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A New Microporous (ca. 25 vol % Void Space) Molybdenum Phosphate Based on the Octahedral–Tetrahedral $Mo_2O_2(PO_4)_2(H_2PO_4)^-$ Framework

This paper describes the synthesis, structure, and sorption properties of the new $Mo_2O_2(PO_4)_2(H_2PO_4)^-$ framework, which, in addition to $(Me_4N)_{1.3}(H_3O)_{0.7}[Mo_4O_8(PO_4)_2]\cdot 2H_2O$,[1] $(NH_4)Mo_2P_2O_{10}\cdot H_2O$,[2] $Mo_8(H_2O)_6P_6O_{34}(OH)_2\cdot 7H_2O$,[3] and $(NH_4)_3Mo_4P_3O_{16}$,[4] represents one of the first examples of a new family of microporous transition-metal oxides with octahedrally coordinated d-block elements. These compounds represent the beginning steps in the preparation of solid-state materials that would display a size or shape discriminatory absorption into molecular sized pores combined with a potentially catalytically active transition element as a covalently bonded part of the lattice within the micropores. The $Mo_2O_2(PO_4)_2(H_2PO_4)^-$ framework, **1**, has a structure that can be conceptually derived from the layers present in the $MoOPO_4$ structure type[5] and is also related to that of $(VOSO_4)_2\cdot H_2SO_4$.[6] The primary difference between the $MoOPO_4$ structure type (layers of corner-sharing octahedra and tetrahedra, space group *P4/n*) and the $Mo_2O_2(PO_4)_2(H_2PO_4)^-$ framework discussed here is that the layers are connected by $PO_2(OH)_2^-$ groups instead of sharing an oxygen atom as in the $MoOPO_4$ structure type. Unlike many zeolites[7] and other of our molybdenum phosphates[1-4] whose framework compositions and structures depend strongly on the nature of the templating cations, the $Mo_2O_2(PO_4)_2(H_2PO_4)^-$ framework is very flexible toward the size, shape, and polarity of the occluded cation. This framework can accommodate these cations by the reorientation of the interlamellar phosphate groups and to some extent by modifying the registry of the layers. This framework was discovered simultaneously by Clearfield and co-workers[8] but with a different cation and crystal system.

When MoO_3, Mo, CH_3NH_2 (or $(CH_3)_2NH$), H_3PO_4, and H_2O are reacted in a mole ratio 5:1:4:36:100 for 4 days at 200 °C, the yellow phosphate $CH_3NH_3[Mo_2O_2(PO_4)_2(H_2PO_4)]$ (**2**) or, if $(CH_3)_2NH$ is used as the template, $(CH_3)_2NH_2[Mo_2O_2(PO_4)_2(H_2PO_4)]$ (**3**) is obtained in ca. 80% yield based on Mo. Elemental analysis shows that there is one cation per Mo_2P_3 formula unit. The IR spectra show a strong N–H stretch near 3260 cm^{-1} and N–H deformations in the range 1550–1650 cm^{-1} for the primary and secondary cations, both of which are diagnostic of ammonium cations,[9] in addition to the bands from the molybdenum phosphate

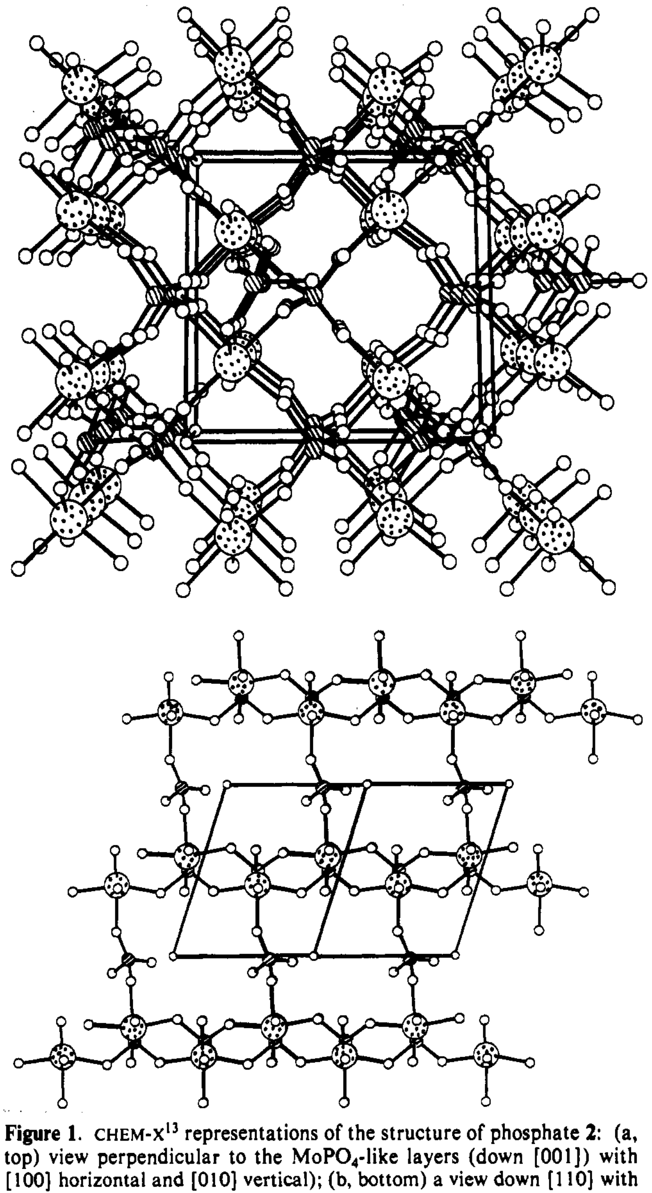

Figure 1. CHEM-X[13] representations of the structure of phosphate **2**: (a, top) view perpendicular to the $MoPO_4$-like layers (down [001]) with [100] horizontal and [010] vertical); (b, bottom) a view down [110] with the [001] axis pointing down, showing the interlamellar phosphate groups and the tunnels where the cations reside.

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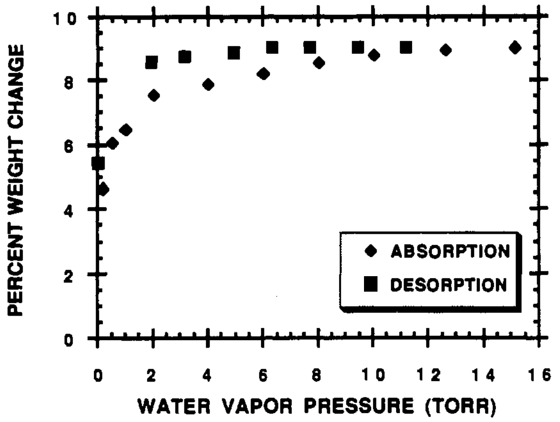

Figure 2. Water absorption isotherm for $(CH_3)_2NH_2[Mo_2O_2(PO_4)_2(H_2PO_4)]$ at 21 °C after the thermal decomposition of the ammonium cation (see text for conditions). The absorption isotherm is type I,[12] indicating the absorption of water into the micropores of the host lattice. The amount absorbed corresponds to filling ca. 25 vol % void space.

framework. The thermogravimetric analysis (TGA) of these materials under He shows a rather abrupt weight loss near 400–450 °C. The sharpness, as well as the relatively high temperature, of the TGA transition is not consistent with the expected thermal behavior of nonentrained methyl- or dimethylammonium cations. The IR absorptions associated with the organic cations disappear at temperatures corresponding to the TGA transition. There is no sharp weight loss in this temperature regime for the $Mo_2P_3O_{12}(OH)_2^-$ frameworks that contain no organics such as $Cs(H_3O)[Mo_2O_2(PO_4)_2(HPO_4)]$[10] and $H_3O[Mo_2O_2(PO_4)_2(H_2PO_4)]$.[10]

The structure of **2**, $(CH_3NH_3)[Mo_2O_2(PO_4)_2(H_2PO_4)]$, was examined with a single-crystal X-ray diffraction study.[11] Figure 1 shows the structure of **2** viewed both parallel and perpendicular to the $MoOPO_4$-like layers, and the interlamellar phosphate groups are obvious. There is a slight disorder of the $P(OH)_2$ portion of the $PO_2(OH)_2$ group about a crystallographic 2-fold axis. All of the Mo atoms are in the 5+ oxidation state and display the characteristic short Mo–O molybdenyl contacts (1.61 (1) Å).

While the analytical data discussed above leave no doubt that there are stoichiometric amounts of $MeNH_3^+$ cations in the molybdenum phosphate framework of **2**, we could find no trace of the cation in the crystal structure. All of the significant peaks in the final difference map (+1.70 to −1.41 $e{\cdot}Å^{-3}$) were near the Mo or P atoms. The simulation of the powder X-ray diffraction pattern of **2** generated from the single-crystal coordinates shows that the bulk material has the same structure found in the crystal used for the single-crystal X-ray diffraction study. The inability to locate the cations is probably due to a combination of three factors: (a) the tunnel in which the cation resides is larger than the cation, thus imposing little preferred orientation; (b) both ends of the $MeNH_3^+$ cation have essentially identical sizes and shapes, facilitating hydrogen bonds in one of two possible directions within the tunnel; (c) there is a 2-fold disorder in the interlamellar phosphate group, which is partially responsible for determining the size and shape of the tunnel, about a crystallographic 2-fold axis (Figure 1b).

To determine if these organic cations could be removed without collapsing the framework, i.e. if it were possible to generate any substantial internal micropore volume, we examined the water absorption isotherms at room temperature after the thermal decomposition of the organic cations. After a sample of $(CH_3)_2NH_2[Mo_2O_2(PO_4)_2(H_2PO_4)]$ was heated from 25 to 400 °C at a linear rate over 24 h under vacuum, the weight of water absorbed as a function of the water vapor pressure was measured. As shown in Figure 2, the shape of the absorption isotherm is type I[12] indicative of the absorption of the guest molecule into the micropores of the host and shows that the sample takes up 9–10 wt % water into the micropores in a nearly reversible manner. During this heating cycle the sample turned from yellow to brown but the powder X-ray diffraction measurements indicated that the sample was still crystalline although with somewhat broader peak widths indicative of a reduction in particle size or a slight reduction in crystalline order. Since the density of the Mo–P–O framework of this phosphate is >2.7 $g{\cdot}cm^{-1}$ and if the density of the adsorbed water is assumed to be less than or equal to 1 $g{\cdot}cm^{-1}$, then the absorbed water comprises ca. 25% of the volume of the hydrated sample. The water uptake, especially on the initial low-pressure absorption points, was rather slow, indicating that the water filled the internal volume of the crystals via a tortuous pathway.

In summary, a new class of molybdenum phosphates based on the $Mo_2O_2(PO_4)_2(H_2PO_4)^-$ framework can be easily prepared by the reaction of a Mo^{5+} source in the presence of phosphoric acid. Unlike many other open framework solids, which yield a specific structure when hydrothermally prepared in the presence of a specific templating cation, the $Mo_2O_2(PO_4)_2(H_2PO_4)^-$ framework is very accommodating in terms of formation in the presence of cations of varying sizes and shapes. Absorption isotherms indicated it was possible, after decomposition of the entrained organic cation, to access essentially all of the internal volume of the solids when water is used as the probe molecule.

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Supplementary Material Available: Table S1, listing experimental crystallographic details, positional and thermal parameters, and bond distances and angles (9 pages); Table S2, listing calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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(10) R. Haushalter and L. Mundi, unpublished results.

(11) X-ray data for **2** (fw 540.86): monoclinic, space group *C*2 (No. 5), $a = 9.126$ (6), $b = 9.108$ (8), $c = 8.654$ (3) Å; $\beta = 114.06$ (4)°; $V = 656.8$ (8) $Å^3$; $Z = 2$. The calculated density is 2.735 $g{\cdot}cm^{-3}$, $\lambda = 0.71069$ Å, and $\mu = 22.99$ cm^{-1} with transmission factors from 0.77 to 1.00. For 60 variables and 678 data with $I > 3.00\sigma(I)$, R (R_w) = 0.061 (0.066). Maximum and minimum residual electron density = +1.70 and −1.41 $e{\cdot}Å^{-3}$.

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(13) CHEM-X, designed and distributed by Chemical Design, Ltd., Mahwah, NJ.

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Novel Titanium(II) Amine Complexes L_4TiCl_2 [L = $^1/_2$ *N,N,N',N'*-Tetramethylethylenediamine (TMEDA), $^1/_2$ *N,N,N'*-Trimethylethylenediamine, Pyridine, $^1/_2$ 2,2'-Bipyridine]: Synthesis and Crystal Structure of Monomeric *trans*-$(TMEDA)_2TiCl_2$

Interest in the chemistry of divalent titanium has been stimulated by the very diverse aspects of its chemical reactivity, including activation of small molecules (N_2,[1] CO,[2] CO_2,[3] H_2[4]), reductive

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