Supplementary Material Available: Tables of NMR and NOE data and figures containing the long-range J_{CH} observed in the HMBC spectrum and ^1H NMR, ^{13}C NMR, H,H COSY, HOHAHA, H,C COSY, HMBC, and NOESY spectra for **1** (10 pages). Ordering information is given on any current masthead page.

Vacant Coordination Sites within the Tunnels of a Microporous, Neutral Framework Molybdenum Phosphate with 35 Vol % Void Space: Structure of $Mo_8O_{12}(PO_4)_4(HPO_4)_2 \cdot 13H_2O$

Linda A. Mundi, Karl G. Strohmaier, David P. Goshorn, and Robert C. Haushalter*

Exxon Research and Engineering Co.
Annandale, New Jersey, 08801

Received June 28, 1990

We are investigating the synthesis and sorption properties of a new class of open framework solids with the goal of being able to carry out shape-selective and size-exclusionary chemical reactions within the pores of a microporous solid. If one could prepare a solid-state material that would have the accessible internal micropore volume, framework rigidity, and thermal stability of a zeolite, combined with a potentially catalytically active transition metal as an integral, covalently bonded part of the framework, then the possibility of performing both catalysis and separations simultaneously in one material may be achievable. In addition to a large number of solid-state alkali-metal Mo phosphates and molecular Mo phosphates with metal-metal bonds,[1] we have reported one previous example of a microporous molybdenum phosphate, $(Me_4N)_{1.3}(H_3O)_{0.7}[Mo_4O_8(PO_4)_2] \cdot 2H_2O$,[2] and there are three other examples of molybdenum phosphates that can be rendered microporous, namely, $(CH_3)_2NH_2[Mo_2P_3O_{12}(OH)_2]$[3] containing Mo^{5+}, $(NH_4)_3Mo_4P_3O_{16}$,[4] containing $Mo^{3.5+}$, and $(NH_4)Mo_2P_2O_{10} \cdot H_2O$[5] with both Mo^{4+} and Mo^{5+}. Here we discuss the synthesis, structural characterization, and sorption properties of $Mo_8O_{12}(PO_4)_4(HPO_4)_2 \cdot 13H_2O$ (**1**). Phosphate **1** contains unusual Mo_4 units, with the MoO_6 octahedra bonded together via both edge- and corner-sharing modes, which together with the phosphate groups form a neutral framework that differs from the anionic frameworks found in all of our other molybdenum phosphates[1,2] as well most other zeolitic solids.[6] Some of the Mo atoms in **1** contain water ligands that can be removed while the crystallinity of the framework is maintained, Mo atoms thereby being generated with vacant coordination sites within the micropores of **1**. At least 35% of the internal volume of crystals of dehydrated **1** is empty space according to water absorption isotherms.

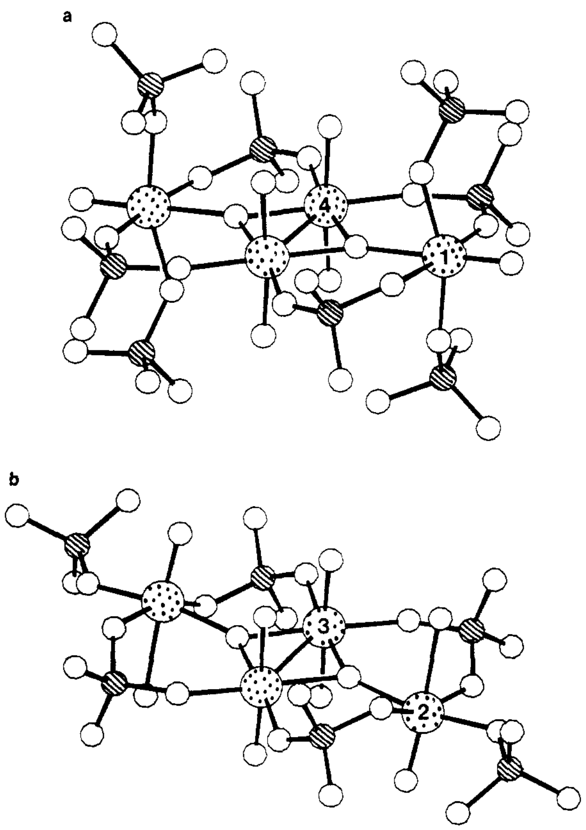

Figure 1. The two Mo_4 tetramers in **1**: (a) tetramer **2** containing Mo(1) and Mo(4) and (b) tetramer **3** containing Mo(2) and Mo(3). Stippled circles, Mo; striped circles, P; remaining circles, O.

The reaction of MoO_3, Mo, H_3PO_4, and H_2O in a mole ratio of 7:1:12:300 for 6 days at 200 °C gives a 40% yield of orange-brown crystalline $Mo_8(H_2O)_6P_6O_{34}(OH)_2 \cdot 7H_2O$ as the only solid precipitating from solution. The product was shown to be single phase by comparison of the powder X-ray diffraction pattern to the powder pattern calculated from the coordinates obtained from the single-crystal structure determination.

Phosphate **1** has a complicated, low-symmetry ($P\bar{1}$) three-dimensional structure[7] with a framework composed of MoO_6 octahedra and PO_4 and $PO_3(OH)$ tetrahedra sharing edges and corners. The structure can be described in terms of the two crystallographically independent, centrosymmetric, nearly planar Mo_4 units present in the unit cell. These two tetramers, labeled **2** and **3** in Figure 1, are both composed of two edge-sharing MoO_6 octahedra, with Mo–Mo single bonds (2.659 (5) and 2.611 (6) Å), with the two O atoms involved in this shared edge also serving as a corner for two additional MoO_6 octahedra, making these particular oxygens each three coordinate to three different Mo atoms.

Tetramer **2** (Figure 1a), centered around the $\bar{1}$ site at ($^1/_2$,0,0), has two of the four Mo atoms (Mo(1)) in the 5+ oxidation state according to bond-strength bond-length calculations[8] and the characteristic geometry.[9] The molybdenyl groups on Mo(1) are trans to three-coordinate O(5). The two Mo(4) atoms in the central edge-sharing octahedral dimer are 2.611 (6) Å apart, consistent with a Mo–Mo single bond and an oxidation state of 5+. Refinement of the X-ray data shows two terminal O atoms on each Mo(4) which appear to be a molybdenyl O and a water O atom disordered over the two sites.[10] In tetramer **3** (Figure

---

(1) (a) $Cs_2Mo_4P_6O_{26}$ and $Cs_4Mo_8P_{12}O_{52}$: Lii, K. H.; Haushalter, R. C. *J. Solid State Chem.* **1987**, *69*, 320. (b) $AgMo_5P_8O_{33}$: Lii, K. H.; Goshorn, D. P.; Johnston, D. J.; Haushalter, R. C. *J. Solid State Chem.* **1987**, *71*, 131. (c) $Cs_3Mo_4P_3O_{16}$: Haushalter, R. C. *J. Chem. Soc., Chem. Commun.* **1987**, 1566. (d) $Cs_3Mo_5P_6O_{25}$: Lii, K. H.; O'Connor, C. J.; Haushalter, R. C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 549. (e) $CsMoP_2O_7$: Haushalter, R. C.; Lii, K. H. *Acta Crystallogr.* **1987**, *C43*, 2036. (f) $Cs_4Mo_{10}P_{18}O_{66}$: Haushalter, R. C.; Lai, F. W. *J. Solid State Chem.* **1988**, *76*, 218. (g) $Cs_2K_2Mo_8P_{12}O_{52}$: Haushalter, R. C.; Lai, F. W. *J. Solid State Chem.* **1989**, *83*, 202. (h) $[Na_{14}Mo_{24}P_{17}O_{97}(OH)_{31}]^{6-}$. (i) Haushalter, R. C.; Lai, F. W. *Angew. Chem.* **1989**, *101*, 802. (j) $Na_3Mo_2P_2O_{11}(OH) \cdot 2H_2O$: Haushalter, R. C.; Mundi, L. A. *Inorg. Chem.* **1990**, *29*, 2879. (k) $[(H_3O)_2NaMo_6P_4O_{24}(OH)_7]^{2-}$: Haushalter, R. C.; Lai, F. W. *Inorg. Chem.* **1989**, *28*, 2904.

(2) Haushalter, R. C.; Strohmaier, K. G.; Lai, F. W. *Science* **1989**, *246*, 1289.

(3) Haushalter, R. C.; Mundi, L. A.; Strohmaier, K. G., submitted for publication.

(4) Haushalter, R. C.; Mundi, L. A.; Strohmaier, K. G.; King, H. E., Jr., submitted for publication.

(5) Haushalter, R. C.; Mundi, L. A.; Strohmaier, K. G.; King, H. E., Jr., submitted for publication.

(6) Barrer, R. M. *Hydrothermal Chemistry of the Zeolites*; Academic Press: London, 1982.

(7) Crystal data for **1**: triclinic, space group $P\bar{1}$ with $a = 10.466$ (5) Å, $b = 12.341$ (4) Å, $c = 8.228$ (7) Å, $\alpha = 94.75$ (4)°, $\beta = 111.46$ (5)°, $\gamma = 89.48$ (3)°, $V = 985$ (2) Å^3, $R(R_w) = 0.067(0.072)$. Framework O atoms: isotropic refinement. All others: anisotropic for 182 variables and 1592 data with $I > 3\sigma(I)$.

(8) (a) Brown, I. D.; Wu, K. K. *Acta Crystallogr.* **1976**, *B32*, 1957. (b) Zachariasen, W. H. *J. Less-Common Met.* **1978**, *62*, 17.

(9) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988.

0002-7863/90/1512-8182$02.50/0 © 1990 American Chemical Society

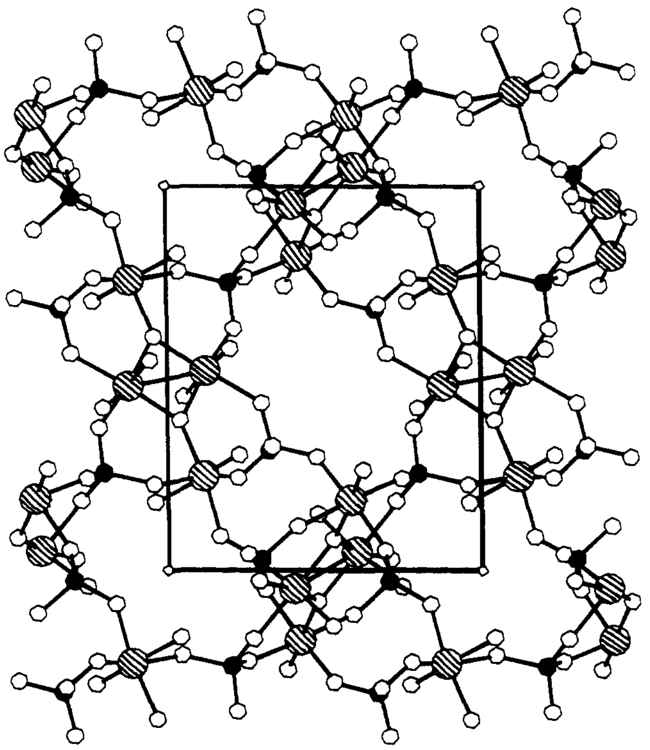

Figure 2. Ball-and-stick projection (as drawn by Chem-X[15]) of the unit cell contents of **1** down [001]. The solvate water molecules residing in the tunnels are not shown. Striped circles, Mo; filled circles, P; remaining circles, O.

1b), centered around the $\bar{1}$ site at $(0,{}^1/_2,{}^1/_2)$, Mo(2) has ordered trans molybdenyl and water oxygens, both of which are cis to three-coordinate O(10), and has a calculated[8] oxidation state of 5+. The Mo(3) pair also has disordered molybdenyl/water oxygen atoms, as with Mo(4) in **2** above, as well as a Mo–Mo single bond at 2.659 (5) Å. These tetramers are topologically quite similar to Fe_4 tetramers found in the mineral amarantite, $Fe_2(SO_4)_2O\cdot 7H_2O$,[11] as well as in some synthetic compounds.[12]

The connection of these tetramers into a three-dimensional array by the phosphate groups is shown in Figure 2, which is a projection of the unit cell contents down [001] showing the tetramers connected into sheets, which lie in the (220) plane, by PO_4 and $PO_3(OH)$ groups. These sheets are connected by PO_4 groups into a 3D lattice. This connectivity generates tunnels parallel to [100], [010], and [001] which are filled with the waters of solvation and into which protrude the waters that are ligated to Mo.

Phosphate **1** is microporous toward water as demonstrated by the Brunauer type I absorption isotherm.[13] Both the absorption isotherm and the TGA data show the loss of 12 wt % H_2O, which is greater than 90% of the theoretical amount calculated from the crystal structure.[14] This 12 wt % corresponds to about 35 vol % internal void space, since the calculated density of **1** based on the X-ray data is near 3 g cm^{-3}, if one assumes that the density of the absorbed water is 1 g cm^{-3} or less. Since nearly half of the water in **1** is ligated to Mo, and since the powder X-ray diffraction pattern indicates rather small distortions of the lattice upon dehydration and the water absorption is totally reversible, one concludes that some of the Mo atoms in the tunnels of dehydrated **1** must possess a vacant coordination site.

Preliminary magnetic measurements on **1** show that $\mu_B = 2.6$ μ_B per four Mo atoms, consistent with the two metal–metal-bonded Mo atoms being diamagnetic and one unpaired electron on each of the other two d^1 Mo^{5+} atoms. Examination of the $\chi^{-1}(T)$ data above 100 °K shows it to be linear with $\theta = -102$ K, indicative of antiferromagnetic interactions, while below 100 °K the $\chi^{-1}(T)$ plot shows nonlinear behavior.

These results show that microporous transition-metal oxides, with coordinatively unsaturated metals and very large internal void volumes, can be easily prepared.

Supplementary Material Available: Tables of experimental crystallographic details, positional parameters and B(eq) values, U values, intramolecular distances and bond angles, and the water absorption isotherm data (9 pages). Ordering information is given on any current masthead page.

---

[10] The Mo(3) and Mo(4) pairs both have Mo–Mo single bonds near 2.6 Å consistent with a d^1 configuration (Mo^{5+}). The water content of **1** observed by TGA requires nearly half of the disordered terminal O atoms on Mo(3) and Mo(4) to be water molecules.

[11] Süsse, P. *Z. Kristallogr.* **1968**, *127*, 261.

[12] Gorun, S. M.; Lippard, S. J. *Inorg. Chem.* **1988**, *27*, 149 and references therein.

[13] Ruthven, D. M. *Principles of Adsorption and Adsorption Processes*; Wiley: New York, 1984; p 49. Absorption data has been deposited as supplementary material.

[14] Possible reasons for removal of less than the theoretical amount of water could be incomplete occupation of the water solvate sites in the crystal (the solvate waters had rather large thermal parameters) or, since water loss starts at just slightly above room temperature according to TGA data, the compound may have lost some water during the isolation and workup.

[15] Chem-X, designed and distributed by Chemical Design Ltd., Mahwah, NJ.

Specific Deuteration Strategy for Enhancing Direct Nuclear Overhauser Effects in High Molecular Weight Complexes

Pearl Tsang, Peter E. Wright, and Mark Rance*

Department of Molecular Biology, MB-2
Research Institute of Scripps Clinic
10666 North Torrey Pines Road
La Jolla, California 92037

Received April 16, 1990

Proton NMR studies of high molecular weight systems are plagued by several problems, including poor resolution and sensitivity. In particular, these problems greatly limit the ability to observe specific nuclear Overhauser effects (NOEs), thus severely hampering structure determination efforts. Poor resolution results from the presence of an enormous number of resonances and inherently large line widths; the latter also significantly reduce the sensitivity of the NMR experiments. Resolution can be greatly improved through the use of isotope-editing techniques[1] which allow selective detection of a subset of NMR resonances. Resonance line-width increases are due to more efficient ^1H-^1H dipolar relaxation as motional correlation times increase; this problem can be alleviated through judicious use of deuterium substitution.[2-7] Another very important benefit of deuterium substitution is the possibility of increasing the size of NOEs via elimination of undesirable magnetization transfer pathways. Such pathways allow magnetization leakage away from the nuclei of interest and also provide indirect magnetization transfer routes between two nuclei, thereby complicating the analysis of NOE data. Substantial improvements in spectral resolution in protein NMR studies through random fractional deuteration have been previously demonstrated.[2-5] However, a significant weakness in such schemes is that unless deuterium incorporation is close to 100%, multispin magnetization transfer pathways will still exist which can lead to erroneous interpretations of NOE measurements, especially if longer mixing times are employed to take advantage of the deuteration. Also, the sensitivity of the fractional deuteration method is far from optimal (except for NOEs between exchangeable protons), due to the low probability of two nuclear

---

[1] Griffey, R. H.; Redfield, A. G. *Q. Rev. Biophys.* **1987**, *19*, 51–82.

[2] Crespi, H. L.; Kostka, A. G.; Smith, U. H. *Biochem. Biophys. Res. Commun.* **1974**, *61*, 1407–1414.

[3] Kalbitzer, H. R.; Leberman, R.; Wittinghofer, A. *FEBS Lett.* **1985**, *180*, 40–42.

[4] LeMaster, D. M.; Richards, F. M. *Biochemistry* **1988**, *27*, 142–150.

[5] Markley, J. L.; Putter, I.; Jardetzky, O. *Science* **1968**, *161*, 1249–1251.

[6] Torchia, D. A.; Sparks, S. W.; Bax, A. *J. Am. Chem. Soc.* **1988**, *110*, 2321–2322.

[7] Shon, K.; Opella, S. J. *J. Magn. Reson.* **1989**, *82*, 193–197.

0002-7863/90/1512-8183$02.50/0 © 1990 American Chemical Society