JOURNAL OF SOLID STATE CHEMISTRY 78, 178–183 (1989)

BRIEF COMMUNICATIONS

$NaMo_2P_4O_{14}$: A Mixed-Valence Molybdenum Phosphate with a Tunnel Structure

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

Received March 2, 1988; in revised form August 25, 1988

The crystal structure of $NaMo_2P_4O_{14}$ has been determined from single-crystal X-ray diffraction data. $NaMo_2P_4O_{14}$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 4.872(1)$, $b = 7.0025(7)$, $c = 8.2620(6)$ Å, $\alpha = 91.468(8)$, $\beta = 92.53(1)$, $\gamma = 106.61(1)°$, $Z = 1$, $R = 0.020$, $R_w = 0.029$, GOF = 1.192 for 1166 reflections with $I > 2.5\,\sigma(I)$. The structure contains two types of tunnels of which the larger one is occupied by sodium atoms. The framework is built up from MoO_6 octahedra and P_2O_7 groups. It is the first molybdenum phosphate in which equal amounts of isolated Mo^{3+} and Mo^{4+} are simultaneously present. A single-phase product can be obtained by heating appropriate amounts of Na_2MoO_4, MoO_2, Mo, and P_2O_5 in a sealed silica tube at 1100°C. © 1989 Academic Press, Inc.

Introduction

Mixed-valence compounds have been the subject of innumerable studies owing to their interesting physical properties. Several series of mixed-valence compounds have been synthesized in the system of phosphate tungsten bronzes (see, e.g., (*1*)). These tungsten phosphates are closely related in that their structures exhibit ReO_3-type slabs. A large number of novel structures have been isolated and elucidated in the system of M–Mo–P–O (M = metal cation) containing Mo in oxidation states less than +6 (*2*). However, mixed-valence molybdenum phosphates have been relatively rare. An interesting result of our recent work was the discovery of two mixed-valence compounds in the Cs–Mo–P–O system, $Cs_3Mo_6P_{10}O_{38}$ (*3*) and $Cs_4Mo_{10}P_{18}O_{66}$ (*4*). We thus initiated a synthetic program to explore novel mixed-valence compounds in the system of molybdenum phosphates. The present paper deals with the preparation and crystal structure of the mixed-valence molybdenum phosphate with a tunnel structure, $NaMo_2P_4O_{14}$.

Experimental

Preparation

Black crystals of $NaMo_2P_4O_{14}$ were obtained by heating a mixture of Na_2MoO_4,

0022-4596/89 $3.00

MoO_2, Mo, and P_2O_5 (mole ratio 2 : 5 : 1 : 6) in a sealed silica tube at 1100°C for 2 days. The solution of the X-ray data showed that the black crystals had the composition Na $Mo_2P_4O_{14}$. Once the stoichiometry was determined from the structural analysis it was possible to prepare $NaMo_2P_4O_{14}$ as an X-ray pure, single-phase material by heating appropriate amounts of Na_2MoO_4, MoO_2, Mo, and P_2O_5 in a sealed silica tube at 1100°C for 2 days.

Determination of the Structure

A black chunk having the dimensions of 0.15 × 0.10 × 0.08 mm was selected for indexing and intensity data collection. Crystallographic data for $NaMo_2P_4O_{14}$: triclinic space group $P\bar{1}$, $a = 4.872(1)$, $b = 7.0025(7)$, $c = 8.2620(6)$ Å, $\alpha = 91.468(8)$, $\beta = 92.53(1)$, $\gamma = 106.61(1)°$, $Z = 1$, $\rho(\text{calc}) = 3.466$ g/cm^3, $\lambda(\text{Mo}K\alpha) = 0.70930$ Å, $\mu(\text{Mo}K\alpha) = 29.8$ cm^{-1}. Of the 1239 unique reflections measured at room temperature ($2\theta_{\max} = 55°$), 1166 were considered observed ($I > 2.5\ \sigma(I)$) after LP and absorption correction ($T_{\max}$, $T_{\min} = 0.999, 0.928$). Corrections for absorption effects were based on ψ scans of a few suitable reflections with χ values close to 90°. The structure was solved by direct methods and refined by full matrix least-squares refinement. All atoms were refined anisotropically: $R = 0.020$, $R_w = 0.029$, GOF = 1.192. In the final difference Fourier map, the deepest hole was -0.91 e/Å^3, and the highest peak 0.45 e/Å^3. Neutral atom scattering factors and anomalous dispersion terms were taken from "International Tables for X-Ray Crystallography" (5).

The molybdenum atoms are at inversion centers and all other atoms are at general positions. There are two major sites for the Na atom which are related by an inversion center and are too closely spaced to be simultaneously occupied. The multiplicity for the Na atom was allowed to vary and the resultant value deviated slightly from a half occupancy (0.473(6)). The Na atom showed a very large thermal parameter along the tunnel direction (U_{11}), suggesting that the Na atom is mobile. The largest residual electron density (0.72 e/Å^3) on the difference map was near the Na atom and was probably due to incomplete modeling of the disordered Na atom. Therefore, the sodium atom was considered half occupied in the final cycles of least-squares refinement. However, the possibility of slight deviation from stoichiometry cannot be excluded.

In order to see whether the two sites of Na^+ are strictly equivalent, the noncentrosymmetric space group $P1$ was considered. A least-squares refinement with fixed atomic and thermal parameters for Mo, P, and O atoms converged at $R = 0.0466$ and $R_w = 0.0604$. A difference Fourier map revealed two peaks in the large tunnel with almost identical intensities, which can be related by an inversion center at ($\frac{1}{2}$,0,0). We conclude that the two sites of Na^+ are equivalent and the very anisotropic thermal parameters do not result from a mean effect due to the superposition of electron densities through the inversion center.

Description and Discussion of the Structure

The atomic coordinates and thermal parameters are listed in Table I. Selected bond distances are given in Table II. The structure of $NaMo_2P_4O_{14}$, viewed along the a-axis, is shown in Fig. 1 and contains two types of tunnels of which one is occupied by Na atoms. The framework consists of MoO_6 octahedra which are connected by pyrophosphate groups. The empty tunnel results from the stacking of rings along the a-axis, each of which is formed by the edges of two octahedra and four tetrahedra. The larger tunnel, which is occupied by Na atoms, is formed by the edges of four octahedra and four tetrahedra. Figures 2a and b

TABLE I

ATOMIC COORDINATES FOR $NaMo_2P_4O_{14}$

Atom	x	y	z	B_{eq} (Å^2)[a]
Na	0.4051(24)	0.0098(10)	−0.0263(10)	6.6(6)
Mo(1)	0.5	0	0.5	0.317(17)
Mo(2)	0	0.5	0	0.343(17)
P(1)	0.11901(21)	0.24162(15)	0.69430(12)	0.47(4)
P(2)	0.52288(21)	0.63153(15)	0.75681(12)	0.43(3)
O(1)	0.3926(7)	0.1928(4)	0.3504(4)	0.94(11)
O(2)	0.7737(7)	0.5568(5)	0.7999(4)	0.97(11)
O(3)	0.3717(6)	0.6786(5)	0.9029(4)	0.88(10)
O(4)	0.9691(7)	0.7539(4)	0.1327(4)	0.81(10)
O(5)	0.1270(6)	−0.1917(4)	0.4327(4)	0.84(10)
O(6)	0.3111(6)	0.1035(4)	0.6808(4)	0.80(11)
O(7)	−0.2978(6)	0.5410(4)	0.3512(4)	0.77(11)

ANISOTROPIC THERMAL PARAMETERS (× 100) (Å^2) FOR $NaMo_2P_4O_{14}$[b]

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	17.4(12)	1.9(3)	5.2(5)	2.4(5)	−2.7(5)	−1.1(3)
Mo(1)	0.39(2)	0.37(2)	0.45(2)	0.13(2)	−0.00(2)	0.02(2)
Mo(2)	0.45(2)	0.50(2)	0.41(2)	0.22(2)	0.04(2)	0.00(2)
P(1)	0.55(4)	0.54(4)	0.66(5)	0.13(4)	0.02(4)	−0.16(3)
P(2)	0.52(4)	0.50(4)	0.58(5)	0.12(3)	−0.01(3)	0.08(3)
O(1)	1.25(14)	0.93(14)	1.37(15)	0.24(11)	−0.02(11)	0.58(11)
O(2)	1.18(14)	1.75(15)	1.03(14)	0.91(12)	−0.24(11)	0.24(12)
O(3)	0.95(14)	1.19(14)	1.05(14)	0.02(11)	0.44(11)	−0.23(11)
O(4)	1.50(14)	0.83(13)	0.88(14)	0.53(11)	0.32(11)	0.03(11)
O(5)	0.91(14)	0.95(14)	1.13(14)	−0.02(11)	−0.18(11)	−0.01(11)
O(6)	1.23(14)	1.09(14)	0.95(14)	0.68(11)	0.19(11)	−0.08(11)
O(7)	0.94(13)	0.71(13)	0.99(14)	−0.19(11)	−0.11(11)	−0.07(11)

[a] $B_{eq} = (8\pi^2/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

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

TABLE II

SOME SELECTED BOND DISTANCES (Å) FOR $NaMo_2P_4O_{14}$

Mo(1)–O(1)	2.014(3) (2×)	P(2)–O(1)	1.505(3)
Mo(1)–O(5)	1.973(3) (2×)	P(2)–O(2)	1.493(3)
Mo(1)–O(6)	2.013(3) (2×)	P(2)–O(3)	1.518(3)
Mo(2)–O(2)	2.057(3) (2×)	P(2)–O(7)	1.600(3)
Mo(2)–O(3)	2.091(3) (2×)	Na –O(3)	2.335(7)
Mo(2)–O(4)	2.111(3) (2×)	Na –O(3)	2.326(8)
P(1) –O(4)	1.512(3)	Na –O(4)	2.764(11)
P(1) –O(5)	1.513(3)	Na –O(4)	3.199(12)
P(1) –O(6)	1.531(3)	Na –O(4)	2.914(8)
P(1) –O(7)	1.587(3)	Na –O(6)	2.579(8)

are each a view of a section of the $NaMo_2P_4O_{14}$ structure and clearly show how the polyhedra are connected. Pentagonal windows (O2-O4-O5-O6-O7) appear on Fig. 2a, but they do not form pentagonal tunnels. Figure 3 is a stereoscopic view of the large tunnel in a direction perpendicular to the *a*-axis. The octagonal rings are inclined with respect to the axis of the tunnel. Adjacent octagonal rings form voluminous cages where the Na atoms are located. This structural characteristic is in agreement with the very large thermal parameter along the tun-

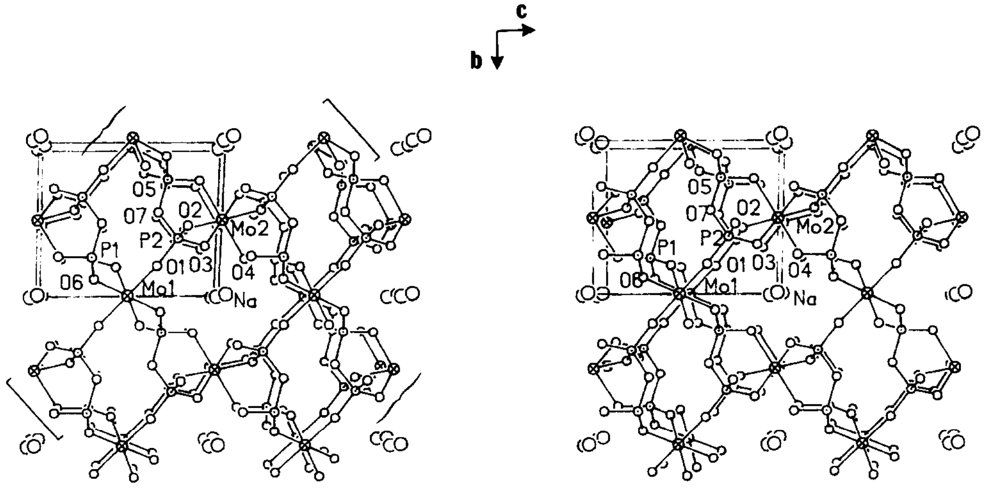

FIG. 1. A stereoscopic view of the $NaMo_2P_4O_{14}$ structure along the *a*-axis. The Mo, P, O, and Na atoms are represented by circles with a cross, a dot, small open circles, and large open circles, respectively.

nel direction for the Na atom. The shortest diameter of the octagonal ring (*d*(O4-O4*a*) = 4.07 Å) is smaller than 4.8 Å, twice the sum of the Na^+-ion and O^{2-}-ion radii. Thus the geometrical feature of the skeleton does not satisfy the criterion for fast Na^+-ion transport. Each Na site is surrounded by six oxygen atoms at distances ranging from 2.326(8) to 3.20(1) Å. Because the Na sites are partially occupied, the anions surrounding unoccupied sites relax toward their bonded cation neighbors and therefore an abnormally large average Na–O bond distance (2.686 Å) is observed.

Each $Mo(1)O_6$ octahedron shares corners with six P_2O_7 groups. Each $Mo(2)O_6$ octa-

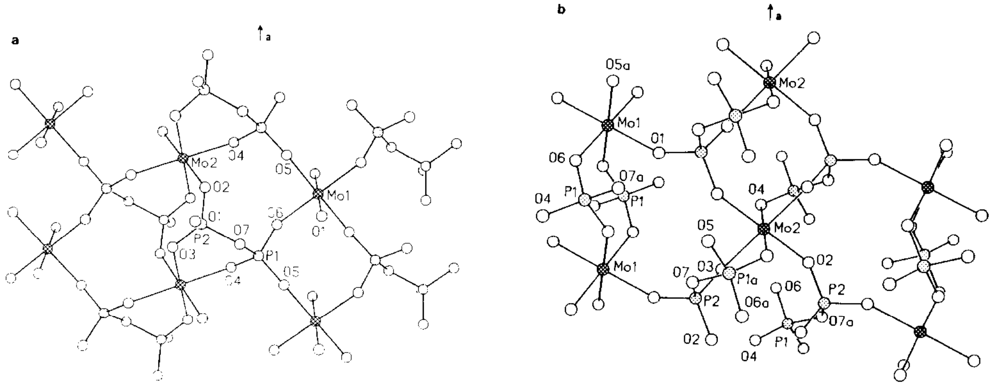

FIG. 2. (a) A view of a section of the $NaMo_2P_4O_{14}$ structure, denoted by the braces in Fig. 1, in a direction approximately parallel to [0$\bar{1}$1]. (b) A view of a section, denoted by the brackets in Fig. 1, in a direction approximately parallel to [011]. The Mo, P, and O atoms are represented by cross-hatched, dotted and open circles, respectively.

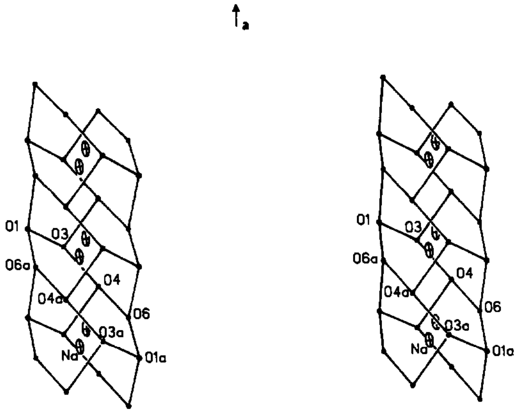

FIG. 3. A stereoscopic view of the large tunnel in $NaMo_2P_4O_{14}$ in a direction perpendicular to the *a*-axis. The tunnel can be considered as resulting from the stacking of octagonal rings (O1-O3-O4-O6-O1a-O3a-O4a-O6a) which are inclined with respect to the *a*-axis.

hedron shares corners with four P_2O_7 groups. Two of the four P_2O_7 groups are trans to each other and each shares two of its corners with the same $Mo(2)O_6$ octahedron. Each P_2O_7 group shares six corners with three $Mo(1)O_6$ octahedra and two $Mo(2)O_6$ octahedra. Both $Mo(1)O_6$ and $Mo(2)O_6$ octahedra exhibit regular Mo–O bond distances, which exclude the possibilities of Mo^{6+} and Mo^{5+} for both Mo atoms. The Mo(1)–O distances are shorter, indicating a higher oxidation state of Mo(1). The Mo(1)–O distances are similar to the Mo^{4+}–O distances (1.972, 1.978, 1.984, 1.995, 2.064, 2.073 Å) in MoO_2 (*6*). The Mo(2)–O distances are almost identical with the Mo^{3+}–O distances (2.080 (3×); 2.100 Å (3×)) in MoP_3SiO_{11} (*7*). An assessment of the oxidation states of the Mo atoms using the bond-length bond-strength formula for the Mo–O bond [$s = (d/1.882\ Å)^{-6}$] (*8*) yields the following results: Mo1, +4.17; Mo2, +3.24. Therefore, the oxidation states +4 and +3 can be assigned to Mo(1) and Mo(2), respectively. In the tetrahedra belonging to the pyrophosphate group each P atom is displaced away from the bridging oxygen atom (O(7)) giving three shorter and one longer P–O bond. The O–O distances in $P(2)O_4$ tetrahedron of the P_2O_7 group range from 2.472(4) to 2.521(4) Å and the mean value, 2.495 Å, is a classical value in a PO_4 tetrahedron. The O–O distances in $P(1)O_4$ tetrahedron cover a wider range (2.416(4)–2.549(4) Å) but with a comparable mean value (2.506 Å). The P(1)–O–P(2) bond angle involving the bridging oxygen atom is 130.3(2)°. The staggered configuration of the P_2O_7 group is rather similar to that in $Cs_4Mo_8P_{12}O_{52}$ (*2*).

$NaMo_2P_4O_{14}$ is the first molybdenum phosphate in which equal amounts of isolated Mo^{3+} and Mo^{4+} are simultaneously present. Magnetic susceptibility measurements on this material would be interesting. This material has empty tunnels available for more counter cations, suggesting the possibility of synthesizing more reduced phases. On the other hand, one might be able to synthesize oxidized phases by removing sodium ions from the tunnels. By using soft chemistry new phases, which are frequently metastable, might be stabilized.

Acknowledgments

Support for this study by the National Science Council and the Institute of Chemistry Academia Sinica is gratefully acknowledged.

References

1. M. GOREAUD, PH. LABBE, AND R. RAVEAU, *J. Solid State Chem.* **56,** 41 (1985); PH. LABBE, M. GOREAUD, AND B. RAVEAU, *J. Solid State Chem.* **61,** 324 (1986); M. LAMIRE, PH. LABBE, M. GOREAUD, AND B. RAVEAU, *J. Solid State Chem.* **66,** 64 (1987).

2. $K_4Mo_8P_{12}O_{52}$: A. LECLAIRE, J. C. MONIER, AND B. RAVEAU, *J. Solid State Chem.* **48,** 147 (1983); $TlMo_2P_3O_{12}$: A. LECLAIRE, J. C. MONIER, AND B. RAVEAU, *J. Solid State Chem.* **59,** 301 (1985); $Cs_4Mo_8P_{12}O_{52}$ and $Cs_2Mo_4P_6O_{26}$: K. H. LII AND R. C. HAUSHALTER, *J. Solid State Chem.* **69,** 320 (1987); $AgMo_5P_8O_{33}$: K. H. LII, D. C. JOHNSTON, D. P. GOSHORN, AND R. C. HAUSHALTER, *J. Solid State*

Chem. **71,** 131 (1987); $Cs_3Mo_5P_6O_{25}$: K. H. LII, R. C. HAUSHALTER, AND C. J. O'CONNOR, *Angew. Chem. Int. Ed. Engl.* **26,** 549 (1987); $CsMoP_2O_7$: K. H. LII AND R. C. HAUSHALTER, *Acta Crystallogr. C* **43,** 2036 (1987); $Cs_3Mo_4P_3O_{16}$: R. C. HAUSHALTER, *J. Chem. Soc. Chem. Commun.*, 1566 (1987); $Cs_3Mo_5P_7O_{24}$: S. L. WANG AND K. H. LII, *J. Solid State Chem.* **73,** 274 (1988); $Mo_3P_5SiO_{19}$: S. L. WANG, C. C. WANG, AND K. H. LII, *J. Solid State Chem.* **74,** 409 (1988).

3. K. H. LII AND C. C. WANG, *J. Solid State Chem.* **77,** 117 (1988).
4. S. L. WANG, C. C. WANG, AND K. H. LII, to be published.
5. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch, Birmingham (1974) (present distributor: Reidel, Dordrecht).
6. B. J. BRANDT AND A. C. SKAPSKI, *Acta Chem. Scand.* **21,** 661 (1967).
7. C. C. WANG, K. H. LII, AND S. L. WANG, unpublished work; A. LECLAIRE AND B. RAVEAU, *J. Solid State Chem.* **71,** 283 (1987).
8. I. D. BROWN AND K. K. WU, *Acta Crystallogr. B* **32,** 1957 (1976).