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A Synchroton Single Crystal X-Ray Structure Determination of $(NH_4)_3Mo_4P_3O_{16}$: A Microporous Molybdenum Phosphate with $Mo_4O_4^{6+}$ Cubes

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Reaction of MoO_3, Mo, $(NH_4)_2HPO_4$, H_3PO_4, and H_2O in a mole ratio of 1.4 : 1 : 3.6 : 6 : 120 at 360°C for 16 hr gives a nearly quantitative yield of black cubes of $(NH_4)_3Mo_4P_3O_{16}$ **(1)**. The structure of **(1)** was solved from data collected on a $30 \times 30 \times 30$ μm^3 crystal at the National Synchrotron Light Source at Brookhaven National Laboratory. The compound is cubic, space group $P\bar{4}3m$, with $a = 7.736(2)$ Å, and was refined to residuals of $R(R_w) = 0.035(0.049)$. Phosphate **(1)** is isotypic with $Cs_3Mo_4P_3O_{16}$ and is related to the iron arsenate mineral pharmacosiderite. Unlike the Cs^+ compound, **(1)** can be rendered microporous by thermal removal of the NH_4^+ cations to give ammonia with the charge compensating proton remaining behind in the lattice. Water absorption isotherms show the reversible uptake of 5.6 wt% water, which corresponds to over 15 vol% void space in **(1)** after the NH_3 removal. The framework consists of $Mo_4O_4^{6+}$ cubes, with six Mo–Mo contacts of 2.570(4) Å, joined together together by $(PO_4)_{6/2}$ along ⟨100⟩ to form a 3-D network composed of tetramers of triply edge-sharing Mo-centered octahedra and phosphate groups alternating along all ⟨100⟩ directions. The windows and cavities in **(1)** are large enough that the NH_4^+ cations occupy several different positions in the unit cell. © 1991 Academic Press, Inc.

We have recently reported several members of a new family of molybdenum phosphates, like $(Me_4N)_{1.3}(H_3O)_{0.7}[Mo_4O_8(PO_4)_2] \cdot 2H_2O$ (*1*), $(CH_3)_2NH_2[Mo_2P_3O_{12}(OH)_2]$ (*2*), $(NH_4)Mo_2P_2O_{10} \cdot H_2O$ (*3*), and $Mo_8(H_2O)_6P_6O_{34}(OH)_2 \cdot 7H_2O$ (*4*), which can be rendered microporous and display internal void volumes ranging from 15 to 35 vol%. One goal of this research is to prepare materials with potentially catalytically active *d*-block elements lining the walls of tunnels in a microporous solid in order to probe the possibility of carrying out shape selective catalysis inside a solid state material. Here we describe synthesis, synchrotron single crystal X-ray structure solution and sorption properties of $(NH_4)_3Mo_4P_3O_{16}$, which contains Mo–Mo-bonded $Mo_4O_4^{6+}$ cubes and has >15 vol% void space, after thermal decomposition of the cations, as determined from water absorption isotherms.

The reaction of MoO_3, Mo, H_3PO_4, $(NH_4)_2HPO_4$, and H_2O in a mole ratio of 1.4 : 1 : 6 : 3.6 : 120 for 16 hr at 360°C gives a nearly quantitative yield of black cubes of $(NH_4)_3Mo_4P_3O_{16}$ **(1)**. The reactions were carried out in 8-mm OD quartz tubes which were heated in a hydrothermal apparatus in which the pressure inside the tube was balanced by an external hydrostatic pressure to keep the tube intact. A Mo : P ratio of 4 : 3 from electron microprobe analysis

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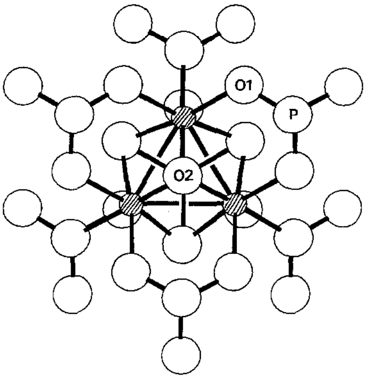

FIG. 1. The $Mo_4O_4^{6+}$ cube in **(1)**, with its 6/2 phosphate groups, projected onto $(\bar{1}\bar{1}\bar{1})$. Note the tetrahedral arrangement of the Mo atoms, which are striped in the figure.

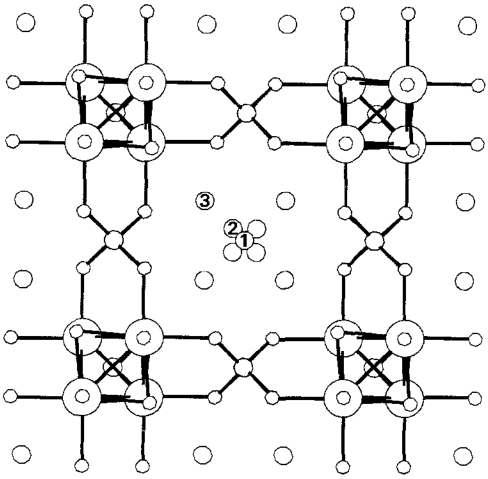

FIG. 2. Ordering of the NH_4^+ cations in the void centered at 0,0,0. In this projection, N(1) appears at the center at $z = 1/2$ while the other N(1) atoms at $z = 0$ are obscured by the phosphate, P, atoms. The atoms labeled N(2) and N(3) have z values of -0.045 and -0.845, respectively.

combined with indexing the powder pattern as primitive cubic with no systematic absences indicated that **(1)** was likely isotypic with our previously determined structure of $Cs_3Mo_4P_3O_{16}$ (*5*) (space group $P\bar{4}3m$, $a = 7.728$ Å). With a 3 kW conventional sealed tube X-ray source the X-ray scattering from the available small crystals of **(1)** was very weak; therefore, we collected a single crystal X-ray diffraction data set on a $30 \times 30 \times 30$ μm^3 crystal using the beamline X10A at the National Synchrotron Light Source at Brookhaven National Laboratory. Structure solution and refinement of such small-molecule structures from single crystal synchrotron data are not commonplace. The difficulty has been the inability to measure high-precision data. A full structure solution and high-precision refinement requires high-quality data and only recently have such data become available using synchrotron sources around the world (*6*). In a recent paper we reported what is, to the best of our knowledge, among the first such full structure solutions from data taken at NSLS (*3*). Here we present the second such study using those same experimental techniques. Further experimental details are given in Table I. The atomic parameters are given in Table II. Bond lengths and angles are given in Table III.

A structure solution using the X-ray data shows that **(1)** contains a three-dimensional octahedral–tetrahedral framework that is essentially identical to that found in

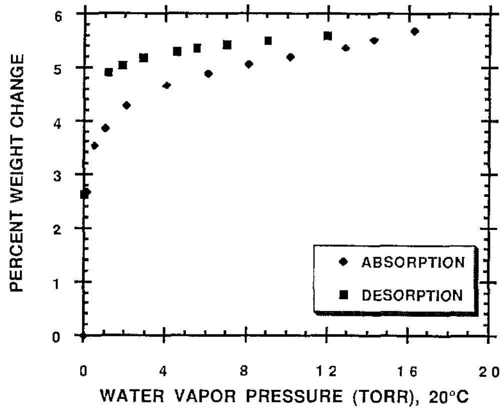

FIG. 3. Water absorption isotherms at 20°C for **(1)**, demonstrating the Type 1 absorption (*7*) isotherms indicative of the absorption of guests into micropores.

TABLE I

EXPERIMENTAL DETAILS

A. Crystal Data	
Formula	$(NH_4)_3MO_4P_3O_{16}$
Molecular weight	786.79
Crystal color, habit	Black, cube
Crystal dimensions	30 × 30 × 30 μm^3
Number of reflections used for unit cell determination	6
Omega scan FWHM	0.1°
Cell parameters	$a = 7.736(2)$ Å $V = 463.03(19)$ Å^3
Space group	$P\bar{4}3m$
Z Value	1
D_{calc}	2.82 g cm^{-3}
F_{000}	374
$\mu_{(\lambda=0.918\ Å)}$	59.30 cm^{-1}
B. Intensity measurements	
Diffractometer	Huber 4-Circle with vertical detector rotation
Radiation, NSLS X10A: 2.5 GeV, ≈125 mA	$\lambda = 0.918(2)$ Å
Monochromator	Double-crystal Ge (111)
Temperature	30°C
Attenuator	Al foil, maximum count rate set to 5 × 10^4 cps
Detector Aperture	12 mm horizontal aperture 10 mm vertical aperture
Crystal to detector distance	345 mm
Scan type	Omega, unequal step size
Scan width, deg	1.0
Steps per scan	100
$2\theta_{max}$, deg	63.5
q range, $q = 2\pi \sin(\theta)/\lambda$)	0.06 Å$^{-1} \le q \le 3.60$ Å^{-1}
Number of reflections measured	Total, including two standards measured every 12 reflections: 249 Unique: 100 ($R_{int} = 0.033$). For subsets of the reflections the following were found: 72 ($F^2 < 1/2\ \overline{F}^2$) $R_{int} = 0.033$; 45 ($F^2 > 1/4\ \overline{F}^2$) $R_{int} = 0.046$; 28 ($F^2 < 1/8\ \overline{F}^2$) $R_{int} = 0.060$
Corrections	Lorentz-polarization, incident beam polarization $I_{\parallel}/I_{\perp} = 13.997$ Extinction (*8*), Parameter = 12(3); The maximum correction is 0.82 applied to F_{001}.
C. Structure solution and refinement	
Structure solution	Fourier difference map
Refinement	Full-matrix least-squares (*9*)
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least-squares weights (σ_F from counting statistics)	$1/\sigma_F^2$
Anomalous dispersion	All nonhydrogen atoms, Mo$K\alpha$ corrections applied
Number of Observations ($I > 3\sigma_I$)	100
Number of Variables	18
Number of Constraints (N(occ) = 3.0)	1
Residuals: $R(R_w)$	0.035(0.049)

$Cs_3Mo_4P_3O_{16}$ which contains metal–metal-bonded $Mo_4O_4^{6+}$ cubes and PO_4^{3-} tetrahedra. This cube is shown, with its 6/2 phosphate groups, in projection down $[\bar{1}\bar{1}\bar{1}]$ in Fig. 1. There are six Mo–Mo bonds at 2.570(4) Å which are similar to those in $Cs_3Mo_4P_3O_{16}$ (2.579(6) Å). Since the four Mo are crystallographically equivalent, the Mo oxidation state is 3.5+ and there are 10 electrons shared among the six Mo–Mo bonds.

The 3-D structure built up from the cubes and tetrahedra contains tunnels running along ⟨100⟩ and smaller tunnels parallel to ⟨110⟩. The larger tunnels have alter-

TABLE IIA

Positional and Thermal Parameters

Atom	Occupancy	x	y	z	U(iso)$^+$
Mo(1)	4	0.6174(2)	$=x$	$=x$	0.010*
P(1)	3	0	1/2	1/2	0.016
O(1)	12	0.616(1)	$=x$	0.890(2)	0.019(3)
O(2)	4	0.360(2)	$=x$	$=x$	0.016(4)
N(1)	0.6(2)	1/2	0	0	0.02(2)
N(2)	1.6(2)	0.955(4)	$=x$	$=x$	=N(1)
N(3)	0.8(2)	0.155(10)	$=x$	$=x$	=N(1)

[a] Coefficients U(iso) of temperature factor T in Å^2; $T = \exp(-8\pi^2 U(\mathrm{iso})[\sin(\theta/\lambda)]^2)$.

[b] U_{eq} given in Å^2; $T = \frac{1}{3}\left(\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j\right)$.

nating voids (at 0,0,0) and constrictions (centered around 1/2, 0, 0) with free diameters at the constrictions of ca. 3.6 Å. In **(1)**, we found significant electron density at three NH_4^+ sites in the unit cell. These sites cannot be fully occupied—the total content would exceed three NH_4 molecules per unit cell and the intersite distances are too short to allow simultaneous occupation. For example we find N(2)–N(2) = 0.98(9) Å and N(2)–N(3) = 2.0(1) Å. We modeled the site occupancy by assuming that the three sites had equal, isotropic thermal parameters then allowed the occupancy to vary with a restraint that the total occupancy summed to equal three N per unit cell. Approximately 20% of the nitrogen atoms are found at N(1), which lies at the center of the constrictions (the Cs^+ location in **(2)**) at the Wyckoff *d* site at 1/2, 0, 0 with $\bar{4}2m$ site symmetry. These are possibly hydrogen bonded, to the O atoms forming the constriction, at 3.2 Å, e.g., we find O(1)–N(1) = 3.219(7) Å. The remaining nitrogen atoms are distributed between N(2) and N(3): both these atoms lie on Wyckoff *e* sites (at x,x,x with $3m$ site symmetry) with x = 0.955 and x = 0.155, respectively. At these positions, both N(2) and N(3) define the vertices of two hypothetical tetrahedra centered in the void at 0, 0, 0 (Fig. 2). The atom at site N(3) may also be hydrogen bonded to the framework atoms. Distances of O(1)–N(3) = 3.24(4) Å and O(2)–N(3) = 2.7(1) Å are found. There is in addition a possibility that the NH_4^+ cations are themselves hydrogen bonded. We find N(2)–N(3) = 2.7(1) Å.

TABLE IIB

Anisotropic Thermal Parameters[a]

Atom	$U11$	$U22$	$U33$	$U12$	$U13$	$U23$
Mo(1)	0.010(1)	$=U11$	$=U11$	−0.0002(7)	$=U12$	$=U12$
P(1)	0.013(5)	0.017(3)	$=U22$	0.0	0.0	0.0

[a] Coefficients U_{ij} of temperature factor T in Å^2; $T = \exp\left(-2\pi^2 \sum_i \sum_j U_{ij} h_i h_j a_i^* a_j^*\right)$.

TABLE III

Bond Lengths (Å) and Angles (deg) for $(NH_4)_3Mo_4P_3O_{16}$

Mo(1)—O(1)	2.108(13)[a]
Mo(1)—O(2)	2.008(16)
Mo(1)—Mo(1)	2.570(4)
Mo(1)—P(1)	3.226(1)
O(1)—Mo(1)—O(1)	90.7(5)
O(1)—Mo(1)—O(2)	84.7(4)
O(1)—Mo(1)—O(2)	173.4(6)
O(2)—Mo(1)—O(2)	99.6(7)
P(1)—O(1)	1.526(12)
O(1)—P(1)—O(1)	112.2(1.0)
O(1)—P(1)—O(1)	108.2(5)
O(1)—O(1)	2.533(24)
O(1)—O(1)	2.472(20)
O(1)—O(1)	2.999(21)
O(1)—O(2)	2.773(11)
O(1)—N(1)	3.219(7)
O(1)—N(3)	3.237(37)
P(1)—O(1)—Mo(1)	124.4(8)
O(2)—O(2)	3.066(39)
O(2)—N(3)	2.7(1)
Mo(1)—O(2)—Mo(1)	79.6(8)
N(1)—N(3)	3.162(6)
N(2)—N(2)	0.98(9)
N(2)—N(3)	2.0(1)
N(2)—N(3)	2.7(1)

[a] One e.s.d. is indicated in parentheses.

Phosphate **(1)** can be rendered microporous by thermally removing NH_3 from the NH_4^+ cations. After heating under vacuum from room temperature to 390°C at a rate of ≈10°C/hr, infrared and TGA analysis both confirmed the absence of the NH_4^+ cations. Powder X-ray diffraction showed that the sample was still crystalline and that the original structure was retained. The absorption properties were studied via water absorption isotherms. As shown in Fig. 3, the weight of water absorbed as a function of water vapor pressure shows a typical Type 1 absorption isotherm (*7*) indicative of the filling of micropores. Since the calculated density of the framework is 2.82 $g \cdot cm^{-3}$, then the 5.6 wt% water absorbed corresponds to the filling of more than 15 vol% internal void space. The relatively small amount of hysteresis shown in Fig. 3 indicates that the absorption is quite reversible.

These results, along with our other examples of microporous molybdenum phosphates (*1–4*), indicate that it is possible to easily prepare a number of microporous transition metal oxides. We are currently beginning to examine the possibility for carrying out chemical reactions within the micropores of these solids.

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