Inorg. Chem. **2005**, *44*, 5273–5277

Inorganic Chemistry
Article

Pillared Layered Structures Based upon M(III) Ethylene Diphosphonates: The Synthesis and Crystal Structures of $M^{III}(H_2O)(HO_3P(CH_2)_2PO_3)$ (M = Fe, Al, Ga)

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Received February 11, 2005

A three-dimensional iron(III) diphosphonate, $Fe^{III}(H_2O)(HO_3P(CH_2)_2PO_3)$, **I**, has been synthesized hydrothermally and characterized by single-crystal X-ray diffraction. The compound crystallizes in the orthorhombic space group *Pbca* (no. 61) where $a = 9.739(5)$ Å, $b = 9.498(5)$ Å, $c = 15.940(8)$ Å, V = 1474.4(1) Å^3, $Z = 8$, and $R_1 = 0.0380$. The structure consists of inorganic sheets pillared by the 1,2-ethylenediphosphonate groups. The sheets are composed of $Fe(H_2O)O_5$ octahedra connected through PO_3C tetrahedra. The corresponding isostructural aluminum (**II**) and gallium (**III**) compounds were also synthesized and indexed: **II**, $a = 9.534(1)$ Å, $b = 9.255(2)$ Å, $c = 15.724(1)$ Å, $V = 1387.5(1)$ Å^3; **III**, $a = 9.670(1)$ Å, $b = 9.357(2)$ Å, $c = 15.862(4)$ Å, $V = 1435.4(1)$ Å^3.

Introduction

Metal–phosphate materials are attractive because of their similarities to zeolites, especially in terms of catalysis[1] and ion exchange.[2] Following Clearfield's pioneering work on crystalline zirconium phosphates,[3] layered organophosphonates were developed by Alberti et al.,[4] and the field quickly expanded to compounds of di-, tri-, tetra-, penta-, and hexavalent metals with a variety of organophosphonic ligands.[5] Because layered compounds tend to cleave and flake, networked or pillared layered structures were developed to avoid this.[6] More recently, structures have been synthesized with the intent of leaving space between layers by using terminal and bifunctional organophosphate acid mixtures (the space is bordered by bifunctional ligands in the plane and by terminal groups above and below), with some success.[7]

In the M(III)/1,2-ethylenediphosphonic acid system (M = Fe, Al, Ga), several structures have been synthesized and characterized. Layered iron(III) compounds were synthesized by Bellito[8] and Altomare.[9] Pillared layered aluminum[10,11] and fluorinated aluminum structures[10,12,13] have also been reported, and pillared layered gallium[14] and fluorinated gallium structures[13,15] have been synthesized. The only three-dimensional (3D) inorganic network structure found in this family is a gallium vanadium diphosphonate, $Ga_2(VO)_3K_2(OH_2)_3(C_2H_4P_2O_6)_4(H_2O)_{13}$.[16] Not surprisingly, iron, gallium, and aluminum often form isostructural compounds.[17] In the

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present work, we describe the synthesis and structure of phases based on the M(III)/1,2-ethylenediphosphonic acid system (M = Fe, Al, Ga) in which the acid remains partly protonated. In the structures referred to above, only one, $(C_3H_7NH_3)\{AlF[(HO)O_2PC_2H_4PO_3]\}$,[10] contains the acid in its protonated form.

Experimental Section

Synthesis of $Fe^{III}(H_2O)(HO_3P(CH_2)_2PO_3)$. A mixture of $FeCl_3 \cdot 6H_2O$ (1.00 mmol) (supplied by Aldrich Chemical Co.) and 1,2-ethylenediphosphonic acid (4.03 mmol) (Lancaster Synthesis) in 1.79 mL of deionized (DI) water was placed in the polytetrafluoroethylene (PTFE) liner of a 23 mL autoclave and stirred for 10 min. The autoclave was then sealed and heated at 200 °C for 2 days (initial and final pH < 1). The final product, consisting of light purple trapezoidal crystals, was washed with water and dried at 60 °C. A suitable single crystal was used for structure determination by single-crystal X-ray diffraction, but the sample was not phase pure. A phase pure sample was synthesized under the same conditions with a reagent mixture change, 2.00 mmol of $FeCl_3 \cdot 6H_2O$, 4.97 mmol of 1,2-ethylenediphosphonic acid, and 3.61 mL of water. Elemental analysis (C, H, N) was carried out by the Marine Sciences Institute Analytical Laboratory at UCSB. Found: H, 2.44; C, 9.26. Calcd: H, 2.33; C, 9.24. FTIR measurements were carried out on a Nicolet Magna 850 IR spectrometer, FTIR frequencies (KBr) above 1400 cm^{-1}: 3552 s, 3394 s, 1630 s, 1419 s.

Synthesis of $Al^{III}(H_2O)(HO_3P(CH_2)_2PO_3)$. A mixture of $AlCl_3 \cdot 6H_2O$ (1.00 mmol) (Johnson and Matthey) and 1,2-ethylenediphosphonic acid (4.03 mmol) in 1.82 mL of DI water was stirred and placed in a 23 mL PTFE lined stainless steel autoclave, which was sealed and heated at 200 °C for 2 days (initial and final pH < 1). The final product consisted of white powder, which was used for unit cell determination. Anal. Found: H, 2.71; C, 10.87. Calcd: H, 2.62; C, 10.40.

Synthesis of $Ga^{III}(H_2O)(HO_3P(CH_2)_2PO_3)$. A mixture of $Ga(NO_3)_3 \cdot xH_2O$ (1.13 mmol) (Alfa Aesar) and 1,2-ethylenediphosphonic acid (4.03 mmol) in 3.61 mL of DI water was stirred and placed in a 23 mL PTFE lined stainless steel autoclave, which was sealed and heated at 180 °C for 2 days (initial and final pH < 1). Colorless crystals that were too small for regular single-crystal X-ray diffraction analysis (XRD) were obtained; these were ground and used for unit cell determination. Anal. Found: H, 2.26; C, 9.12; Calcd: H, 2.21; C, 8.78.

Structure Determination of the $Fe^{III}(H_2O)(HO_3P(CH_2)_2PO_3)$ (I). A suitable single crystal of $Fe^{III}(H_2O)(HO_3P(CH_2)_2PO_3)$ was carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (Superglue) adhesive. Crystal structure determination by XRD was performed on a Bruker SMART-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature. An empirical correction on the basis of symmetry equivalent reflections was applied using the SADABS program.[18] The structure was solved by direct methods using SHELX-97 and difference Fourier syntheses.[19] The relevant details of structure determination are presented in Table 1. Full matrix least-squares refinement against $|F^2|$ was carried out using the SHELXTL-PLUS package of programs.[20] The hydrogen atoms were found in the Fourier difference map; the proton remaining on the acid was restrained with an antibumping restraint to be at a distance no less than the shortest O−H distance in the ethylenediphosphonic acid ligand.[21] The last cycles of refinement included atomic positions and anisotropic thermal parameters for all of the atoms except hydrogen, which used isotropic thermal parameters. The asymmetric unit is shown in Figure 1. The bond valence sums obtained by using the program VALIST[22] confirm the assignment of the iron as trivalent. The program PLATON[23] determined that no obvious space group change is needed or suggested.

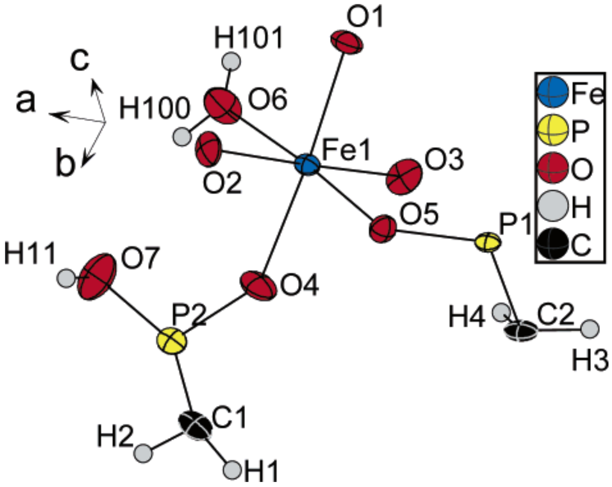

Figure 1. Octant-view plot of the asymmetric unit of $Fe^{III}(H_2O)(HO_3P(CH_2)_2PO_3)$, **I.** Thermal ellipsoids are given at 50% probability (hydrogen at 20% probability).

Table 1. Crystal Data and Structure Refinement Parameters for **I**

structural parameter	
chemical formula	$[Fe(H_2O)(HO_3P(CH_2)_2PO_3)]$
formula mass	260.87
crystal system	orthorhombic
space group	*Pbca* (61)
T (K)	293
a/Å	9.739(5)
b/Å	9.498(5)
c/Å	15.940(8)
V/Å^3	1474.4(1)
Z	8
μ/mm^{-1}	2.477
2θ range data collected	5.12, 55.72
total data collected	8286
unique data	1617
observed data ($I > 2\sigma(I)$)	1181
R_{int}	0.0877
R_1, wR_2 ($I > 2\sigma(I)$)	0.0380, 0.0920
R (all data)	0.0592, 0.0997

Indexing of $Al^{III}(H_2O)(HO_3P(CH_2)_2PO_3)$ (II) and $Ga^{III}(H_2O)(HO_3P(CH_2)_2PO_3)$ (III). X-ray powder diffraction data were

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Table 2. Unit Cell Parameters for **II** and **III**[a]

parameter	I	II	III	Bujoli-Doeuff et al. Ga analogue
space group	*Pbca* (61)	*Pbca* (61)	*Pbca* (61)	*Pbca* (61)
a/Å	9.739(5)	9.534(1)	9.670(1)	9.6790(5)
b/Å	9.498(5)	9.255(2)	9.357(2)	9.3600(7)
c/Å	15.940(8)	15.724(1)	15.862(4)	15.8583(8)
V/Å^3	1474.4(1)	1387.5(1)	1435.4(1)	1436.7(1)

[a] Values for **I** and for the Bujoli-Doeuff et al. Ga analogue structure are provided for reference.

collected on a Scintag X2 θ-θ diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). The powder diffraction pattern was scanned over an angular range of 5−90° (2Θ) with a step size of 0.01° and a counting time of 2 s·step^{-1}. Pattern indexing was performed from the first 20 lines (**III**) (10 lines for **II**) using the computer program DICVOL04.[24] The orthorhombic solutions found for **II** (FOM = 61) and **III** (FOM = 28) are the same as that for the iron compound, **I**, with slightly smaller unit cell lengths; **II** has the smallest unit cell. The relative cell volumes follow the trend in the relative ionic radii, with $\mathrm{Fe^{III}}$(h.s.) = 64.5 pm > $\mathrm{Ga^{III}}$ = 62 pm > $\mathrm{Al^{III}}$ = 53.5 pm.[25] Table 2 shows the cell parameters of **I**, **II**, and **III**.

Thermal Analysis. Thermogravimetric analyses were carried out with a heating rate of 10 °C (20°) min^{-1} on a Mettler 851eTG/sDTA coupled to a Blazers ThermoStar 300 AMU mass spectrometer. Dehydration and rehydration of **I** were tested by dehydrating the sample and attempting to dehydrate again after the sample sat in air to rehydrate. X-ray thermodiffractometry (Cu Kα radiation, $\lambda = 1.5418$ Å) was performed under static air in a Bruker D8 Advance diffractometer outfitted with a M. Braun Position Sensitive Detector and an Anton Paar HTK 16 high-temperature stage. Patterns were scanned at plateaus in the thermogravimetric analysis (TGA) curve and in the regions where mass was lost, with a temperature ramp of 0.5 °C min^{-1}.

Results and Discussion

Structure of $\mathrm{Fe^{III}}$ $(H_2O)(HO_3P(CH_2)_2PO_3)$ (I). $\mathrm{Fe^{III}}$-$(H_2O)(HO_3P(CH_2)_2PO_3)$, **I**, possesses a three-dimensional architecture and is built from FeO_6 and CPO_3 moieties. The iron−oxygen octahedra link through corner sharing to phosphorus−oxygen−carbon tetrahedra, forming a continuous network. The structure can be described as an inorganic layer perpendicular to the *c*-axis of $FeO_6P_2(H_2O)$ (see Figure 2), pillared with the alkyl part of the diphosphonate group (see Figure 3) to form a three-dimensional structure. The inorganic layers are composed of $FeO_5(H_2O)$ octahedra connected to each other through PO_3C tetrahedra. The layer is corrugated in the *a* direction. There are no accessible pores in this structure. This is consistent with the model shown in Figures 2 and 3, where there does not appear to be any space for molecules to fit between pillars or within the layers.

The asymmetric unit of **I** (Figure 1) consists of the 18 framework atoms and no guest species. There is one crystallographically independent iron and two phosphorus atoms. Of the seven oxygen atoms present in the asymmetric unit, five (O(1), O(2), O(3), O(4), O(5)) are two-coordinated, one (O(6)) is a water molecule, and O(7) is the remaining protonated oxygen from the acid. As no oxygens (except those also on P(2)) are within 3 Å of the protonated oxygen, hydrogen bonding does not take place in this structure and the OH is a pendant group. Further evidence of the absence of hydrogen bonding through the pendant OH group is to be found in the FTIR spectrum, which shows a sharp peak at 3550 cm^{-1} (the peak is higher frequency and sharper than expected for hydrogen bonded OH). The iron is six-coordinated and possesses a distorted octahedral geometry. The Fe−O distances lie in the range 1.948−2.123 Å, and the O−Fe−O bond angles lie in the range 85.19−94.32° (Table 3). The large variation in bond distances and angles show the distortion of the FeO_6 octahedra. Both phosphorus atoms are tetrahedrally coordinated, with P−O distances in the range 1.503−1.573 Å ($(P(1)-O)_{av} = 1.523$, $(P(2)-O)_{av} = 1.527$ Å) and P−C distances in the range 1.794−1.795 Å; the O−P−O angles range 108.68−115.29° ($(O-P(1)-O)_{av} = 111.38$, $(O-P(2)-O)_{av} = 111.54°$) and the O−P−C angles range 103.99−109.97° ($(O-P(1)-C)_{av} = 107.49$, $(O-P(2)-C)_{av} = 107.19°$) (Table 3). The iron octahedra are elongated along one bond, with the water molecule Fe−O bond being the longest; the phosphate tetrahedra are elongated along the P−C bond, and the difference in bond lengths

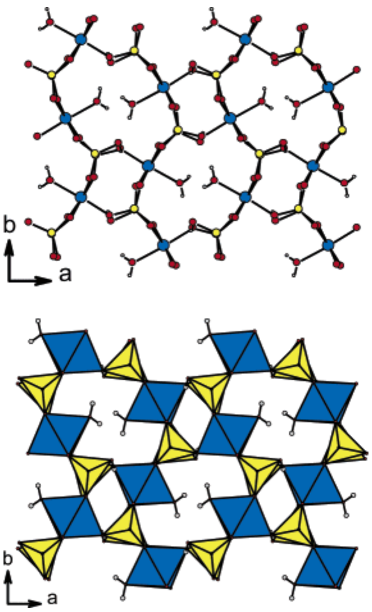

Figure 2. View of the inorganic layer of the structure of **I** along the *c*-axis in ball-and-stick representation (top) and with polyhedra of FeO_6 in blue and PO_3C in yellow (bottom).

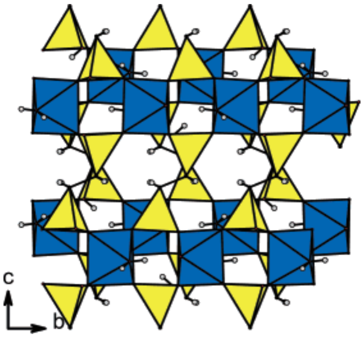

Figure 3. Projection of the structure of **I** along the *a*-axis showing the alkyl chains linking the inorganic layers.

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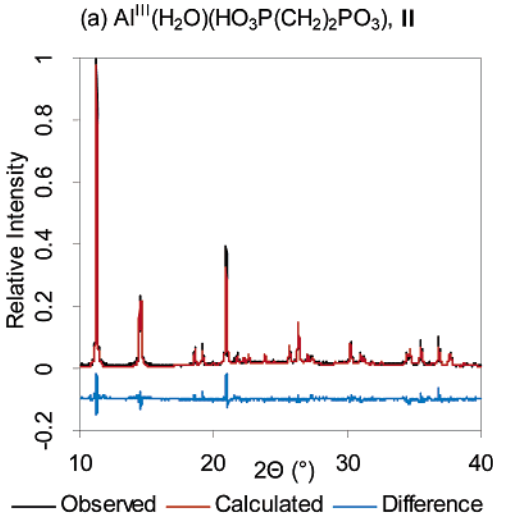
Table 3. Selected Bond Lengths and Angles in **I**]

moiety	length (Å) or angle (deg)	moiety	length (Å) or angle (deg)
Fe(1)−O(1)	1.948(3)	P(1)−O(5)	1.538(3)
Fe(1)−O(2)	1.958(3)	P(1)−C(2)	1.795(4)
Fe(1)−O(3)	1.971(3)	P(2)−O(4)	1.503(3)
Fe(1)−O(4)	1.980(3)	P(2)−O(3)	1.505(3)
Fe(1)−O(5)	1.989(3)	P(2)−O(7)	1.573(3)
Fe(1)−O(6)	2.123(3)	P(2)−C(1)	1.794(4)
P(1)−O(1)	1.515(3)	C(1)−C(2)	1.519(5)
P(1)−O(2)	1.515(3)		
O(1)−Fe(1)−O(2)	85.19(11)	O(5)−Fe(1)−O(6)	175.75(12)
O(1)−Fe(1)−O(3)	94.32(12)	O(1)$^{\#1}$−P(1)−O(2)$^{\#2}$	112.86(16)
O(2)−Fe(1)−O(3)	177.71(12)	O(1)$^{\#1}$−P(1)−O(5)	111.72(15)
O(1)−Fe(1)−O(4)	175.95(11)	O(2)$^{\#2}$−P(1)−O(5)	109.56(15)
O(2)−Fe(1)−O(4)	91.41(12)	O(1)$^{\#1}$−P(1)−C(2)	106.89(16)
O(3)−Fe(1)−O(4)	88.98(12)	O(2)$^{\#2}$−P(1)−C(2)	107.37(16)
O(1)−Fe(1)−O(5)	93.51(11)	O(5)−P(1)−C(2)	108.22(16)
O(2)−Fe(1)−O(5)	89.64(11)	O(4)−P(2)−O(3)$^{\#3}$	115.29(16)
O(3)−Fe(1)−O(5)	92.63(11)	O(4)−P(2)−O(7)	108.22(16)
O(4)−Fe(1)−O(5)	88.67(11)	O(3)$^{\#3}$−P(2)−O(7)	110.65(17)
O(1)−Fe(1)−O(6)	90.71(12)	O(4)−P(2)−C(1)	107.62(17)
O(2)−Fe(1)−O(6)	90.22(13)	O(3)$^{\#3}$−P(2)−C(1)	109.97(18)
O(3)−Fe(1)−O(6)	87.55(12)	O(7)−P(2)−C(1)	103.99(19)
O(4)−Fe(1)−O(6)	87.09(12)		

between the P−O and P−C bonds is greater for the phosphate tetrahedra with the protonated oxygen.

In addition to the structures mentioned in the Introduction, Bujoli-Doeuff et al. also synthesized **III**, but the sample was so poorly crystalline that, although the unit cell was indexed, the structure could not be determined.[14] Their lattice parameters agree well with the values determined here for **III**.[14] The structures of **II** and **III** were refined with the Rietveld method using FULLPROF.[26] Atomic positions were refined starting from the positions for **I**; the positions of the hydrogen atoms were not refined. Preferred orientation was severe but was treated by using the usual Rietveld function, with a preferred orientation vector along the *c**-axis. Final Rietveld plots are given in Figure 4, and final agreement factors are given in Table 4.[27] The refined atomic coordinates for **II** and **III** are given in the Supporting Information. Because of the similarity of synthesis conditions, the indexing of the powder patterns, and the Rietveld analysis, it is clear that compounds **II** and **III** are isostructural with compound **I**.

Bujoli-Doeuff concluded that **III** is unstable under hydrothermal synthesis conditions, "probably due to the non-coordinated P−OH function that tends to react to form $Ga_4(O_3PC_2H_4PO_3)_3$".[14] The structure of $Ga_4(O_3PC_2H_4PO_3)_3$ exhibits sheets of GaO_5 and GaO_4 polyhedra together with ethylenediphosphonate groups; these sheets are then pillared by further diphosphonate groups.[14] With respect to the conditions described by Bujoli-Doeuff et al. that give rise to $Ga_4(O_3PC_2H_4PO_3)_3$,[14] the conditions described herein are slightly more acidic (P/Ga ratio > 7, pH < 1 vs P/Ga ratio > 5, pH ∼ 1) and have a shorter reaction time. However, at 200 °C, 20 °C above the temperature that yields **III**, a poorly crystalline structure of $Ga_4(O_3PC_2H_4PO_3)_3$ forms. Our acidic conditions, relatively low temperature and shorter reaction time may stabilize the P−OH function in **III** and allow it to exist without reacting further to form a Ga−O bond.


(a) $Al^{III}(H_2O)(HO_3P(CH_2)_2PO_3)$, **II**

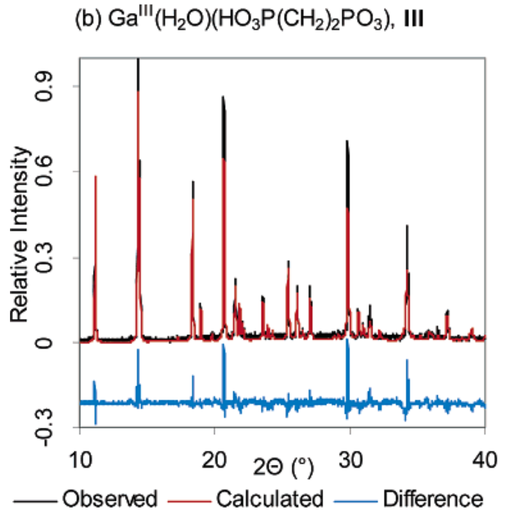

(b) $Ga^{III}(H_2O)(HO_3P(CH_2)_2PO_3)$, **III**

Figure 4. Observed and calculated profiles of the Rietveld refinement of **II** (top) and **III** (bottom).

Table 4. Final Rietveld Agreement Factors and Cell Parameters for **II** and **III**[a]

final Rietveld agreement factors	II	III	final Rietveld agreement factors	II	III
R_p	24.9	31.2	R_F	7.90	9.76
R_{wp}	27.9	39.5	χ^2	1.54	1.36
Bragg *R*	11.5	16.0			

[a] Definitions for agreement factors in ref 27.

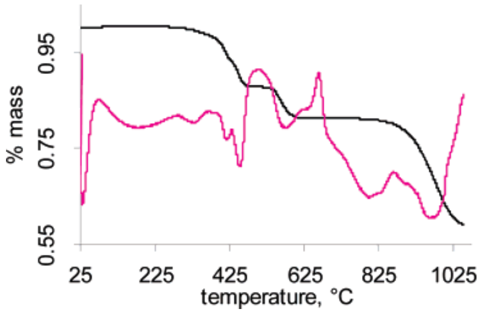


Figure 5. TGA trace (black) and DTA (pink) of the mass loss of **I**.

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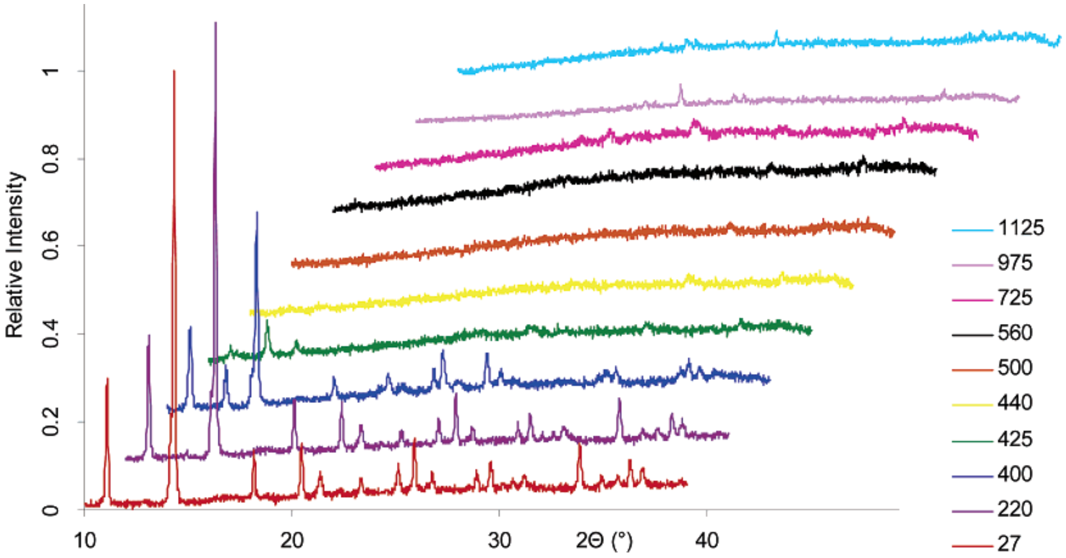

Figure 6. Thermodiffraction patterns for **I**.

Thermal Behavior of I. Mass loss occurs in four distinct stages (Figure 5) during heating. The first mass loss, between 185 and 429 °C (which is more apparent in the differential thermal analysis (DTA) curve than the TGA curve) is attributed to the loss of coordinated water, O(6): found, 7.23%; calcd, 6.93%. As shown in the variable temperature X-ray diffractogram (Figure 6), the sample becomes amorphous at this point. This is consistent with the observation that a dehydrated sample does not rehydrate on standing in air. There is some evidence (Figure 6) that other transient phases may be formed during the heating cycle.

Thermal Behavior of II and III. The thermal behaviors of **II** and **III** are less complicated than that of the iron compound, losing mass in two stages. For **II**, the first mass loss (of coordinated water) occurs between 135 and 350 °C, while the second mass loss starts at 560 °C. For **III**, the first mass loss (of coordinated water) occurs between 155 and 300 °C, while the second mass loss starts at 540 °C. Compounds **II** and **III** do not rehydrate on standing in air.

Conclusions

The synthesis and structure determination of $Fe^{III}(H_2O)(HO_3P(CH_2)_2PO_3)$ are described in this paper, together with the identification of the aluminum and gallium analogues. The gallium phase had previously been synthesized and indexed by Bujoli-Doeuff et al.,[14] but the structure remained unknown until now. The structure is one of the few that contains a pendant protonated oxygen from the original acid. While rare in the iron/aluminum/gallium−ethylenediphosphonate system, a fair number of methylenediphosphonates contain a P−OH function, including MIL-13 from Riou-Cavellec et al.[28] and two gallium structures synthesized by Harvey et al.[29]

Acknowledgment. We thank Unilever plc for financial support. This work made use of facilities by the MRL program of the National Science Foundation under Award No. DMR00-80034. Neeraj Sharma is acknowledged for helping with the single crystal X-ray diffraction measurements, and Paul Forster is thanked for useful discussions.

Supporting Information Available: Atomic coordinates available for compounds **II** and **III** as well as the IR spectrum of compound **I**. CIF also available. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0502269

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