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Articles

Hydrothermal Synthesis and Structure of $Fe(NH_3)_2PO_4$: A Novel Monophosphate

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$Fe(NH_3)_2PO_4$ is synthesized under mild hydrothermal conditions in the presence of urea. The crystal structure is solved for powder X-ray diffraction data. The unit cell is orthorhombic, $a = 10.1058(2)$ Å, $b = 6.3676(2)$ Å, $c = 7.5714(2)$ Å, space group *Pnma*, $Z = 4$. The structure consists of a three-dimensional network of FeO_4N_2 octahedra and PO_4 tetrahedra linked by vertex sharing. Two crystallographically independent ammonia molecules are linked to the iron atom. This compound is the first three-dimensional solid structurally characterized containing $Fe-NH_3$ bonds.

Introduction

Under natural conditions many minerals crystallize from hot and rich water solutions. By using autoclaves, hydrothermal growth in the laboratory closely duplicates the natural process. Recently, by exploiting the presence of cationic organic templates in hydrothermal preparations of d-block metal phosphates, a large variety of metastable phases with layered and open frameworks have been synthesized. It was found that the type of compound formed depends on the exquisitely sensitive relationship between the charge, shape, and volume of the cationic template and the nature of the void formed in the anionic framework.[1−8]

Iron(III) phosphates have been extensively studied because they find applications in such diverse fields as heterogeneous catalysis, ion exchange or passivation of a metal surface. Several new compounds in the iron(III) phosphate family have been synthesized recently by using hydrothermal methods.[9−11] Since the use of structure-directing organic molecules has evolved into a successful strategy for the synthesis of layered and zeolitic materials, we sought to expand to there groups of the iron(III) phosphate family of solids by exploiting the introduction of urea as a template under hydrothermal conditions.

We report here the syntheses and structural characterization of a new iron(III) phosphate: $Fe(NH_3)_2PO_4$.

Experimental Section

Sample Preparation. Hydrothermal crystallization of $Fe(NH_3)_2PO_4$ was carried out in a stainless steel (100 mL) Teflon-lined vessel under autogenous pressure. $(NH_2)_2CO$ (solid), 85% H_3PO_4, and freshly prepared $FeCl_3 \cdot 6H_2O$ (1 M) were mixed in the molar ratio 1:10:20:63 ($FeCl_3$:H_3PO_4:$(NH_2)_2CO$:H_2O) in a total volume of 40 mL. The autoclave was sealed and heated at 170 °C for 6 days. The obtained solid was filtered off, washed with an excess of the distilled water, and dried in air at room temperature. Microanalytical data (C, H, and N) were obtained with a Perkin-Elmer model 2400B elemental analyzer. The phosphorus and iron contents were determined with a SpectraSpectrometer DCP-AEC after dissolving a weighed amount of sample in HF(aq). Elemental analysis: Fe 30.2, P 16.8, N 15.2, H 3.1 (calcd for $Fe(NH_3)_2PO_4$: Fe 30.23, P 16.77, N 15.14, H 3.25). Thermogravimentric analysis was carried out at a rate of 10 °C min^{-1} under a flow of nitrogen. The total weight loss up to 800 °C was 19.0% (calcd 18.39%), which corresponds to release of the two molecules of NH_3. The weight loss occurs in two steps (the desorption of the first molecule takes place at ca. 270 °C, whereas the second molecule is released at ca. 340 °C). The final product after thermal decomposition was $FePO_4$ (low-temperature quartz structure).

X-ray Diffraction Study. An X-ray powder diffraction pattern was obtained using a Philips 1050 conventional powder diffractometer (Cu Kα, 40 kV and 30 mA). The data were collected at room temperature over the angular range 13−110° 2θ with a step of 0.02° (time constant

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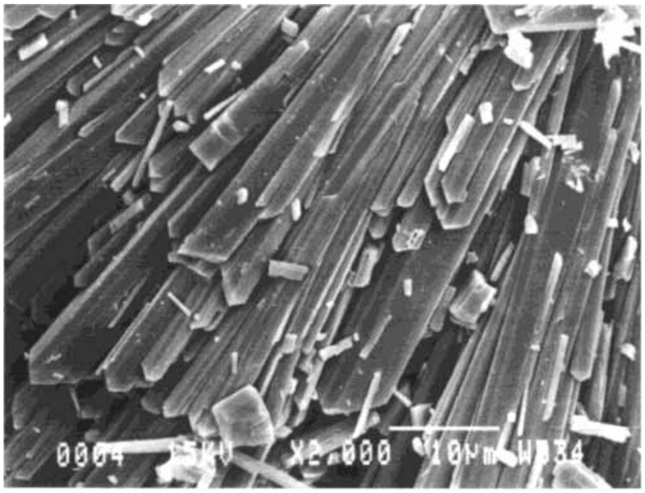

Figure 1. Scanning electron micrograph of $Fe(NH_3)_2PO_4$.

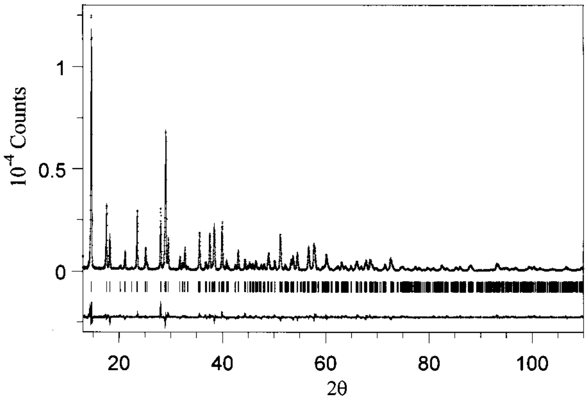

Figure 2. Powder X-ray diffraction pattern and Rietveld analysis for $Fe(NH_3)_2PO_4$. Points correspond to observed data; the solid line is the calculated profile. Tick marks represent the positions of allowed reflections, and a difference curve on the same scale is plotted at the bottom of the pattern.

10 s). The pattern was indexed using the program TREOR.[12] Initially the structure was solved in space group $P2_12_12_1$, one of the space groups consistent with the observed systematic absences. Reflection intensities were extracted from the diffraction pattern using the Le Bail method;[13] 214 F^2 values extracted from the data were used as input for the direct method program SIRPOW.[14] The solution with the best figure of merit was selected, and after 20 cycles of Fourier recycling, plausible values of the coordinates of all atoms were revealed. The starting structural model was refined in RIET94, a local version of a Wiles & Young program.[15] Later, additional symmetry was detected, coordinates were converted to *Pnma*, and the refinement was concluded in this group. During the refinement a preferred orientation correction along 010 was included using the March model,[16] resulting in a value $G = 1.34$ indicating a strong fibrous orientation in accord with the observed morphology (see Figure 1) and showing that the fibers grow along the channel direction.

Table 1. Crystallographic Parameters for the Powder X-ray Diffraction Study of $Fe(NH_3)_2PO_4$

empirical formula	$FePO_4N_2H_6$
fw	178.8
color	pale green
cryst syst	orthorhombic
wavelength (Å)	1.5418
2θ range (deg)	13−110
a (Å)	10.1058(2)
b (Å)	6.3676(2)
c (Å)	7.5714(2)
V (Å^3)	487.21(2)
Z	4
ρ_{calc} (g cm^{-3})	2.52
space group	*Pnma* (No. 62)
contributing reflns (K_α doublets)	341
structural params	22
profile params	16
R_{wp}	12.3
R_F	5.6
R_{exp}	6.1

Table 2. Fractional Atomic Coordinates and Isotropic Displacement Parameters (Å^2) for $Fe(NH_3)_2PO_4$

atom	Wyckoff	*x*	*y*	*z*	*B*
Fe	4*c*	0.1578(2)	$^1/_4$	−0.0874(2)	3.00(5)
P	4*c*	0.1614(3)	$^3/_4$	0.0375(3)	2.80(6)
O(1)	8*d*	0.1633(4)	0.5674(8)	−0.0817(5)	1.72(9)
O(2)	4*c*	0.2822(6)	$^3/_4$	0.1566(8)	4.4(2)
O(3)	4*c*	0.0346(5)	$^3/_4$	0.1543(6)	2.4(2)
N(1)	4*c*	0.3578(7)	$^1/_4$	0.0146(9)	3.3(2)
N(2)	4*c*	0.0995(6)	$^1/_4$	0.1893(8)	1.1(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Fe(NH_3)_2PO_4$

Fe−O(1)	2.022(5) × 2	Fe−O(3)	2.009(5)
Fe−N(1)	2.164(7)	P−O(1)	1.472(5) × 2
Fe−N(2)	2.176(6)	P−O(2)	1.518(7)
Fe−O(2)	2.031(6)	P−O(3)	1.557(6)

N(1)···O(3)	2.937(8) intra	N(1)···N(2)	3.316(9)
N(1)···O(1)	3.277(7) × 2 inter	N(1)···O(2)	3.446(4) × 2 intra
N(2)···O(1)	3.011(7) × 2 intra	N(2)···O(1)	3.179(7) × 2 inter
N(2)···O(3)	3.262(2) × 2 intra		

O(1)−Fe−N(1)	88.1(1) × 2	O(3)−Fe−N(2)	88.9(2)
O(1)−Fe−N(2)	89.3(1) × 2	O(2)−Fe−O(3)	92.8(2)
O(1)−Fe−O(2)	90.7(1) × 2	O(1)−P−O(2)	110.7(2) × 2
O(1)−Fe−O(1)	176.0(2)	O(1)−P−O(3)	111.0(2) × 2
O(1)−Fe−O(3)	91.8(1) × 2	O(1)−P−O(1)	104.3(3)
N(1)−Fe−N(2)	84.8(2)	O(2)−P−O(3)	108.9(3)
O(2)−Fe−N(1)	93.5(3)	Fe−O(1)−P	143.3(3)
O(3)−Fe−N(1)	173.7(2)	Fe−O(2)−P	143.9(4)
O(2)−Fe−N(2)	178.3(3)	Fe−O(3)−P	130.8(3)

Results

Figure 2 shows the powder X-ray diffraction pattern and the difference between the calculated pattern, including the refined background, and the observed pattern. Crystallographic parameters are collected in Table 1. Final atomic coordinates and isotropic displacement parameters are reported in Table 2, with bond distances and selected angles in Table 3. A projection of the structure down the *b* axis is shown in Figure 3.

The structure of $Fe(NH_3)_2PO_4$ can be described by metal-centered octahedra linked together via [PO_4] tetradentate tetrahedra to form a three-dimensional network. Two crystallographically independent ammonia molecules in relative cis positions complete the octahedral environment of the iron atom. The channels along the *b* axis are fully occupied by the ammonia molecules. The process of partial decomposition may be explained by the different positions occupied by the two ammonia molecules within the channels: one of them is located in the middle of the channel whereas the other is near the edge. The channels are large enough to allow the diffusion of one ammonia molecule.

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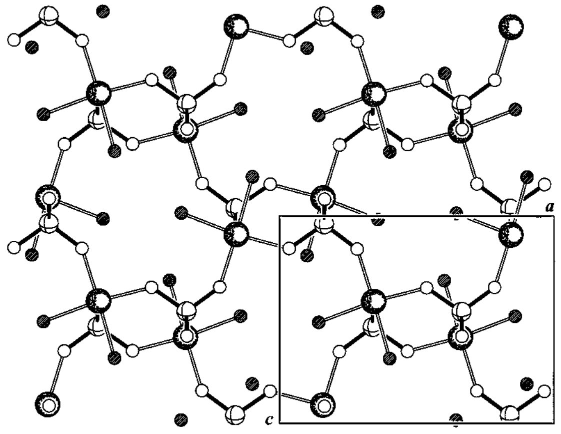

Figure 3. View of $Fe(NH_3)_2PO_4$ along the *b* axis (Fe, large shadowed spheres; N, small shadowed spheres; P, large white spheres; O, small white spheres).

Discussion

It is surprising that a compound with that simple formula was not known up to the present. Only a few examples of phosphates containing NH_3 molecules are known, basically compounds of Co and Cr. As far as we know this is the first reported iron(III) phosphate containing ammonia molecules and its crystalline structure does not belong to any previously described type. Furthermore this compound is also the first structurally characterized three-dimensional solid containing $Fe-NH_3$ bonds. Up to the moment in our knowledge this bond was reported only in molecular solids containing complexes like $Fe(NH_3)_6Cl_2$ or $Na_2[Fe(CN)_5(NH_3)]\cdot 2H_2O$.

The $Fe(NH_3)_2PO_4$ compound is related to $Fe(H_2O)_2PO_4$, which is present in the mineral kingdom in two forms: strengite (orthorhombic, *Pbca*, $a = 10.05$ Å, $b = 8.65$ Å, $c = 9.80$ Å) and metastrengite, also named fosfosiderite (monoclinic, $P2_1/n$, $a = 5.30$ Å, $b = 9.77$ Å, $c = 8.73$ Å, $\beta = 90.6°$). Each solid belongs to an isotypic family of natural and synthetic phosphates. In the case of strengite also are known the arsenates.

It is interesting to compare the structure of $Fe(NH_3)_2PO_4$ with the structure of strengite and metastrengite.[17,18] All of these structures are formed by octahedra centered in the metal joined through $[PO_4]$ tetrahedra forming a three-dimensional network. In the case of these minerals, two water molecules are associated with each octahedron, the configuration being *cis*-$Fe(O_p)_4(O_h)_2$, where O_p is an oxygen atom also joined to a phosphate and O_h is the oxygen atom of a water molecule. Of the three structures, the $Fe(NH_3)_2PO_4$ is the most open (density of 2.52 g cm^{-3} versus 2.87 and 2.76 for strengite and metastrengite, respectively). The basic unit in these structures is the cluster formed by the disposition of the tetrahedra about the octahedron, as shown in Figure 4 (for the strengite series we have chosen the iron(III) arsenate, scorodite). The changes in the disposition of tetrahedra can be associated with the different interactions with the water (ammonia) molecules. In fact, the configuration of the cluster in the strengite and metastrengite is quite similar, and it is not surprising that a structural relationship exists between both structures.[17,18] For metastrengite the disposition is slightly more open than for strengite. In Table 4 are collected the torsion angles that describe the conformation of each tetrahedron around the central atom.

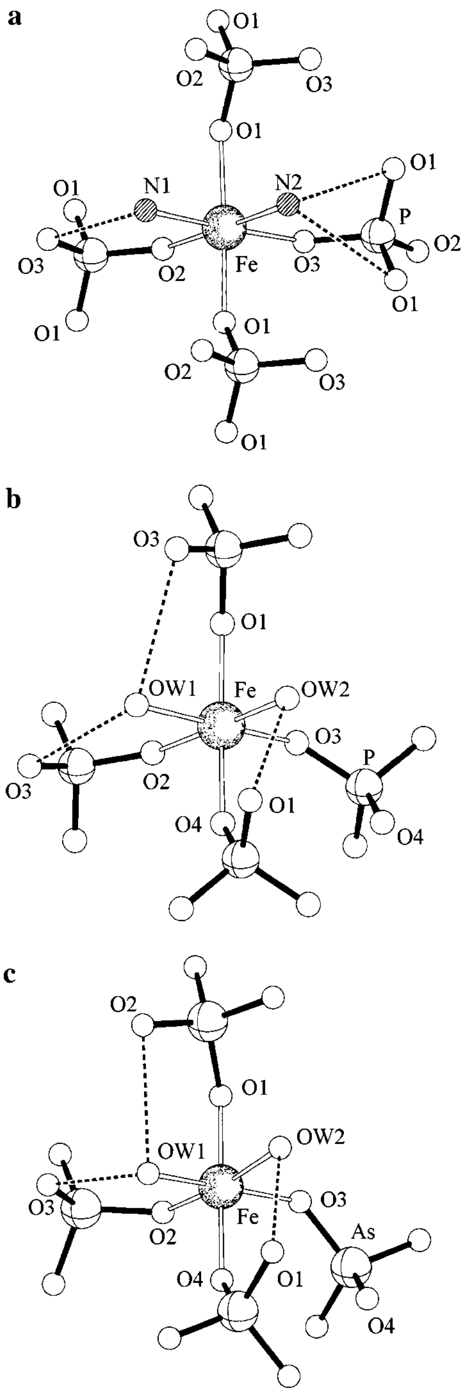

Figure 4. Disposition of tetrahedra and NH_3 (H_2O) molecules about the Fe atom: (a) $Fe(NH_3)_2PO_4$, (b) metastrengite, and (c) scorodite. Dotted lines indicate short interatomic contacts.

In the three cases there are three short interatomic contacts between the oxygens of the water molecules (or the nitrogen of the ammonia molecules) and two other oxygens inside the cluster. In metastrengite and scorodite one of the water molecules, O(W1), is close to two oxygen atoms belonging to different phosphate groups, one equatorial and one axial, and the other water molecule, O(W2), is close to an oxygen of the remaining axial phosphate. In the case of $Fe(NH_3)_2PO_4$ the three shortest contacts are located in the equatorial plane (see Table 3 where intra and inter means inside the same cluster or between different clusters, respectively). Then one nitrogen atom interacts with two oxygen atoms of the same phosphate, N(2)···O(1) twice by symmetry.

Some of these intracluster contacts occur with the formation of five-membered rings with a high degree of planarity. In Table

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Table 4. Torsion Angles (deg) for the Geometry of the Octahedral Cluster

$Fe(NH_3)_2PO_4$		metastrengite		scorodite	
N(2)−Fe−O(3)−P	0.00	O(W2)−Fe−O(3)−P	53.44	O(W2)−Fe−O(3)−As	91.40
Fe−O(3)−P−O(1)	57.78	Fe−O(3)−P−O(4)	−6.80	Fe−O(3)−As−O(4)	−43.79
N(1)−Fe−O(2)−P	*0.00*	O(W1)−Fe−O(2)−P	*−3.12*	O(W1)−Fe−O(2)−As	*12.10*
Fe−O(2)−P−O(3)	*0.00*	Fe−O(2)−P−O(3)	*−11.19*	Fe−O(2)−As−O(3)	*−6.89*
N(2)−Fe−O(1)−P	−12.38	O(W1)−Fe−O(1)−P	50.63	O(W1)−Fe−O(1)−As	33.91
Fe−O(1)−P−O(3)	57.66	Fe−O(1)−P−O(3)	−39.03	Fe−O(1)−As−O(2)	−42.63
N(2)−Fe−O(1)−P	12.38	O(W2)−Fe−O(4)−P	*18.59*	O(W2)-Fe−O(4)−As	*20.50*
Fe−O(1)−P−O(3)	−57.66	Fe−O(4)−P−O(1)	*11.80*	Fe−O(4)−As−O(1)	*−13.22*

4 this is shown by low torsion angles (in italics). For $Fe(NH_3)_2PO_4$ this geometry occurs in the contact N(1)···O(3) where the disposition is exactly planar with the five atoms on a mirror plane. In the case of $Fe(NH_3)_2PO_4$, due to the absence of interaction with axial phosphates the cluster arrangement is more relaxed and open.

On the other hand, the difference in the geometry of the cluster between scorodite and metastrengite is related to the formation of hydrogen bonds by the O(W1). Whereas in the orthorhombic phase only one hydrogen bond is formed with the O(3) (equatorial phosphate), in the monoclinic phase the distortion of cluster geometry favors the formation of two less strong hydrogen bonds with the equatorial and axial phosphates. This conclusion can be extracted from the hydrogen atom positions founds in the single-crystal studies carried out in variscite,[19] scorodite[20] and metavariscite.[21] It is clear in all of these cases that the geometry of the planar ring discussed before is favored by the formation of hydrogen bonding in this type of structure.

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