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Synthesis of Open-Framework Transition-Metal Phosphates Using Organometallic Precursors in Acidic Media. Preparation and Structural Characterization of $Fe_5P_4O_{20}H_{10}$ and $NaFe_3P_3O_{12}$[1]

Sir:

We wish to report the synthesis and single-crystal X-ray structural characterization of two open-framework transition-metal phosphates by a novel synthetic procedure, namely the reaction of metal carbonyls with a protonated anion at neutral to acid pH in a biphasic water–acetone solution. Specifically, this procedure is shown to be applicable to the synthesis of materials isostructural with the iron–manganese phosphate minerals hureaulite[2–4] and alluaudite.[5]

The pure iron-containing forms of these minerals may be prepared by a hydrothermal synthesis procedure in which a mixture of H_3PO_4 (46.7 g), 40% tetrapropylammonium hydroxide ((TPA)OH, 90 g) or 40% tetrabutylammonium hydroxide ((TBA)OH, 114.8 g), $Fe(CO)_5$ (59 g), H_2O (192 g), and acetone (300 cm^3) are heated to 150 °C for 43 h under autogenous pressure. The primary product of the reaction, as determined by X-ray powder diffraction techniques, is a pure iron-containing analogue, $Fe_5P_4O_{20}H_{10}$ (I), of the mineral hureaulite, $(Mn_{1-x},Fe_x)\cdot 5H_2(PO_4)_4\cdot 4H_2O$. A second phase, $NaFe_3P_3O_{12}$ (II), corresponding to the pure iron-containing form of the mineral alluaudite, $W_{4-8}(X+Y)_{12}(PO_4)_{12}$, where W = Na, Ca, K, and/or Mn, X = Mn(II), Fe(II), Mg, Ca, Li, and/or Na, and Y = Fe(III), was also isolated from the products of the reaction mixture containing (TBA)OH with 0.4% sodium ion present. Single crystals of I and II were isolated and structurally characterized.[6,7]

The structure of I consists of an open-framework network of $[Fe_5P_4O_{20}H_4]^{6-}$ ions with octahedrally coordinated iron atoms and tetrahedrally coordinated phosphorus atoms. Preliminary Mössbauer results have established the presence of three iron(II) sites. The anion, $[Fe_5P_4O_{20}H_4]^{6-}$, has a twofold axis of symmetry and contains two water molecules coordinated to the two equivalent Fe(2) atoms, projecting into the cavity formed by the other three oxygen atoms. Although only three of the hydrogen atoms were found in the structural analysis, TGA results showed a weight loss consistent with a sturctural formula of $Fe_5H_2(PO_4)_4\cdot 4H_2O$.

A prominent set of channels runs along the *c* axis as shown in Figure 1. Two sets of small channels, roughly perpendicular to the *b* axis, are also present. By rotation about the *c*–sin β axis, a third set of small channels is observed.

In their structural characterization of the alluaudite-like product of the system $NaCl–Fe_2O_3–(NH_4)_2HPO_4–H_2O$, Yakubovich and co-workers[8] found the structural formula to be $Na_2Fe^{III}Fe^{II}{}_2(PO_4)_3$. From our system, $Fe(CO)_5$–(TBA)OH–H_3PO_4, with 0.4% sodium ion present in the (TBA)OH solution, crystals of I and II were isolated. The open-framework nature of II is seen in the view down the *c* glide shown in Figure 2. The coordination about the iron atoms is octahedral, and that about the phosphorus atoms is

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(1) Contribution No. 3846 from the Central Research and Development Department, Experimental Station, E. I. du Pont de Nemours and Co.

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(6) For $Fe_5P_4O_{20}H_{10}$, a crystal of dimensions 0.10 × 0.02 × 0.25 mm was mounted in a glass capillary. Forty-four reflections were computer-centered on the diffractometer at −100 °C and cell parameters refined by least squares to the values $a = 17.492$ (3) Å, $b = 9.038$ (2) Å, $c = 9.349$ (2) Å, and $\beta = 96.23$ (2)°. Intensity data were collected at −100 °C by the ω-scan method using Mo Kα radiation on a Syntex P3 diffractometer equipped with a graphite crystal monochromator. Several ω scans showed typical peak widths at half-height to be 0.28°. Data were collected with use of a scan rate of 1.3–4.0°/min and a scan range of 1.0°. The ratio of scan time to background counting time was 1.0. Measurements were made from $2\theta = 4°$ to $2\theta = 54°$, giving a total of 1858 reflections, of which 1356 were independent. With use of the criterion $F_o^2 > 2\sigma(F_o^2)$, 1241 reflections were considered observed. Three standard reflections were measured every 200 reflections and showed no systematic variations. Intensities were corrected for Lorentz and polarization effects. An absorption correction ($\mu = 94.86$ cm^{-1}) was applied. The transmission factors varied from 0.097 21 to 0.126 95. The structure was solved in the space group *C*2/*c* with use of direct methods (MULTAN). Three of the hydrogen atoms were found in the difference Fourier. The function minimized during the least-squares refinement was $w(|F_o| - |F_c|)^2$, where w was taken as $1/\sigma(F_o)$ and $\sigma(F_o) = [\sigma(I^2) + 0.003(I^2)]^{1/2}$. Refinement of the positional parameters using anisotropic thermal parameters for all atoms except for hydrogen gave $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.039$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 0.046$. The final values of the positional parameters, anisotropic thermal parameters, interatomic distances, intramolecular angles, intramolecular nonbonding distances, intermolecular distances, symmetry operation codes, and structure factors for I are available in Tables I–VIII, respectively, of the supplementary material.

(7) For $NaFe_3P_3O_{12}$, a crystal of dimensions 0.033 × 0.066 × 0.10 mm was mounted on a fiber in air. Twenty-five reflections were computer-centered on the diffractometer at 26 °C and the cell parameters refined by least squares to the values $a = 11.998$ (1) Å, $b = 12.328$ (1) Å, $c = 6.500$ (1) Å, and $\beta = 114.185$ (6)°. Intensity data were collected at 26 °C by the ω-scan method using Mo Kα radiation on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal monochromator. ω scans showed typical peak widths at half-height to be 0.20°. Data were collected with use of a scan rate of 2°/min and a scan range of $\omega = 0.8 + 0.35(\tan\theta)$. Measurements were made from $2\theta = 4°$ to $2\theta = 55°$, giving a total of 2219 (1911 observed) reflections, of which 915 were independent. Three standard reflections were measured every 200 reflections and showed no systematic variations. An absorption correction was applied ($\mu = 55.607$ cm^{-1}). Prior to the correction, the variance was 11.97, and after correction, 5.04. The structure was solved in the space group *C*2/*c* with use of the heavy-atom (Patterson) method. No problems were encountered during the solution. The function minimized during the least-squares refinement was $w(|F_o| - |F_c|)^2$, where w was taken as $1/\sigma(F_o)$ and $\sigma(F_o) = [\sigma(I^2) + 0.003(I^2)]^{1/2}$. Refinement of the positional parameters using anisotropic thermal parameters for all atoms gave $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.024$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 0.029$. The final values of the positional parameters, anisotropic thermal parameters, interatomic distances, intramolecular angles, intramolecular nonbonding distances, intermolecular distances, symmetry operation codes, and structure factors for II are available in Tables IX–XVI, respectively, of the supplementary material.

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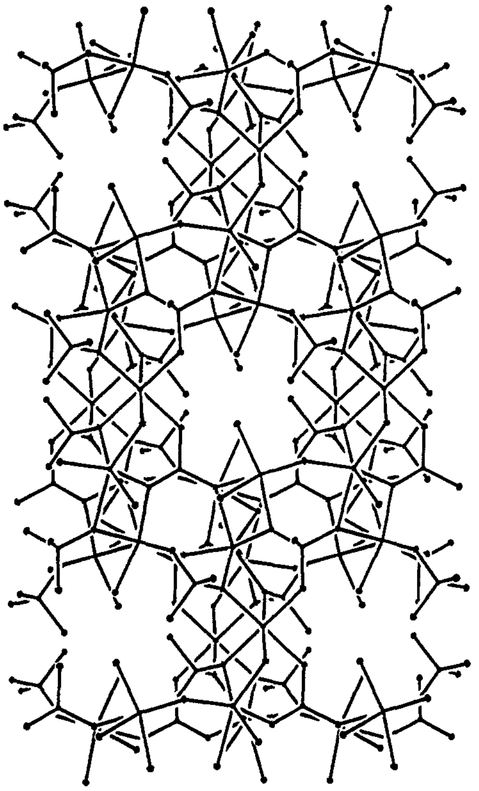

Figure 1. View of I along the *c* axis with the *b* axis horizontal.

tetrahedral. The sodium ion, lying within one of the two channels found in this structure, is bound to four oxygen atoms and is interacting with at least six others.

In the preparation of I, $Fe(CO)_5$ is reacted with concentrated H_3PO_4 in a water and acetone mixture. The pure manganese and mixed manganese/iron forms are prepared by a similar procedure using $Mn_2(CO)_{10}$ and $Mn_2(CO)_{10}$–$Fe(CO)_5$ mixtures, respectively. Tetrapropylammonium hydroxide is also added. The reaction yield is directly related to the amount of (TPA)OH present. In its absence, the reaction does not proceed to the desired product but apparently gives an amorphous acid-soluble iron carbonate phase. The use of tetraalkylammonium salts as phase-transfer catalysts in metal carbonyl systems has been discussed.[9] In this reaction, we believe (TPA)OH is acting to neutralize the acid to give the $H_2PO_4^-$ species, which reacts with the metal carbonyl. No reaction occurs when (TPA)Br is used in place of (TPA)OH. There is also no evidence that the TPA^+ ion is behaving as a templating agent as it does in the synthesis of the molecular sieve silicalite.[10]

Gas chromatographic analysis of the headspace from the autoclave shows H_2, CO, and CO_2 as products. Similar analysis prior to heating revealed CO and CO_2 but no H_2. We believe that these results indicate that the $H_2PO_4^-$ ion is the reactive species and is perhaps "phase-transferred" into the organic phase (acetone–$Fe(CO)_5$) as the ion pair $(TPA^+)(H_2PO_4^-)$ with subsequent oxidative addition of an hydroxyl group to the iron atom.

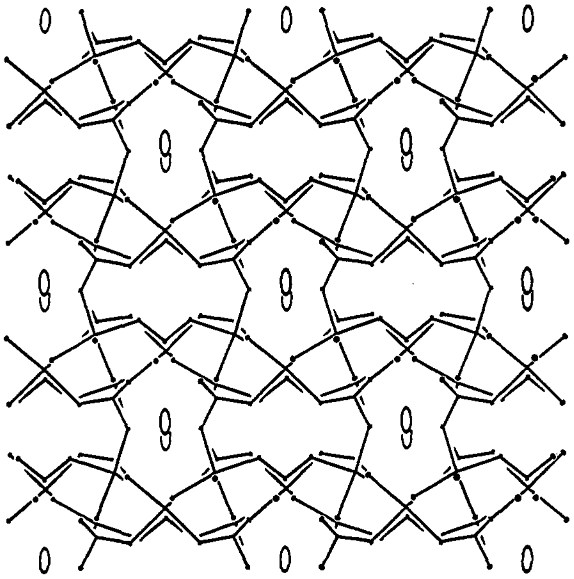

Figure 2. View of II down the *c* glide perpendicular to the twofold axis showing a total of 4 unit cells on the face and $1^1/_2$ unit cells in depth.

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Registry No. I, 14485-26-8; II, 102307-38-0; $Fe(CO)_5$, 13463-40-6; H_3PO_4, 7664-38-2; (TPA)OH, 4499-86-9; (TBA)OH, 2052-49-5.

Supplementary Material Available: Final values of the positional parameters, anisotropic thermal parameters, interatomic distances, intramolecular angles, intramolecular nonbonding distances, intermolecular distances, and symmetry operation codes for I and II (Tables I–VII and IX–XV, respectively) (17 pages). Ordering information is given on any current masthead page.

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