

Synthesis and crystal structures of aluminum and iron phosphites

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Received June 28, 1993

The hydrated forms of aluminum and iron phosphite were prepared and their structure was solved using X-ray powder diffraction data. The diffraction data for the aluminum phosphite powder sample was collected using synchrotron radiation ($\lambda = 1.3087 \text{ \AA}$) while that for iron phosphite was obtained from a rotating anode X-ray source. Both compounds crystallize in the monoclinic space group, $P2_1$. Unit cell parameters for the Al compound: $a = 8.0941(1)$, $b = 9.9137(1)$, $c = 7.6254(1) \text{ \AA}$, $\beta = 111.95^\circ$; Fe compound: $a = 8.2548(1)$, $b = 10.1814(1)$, $c = 7.7964(1) \text{ (\AA)}$, $\beta = 111.94(1)^\circ$. The Rietveld refined formula is $M_2(\text{PO}_3\text{H})_3 \cdot 4\text{H}_2\text{O}$ ($M = \text{Al, Fe}$). There are two independent metal atoms in the structure and both are six-coordinated. One of them is coordinated by two water molecules and four phosphite oxygens. The other atom is surrounded by one water molecule and five phosphite oxygens. All the phosphite oxygens are involved in bridging the Al atoms. The geometry about Al, Fe, and P atoms is normal and they display expected bond parameters. The Lattice water is located in the cavity and is hydrogen bonded to phosphite oxygen and water molecules.

Introduction

Recently, there has been a growing interest in the chemistry of metal phosphates, metal phosphites, metal phosphonates, and their derivatives (Clearfield, 1989). These compounds can provide porous structures which may have applications in catalysis, sorption and ion exchange. Our research in this field is mainly focused on the synthesis and structural studies of these materials. We have prepared a number of metal phosphite compounds and their structures were solved using single crystal data (Zhang *et al.*, 1992; Ortiz-Avila *et al.*, 1989). The Al and the Fe phosphites were found to be isostructural on the basis of their powder diffraction data, but attempts to grow them in the single crystal form were

unsuccessful. The powder patterns of these samples showed good quality Bragg reflections with high resolution. Although these compounds consist of 18 non-hydrogen atoms in the asymmetric unit which is a relatively difficult problem to be attempted by powder methods, we were encouraged by our previous results (Rudolf *et al.*, 1986) in which a 26 atom problem was solved by ab initio methods. Therefore it was decided to undertake the structure solution of these compounds to demonstrate the power of powder diffraction data in resolving the structure of compounds containing a large number of atoms. Further incentive for obtaining the structure was to round out our knowledge of metal phosphites. In particular, several lanthanide phosphite structures have been solved (Zhang *et al.*, 1992; Loukili *et al.*, 1988; Tijani *et al.*, 1988) and it is of interest to compare these structures with those of trivalent transition elements. The only known structures of trivalent transition elements are those of anhydrous $\text{Fe}_2(\text{O}_3\text{PH})_3$ (Sghyar *et al.*, 1991b) and $\text{Fe}(\text{HO}_3\text{PH})_3$ (Sghyar *et al.*, 1991a). The powder data for the Al sample was collected using synchrotron radiation and its structure was

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solved without any prior knowledge of the structure. When this manuscript was in preparation we came to know that this compound is isostructural to that of gallium phosphite whose structure was determined using neutron and synchrotron powder data (Morries *et al.*, 1992).

Experimental

Solid-state MAS NMR spectra were obtained on a Bruker MSL-300 solid state NMR spectrometer. The ^{31}P chemical shifts are referenced to 85% H_3PO_4 aqueous solution. The aluminum chemical shifts were referred to external $\text{Al}(\text{H}_2\text{O})_6^{3+}$ as derived from an $\text{Al}(\text{NO}_3)_3$ aqueous solution. Thermogravimetric analysis (TGA) was carried out with a Du Pont Model 951 unit at a rate of $10^\circ\text{C}/\text{min}$. Infrared spectra were recorded on a Digilab Model FTS-40 FTIR unit by the KBr method.

Preparation of the Aluminum phosphite

8.45 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (MCB) was dissolved in deionized water which was added to 60 ml aqueous solution of 1.0M H_3PO_3 . The pH of this mixture was then raised to 1.8 by the addition of NaOH. One third of this solution was kept at 65°C in an oil bath for 24 hr. A white solid (1, 14 g, 81% yield) was obtained after filtration, washing with water and air drying. Analytical data: Al, 13.9%; P 25.0%. Calculated for $\text{Al}_2(\text{O}_3\text{PH})_3 \cdot 4\text{H}_2\text{O}$: Al, 14.7%; P 25.4%.

Preparation of the iron phosphite

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Baker) (14.40 g) was dissolved in 25 ml of an aqueous solution of 1.0 M H_3PO_3 . The resulting red brown clear solution was then refluxed for 24 hr. 5.8 g (77% yield) of a slightly pink solid was recovered by filtration, washed, and then air dried.

Data collection

Powder diffraction data for the aluminum sample were obtained at the National Synchrotron Light Source on beam line X7A using a wavelength of 1.3087 \AA from a Ge (111) monochromator using a Ge (220) analyzer crystal. The sample was contained in a capillary and the data were collected every $0.01^\circ 2\theta$ from 5 to $88.8^\circ 2\theta$ with a count time of 1 s per step. The raw data were transferred to the GRAPH (Rudolf *et al.*, 1985) format and the peaks were indexed. The unit cell parameters were refined by least-squares procedures (Rudolf, 1982).

Step scanned X-ray powder data for the iron sample (packed on a flat aluminum sample holder) were collected on the finely ground sample by means of a Rigaku RU200 computer automated diffractometer. The X-ray source was a rotating anode operating at 50 KV and 180 mA with a copper target and graphite monochromated radiation. Data were collected between 10 and 90° in 2θ with a step size of 0.01° and a count time of 6 s per step. The data were transferred to a DEC microVAX II computer and the pattern processed as described earlier (Rudolf *et al.*, 1985). Indexing was carried out by trial and error methods (Werner, 1965) and refined by least-squares procedures. Crystallographic data are given in Table 1.

Structure solution and refinement

Aluminum phosphite

The pattern was indexed by the trial and error method. The systematic absences indicated the space group to be either $\text{P}2_1$ or $\text{P}2_1/\text{m}$. There were 60 singly indexed reflections up to a 2θ limit of 57° corresponding to a d-spacing of 1.38 \AA . Peaks which could not be

Table 1. Crystallographic data for aluminum and iron phosphites

	Al	Fe
Pattern range (2θ), deg.	9-88.8	4-80
Step scan increment (2θ), deg.	0.01	0.01
Step scan time, s	1	6
Radiation Source	Synchrotron	Rotating anode
Wavelength, \AA	1.3087	1.5406, 1.5444
Space group	$\text{P}2_1$	$\text{P}2_1$
<i>a</i> , \AA	8.0942(1)	8.2548(1)
<i>b</i> , \AA	9.9138(1)	10.1814(1)
<i>c</i> , \AA	7.6255(1)	7.7964(1)
β , deg.	111.95(1)	111.94(1)
No. of contributing reflections	781	533
No. of geometric and observations	61	61
P-O distances and tolerance (\AA)	1.53(1)	1.53(1)
MO_6 distances and tolerance (\AA)	1.85(1)	2.0(1)
O-O distances for PO_4 (\AA)	2.55(1)	2.55(1)
O-O distances for MO_6 (\AA)	2.66(1)	2.66(1)
No. of structural parameters	51	51
No. of profile parameters	11	11
Statistically expected <i>Rwp</i>	0.072	0.034
<i>Rp</i>	0.133	0.164
<i>Rp</i>	0.101	0.122
<i>R_F</i>	0.042	0.041
$R_{wp} = (\sum w(I_o - I_c)^2 / \sum w I_o^2)^{1/2}$		$R_p = (\sum I_o - I_c / \sum I_o)$
Expected $R_{wp} = R_{wp} / (\chi^2)^{1/2}$		$\chi^2 = \sum w(I_o - I_c)^2 / (N_{obs} - N_{var})$
$R_F = \langle F_o - F_c \rangle / \langle F_o \rangle$		

decomposed into their individual reflections were treated as unobserved data. These 60 singly indexed reflections along with an equal number of unobserved data were input to the direct method package in TEXSAN (TEXSAN, 1987). In the space group $P2_1$, the E-map revealed the positions of all the P and Al atoms along with two oxygen atoms. The positions of most of these Al and P atoms were also confirmed by the Patterson map computed with the same data set. A limited refinement was conducted on these atoms with heavy damping and selective refinement of a few parameters per cycle. Difference Fourier maps computed at this stage allowed the positioning of an additional five oxygen atoms of the phosphite groups. The geometry about the Al atoms with these oxygen atoms could not be decided and therefore tetrahedral coordination was assumed at this stage.

Using a utility program Graph (Rudolf *et al.*, 1985) the raw data were transferred to the GSAS (Larsen *et al.*, 1985) program package for Rietveld method (Rietveld, 1969) of full-profile refinement. The refinement was started in the space group $P2_1$ with the positional parameters obtained above. Initial refinement of the scale, background, the unit cell parameters and the profile coefficients led to a satisfactory agreement between the observed and calculated patterns. Refinement of the atomic positions were carried out with soft constraints consisting of both Al—O and P—O bond distances and O—O nonbonded distances. A difference Fourier map obtained at this stage revealed the positions of the missing phosphite oxygens along with peaks at bonding distances (1.7–2.4 Å) from the Al atoms. There were two such peaks near Al1 and one near Al2. These peaks were input as water molecules and the soft constraints were adjusted for octahedral geometry of the Al atoms. With this model the refinement progressed very well and the lattice water molecule was located in the final difference Fourier map. In the last stages of refinement the atom isotropic thermal parameters were refined. In the final refinement the shifts in all the parameters were less than their estimated standard deviations. Neutral atomic scattering factors were used for all atoms. No corrections were made for anomalous dispersion, absorption or preferred orientation.

Iron phosphite

The atomic positions obtained from the refinement of the aluminum phosphite was used as a starting model. The pairs of peaks arising from $K\alpha_1$ and $K\alpha_2$ doublets were treated as separate reflections in the fixed intensity ratio of 2:1. The refinement was carried out in a manner similar to that for the Al compound. Details of the structure refinement are given in Table 1.

Table 2. Positional and thermal parameters for aluminum phosphite

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{iso}, \text{\AA}^2$ ^a
Al1	0.3677(5)	0.9278 ^b	0.0890(5)	0.004(1)
Al2	0.9752(5)	0.1481(6)	0.4359(5)	0.001(1)
P1	0.6528(4)	0.1275(6)	0.0435(5)	0.003(1)
P2	0.0769(5)	0.8710(6)	0.2752(6)	0.003(1)
P3	0.9906(5)	0.9244(6)	0.7515(6)	0.001(1)
O1	0.2197(8)	0.8480(7)	0.1919(9)	0.005(3)
O2	0.0462(8)	0.2774(7)	0.3024(9)	0.007(3)
O3	0.0660(9)	0.0199(7)	0.3192(9)	0.015(3)
O4	0.8934(8)	0.2806(8)	0.5534(9)	0.006(3)
O5	0.5223(8)	0.0090(7)	0.9901(8)	0.007(3)
O6	0.1874(7)	0.9541(7)	0.8601(7)	0.016(3)
O7	0.4360(9)	0.7620(6)	0.0301(1)	0.004(3)
O8	0.9178(8)	0.0179(7)	0.5774(8)	0.014(3)
O9	0.7501(6)	0.1320(9)	0.2576(7)	0.001(3)
O(W1)	0.3100(8)	0.1052(6)	0.1671(9)	0.005(3)
O(W2)	0.5647(8)	0.9178(9)	0.3384(7)	0.009(3)
O(W3)	0.2148(7)	0.1608(10)	0.6356(8)	0.020(3)
O(W4)	0.4949(13)	0.8506(12)	0.6624(13)	0.020(3)

^a $U_{iso} = \frac{B_{iso}}{8\pi^2}$ as defined in GSAS, 1985.

^bHeld fixed in least-squares refinement.

Results and discussion

Crystallographic and experimental parameters are given in Table 1, and final positional and thermal parameters in Table 2 and 3. Bond lengths and angles for the two samples are shown in Tables 4 and 5. The final Rietveld refinement difference plot is shown in Fig. 1.

Table 3. Positional and thermal parameters for iron(III) phosphite

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{iso}, \text{\AA}^2$
Fe1	0.3701(5)	0.9278 ^a	0.0899	0.015(1)
Fe2	0.9733(5)	0.1516(6)	0.4324(5)	0.018(1)
P1	0.6555(8)	0.1263(9)	0.0380(9)	0.019(3)
P2	0.0786(9)	0.8741(8)	0.2722(10)	0.013(3)
P3	0.9956(8)	0.9314(10)	0.7359(9)	0.012(2)
O1	0.220(1)	0.851(1)	0.197(2)	0.012(6)
O2	0.049(2)	0.284(1)	0.304(2)	0.042(7)
O3	0.064(2)	0.022(1)	0.318(2)	0.041(7)
O4	0.897(2)	0.289(1)	0.559	0.040(7)
O5	0.524(2)	0.011(1)	0.988(2)	0.044(7)
O6	0.188(1)	0.955(1)	0.860(1)	0.012(6)
O7	0.434(2)	0.761(1)	0.029(2)	0.041(6)
O8	0.918(1)	0.020(1)	0.581(2)	0.011(6)
O9	0.748(1)	0.138(2)	0.256(1)	0.026(5)
O(W1)	0.324(2)	0.104(1)	0.175(2)	0.027(6)
O(W2)	0.561(1)	0.912(2)	0.345(1)	0.005(5)
O(W3)	0.213(1)	0.166(2)	0.639(2)	0.025(5)
O(W4)	0.492(2)	0.850(2)	0.648(2)	0.032(6)

^aHeld fixed in least-squares refinement.

Table 4. Average and ranges in bond lengths (Å) and bond angles (°) for aluminum phosphite

	Distance	Range	Average
Al1—O	1.828(5) — 1.843(6)		1.84
Al1—O(W)	1.968(5) — 1.976(6)		1.97
Al2—O	1.828(5) — 1.857(5)		1.85
Al2—O(W)	1.972(5)		
P1—O	1.519(7) — 1.529(5)		1.52
P2—O	1.523(5) — 1.530(5)		1.53
P3—O	1.513(5) — 1.544(5)		1.53

Atoms	Angle	Range	Average
O—Al1—O (<i>cis</i>)	88.1(3) — 95.7(3)		90
O—Al1—O (<i>trans</i>)	174.7(4) — 178.7(4)		177
O—Al2—O (<i>cis</i>)	87.2(3) — 94.6(3)		90
O—Al2—O (<i>trans</i>)	176.8(3) — 177.6(3)		177
O—P1—O	109.6(4) — 113.0(4)		111
O—P2—O	110.5(5) — 112.6(5)		111.5
O—P3—O	109.7(4) — 113.1(4)		111.5

Atoms	Angle	Range	Average
P—O—Al	136.4(4) — 149.5(5)		142

Atoms	Distance	Atoms	Distance
O(W1)—O3	2.770(9)	O(W2)—O(W4)	2.81(1)
O(W1)—O(W4)	2.93(1)	O(W3)—O6	2.73(1)
O(W2)—O8	2.93(1)	O(W4)—O5	2.89(1)
O(W2)—O9	2.80(1)		

Table 5. Average and ranges in bond lengths (Å) and bond angles (°) for iron(III) phosphite

	Distance	Range	Average
Fe1—O	1.88(1) — 1.93(1)		1.90
Fe1—O(W)	2.00(1) — 2.03(1)		2.01
Fe2—O	1.86(1) — 1.94(1)		1.91
Fe2—O(W)	2.04(1)		
P1—O	1.55(1) — 1.59(1)		1.56
P2—O	1.51(1) — 1.56(1)		1.53
P3—O	1.51(1) — 1.57(1)		1.54

Atoms	Angles	Range	Average
O—Fe1—O (<i>cis</i>)	88.2(5) — 95.2(6)		90
O—Fe1—O (<i>trans</i>)	174.5(6) — 177.8(6)		176
O—Fe2—O (<i>cis</i>)	87.2(5) — 95.5(6)		90
O—Fe2—O (<i>trans</i>)	174.7(6) — 176.2(7)		176
O—P1—O	109.9(8) — 112.5(8)		109
O—P2—O	110.4(9) — 112.3(8)		111
O—P3—O	109.3(8) — 113.2(7)		112

Atoms	Angle	Range	Average
P—O—Fe	137.3(8) — 152(1)		143

The X-ray powder pattern for the Fe compound is shown in Fig. 2. The bridging nature of the phosphite groups and the coordination surrounding the Al atoms is presented in Fig. 3. Fig. 4 shows the packing of the groups in the lattice.

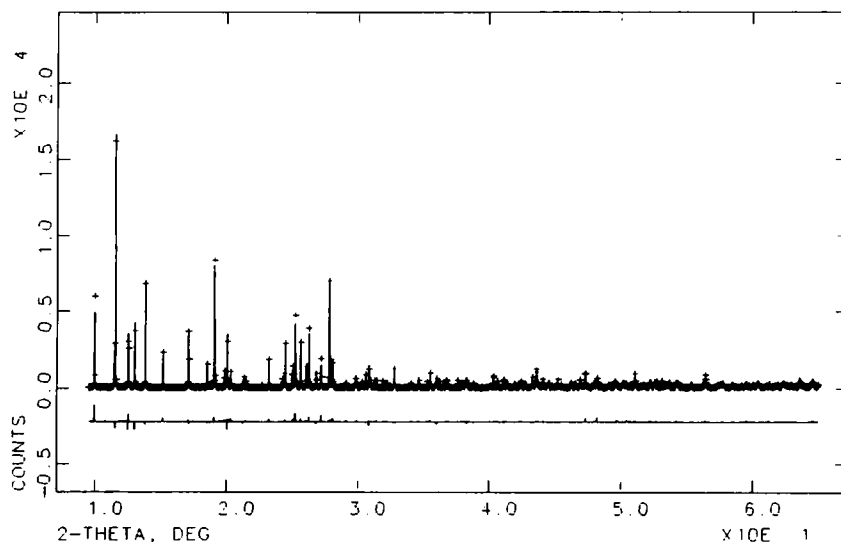


Fig. 1. A portion of the observed (+) and calculated (−) profiles (X-ray intensity versus 2θ) for the Rietveld refinement of the Al sample. The diffraction data was collected using synchrotron radiation. The bottom curve is the difference plot on the same intensity scale.

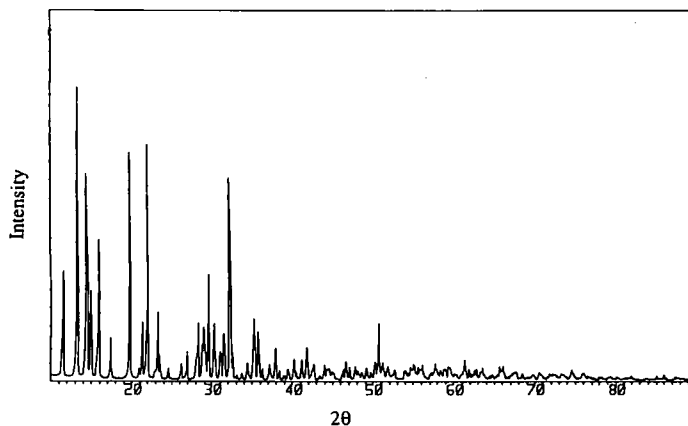


Fig. 2. X-ray powder pattern of the iron phosphite. Intensity data for this sample was collected using Cu $K\alpha$ radiation from a Rigaku Rotating Anode.

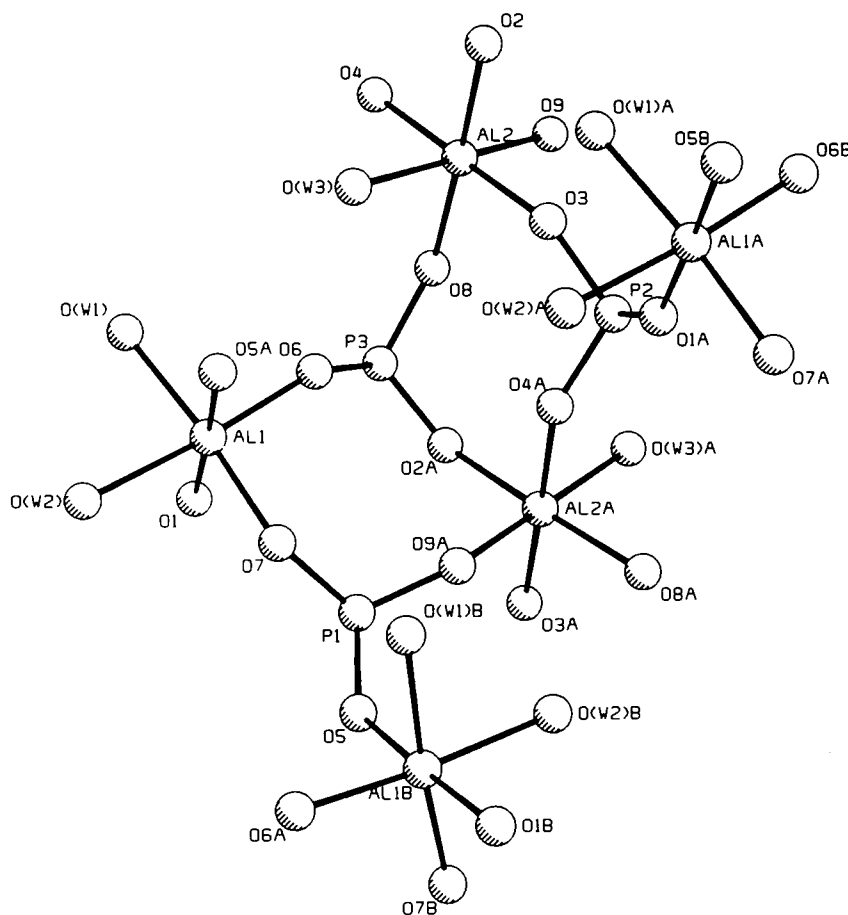


Fig. 3. Plot of the Al phosphite structure showing the numbering scheme and the bridging nature of the phosphite groups.

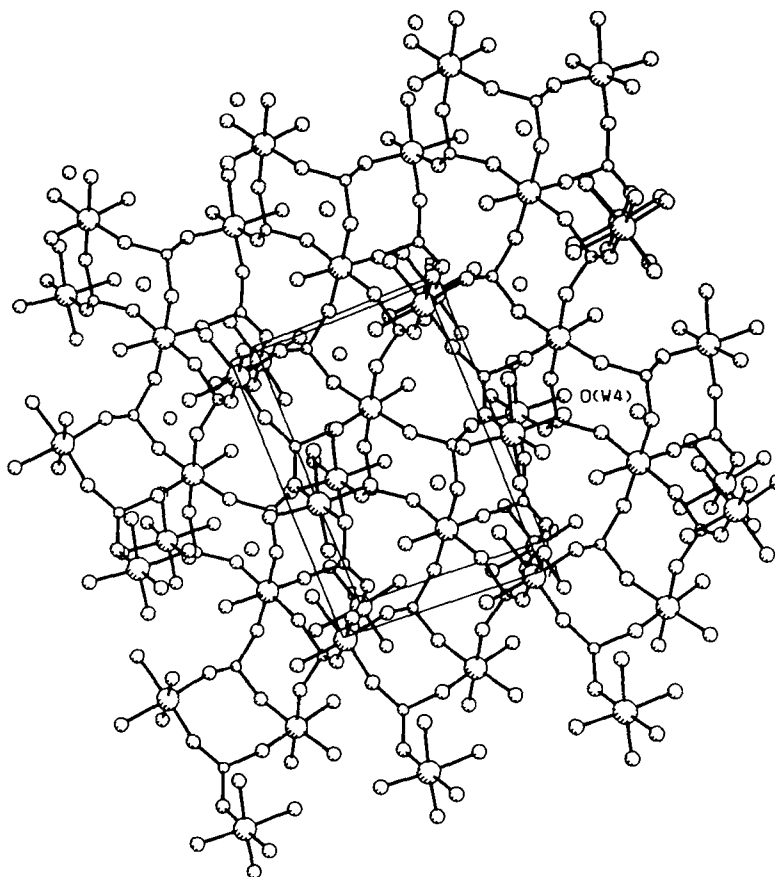


Fig. 4. Packing of the structure in the unit cell.

Since these compounds are isostructural the structural discussion is presented only for the aluminum phosphite compound. The structure consists of three phosphite groups and two octahedrally coordinated Al atoms as shown in Fig. 3. Each phosphite group bridges to three Al atoms. Al1 is coordinated by two water molecules and four phosphite oxygen atoms (O5 and O7 from different P1, O1 from P2 and O6 from P3). The aluminum atom, Al2, is coordinated to one water molecule and five phosphite oxygen atoms (O9 from P1, O3 and O4 from different P2, O2 and O8 from P3). P1 is linked to two Al1 atoms and one Al2 atom while P2 and P3 have the environment of two Al2 atoms and one Al1 atom. This bridging of phosphite groups leads to a three dimensional network of the structure as shown in the Fig. 4. The lattice water is located in a small cavity and is hydrogen bonded to one phosphite oxygen and two coordinated water molecules (Table 4). The metal atoms in both the compounds display a regular octahedral geometry. Bond angles and bond lengths about all the phosphite groups are close to the expected values.

The number of water molecules obtained from the X-ray crystallographic study is consistent with the TGA results. The Al phosphite showed a weight loss of 21.2% up to 200°C while for the Fe compound the weight loss in this temperature range is 16.2%. The calculated value for $M_2(HPO_3)_3 \cdot 4H_2O$ is 19.7% and 17% for the Al and Fe compounds, respectively. The IR spectrum of the Al phosphite (Fig. 5) shows three sharp bands at 2474, 2452 and 2414 cm^{-1} while for the iron phosphite the bands are at 2453, 2430 and 2405 cm^{-1} . These frequencies are characteristic of P—H stretching and indicate the different environments to the three phosphite groups. The spectra also contained bands in the range of 3505–3330 cm^{-1} corresponding to —OH stretching of the water molecules. Two bands are present in the water bend region, perhaps indicating coordinated and hydrogen bonded water. The bands due to the PO_3 group vibrations are seen in the region of 1000–1200 cm^{-1} . The solid-state ^{31}P MAS NMR spectrum of the Al sample showed three peaks of equal intensities at -5.3 , -11.9 and -15.3 ppm (Fig. 6). The ^{27}Al NMR spec-

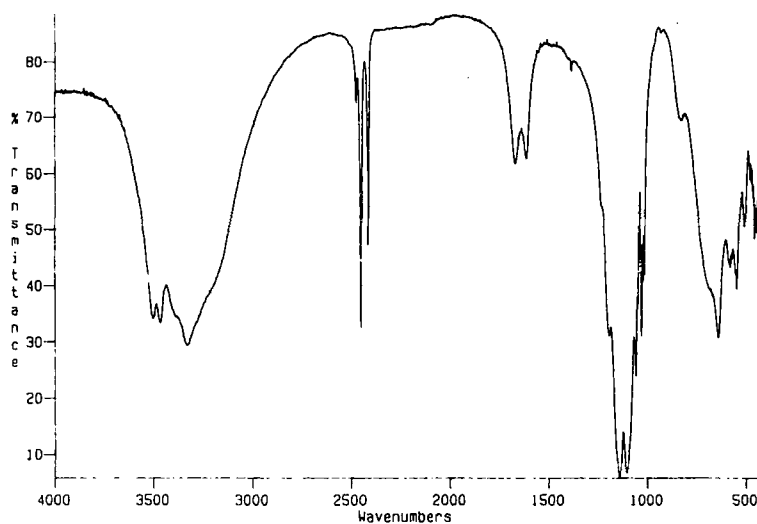


Fig. 5. Infrared transmittance spectrum of $\text{Al}_2(\text{O}_3\text{PH})_3 \cdot 4\text{H}_2\text{O}$.

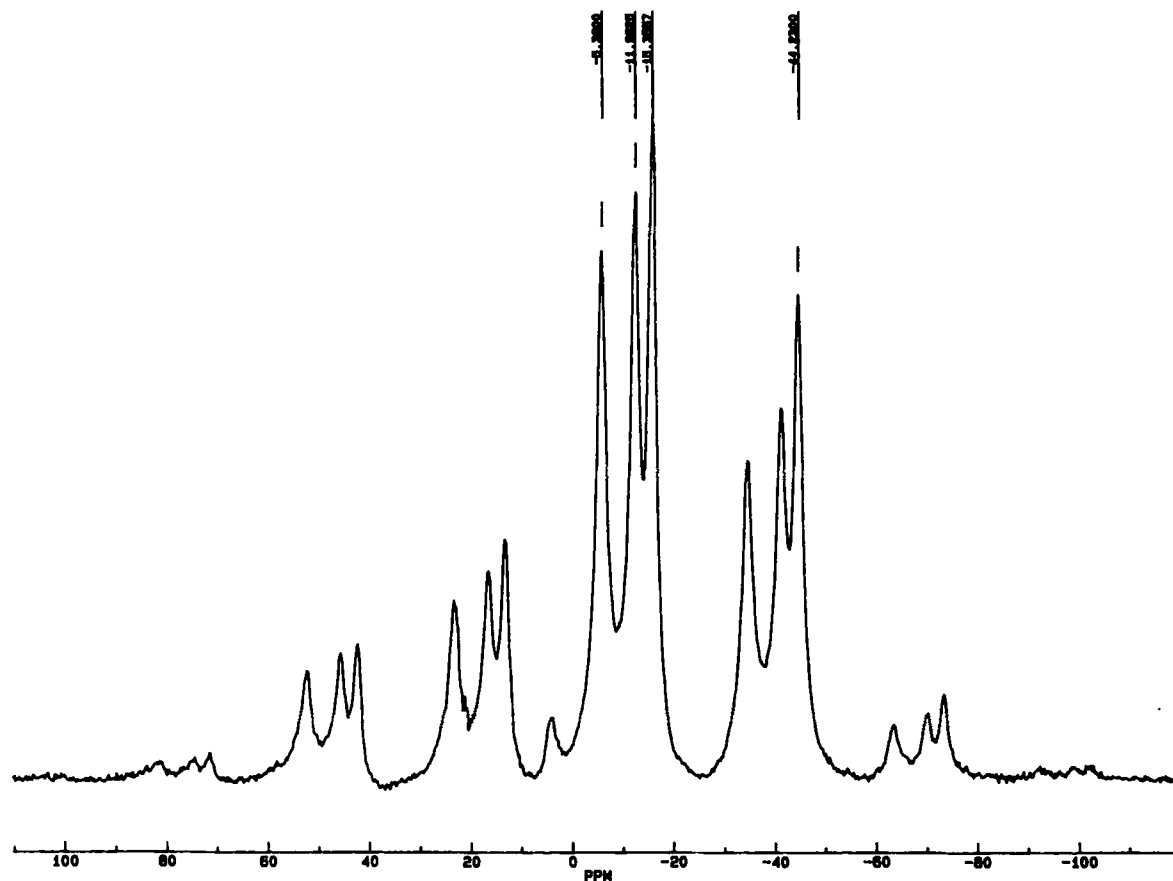


Fig. 6. ^{31}P MAS solid state NMR of $\text{Al}_2(\text{PO}_3)_3 \cdot 4\text{H}_2\text{O}$.

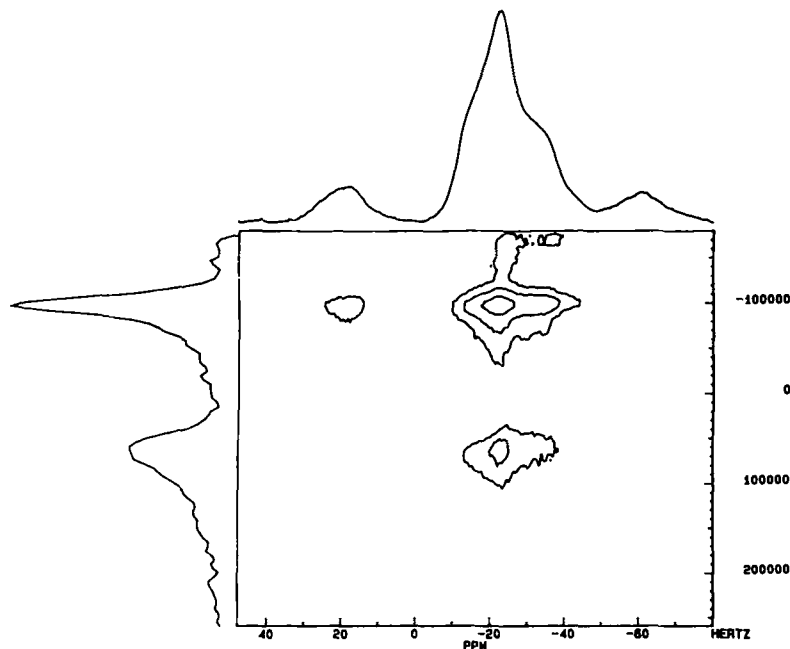


Fig. 7. ^{27}Al 2D-NMR of $\text{Al}_2(\text{PO}_3)_3 \cdot 4\text{H}_2\text{O}$.

trum showed a single peak centered at -20 ppm with a broad shoulder. However, the 2D-NMR clearly showed two peaks of nearly the same intensities (Fig. 7). These results are in agreement with the crystal structure which contain three independent Phosphite groups and two chemically distinct Al atoms.

As mentioned in the introduction, these structures are similar to that of Ga phosphite, $\text{Ga}_2(\text{HPO}_3)_3 \cdot 4\text{H}_2\text{O}$. The dehydrated forms of Fe, Al, and Ga phosphite also contain the same type of structural units. These compounds have a general formula of the type, $\text{M}_2(\text{HPO}_3)_3$ ($\text{M} = \text{Al}, \text{Fe}, \text{Ga}$). The structures of $\text{Fe}(\text{HPO}_3\text{H})_3$ (Sghyar *et al.*, 1991a), $\text{La}(\text{HPO}_3\text{H})_3 \cdot \text{H}_2\text{O}$ (Tijani *et al.*, 1988), $\text{Ce}(\text{HPO}_3\text{H})(\text{HPO}_3) \cdot 2\text{H}_2\text{O}$,² and $\text{La}(\text{HPO}_3\text{H})(\text{HPO}_3) \cdot 3\text{H}_2\text{O}$, (Zhang *et al.*, 1992) on the other hand, are layered. In these cases, the metal atoms are situated in a plane which are bridged by phosphite groups lying slightly above and below the metal plane. The main difference in the structures of the lanthanides from those of the regular elements is the higher coordination number, eight versus six. This high coordination is achieved by one of the phosphite groups chelating the metal atom while at the same time one or both of its oxygen atoms coordinate to adjacent metal atoms. This type of bonding is common among metal phosphonate complexes (Zhang and Clearfield, 1992). It is interesting to note that in all these layered structures the phosphite oxygen carrying the proton is not involved in coordination and it projects away toward the interlayer

region. In the case of $\text{Zn}(\text{H}_2\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$, (Ortiz-Avila *et al.*, 1989) the octahedral metal atoms are linked to HPO_3H anions to form infinite helical chains. A more detailed discussion of the structures involving the phosphite groups and nature of metal coordination was given in Zhang *et al.*, (1992).

Obviously, the accuracy of the structure derived from powder diffraction data is no parallel to that obtained from single crystal study. Nevertheless, the powder data can provide valuable structural information on compounds which can be obtained only in the polycrystalline form. We had earlier solved the structure of a aluminum phosphate molecular sieve, $(\text{AlPO}_4)_3 \cdot (\text{CH}_3)_4\text{NOH}$ using powder data from a conventional X-ray sealed tube. This structure consists of 26 nonhydrogen atoms in the asymmetric unit. Nowadays, with the use of high quality powder data from synchrotron sources and from neutron beams it is possible to improve the precision of the refinement and also to attempt the solution of much more complex crystal structures. The structures presented here and the Ga phosphite contain 18 nonhydrogen atoms in the asymmetric unit. Morris *et al.* (1992) were also able to locate and refine all the hydrogen atoms of the phosphite groups and the water molecules using an additional neutron diffraction data set. The complete structure solution of these phosphite structures is clearly a major step in demonstrating the quality of structural results from powder diffraction data.

Acknowledgments

We gratefully acknowledge financial support of this study by the Regents of Texas A&M University through the commitment to Texas Program and the State of Texas through the Advanced Technology Program. We also wish to thank Dr. David Cox for assistance in obtaining the synchrotron data at the National Synchrotron Light Source at Brookhaven National Laboratory, which is supported by the United States Department of Energy, Division of Materials Sciences, and Division of Chemical Sciences.

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