

Hydrothermal Synthesis, Structure, and Sorption Properties of $\text{Cs}(\text{H}_3\text{O})[\text{Mo}_2\text{O}_2(\text{PO}_4)_2(\text{HPO}_4)]$

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Yellow plates of $\text{Cs}(\text{H}_3\text{O})[\text{Mo}_2\text{O}_2(\text{PO}_4)_2(\text{HPO}_4)]$, (**1**), obtained in 60% yield from the reaction of Cs_2MoO_4 , Mo, H_3PO_4 , and H_2O in a mole ratio of 5 : 1 : 30 : 57 for 24 hrs at 200°C, crystallize in the monoclinic space group $P2_1/a$ with $a = 9.166(4)$, $b = 9.073(2)$, $c = 15.808(3)\text{\AA}$, $\beta = 96.85^\circ$, $V = 1305(1)\text{\AA}^3$, $Z = 4$, and $R(R_w) = 0.087(0.085)$. The structure has MoOPO_4 -like layers held together with HPO_4 groups and is structurally similar to $(\text{VO})_2(\text{SO}_4)_2(\text{H}_2\text{SO}_4)$. The interlamellar space is compartmentalized into tunnels containing one-dimensional H-bonded strings of HPO_4 groups alternating with strings of Cs^+ and H_3O^+ cations. It is possible to remove water from the structure in a reversible manner as shown from water absorption isotherms. This same composition framework was prepared in a different crystal system and with a different cation by Clearfield and Peascoe (see *J. Solid State Chem.* **95**(1), 83 (1991)). © 1991 Academic Press, Inc.

Introduction

Although microporosity exists in a large number of tetrahedral framework materials like zeolites and aluminophosphates, this property is much less common in nonmineralogical materials containing octahedrally coordinated d -block elements. We have recently prepared five new microporous molybdenum phosphates (MoPO's) that have internal void volumes in the range of 15-40 volume% (1-5). One goal of this research involving microporous transition metal oxides is to prepare materials that have large internal surface areas, like the traditional zeolitic aluminosilicates, capable of sorbing molecules but combined with a potentially catalytically active, octahedrally coordi-

nated d -block element. In this paper we describe the synthesis, single crystal X-ray diffraction structure, magnetic properties, and sorption properties of $\text{Cs}(\text{H}_3\text{O})[\text{Mo}_2\text{O}_2(\text{PO}_4)_2(\text{HPO}_4)]$, (**1**). Unlike most of our other hydrothermally prepared microporous phosphates, whose MoPO framework geometries and compositions depend very strongly on the nature of the templating cation, this particular framework can accommodate several different cations, primarily by reorientation of the interlamellar PO_4 groups. Molybdenum phosphate frameworks of this composition were reported previously by us (5) and in the accompanying paper by Clearfield and Peascoe (10).

Experimental

The reaction described here was carried out in polytetrafluoroethylene lined stainless steel containers under autogeneous

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pressure. The Mo metal should be less than $2\mu\text{m}$ particle size.

$\text{Cs}(\text{H}_3\text{O})[\text{Mo}_2\text{O}_2(\text{PO}_4)_2(\text{HPO}_4)]$, **(1)**. The reaction of Cs_2MoO_4 , Mo, H_3PO_4 , and H_2O in a mole ratio of 5 : 1 : 30 : 57 for 24 hrs at 200°C gives a 60% yield of yellow crystals of **(1)** as the only product precipitating from solution. Simulation of the X-ray powder pattern based on the coordinates from the single crystal study shows the solid to be single phase.

Results and Discussion

We have recently investigated the synthesis and sorption properties of a new class of microporous solids based on octahedral-tetrahedral molybdenum phosphate frameworks. These materials are built up from the following units: (a) $\text{Mo}_4\text{O}_4(\text{PO}_4)_{6/2}^-$ cubes and tetrahedra; (b) $\text{Mo}_4\text{O}_8(\text{PO}_4)_{4/2}^-$ cubes and tetrahedra; (c) $\text{Mo}_6\text{O}_{15}(\text{H}_2\text{PO}_4)_3(\text{HPO}_4)^{5-}$ rings; (d) planar Mo_4 tetramers with single and double Mo-Mo

bonds; (e) MoOPO_4 -like layers connected by phosphate groups.

We have now isolated several examples of the type (e) above containing various cations in an octahedral-tetrahedral framework composed of MoOPO_4 -like layers bonded together covalently by interlamellar phosphate groups. We recently reported the synthesis and sorption properties of $\text{CH}_3\text{NH}_3[\text{Mo}_2\text{O}_2(\text{PO}_4)_2(\text{H}_2\text{PO}_4)]$, **(2)**, which could be rendered microporous via thermal decomposition of the ammonium cation and contained >25 volume% void space (5). The accompanying paper by Clearfield and Peascoe (10) also describes the same framework with a different cation in a different Laue class. There are also other examples of solids with frameworks that are topologically quite similar to this structure type but with different elements.

The structure of the cesium phosphate **(1)** was determined from single crystal X-ray diffraction data and is shown in Fig. 1, with the experimental X-ray data in Table I, the

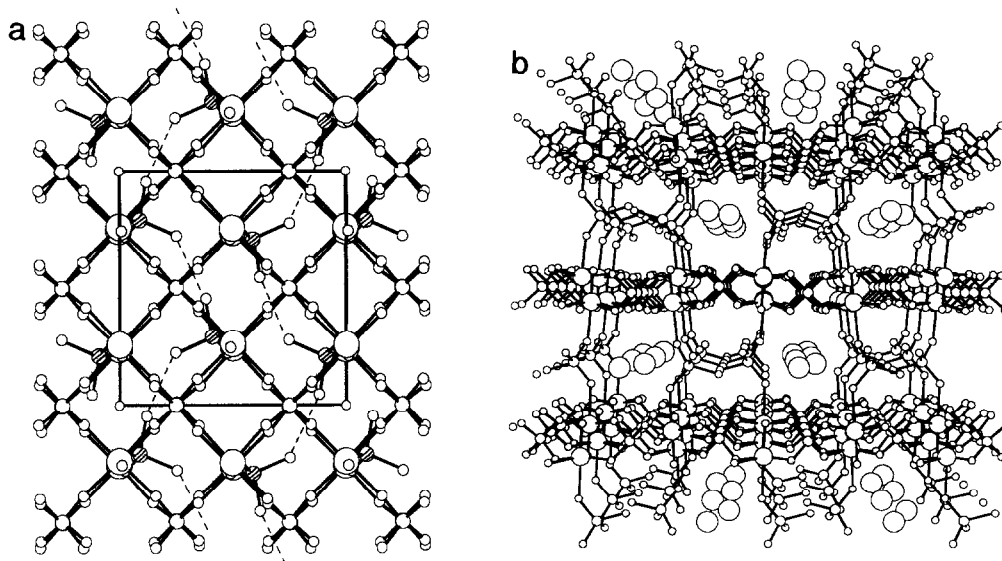


FIG. 1. The structure of phosphate **(1)** shown (a) perpendicular to the layers. The hydrogen bonded network involving the interlamellar phosphate groups (interlamellar P atoms striped) is shown as a dashed line (see also Figure 4); (b) perspective view parallel to the layers with the Cs^+ represented as large circles. Note that the interlamellar PO_4 groups do not share a common O atom (see Fig. 4). The H_3O^+ cation (O(15)) is not shown, but see Fig. 3.

TABLE I
EXPERIMENTAL DETAILS

A. Crystal data	
Empirical formula	Mo ₂ P ₃ O ₁₅ Cs
Formula weight	657.70
Crystal color, habit	yellow, trigonal-plate
Crystal dimensions (mm)	0.150 × 0.200 × 0.100
Crystal system	monoclinic
Lattice parameters:	$a = 9.166$ (4) Å $b = 9.073$ (2) Å $c = 15.808$ (3) Å $\beta = 96.85$ (2)°
Space group	$P2_1/a$ (#14)
Z value	4
D_{calc}	3.346 g/cm ³
$\mu(\text{MoK}\alpha)$	50.47 cm ⁻¹
B. Intensity measurements	
Diffractometer	Rigaku AFC6R
Radiation	MoK α ($\lambda = 0.71069$ Å)
Temperature	23°C
$2\theta_{\text{max}}$	50.0°
No. of reflections measured	Total: 2623 Unique: 2462 ($R_{\text{int}} = .061$)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.86–1.00) Decay (-0.40% decline)
C. Structure solution and refinement	
Structure solution	Patterson method
Refinement	Full-matrix least-squares
Function minimized	$\sum w(F_o - F_c)^2$
Anomalous dispersion	All nonhydrogen atoms
No. observations ($I > 3.00\sigma(I)$)	1403
No. variables	115
Reflection/parameter ratio	12.20
Residuals: R ; R_2	0.087; 0.085
Maximum peak in final diff. map	5.83 e ⁻ /Å ³
Minimum peak in final diff. map	-5.02 e ⁻ /Å ³

fractional coordinates in Table II, and some selected interatomic distances in Table III. The solid state structure is topologically quite similar to both the structure found in (VO)₂(SO₄)(H₂SO₄) (6) and some very recently reported niobium phosphates (7). These structures all contain MoOPO₄-like layers (8), which consist of corner sharing

octahedra and tetrahedra as shown in Fig. 2. The structure of these layers as found in MoOPO₄ itself (space group $P4/n$) is shown in Fig. 2, which is a projection onto (001). The molybdenum in the 5+ oxidation state, as in (1), very often shows a short Mo=O (molybdenyl group, Mo=O, ca. 1.6 Å) bond *trans* to a long (ca. 2.3 Å) Mo-O bond. The

TABLE II
POSITIONAL PARAMETERS AND $B(\text{eq})$ FOR (1)

Atom	x	y	z	$B(\text{eq})$
Cs(1)	0.1067(3)	0.1968(3)	0.2425(2)	3.4(1)
Mo(1)	0.2616(2)	0.4991(3)	0.0411(1)	0.27(8)
Mo(2)	0.2444(2)	0.4980(3)	0.4584(1)	0.47(9)
P(1)	0.500(1)	0.7499(7)	0.0038(5)	0.3(2)
P(2)	0.2919(8)	0.5888(9)	0.2524(5)	1.1(3)
P(3)	0.503(1)	0.7517(7)	0.5104(5)	0.7(3)
O(1)	0.611(2)	0.842(2)	0.060(1)	0.9(4)
O(2)	0.581(2)	0.656(2)	-0.059(1)	0.6(4)
O(3)	0.390(2)	0.844(2)	-0.053(1)	0.6(4)
O(4)	0.422(2)	0.652(2)	0.064(1)	0.8(4)
O(5)	0.247(2)	0.509(2)	-0.063(1)	1.3(4)
O(6)	0.288(2)	0.488(2)	0.178(1)	0.5(3)
O(7)	0.221(2)	0.522(2)	0.323(1)	0.8(3)
O(8)	0.457(2)	0.623(2)	0.287(1)	1.9(4)
O(9)	0.220(3)	0.765(3)	0.232(2)	3.9(6)
O(10)	0.271(2)	0.487(2)	0.564(1)	0.5(3)
O(11)	0.401(2)	0.655(2)	0.448(1)	1.6(4)
O(12)	0.415(2)	0.844(2)	0.567(1)	1.6(4)
O(13)	0.585(2)	0.850(2)	0.452(1)	1.2(4)
O(14)	0.608(2)	0.654(2)	0.572(1)	1.5(4)
O(15)	-0.098(3)	0.464(3)	0.261(2)	6.1(8)

Note.

$$B_{\text{eq}} = \frac{8\pi^2}{3} [U_{22} + \frac{1}{\sin^2\beta} (U_{11} + U_{33} + 2U_{13} \cos \beta)].$$

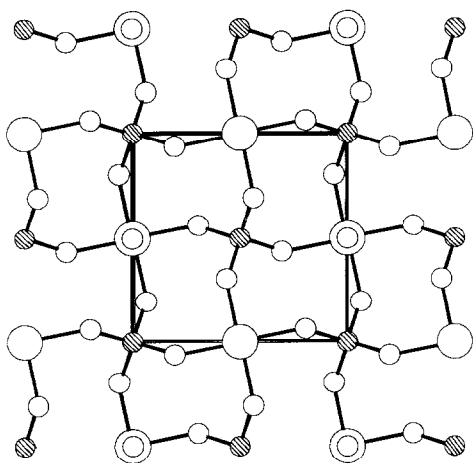


FIG. 2. Projection of the MoOPO_4 structure onto (001) with large circles Mo, P atoms striped, and remaining circles O.

5+ oxidation is confirmed by magnetic susceptibility measurements which shows $\mu = 2.0$ BM per Mo atom consistent with one unpaired electron for each Mo atom. In both (1) and in MoOPO_4 the $\text{Mo}=\text{O}$ vector is perpendicular to the layers. In MoOPO_4 the layers are connected by an oxygen that is a shared vertex between octahedra of two layers in a manner in which the molybdenyl oxygen from one layer forms the long $\text{Mo}-\text{O}$ contact, which is *trans* to the molybdenyl group, up to the next layer. In (1) and (2) however, the layers are connected by phosphate tetrahedra, two of whose vertices form the long $\text{Mo}-\text{O}$ contact between two layers (Fig. 1).

In (1) the interlayer phosphate group is formulated as HPO_4 based on the rather

TABLE III
INTRAMOLECULAR DISTANCES

Atoms	Distance
Mo(1)–O(1)	2.04(2)
Mo(1)–O(2)	2.01(2)
Mo(1)–O(3)	2.00(2)
Mo(1)–O(4)	2.02(2)
Mo(1)–O(5)	1.63(2)
Mo(1)–O(6)	2.15(2)
Mo(2)–O(7)	2.14(2)
Mo(2)–O(10)	1.67(2)
Mo(2)–O(11)	2.04(2)
Mo(2)–O(12)	2.03(2)
Mo(2)–O(13)	2.00(2)
Mo(2)–O(14)	2.03(2)
P(1)–O(1)	1.52(2)
P(1)–O(2)	1.56(2)
P(1)–O(3)	1.53(2)
P(1)–O(4)	1.53(2)
P(2)–O(6)	1.48(2)
P(2)–O(7)	1.48(2)
P(2)–O(8)	1.58(2)
P(2)–O(9)	1.75(3)
P(3)–O(11)	1.44(2)
P(3)–O(12)	1.53(2)
P(3)–O(13)	1.54(2)
P(3)–O(14)	1.56(2)

large difference in bond lengths between the two terminal P–O bonds of P–O = 1.58(2) and P–O = 1.74(3) Å. This contrasts to the corresponding interlamellar phosphate in (2), which was formulated as H_2PO_4 . Therefore the framework has a 2- charge per formula unit and this charge is compensated by the Cs^+ and H_3O^+ cations. This hydronium ion, (O(15)), which is bonded to the Cs^+ at 3.10(3) and 3.06(3) Å, bridges the Cs^+ into one-dimensional strings running parallel to [100] as shown in Fig. 3. This hydronium ion also has probable H-bonded contacts at 2.98(4) and 3.01(3) Å to some of the framework O atoms.

As shown in Fig. 1(b) the $\text{Cs}^+/\text{H}_3\text{O}^+$ strings and the phosphate tetrahedra fill the space between the MoOPO_4 -like layers. The phosphate groups also form one-dimensional hydrogen bonded strings parallel to the [100] direction as shown in Figs. 1(b) and 4.

To determine if the water in (1), which was present in the form of a hydronium ion, could be reversibly removed, the thermal behavior and water absorption isotherms were investigated. The TGA of (1) showed a weight loss of 2.2% at ca. 100°C, which

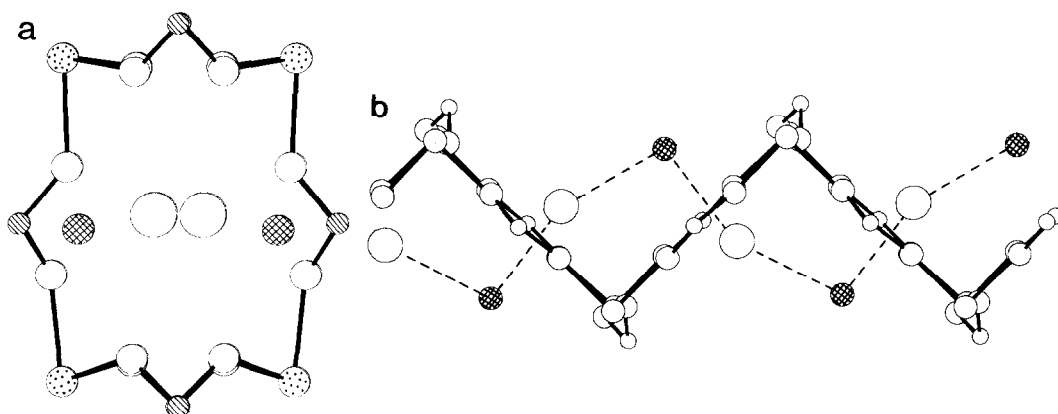


FIG. 3. Views of the tunnel where Cs^+ and H_3O^+ cations reside. (a) View parallel to the tunnel direction with large circles Cs^+ , stippled circles Mo, striped circles P, cross-hatched circles H_3O^+ , and remaining circles framework O. (b) View about 90° from (a) showing how the Cs^+ and H_3O^+ cations are bonded into one dimensional strings (dashed line).

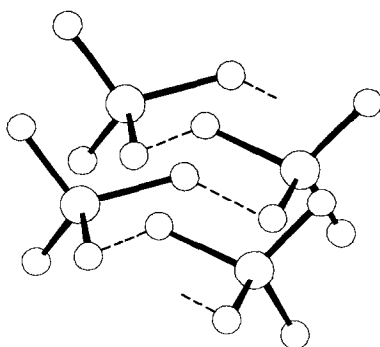


FIG. 4. The hydrogen bonded strings of the interlamellar phosphate groups.

can be compared with a weight loss of 2.9% calculated from the chemical formula. The water absorption isotherm of **(1)** was investigated at 20°C and the results are shown in Fig. 5. The absorption-desorption loops show some hysteresis but the shape of the isotherm is approximately Type I (9), indicating that the absorption of water into **(1)** is fairly reversible. There is additional weight loss in the 350°C range, which might be due to the dehydration of adjacent H_2PO_4 groups.

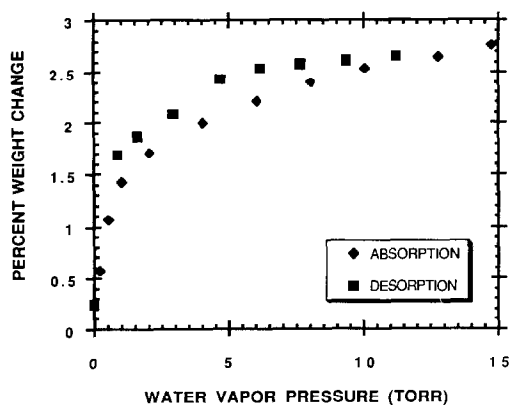


FIG. 5. The water absorption/desorption isotherm for **(1)** at 20°C. For the initial cycle the compound was degassed for 1 hr at 150°C under vacuum.

Summary

The molybdenum phosphate framework discussed here has now been structurally characterized with three different cations (MeNH_3^+ , Cs^+ , and Na^+) which crystallized in three different Laue classes. This differs from most of our other molybdenum phosphates, as well as most zeolites, in that usually a specific cationic template directs the crystallization of a specific framework. The reason that this framework is so accommodating in terms of the template charge and geometry is that the framework is flexible due to both the possibility of various orientations of the interlamellar phosphate tetrahedra as well as changes due to the registry of the layers relative to one another.

Finally, water absorption isotherms show that the water in **(1)** can be removed easily and in a reversible manner.

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