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

K. H. LII AND J. J. CHEN

Institute of Chemistry Academia Sinica, Nankang, Taipei, Taiwan, Republic of China

AND S. L. WANG

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, Republic of China

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*), α-, β-, and γ-$CsMo_2P_3O_{13}$ (*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

of Mo_2O_{11} units, P_2O_7 groups and PO_4 tetra-hedra, the sodium compound has a mark-edly 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 $Na Mo_2P_3O_{12}$.

Experimental

The starting materials used for prepara-tion 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 pre-pare "$Na_2Mo_3P_4O_{17}$" in a sealed fused sil-ica tube at 1000°C for 4 days. Its stoichiom-etry was not known until a complete single crystal X-ray structure determination. Sub-sequently, a few reactions using appropri-

ate amounts of the starting materials were conducted at several different temperatures ranging from 850 to 1000°C. However, pow-der X-ray diffraction patterns showed that the products were always contaminated with a small amount of MoO_2 and $NaMo_2 P_4O_{14}$ (8).

A black crystal having the dimensions of $0.08 \times 0.09 \times 0.09$ mm was selected for indexing and intensity data collection. The unit cell parameters were obtained by least-squares refinement of 25 reflections with 2θ ranging from 16 to 29°. Based on the statis-tical analysis of intensity distribution, sys-tematic extinctions, and the successful so-lution 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 po-larization effects. Atomic scattering factors and anomalous dispersion terms were taken from *International Tables for X-ray Crys-tallography* (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 an-gles 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. (MoKα)	32.0 cm^{-1}
Intensity measurement	
λ(MoKα)	0.70930 Å
Scan mode	$\omega/2\theta$
Scan rate	5.5°/min
Scan width	$0.65° + 0.35°$ tan θ
Max 2θ	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 $Na Mo_2P_3O_{12}$ is composed of corner-sharing MoO_6 octahedra, NaO_6 trigonal antiprisms, and PO_4 tetrahedra. Each MoO_6 octahe-

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

TABLE II

POSITIONAL AND THERMAL PARAMETERS
FOR NaMo$_2$P$_3$O$_{12}$[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$_2$P$_3$O$_{12}$ 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-
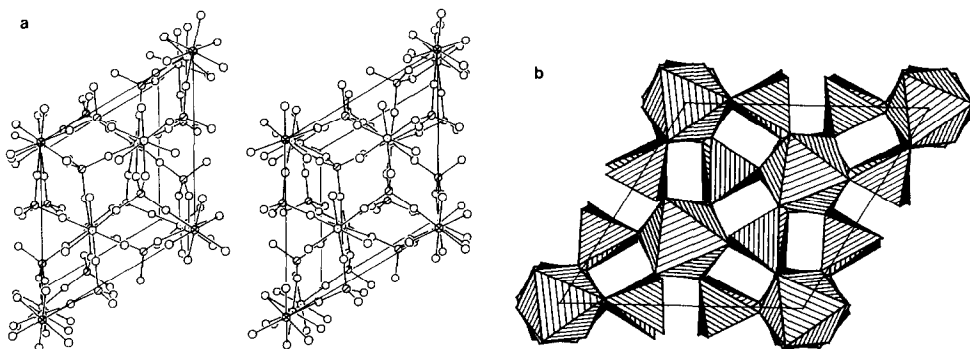

FIG. 1. (a) A stereoscopic view of the NaMo$_2$P$_3$O$_{12}$ structure along the c-axis. The Na, Mo, P, and O atoms are represented by circles with a cross, a dot, a slash, and open circles, respectively. For clarity, only half of the unit cell content along the c-axis is shown in the figure. (b) A polyhedron representation of the NaMo$_2$P$_3$O$_{12}$ 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.

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 $Na Mo_2P_4O_{14}$ ($\Delta \times 10^4 = 0.91$), 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 $NaZr_2P_3O_{12}$.
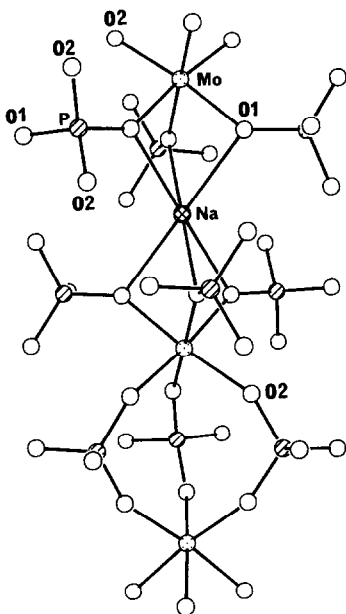

FIG. 2. A section of a string of MoO_6 octahedra and NaO_6 trigonal antiprisms connected through PO_4 tetrahedra.

According to our knowledge NaMo$_2$P$_3$O$_{12}$ 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$_2$P$_3$O$_{12}$ (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.

Acknowledgments

References

1. A. Leclaire, J. C. Monier, and B. Raveau, *J. Solid State Chem.* **48**, 147 (1983).

2. α-, β-CsMo$_2$P$_3$O$_{13}$: K. H. Lii and R. C. Haushalter, *J. Solid State Chem.* **69**, 320 (1987); γ-CsMo$_2$P$_3$O$_{13}$: 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).