO_6$ trigonal antiprisms, and $PO_4$ tetrahedra. Its structure is isostructural with $NaZr_2P_3O_{12}$ and closely related to $MoP_3SiO_{11}$. © 1989 Academic Press, Inc.

## Introduction

A large number of new compounds have been isolated and characterized in the system of $M$–Mo–P–O ($M$ = metal cation) containing Mo in oxidation states less than +6, indicating the great ability of $PO_4$ tetrahedra to form various frameworks with $MoO_6$ octahedra. The investigation of the system $M$–Mo(V)–P–O has shown the formation of $K_4Mo_8P_{12}O_{52}$ (*1*), $\alpha$-, $\beta$-, and $\gamma$-$CsMo_2P_3O_{13}$ (*2*), and $MMo_5P_8O_{33}$ ($M$ = Li, Na, Ag) (*3*). The phosphates containing Mo(IV) have been observed in $MMo_2P_3O_{12}$ ($M$ = Tl, Rb, K) (*4*) and the mixed-valence compounds $MMo_3P_6Si_2O_{25}$ ($M$ = Cs, Rb, Tl) (*5*), $Cs_3Mo_6P_{10}O_{38}$ (*6*), $Cs_2Mo_5P_9O_{33}$ (*7*), and $NaMo_2P_4O_{14}$ (*8*), in which Mo(IV) and Mo(III) are simultaneously present. Interestingly, several compounds exhibit metal–metal bondings. For example, $Cs_3Mo_5P_6O_{25}$ (*9*), $Cs_3Mo_4P_3O_{16}$ (*10*), and $Cs_3Mo_5P_7O_{24}$ (*11*) contain cubane-like $Mo_4O_4$ and $Mo_4O_3P$ clusters each with six Mo–Mo bonds. A confacial bioctahedral $Mo_2O_9$ cluster with a Mo–Mo bond has been observed in $Mo_3P_5SiO_{19}$ (*12*). The phosphates containing isolated Mo(III) only have also been found in $MMoP_2O_7$ ($M$ = Cs, Rb, K) (*13*) and $MoP_3SiO_{11}$ (*14*).

The Mo(IV) phosphates $MMo_2P_3O_{12}$ ($M$ = Tl, Rb, K) have been unusual among molybdenum phosphates with respect to the corner-sharing $Mo_2O_{11}$ units in their framework. Since phosphates containing Mo(IV) only have been relatively rare, efforts have been made to add new members to the family of $M$–Mo(IV)–P–O. In an attempt to prepare "$Na_2Mo_3P_4O_{17}$" a new Mo(IV) phosphate has been discovered. In contrast to $MMo_2P_3O_{12}$ ($M$ = Tl, Rb, K) which adopt a tunnel structure and are built

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of $Mo_2O_{11}$ units, $P_2O_7$ groups and $PO_4$ tetrahedra, the sodium compound has a markedly different structure and is composed of $MoO_6$ octahedra, $NaO_6$ trigonal antiprisms, and $PO_4$ tetrahedra. We report in this paper the preparation and crystal structure of $NaMo_2P_3O_{12}$.

## Experimental

The starting materials used for preparation were $Na_2MoO_4$ (99.9%), $MoO_3$ (99.9%), Mo (99.9%), and $P_2O_5$ (99.9%). The title compound was first obtained as black chunky crystals in an attempt to prepare "$Na_2Mo_3P_4O_{17}$" in a sealed fused silica tube at 1000°C for 4 days. Its stoichiometry was not known until a complete single crystal X-ray structure determination. Subsequently, a few reactions using appropriate amounts of the starting materials were conducted at several different temperatures ranging from 850 to 1000°C. However, powder X-ray diffraction patterns showed that the products were always contaminated with a small amount of $MoO_2$ and $NaMo_2P_4O_{14}$ (*8*).

A black crystal having the dimensions of 0.08 × 0.09 × 0.09 mm was selected for indexing and intensity data collection. The unit cell parameters were obtained by least-squares refinement of 25 reflections with $2\theta$ ranging from 16 to 29°. Based on the statistical analysis of intensity distribution, systematic extinctions, and the successful solution and refinement of the structure, the space group was determined to be $R\bar{3}c$ (No. 167). The structure was solved by direct methods and refined by full matrix least-squares refinement based on $F$ values to $R = 0.015$, $R_w = 0.018$, and GOF = 1.613. The occupancy factor for Na was initially refined but the resultant value indicated full occupancy. Subsequently it was learned that the structure was isostructural with $NaZr_2P_3O_{12}$ (*15*). The intensity data were corrected for absorption, Lorentz, and polarization effects. Atomic scattering factors and anomalous dispersion terms were taken from *International Tables for X-ray Crystallography* (*16*). Crystal data, intensity measurements, and structure refinement parameters are collected in Table I. Final positional and thermal parameters are listed in Table II. Selected bond distances and angles are given in Table III.[1]

TABLE I

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENT, AND STRUCTURE REFINEMENT PARAMETERS FOR $NaMo_2P_3O_{12}$

| | |
|---|---|
| Crystal data | |
| Space group | $R\bar{3}c$ |
| Cell constants | $a = 8.6160(7)$, $c = 22.075(3)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 1419.2$ Å |
| $Z$ | 6 |
| Density (calcd) | 3.509 g/cm$^3$ |
| Abs. coeff. (Mo$K\alpha$) | 32.0 cm$^{-1}$ |
| Intensity measurement | |
| $\lambda$(Mo$K\alpha$) | 0.70930 Å |
| Scan mode | $\omega/2\theta$ |
| Scan rate | 5.5°/min |
| Scan width | $0.65° + 0.35° \tan\theta$ |
| Max $2\theta$ | 60° |
| Standard reflections | Three measured every 2 hr (no decay) |
| Reflections measured | 889 total, 466 unique |
| Structure solution and refinement | |
| Reflections included | 406 with $I > 2.5\,\sigma(I)$ |
| Parameters refined | 30 |
| Agreement factors | $R = 0.015$, $R_w = 0.018$ |
| GOF | 1.613 |
| $(\Delta\rho)_{max}$; $(\Delta\rho)_{min}$ | 0.48; −0.39 e/Å$^3$ |

## Description and Discussion of the Structure

As shown in Fig. 1 the framework of $NaMo_2P_3O_{12}$ is composed of corner-sharing $MoO_6$ octahedra, $NaO_6$ trigonal antiprisms, and $PO_4$ tetrahedra. Each $MoO_6$ octahe-

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[1] A table of structure factors is available on request from the author.

TABLE II

POSITIONAL AND THERMAL PARAMETERS FOR $NaMo_2P_3O_{12}$[a,b]

| Atom | $x$ | $y$ | $z$ | $B$(iso) (Å$^2$) |
|---|---|---|---|---|
| Na | 0.0 | 0.0 | 0.0 | 2.06(9) |
| Mo | 0.0 | 0.0 | 0.14443(1) | 0.37(1) |
| P | 0.2891(1) | 0.2891 | 0.25 | 0.44(2) |
| O1 | 0.1917(2) | 0.0250(2) | 0.08676(8) | 0.92(8) |
| O2 | 0.0201(3) | −0.1813(3) | 0.19315(9) | 1.19(8) |

| | Anisotropic thermal parameters (Å$^2$ × $10^2$) | | | | | |
|---|---|---|---|---|---|---|
| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
| Na | 3.4(1) | 3.4 | 1.0(1) | 1.7 | 0.0 | 0.0 |
| Mo | 0.50(2) | 0.50 | 0.41(2) | 0.25 | 0.0 | 0.0 |
| P | 0.50(3) | 0.50 | 0.63(4) | 0.21(3) | 0.08(1) | −0.08 |
| O1 | 0.83(9) | 1.63(9) | 1.14(8) | 0.70(7) | 0.20(7) | −0.02(7) |
| O2 | 2.0(1) | 1.43(9) | 1.36(9) | 1.06(8) | −0.12(7) | 0.64(7) |

[a] $B$(iso) is the mean of the principal axes of the thermal ellipsoid.

[b] The anisotropic thermal parameters take the form: $2\Pi^2(h^2(a^*)^2U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)$.

TABLE III

SELECTED BOND DISTANCES (Å) AND BOND ANGLES (DEGREE)

| Bond distances | | Bond angles | |
|---|---|---|---|
| Na–O1 | 2.467(2) (6×) | O1–Na–O1 | 180.0 (3×) |
| Mo–O1 | 2.010(2) (3×) | O1–Na–O1 | 66.2(2) (6×) |
| Mo–O2 | 1.974(2) (3×) | O1–Na–O1 | 113.8(1) (6×) |
| P–O1 | 1.527(2) (2×) | O1–Mo–O1 | 84.2(1) (3×) |
| P–O2 | 1.520(2) (2×) | O1–Mo–O2 | 92.05(8) (3×) |
| | | O1–Mo–O2 | 90.2(1) (3×) |
| | | O1–Mo–O2 | 173.5(1) (3×) |
| | | O2–Mo–O2 | 93.3(1) (3×) |
| | | O1–P–O1 | 109.4(1) (1×) |
| | | O1–P–O2 | 111.1(2) (2×) |
| | | O1–P–O2 | 106.2(2) (2×) |
| | | O2–P–O2 | 112.9(1) (1×) |
| | | Na–O1–Mo | 90.23(7) |
| | | Na–O1–P | 126.2(1) |
| | | Mo–O1–P | 143.5(1) |
| | | Mo–O2–P | 154.7(2) |

dron shares its six corners with six $PO_4$ tetrahedra. Similarly, each $NaO_6$ trigonal antiprism is linked to six $PO_4$ tetrahedra. Each $NaO_6$ trigonal antiprism shares its opposite faces with two $MoO_6$ octahedra (Fig. 2). Along a threefold axis the $MoO_6$ and $NaO_6$ polyhedra alternate in the following sequence . . ./ /$(NaO_6)(MoO_6)(MoO_6)(NaO_6)(MoO_6)(MoO_6)$/ /. . . . The structure of $NaMo_2P_3O_{12}$ can be described as strings of $MoO_6$ octahedra and $NaO_6$ trigonal antiprisms directed along the $c$-axis which are linked together through $PO_4$ tetrahedra. Each $PO_4$ tetrahedron is linked with three neighboring strings. Each $PO_4$ group shares two corners with two $MoO_6$ octahedra within one of the three strings and two cor-

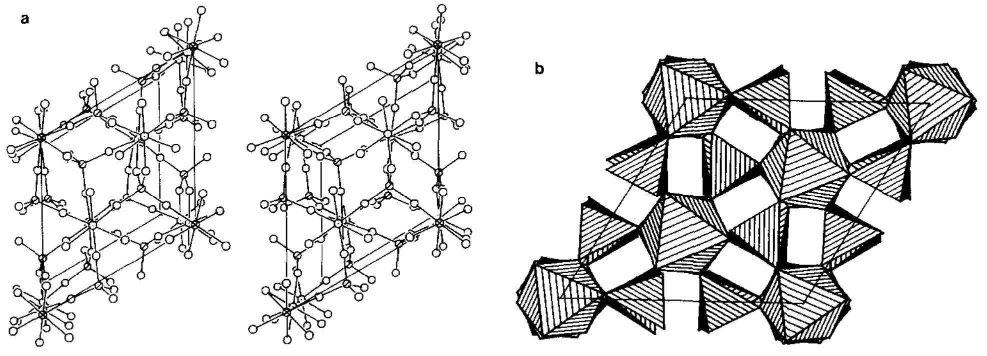

FIG. 1. (a) A stereoscopic view of the $NaMo_2P_3O_{12}$ structure along the $c$-axis. The Na, Mo, P, and O atoms are represented by circles with a cross, a dot, a slash, and open circles, respectively. For clarity, only half of the unit cell content along the $c$-axis is shown in the figure. (b) A polyhedron representation of the $NaMo_2P_3O_{12}$ structure along the $c$-axis.

ners each with a $MoO_6$ and a $NaO_6$ polyhedron within a neighboring string. Oxygen 1 is simultaneously bonded to P, Mo, and Na atoms and the four atoms are coplanar. However, O2 is only bonded to P and Mo atoms.

The structure of $NaMo_2P_3O_{12}$ is closely related to that of $MoP_3SiO_{11}$, which is built of corner-sharing $Mo(III)O_6$ octahedra, $P_2O_7$ groups, and $Si_2O_7$ groups. $NaMo_2P_3O_{12}$ can be deduced from $MoP_3SiO_{11}$ by simple replacement of the $Si_2O_7$ groups with $NaO_6$ trigonal antiprisms, and the $P_2O_7$ groups with $PO_4$ tetrahedra. The framework of the sodium compound is formed of $[NaMo_2(PO_4)_3]_\infty$ slabs parallel to the (001) plane, which are stacked along the *c*-axis and mutually linked in such a way that the three $PO_4$ tetrahedra in a slab unit share their corners with the $MoO_6$ octahedra and the $NaO_6$ trigonal antiprisms of an adjacent slab. Whereas in $MoP_3SiO_{11}$, the three $PO_4$ tetrahedra in a slab unit share their corners with the three other $PO_4$ tetrahedra of a neighboring slab.

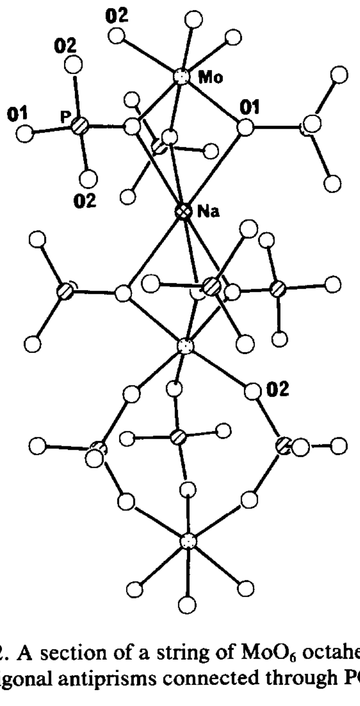

FIG. 2. A section of a string of $MoO_6$ octahedra and $NaO_6$ trigonal antiprisms connected through $PO_4$ tetrahedra.

For each $MoO_6$ octahedron two sorts of Mo–O bond distances are observed. The longer Mo–O bonds correspond to the oxygen atom (O1) common to a $PO_4$ tetrahedron, a $MoO_6$ octahedron, and a $NaO_6$ trigonal antiprism. The shorter Mo–O bonds correspond to the oxygen atom (O2) shared by a $PO_4$ tetrahedron and a $MoO_6$ octahedron. The $MoO_6$ octahedron is distorted as shown by the O–O distances ranging from 2.697(3) to 2.870(2) Å. The octahedral distortion can be estimated by using the equation $\Delta = (1/6)\Sigma((R_i - \bar{R})/\bar{R})^2$ where $R_i$ = an individual bond length and $\bar{R}$ = average bond length (*17*). The calculation result ($\Delta \times 10^4 = 0.82$) shows that the distortion is almost identical with the $Mo^{4+}$–O octahedra in the mixed-valence compound $NaMo_2P_4O_{14}$ ($\Delta \times 10^4 = 0.91$), but much smaller than the $Mo^{4+}$–O octahedra in $TlMo_2P_3O_{12}$ ($\Delta \times 10^4 = 11.2$). The P atom is bonded to four oxygen atoms at two nearly equal distances (see Table III). The $PO_4$ tetrahedron is slightly distorted as indicated by the O–O distances ranging from 2.438(3) to 2.530(4) Å. The sums of bond strengths using the equations derived by Brown and Wu (*18*) led to +0.99 for Na and +4.28 for Mo, which is a little higher than the formal oxidation state +4 of Mo in this compound. The Na atom is bonded to six oxygen atoms at a distance of 2.467(2) Å forming a regular trigonal antiprism with the edge lengths of 2.697(3) Å (6×) and 4.134(3) Å (6×). It should be noted that the $U_{11}$ and $U_{22}$ values for the Na atom are much larger than the $U_{33}$ value. The anomalously large thermal parameters suggest that the sodium atom is mobile. Hong showed that the network of $NaZr_2P_3O_{12}$ contains empty interstitial space along the *a*-axis and the interstitial space satisfies the criteria for fast $Na^+$-ion transport (*19*). Large thermal parameters for the Na atom were also observed in $NaZr_2P_3O_{12}$.

According to our knowledge $NaMo_2P_3O_{12}$ has been unique in the system of $M$–Mo–P–O with respect to the isolated Mo(IV)$O_6$ octahedra in its framework. Interestingly, the sodium compound adopts a drastically different structure from those of $MMo_2P_3O_{12}$ ($M$ = Tl, Rb, K). It is one of the examples showing the effect of the size of the counter cation on the crystal structure. This structural study once again shows the great ability of $PO_4$ tetrahedra to form a variety of frameworks with $MoO_6$ octahedra.

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## References

1. A. Leclaire, J. C. Monier, and B. Raveau, *J. Solid State Chem.* **48,** 147 (1983).
2. $\alpha$-, $\beta$-$CsMo_2P_3O_{13}$: K. H. Lii and R. C. Haushalter, *J. Solid State Chem.* **69,** 320 (1987); $\gamma$-$CsMo_2P_3O_{13}$: J. J. Chen, K. H. Lii, and S. L. Wang, *J. Solid State Chem.* **76,** 204 (1988).
3. K. H. Lii, D. C. Johnston, D. P. Goshorn, and R. C. Haushalter, *J. Solid State Chem.* **71,** 131 (1987).
4. A. Leclaire, J. C. Monier, and B. Raveau, *J. Solid State Chem.* **59,** 301 (1985); A. Leclaire and B. Raveau, *Acta Crystallogr. C* **44,** 226 (1988).
5. A. Leclaire, J. C. Monier, and B. Raveau, *Acta Crystallogr. B* **40,** 180 (1984).
6. K. H. Lii and C. C. Wang, *J. Solid State Chem.*, in press.
7. K. H. Lii, C. C. Wang, and S. L. Wang, to be published.
8. J. J. Chen, K. H. Lii, and S. L. Wang, *J. Solid State Chem.*, in press.
9. K. H. Lii, R. C. Haushalter, and C. J. O'Connor, *Angew. Chem. Int. Ed. Engl.* **26,** 549 (1987).
10. R. C. Haushalter, *J. Chem. Soc. Chem. Commun.*, 1566 (1987).
11. S. L. Wang and K. H. Lii, *J. Solid State Chem.* **73,** 274 (1988).
12. S. L. Wang, C. C. Wang, and K. H. Lii, *J. Solid State Chem.* **74,** 409 (1988).
13. K. H. Lii and R. C. Haushalter, *Acta Crystallogr. C* **43,** 2036 (1987); K. H. Lii, C. C. Wang, and J. J. Chen, unpublished work.
14. A. Leclaire and B. Raveau, *J. Solid State Chem.* **71,** 283 (1987).
15. L. Hagman and P. Kierkegaard, *Acta Chem. Scan.* **22,** 1822 (1968).
16. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch, Birmingham (1974).
17. R. D. Shannon, *Acta Crystallogr. A* **32,** 751 (1976).
18. I. D. Brown and K. K. Wu, *Acta Crystallogr. B* **32,** 1957 (1976).
19. H. Y-P. Hong, *Mat. Res. Bull.* **11,** 173 (1976).