

Synthesis and X-Ray Powder Structures of Three Novel Titanium Phosphate Compounds

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INTRODUCTION

Three titanium phosphate porous compounds were prepared hydrothermally and their structures solved from their X-ray powder diffraction patterns collected on a laboratory X-ray source. The compound, $[\text{Ti}_3(\text{PO}_4)_4(\text{H}_2\text{O})_2] \cdot \text{NH}_3$ (1), crystallizes in triclinic symmetry with $a = 8.2506(4)$, $b = 8.7879(4)$, $c = 5.1022(2)$ Å; $\alpha = 90.703(1)$, $\beta = 91.083(1)$, $\gamma = 110.158(1)^\circ$; space group $P\bar{1}$, and $Z = 1$. The structure was solved *ab initio* by direct methods and refined by Rietveld methods. The structure consists of two octahedrally coordinated titanium atoms, one of which is bound only by phosphate oxygens and the other by phosphate oxygens and water molecules. The bridging of titanium atoms by phosphate oxygens creates a framework consisting of one-dimensional channels oriented along the c -axis. The ammonia molecules are located in these channels. Compound (2), $[\text{Ti}_2\text{O}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$, also crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.818(1)$, $b = 9.654(1)$, $c = 5.109(1)$ Å; $\alpha = 93.818(2)$, $\beta = 93.665(3)$, $\gamma = 73.313(3)^\circ$; and $Z = 2$. The complete structure was solved by direct methods. The two independent titanium atoms are bridged by an oxygen atom. The remaining coordination sites of the octahedra are completed by phosphate oxygens and water oxygen atoms. As in the case of compound (1) the water molecules are coordinated to only one type of Ti atom. The structure consists of one-dimensional channels into which the water oxygens are projected. The compound $(\text{NH}_4)_2[\text{Ti}_3\text{O}_2(\text{HPO}_4)_2(\text{PO}_4)_2]$ (3) crystallizes in the noncentric space group $P2_1$, with $a = 8.5165(3)$, $b = 16.7331(5)$, $c = 5.1813(2)$ Å; $\beta = 91.173(2)^\circ$; and $Z = 2$. A partial structural model was obtained from direct methods procedures and the structure was completed by Fourier methods following Rietveld refinement of the full pattern. In this case there are three independent titanium atoms and they are bridged by oxygen atoms of the Ti_3O_2 group. All the Ti atoms are octahedrally coordinated. As in the case of compounds (1) and (2), compound (3) forms a framework structure containing one-dimensional channels. The hydroxyl groups of the monohydrogen phosphate and the ammonium cations are located in the channels. In the channel the $\text{Ti}-\text{PO}_4$ framework and the hydroxyl groups create cavities around the ammonium cations which block its exchange with other cationic species. © 1997

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The interest in research concerning preparation and characterization of materials based on group IV metal phosphates is largely due to their properties, such as thermal, radiation, and chemical stability and resistance to oxidation. These materials have potential applications in the areas of ion-exchange (1–4), catalysis (5,6), conductivity (7,8), nonlinear optics (9), etc. The titanium phosphate and silicate compounds, in particular, have been shown to form diverse compound types including porous compounds which may have important applications in the removal and safe storage of radioactive species (10). For example, a compound with an ideal formula $\text{Na}_2\text{Ti}_2\text{O}_3(\text{SiO}_4) \cdot 2\text{H}_2\text{O}$ has been shown to selectively absorb trace amounts of Cs^+ ions from solutions containing molar amounts of other alkaline metal ions (11). This special property of this compound was found to be due to its unique three-dimensional structure (12). The structure consists of unidimensional channels which are ideally suited for the optimal binding of Cs^+ ions in the presence of large amounts of Na^+ . Titanium phosphate compounds with layer structures are also well known which include $\alpha\text{-Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (13) and $\gamma\text{-Ti}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ (14). These layered compounds were studied extensively with respect to their ion-exchange properties and also in preparing organically or inorganically pillared compounds (15, 16). In this paper we report three new titanium phosphate compounds the structures of which were solved *ab initio* from X-ray powder diffraction data. The compounds contain respectively monomeric, dimeric, and trimeric TiO_6 octahedra and they form three-dimensional structures consisting of large one-dimensional channels.

EXPERIMENTAL

Materials and methods. All reagents were of analytical grade (Aldrich) and used without further purification. Thermogravimetric analysis was carried out with a TA 4000 unit, at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. The IR spectrum was recorded on a Perkin–Elmer 1720-X

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FTIR unit by the KBr disk method. The solids were dissolved in HF and the titanium and phosphorus contents were determined using a SpectraSpec spectrometer DCP-AEC. ^{31}P MAS solid state NMR spectra were recorded on a Bruker MSL-300 spectrometer where proton and phosphorus nuclei resonate at 300.1 and 12.5 MHz, respectively. The ^{31}P chemical shifts were referenced to 85% H_3PO_4 aqueous solution.

Synthesis of $[\text{Ti}_3(\text{PO}_4)_4(\text{H}_2\text{O})_2] \cdot \text{NH}_3$ (1). To a TiCl_3 solution in 20% HCl (24 mL, $\sim 1.4\text{ M}$) 4.32 mL of 85% H_3PO_4 and 2 g of urea (dissolved in 30 mL of water) were added. The reaction mixture was placed in a 100 mL stainless steel Teflon-lined vessel, and heated at 190°C for 7 days. The white product was filtered, washed with an excess of water and air dried. The preparation of this compound was also attempted by using TiCl_4 but was not successful. Anal. found: Ti, 24.88%; P, 21.19%; N, 2.4%. Calc. for the above formula: Ti, 24.53%; P, 21.12%, N, 2.39%.

Synthesis of $[\text{Ti}_2\text{O}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$ (2). A 3 mL solution of TiCl_4 (2 M) was mixed with 57 mL of 4.5 M H_3PO_4 . The mixture was placed in a Teflon-lined stainless steel vessel and heated at 190°C for 1 week. The product formed was filtered, washed with water, and air dried. Anal. found: Ti, 28.33%; P, 18.25%. Calc. for the above formula: Ti, 28.4%; P, 18.34%.

Synthesis of $(\text{NH}_4)_2[(\text{Ti}_3\text{O}_2)(\text{HPO}_4)_2(\text{PO}_4)_2]$ (3). To a 12 mL solution of TiCl_4 (2 M) 15.5 mL of concentrated H_3PO_4 and 7.2 g of urea (dissolved in 15 mL of water) were added. The reaction mixture was heated to 190°C for 5 days in a Teflon-lined steel vessel. The white powder was separated by filtration, washed with water, and air dried. Anal. found: Ti, 25.08%; P, 20.35%; N, 4.6%. Calc. for the above formula: Ti, 24.2%; P, 20.8%, N, 4.7%.

X-ray data collection. Initially, X-ray powder data for the samples were collected using a flat aluminum sample holder by means of a Rigaku 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. During the course of study it was found that the data were severely affected by preferred orientation effects. To overcome this problem, the samples for the data collection were prepared by using a tubular aerosol suspension chamber developed by Davis Consulting (17). In this case the finely ground sample particles were dispersed into an aerosol through the action of a fluidized bed of spherical beads. The aerosol is then carried up through a column and is captured by a filter paper mounted on a cassette by the action of a vacuum pump. In this way the powder particles were deposited in a random orientation within the pores of the filter paper thereby reducing the effect of preferred orientation to a minimum level. Data for compound (1) were collected at room temperature between

8° and 100° , in 2θ with a step size of 0.01° and a count time of 9 s per step. For compounds (2) and (3) the same 2θ range and step sizes were used but the exposure times were 8 and 10 s, respectively. The powder patterns were indexed by Ito methods (18). The initial unit cell dimensions obtained were compound (1) $a = 8.25$, $b = 8.787$, $c = 5.1\text{ \AA}$, $\alpha = 90.7$, $\beta = 91.07$, $\gamma = 110.15^\circ$ (FOM = 63); compound (2) $a = 8.83$, $b = 9.67$, $c = 5.12\text{ \AA}$, $\alpha = 93.83$, $\beta = 93.68$, $\gamma = 73.33^\circ$ (FOM = 84); compound (3) $a = 8.52$, $b = 16.74$, $c = 5.18\text{ \AA}$, $\beta = 91.18^\circ$ (FOM = 57). Initially the triclinic centric space group was selected for compounds (1) and (2) which was confirmed by the successful refinement of the structures. In the case of compound (3) the systematic absences indicated the space group to be either $P2_1/m$, $P2_1$, or $P2_1/n$.

Structure solution and refinement. The structure factor amplitudes were extracted from the profile using the Le Bail method (19). For compounds (1) and (3) Le Bail extraction was carried out in GSAS (20) while for (2) the program EXTRA (21) was used. In the case of compound (1) the extraction procedure yielded 754 $K\alpha_1$ reflections which were input to the direct method program MITHRIL (22) in TEXSAN (23) series of programs. An E-map calculated with the set with the best figure of merit (Abs. FOM = 1.6, Psi Zero = 4.0, Resid = 14.24) revealed the positions of all the 14 atoms in the structure. These positions were used for Rietveld refinement of the full pattern in GSAS. After the initial refinement of scale, background function, unit cell parameters, and profile parameters, the positions were refined with soft constraints only for the phosphate groups. As the refinement progressed, the weights of these constraints reduced to a minimum value so as to keep the refinement from diverging. In the final stages of refinement, the preferred orientation factor was allowed to refine. The diffraction vector is along the c^* -axis and the ratio of the effect along this axis to that along the perpendicular plane was refined. The ratio was refined to a value very close to 1.0, indicating that the effect was almost eliminated by the sample preparation method. All the atoms were refined isotropically. Neutral atomic scattering factors, as stored in GSAS, were used for all atoms. No absorption corrections were made.

For compound (2), Le Bail extraction using EXTRA produced 854 independent reflections in the 2θ range 7° – 100° . The structure was solved by SIRPOW.92 (24). An E-map calculated for a set with the best figure of merit (CFOM = 0.90) yielded the positions of all 15 nonhydrogen atoms in the structure. The R factor for these atoms was 17%. These positions were then transferred to GSAS for full pattern refinement. The refinement was carried out in a manner similar to that described for compound (1).

As mentioned in the X-ray data collection section, if some very low intensity peaks are ignored the space group can be determined as $P2_1/n$. On the other hand, if these minor peaks are included the space group is either $P2_1$ or $P2_1/m$.

Initial efforts to solve the structure in $P2_1/n$ failed to produce any reasonable structural fragment. Attempts were also made to solve the structure in $P2_1/m$. Again, no solution produced any starting model for the structure. At this stage a ^{31}P MAS NMR spectrum (Fig. 2C) was obtained for the compound to obtain some information about the type and number of phosphate groups in the structure. The spectrum shows clearly three peaks with intensity ratio 1:2:1. If the space groups were $P2_1/m$ or $P2_1/n$, the NMR spectrum should have shown only two peaks corresponding to two types of phosphate groups in the structure. The presence of three peaks with intensity ratio 1:2:1 clearly indicates the formula $(\text{NH}_4)_2[(\text{Ti}_3\text{O}_2)(\text{HPO}_4)_2(\text{PO}_4)_2]$ consisting of four independent phosphate groups rather than two independent phosphate groups. In other words, the NMR data is consistent with the noncentric space group $P2_1$. The subsequent calculations were therefore carried out in $P2_1$. Intensities for a total of 812 $K\alpha_1$ reflections were extracted in the 2θ range 10° – 100° using GSAS. A direct method run using MITHRIL (Abs. FOM = 1.82, Psi Zero = 2.49, Resid = 19.9) revealed the positions of three titanium atoms, two phosphorus atoms, and five oxygen atoms in the E-map. These positions were used as a starting model for full pattern refinement in GSAS. After the initial refinement of nonstructural parameters (scale, unit cell parameters, background terms, and profile parameters) a series of difference Fourier maps were calculated. These maps allowed the positioning of all the remaining nonhydrogen atoms in the structure. Final refinements were carried out similar to that for compound (1).

Crystallographic and experimental parameters are given in Table 1, final positional and thermal parameters in Tables 2–4, and bond lengths and angles in Tables 5–7. The final Rietveld refinement difference plots are shown in Figs. 1A–1C.

RESULTS

TGA and spectral characterization of the compounds. The TGA curve for compound (1) shows the release of the coordinated water molecules in two steps, one in the range 230 – 360°C (weight loss, 3.7%) and the other in the range 360 – 470°C (weight loss, 2.46%). The dehydrated phase retained the ammonia molecule and it was confirmed by the presence of the characteristic NH_3 band (1430 cm^{-1}) in the IR spectrum of the sample heated to 450°C . The ammonia molecule is released in two steps, 470 – 570°C and 570 – 680°C accounting for 0.43 and 0.48 moles of ammonia, respectively. The ^{31}P MAS NMR spectrum (Fig. 2A) shows two distinct signals at -23.4 and -25.6 ppm with equal intensities.

Compound (2) does not show any weight loss up to 150°C indicating the absence of any lattice water molecules. The coordinated water molecules are released in the temperature range 150 – 366°C . The total weight loss of 10.51% found in the TGA curve agrees very well to that calculated (10.65%) for $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. The ^{31}P MAS NMR spectrum (Fig. 2B) shows two sharp peaks of equal intensities at -12.3 and -26.0 ppm, which is in agreement with the structure derived from the X-ray diffraction.

TABLE 1
Crystallographic Data for the Titanophosphate Phases

Formula	(1) $[\text{Ti}_3(\text{PO}_4)_4(\text{H}_2\text{O})_2] \cdot \text{NH}_3$	(2) $[\text{Ti}_2\text{O}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$	(3) $(\text{NH}_4)_2[(\text{Ti}_3\text{O}_2)(\text{HPO}_4)_2(\text{PO}_4)_2]$
Formula weight	576.7	337.8	593.7
Space group	$P\bar{1}(\#2)$	$P\bar{1}(\#2)$	$P2_1(\#4)$
a (Å)	8.2506(4)	8.818(1)	8.5165(3)
b (Å)	8.7879(9)	9.654(1)	16.7331(5)
c (Å)	5.1022(2)	5.109(1)	5.1813(5)
α (°)	90.703(1)	93.818(2)	
β (°)	91.083(1)	93.665(3)	91.173(2)
γ (°)	110.158(1)	73.313(3)	
Z	1	2	2
V (Å ³)	347.14(4)	415.2(1)	738.22(5)
d_{calcd} (g/cm ³)	2.76	2.7	2.67
μ (cm ⁻¹)	198.56	206.84	187.22
Pattern range (2θ)	9–100	7.5–100	10.5–90
No. of reflections	710	846	622
No. soft constraints	20	20	40
R_{wp}^a	0.104	0.116	0.143
R_{p}^a	0.073	0.088	0.104
R_{F}^a	0.043	0.052	0.036

^a See Ref. 20 for definitions.

TABLE 2
Positional and Thermal Parameters for
[Ti₃(PO₄)₄(H₂O)₂] · NH₃

	x	y	z	$U_{\text{iso}}, \text{\AA}^2$ ^a
Ti1	0.0	0.0	0.0	0.024(4)
Ti2	0.7270(3)	0.4332(3)	0.2692(5)	0.008(3)
P1	0.8681(5)	0.2921(4)	0.7528(6)	0.010(3)
P2	0.3114(5)	0.3293(4)	0.2110(6)	0.010(3)
O1	0.9129(8)	0.1419(8)	0.8010(11)	0.017(4)
O2	0.7734(8)	0.2617(7)	0.4943(10)	0.017
O3	0.0269(7)	0.4401(8)	0.7517(11)	0.017
O4	0.7528(8)	0.3046(8)	0.9681(11)	0.017
O5	0.7066(9)	0.5631(8)	0.5805(11)	0.017
O6	0.4766(7)	0.2938(7)	0.2688(12)	0.017
O7	0.1595(8)	0.1693(8)	0.2223(11)	0.017
O8	0.3245(8)	0.4013(8)	0.9408(11)	0.017
O9 ^b	0.1923(9)	0.0185(9)	0.7315(13)	0.107
N1	0.5	0.0	0.0	0.017

^a $U_{\text{iso}} = B_{\text{iso}}/8\pi^2$.

^b Water oxygen atom.

The TGA experiment for compound (3) was carried out up to 1000°C and the final product was analyzed as a mixture of TiP₂O₇ and Ti₂O(PO₄)₂. The compound is stable up to 415°C and the weight loss concerning the release of one mole of ammonia (weight loss 3.3%) starts around 415°C and appears to be complete at 635°C. In the next step 635–725°C a weight loss of 7.7% was observed which corresponds to the release of the remaining mole of ammonia and two water molecules. The total weight loss of 10.99% observed is close to that expected (11.78%) for the formula (NH₄)₂[(Ti₃O₂)(HPO₄)₂(PO₄)₂]. The compound shows

TABLE 3
Positional and Thermal Parameters for [Ti₂O(PO₄)₂(H₂O)]

	x	y	z	$U_{\text{iso}}, \text{\AA}^2$
Ti1	-0.1241(5)	0.2995(4)	-0.5307(8)	0.024(2)
Ti2	0.2694(5)	0.1651(4)	-0.7518(7)	0.010(2)
P1	0.3302(7)	-0.0750(6)	-0.2758(10)	0.018(2)
P2	0.1790(6)	0.3817(6)	-0.2427(10)	0.010(2)
O1	0.5029(6)	-0.1196(9)	-0.1953(15)	0.022(5)
O2	0.3026(11)	-0.0156(7)	-0.5465(12)	0.022
O3	0.2581(11)	-0.2092(9)	-0.2488(17)	0.022
O4	0.2433(10)	0.0425(8)	-0.0809(13)	0.022
O5	0.2509(11)	0.3275(9)	0.0254(13)	0.022
O6	0.2846(8)	0.2911(7)	-0.4447(12)	0.022
O7	0.0049(9)	0.3667(11)	-0.2609(17)	0.022
O8	-0.1916(12)	0.4617(7)	-0.7639(19)	0.022
O9	0.0334(6)	0.2058(10)	-0.7481(16)	0.022
O10 ^a	-0.0805(12)	0.1399(10)	-0.2696(17)	0.022
O11 ^a	-0.3289(11)	0.4159(11)	-0.3230(19)	0.022

^a Water oxygen atoms.

TABLE 4
Positional and Thermal Parameters for
(NH₄)₂[(Ti₃O₂)(HPO₄)₂(PO₄)₂]

	x	y	z	$U_{\text{iso}}, \text{\AA}^2$
Ti1	0.2516(11)	0.0	-0.241(2)	0.030(3)
Ti2	0.4138(8)	0.1741(6)	0.458(1)	0.008(4)
Ti3	0.0953(8)	-0.1737(6)	0.059(1)	0.012(5)
P1	0.1674(11)	0.1820(6)	-0.056(2)	0.007(6)
P2	-0.0760(11)	-0.0904(7)	0.546(2)	0.027(7)
P3	0.5871(12)	0.0841(7)	-0.036(2)	0.028(6)
P4	0.3248(10)	-0.1823(7)	-0.406(2)	0.016(7)
O1	0.2608(11)	0.2147(7)	0.716(2)	0.030(8)
O2	0.1514(12)	0.0905(5)	-0.057(2)	0.030
O3	0.0036(8)	0.2172(6)	-0.040(2)	0.030
O4	0.2659(11)	0.2095(6)	0.180(2)	0.030
O5	0.0474(11)	-0.0231(6)	-0.434(2)	0.030
O6	-0.0831(11)	-0.1277(7)	0.275(2)	0.030
O7	-0.0318(14)	-0.1583(7)	0.735(2)	0.030
O8	-0.2391(12)	-0.0534(10)	0.613(3)	0.030
O9	0.4575(10)	0.0207(6)	-0.052(2)	0.030
O10	0.5673(11)	0.1404(7)	-0.269(2)	0.030
O11	-0.4307(11)	0.1332(7)	-0.790(2)	0.030
O12	-0.2491(12)	0.0451(10)	-0.031(3)	0.030
O13	0.3533(11)	-0.0925(5)	-0.411(2)	0.030
O14	0.5153(11)	0.2817(6)	0.452(2)	0.030
O15	0.2781(11)	-0.2143(9)	-0.148(3)	0.030
O16	0.2110(14)	-0.2063(7)	0.385(2)	0.030
N1	-0.0772(30)	0.1290(21)	-0.582(5)	0.030
N2	0.6213(26)	-0.1338(19)	0.043(4)	0.030

three signals in the ³¹P MAS NMR spectrum at -3.0, -10.3, and -19.0 ppm with an intensity ratio of about 1:2:1. The NMR spectrum for the compound is presented in Fig. 2c.

TABLE 5
Bond Lengths (Å) and Bond Angles (°) for
[Ti₃(PO₄)₄(H₂O)] · NH₃

Atoms	Distance	Atoms	Distance
Ti1–O1	1.930(5)	2 × Ti1–O9	2.081(6) 2 ×
Ti1–O7	1.946(5)	2 × Ti2–O2	2.040(6) 2 ×
Ti2–O3	1.956(6)	Ti2–O4	1.954(6)
Ti2–O5	1.988(6)	Ti2–O6	2.006(6)
Ti2–O8	1.972(6)	P1–O1	1.510(7)
P1–O2	1.493(6)	P1–O3	1.495(6)
P1–O4	1.494(5)	P2–O5	1.458(5)
P2–O6	1.524(6)	P2–O7	1.530(6)
P2–O8	1.514(6)		
Atoms	Angle range	Average	
O–Ti1–O (<i>cis</i>)	83.9(3)–96.1(3)	90	
O–Ti1–O (<i>trans</i>)	180	180	
O–Ti2–O (<i>cis</i>)	86.0(3)–95.3(3)	90.0	
O–Ti2–O (<i>trans</i>)	175.9(3)–178.4(3)	177.4	
O–P1–O	105.2(4)–111.1(5)	109.5	
O–P2–O	107.5(4)–113.7(5)	109.4	

TABLE 6
Bond Lengths (Å) and Bond Angles (°) for $[\text{Ti}_2\text{O}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$

Atoms	Distance	Atoms	Distance
Ti1–O3	1.928(7)	Ti1–O7	1.929(7)
Ti1–O8	1.961(6)	Ti1–O9	1.823(6)
Ti1–O10	2.042(7)	Ti1–O11	2.138(7)
Ti2–O1	1.961(6)	Ti2–O2	2.034(6)
Ti2–O4	2.030(6)	Ti2–O5	1.962(6)
Ti2–O6	1.942(6)	Ti2–O9	2.004(6)
P1–O1	1.497(7)	P1–O2	1.511(7)
P1–O3	1.615(6)	P1–O4	1.521(7)
P2–O5	1.532(7)	P2–O6	1.493(6)
P2–O7	1.579(7)	P2–O8	1.546(7)
Atoms	Angle range	Average	
O–Ti1–O (<i>cis</i>)	78.3(4)–103.1(4)	90.0	
O–Ti1–O (<i>trans</i>)	169.3(5)–173.0(5)	171.5	
O–Ti2–O (<i>cis</i>)	83.2(2)–95.0(4)	90.0	
O–Ti2–O (<i>trans</i>)	172.5(4)–176.8(4)	174.6	
O–P1–O	105.2(5)–113.5(5)	109.6	
O–P2–O	103.8(5)–115.4(6)	109.3	

Structure of $[\text{Ti}_3(\text{PO}_4)_4(\text{H}_2\text{O})_2] \cdot \text{NH}_3$. The structure consists of two independent monomeric titanium octahedra and two phosphate groups. One of the titanium atoms occupies the center of symmetry (0, 0, 0) and is coordinated by two oxygens (O1, O1a) from the P1 phosphate, 2 oxygens (O7, O7a) from P2 phosphate, and two water oxygen atoms (O9, O9a). The other titanium atom is located on a general position and all its octahedral coordination sites are occupied by phosphate oxygens. Phosphate oxygens that do not bind to Ti1 are involved in Ti2 coordination as shown in Fig. 3. The titanium octahedra and phosphate tetrahedra display normal bond parameters.

The linking of titanium octahedra by phosphate oxygens via Ti–O–P leads to a three-dimensional structure consisting of one-dimensional channels. These channels run along the *c*-axis of the crystal. As shown in Fig. 4, the channels contain pores consisting of a 16-membered ring (–Ti1–O1–P1–O2–Ti2–O6–P2–O7–Ti1– and its symmetry related positions) in the *ab*-plane. These pores have an approximately circular opening in the *ab*-plane with dimensions of 5.6 and 5.8 Å along the *a*-axis and *b*-axis, respectively. The ammonia molecules are located at the center of these channels (center of symmetry, at 1/2, 0, 0). The arrangement leads to alternating titanium atoms (Ti1) and ammonia molecules along the *a*-axis separated by about 4.12 Å (1/2 of *a*-axis length). The coordinated water molecules (O9) of the neighboring Ti1 octahedra (along *a*-axis) are involved in hydrogen bonding with the ammonia molecule (O9---N1 = 2.92 Å, O9---N1---O9 = 180°). The ammonia molecules are also at hydrogen bonding distances from O4 (N1---O4 = 2.78 Å) and O6 (N1---O6 = 2.98 Å).

TABLE 7
Bond Lengths (Å) and Bond Angles (°) for $(\text{NH}_4)_2[(\text{Ti}_3\text{O}_2)(\text{HPO}_4)_2(\text{PO}_4)_2]$

Atoms	Distance	Atoms	Distance
Ti1–O2	1.990(7)	Ti1–O5	2.026(7)
Ti1–O9	2.020(7)	Ti1–O13	1.989(7)
Ti1–O17	1.984(7)	Ti1–O18	1.971(7)
Ti2–O1	2.002(6)	Ti2–O4	1.985(7)
Ti2–O10	1.986(7)	Ti2–O11	1.986(7)
Ti2–O14	1.998(7)	Ti2–O17	1.971(7)
Ti3–O3	2.012(7)	Ti3–O6	2.055(6)
Ti3–O7	1.997(6)	Ti3–O15	2.027(7)
Ti3–O16	2.103(7)	Ti3–O18	1.989(7)
P1–O1	1.540(8)	P1–O2	1.537(7)
P1–O3	1.518(7)	P1–O4	1.540(8)
P2–O5	1.543(7)	P2–O6	1.536(7)
P2–O7	1.541(8)	P2–O8	1.567(8)
P3–O9	1.533(8)	P3–O10	1.539(8)
P3–O11	1.527(8)	P3–O12	1.539(8)
P4–O13	1.522(8)	P4–O14	1.512(8)
P4–O15	1.501(15)	P4–O16	1.493(8)
Atoms	Angle range	Average	
O–Ti1–O (<i>cis</i>)	84.4(4)–93.6(4)	90.0	
O–Ti1–O (<i>trans</i>)	177.1(5)–178.6(5)	177.8	
O–Ti2–O (<i>cis</i>)	85.6(4)–93.1(4)	90.0	
O–Ti2–O (<i>trans</i>)	178.2(5)–179.4(5)	178.7	
O–Ti3–O (<i>cis</i>)	81.7(5)–94.3(4)	90.0	
O–Ti3–O (<i>trans</i>)	171.3(5)–177.1(5)	174.8	
O–P1–O	102.8(5)–113.5(6)	109.5	
O–P2–O	106.6(6)–111.9(6)	109.5	
O–P3–O	108.3(7)–111.0(7)	109.5	
O–P4–O	104.3(6)–114.4(10)	109.4	

Structure of $[\text{Ti}_2\text{O}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$. This compound contains an oxygen bridged dimeric titanium octahedra and two independent phosphate groups. The coordination about the titanium atoms is shown in Fig. 5. Ti1 is coordinated by one oxygen (O3a) from P1 phosphate, two oxygens (O7, O8) from P2 phosphate, two water oxygens (O10, O11), and an oxygen (O9) of the Ti_2O group. As in the case of compound (1) the water molecules are involved in binding to only one type of titanium atoms. The octahedral coordination sites of Ti2 are occupied by three oxygens (O2, O1a, O4a) of P1 phosphate, two oxygens (O5a, O6) of P2 phosphate and O9. The titanium octahedra and P tetrahedra display near-perfect geometries. The Ti–O bond lengths in the Ti_2O group are Ti1–O9 = 1.823(6) Å and Ti2–O9 = 2.004(6) Å. The Ti_2O group is bent by about 43° from linearity (angle Ti1–O9–Ti2 is 137.4(5)°). The angle at the oxygen in this linking group is in the range of values observed for that in Ti–O–P links. The Ti–O–P angle in the structure for different atoms ranges between 134.7(7)° and 155.6(6)° with an average value of 141°.

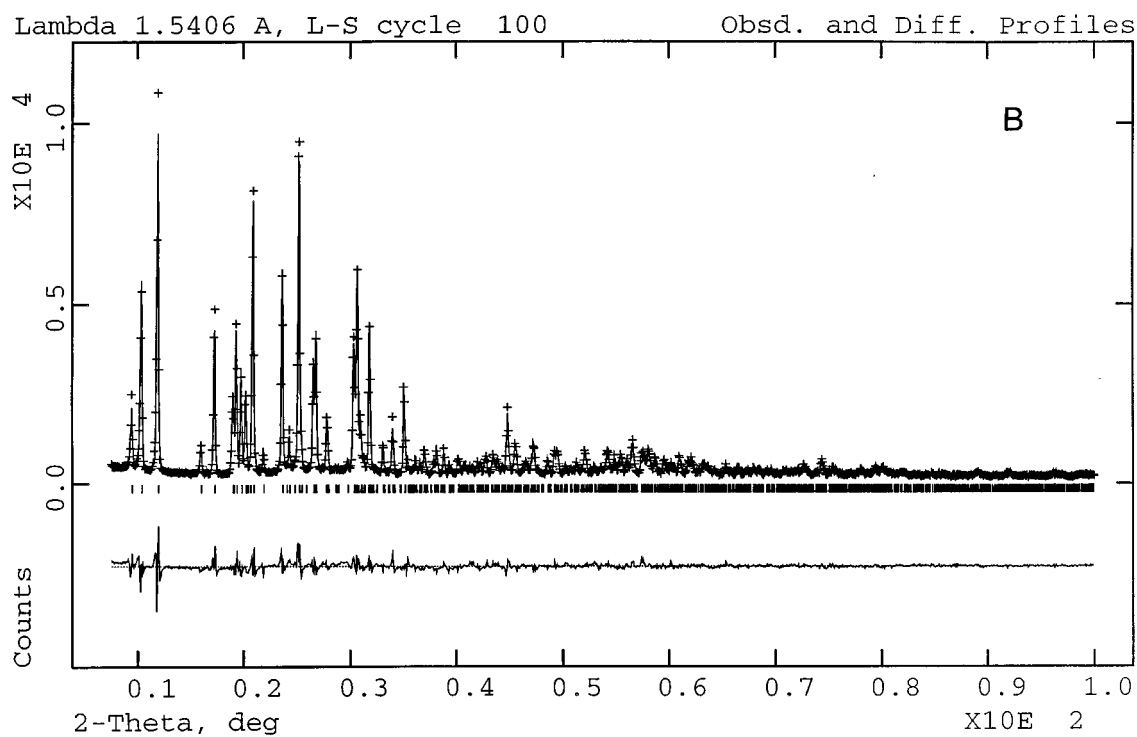
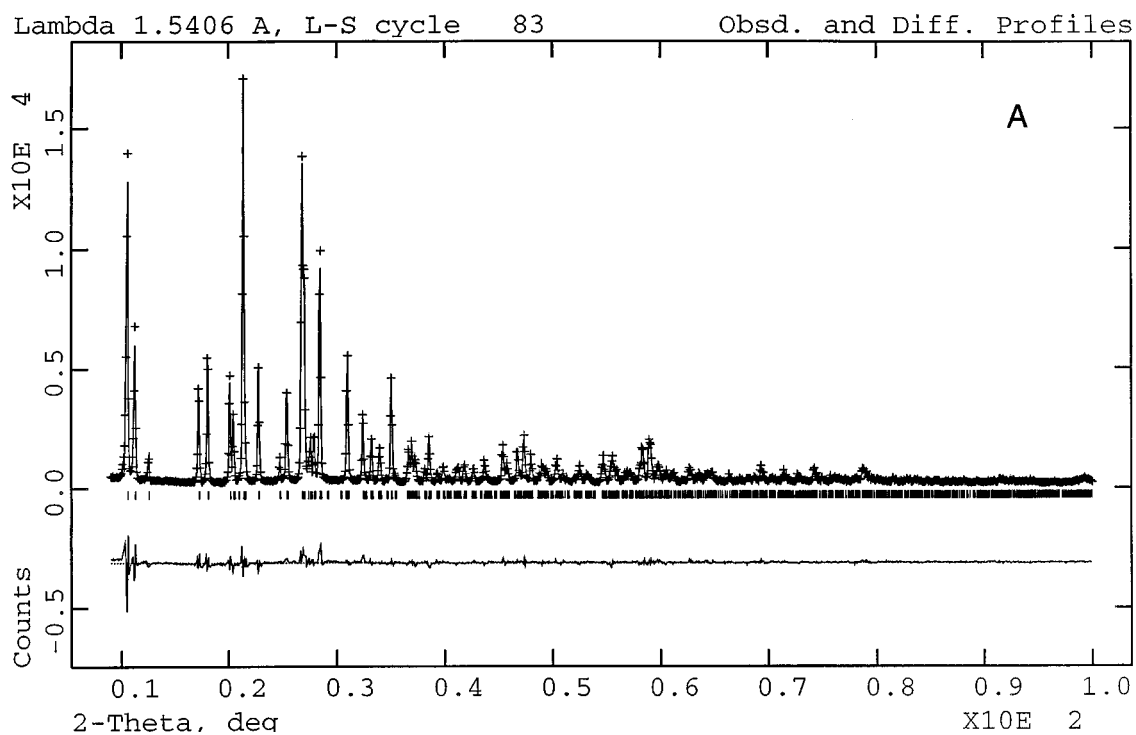


FIG. 1. Observed (+) and calculated (-) profiles for the Rietveld refinement for (A) $[\text{Ti}_3(\text{PO}_4)_4(\text{H}_2\text{O})_2] \cdot \text{NH}_3$ (1), (B) $[\text{Ti}_2\text{O}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$ (2), and (C) $(\text{NH}_4)_2[\text{Ti}_3\text{O}_2(\text{HPO}_4)_2(\text{PO}_4)_2]$ (3). The bottom curve is the difference plot on the same intensity scale.

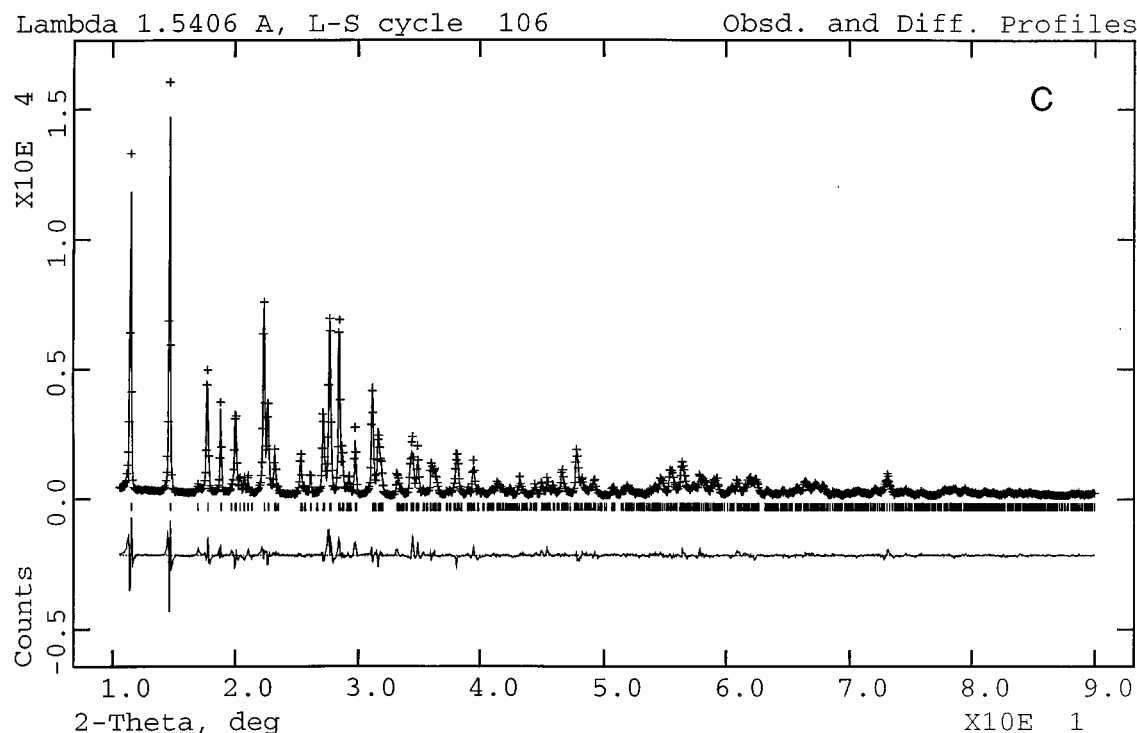


FIG. 1—Continued

The structure consists of one-dimensional channels along the c -axis of the crystal. There are two types of channels in the structure as can be seen in Fig. 6. One of them is a large channel consisting of a 16-membered ring ($-\text{Ti1}-\text{O3}-\text{P1}-\text{O1}-\text{Ti2}-\text{O6}-\text{P2}-\text{O8}-\text{Ti1}-$ and their symmetry related positions) in the ab -plane as in the case of compound (1). The center of this ring is located at a center of symmetry ($1/2, 1/2$) in the c -axis projection. Water molecules, designated by O11, are projected into this channel and the distance between two such neighboring water oxygens is about 3.5 \AA . Although the effective dimension (without water oxygens) of the open space is on the order of $6.7 \times 7.8 \text{ \AA}$, the projection of the coordinated water molecules reduces this free space to a level such that no guest molecules or ions could be incorporated in the channel. The other channel has a 12-membered ring opening in the ab -plane. The center of this ring coincides with another center of symmetry (0, 0) of the ab -plane. In this case the ring consists of two Ti_2O groups linked by two phosphate groups. The effective open space of this channel is also very small as it is occupied by the other water molecule, designated by O10. The two symmetry-related water oxygens are at a distance of about 3.5 \AA in this pore.

Structure of $(\text{NH}_4)_2[(\text{Ti}_3\text{O}_2)(\text{HPO}_4)_2(\text{PO}_4)_2]$. The structure consists of three independent Ti atoms, four phosphate

groups, two bridging oxygens (O17, O18) of the Ti_3O_2 group, and two charge neutralizing ammonium anions. Unlike compounds (1) and (2) this compound contains trimeric TiO_6 octahedra. Figure 7 shows the coordination of the titanium atoms and their connections by phosphate groups along the c -axis of the crystal. All three titanium atoms are octahedrally coordinated. The coordination is completed by phosphate oxygens and oxygens of Ti_3O_2 groups. Oxygen atom O17 bridges Ti2 to Ti1 which in turn is connected to Ti3 through oxygen atom O18. Four phosphate oxygens, O2, O5, O9, and O13, complete the coordination of Ti1. The remaining five coordination sites of Ti2 and Ti3 are occupied by O1, O4, O10, O11, and O14 and O3, O6, O7, O15, and O16, respectively. The Ti-O bond lengths in the Ti_3O_2 group are in the range $1.97-1.99 \text{ \AA}$ and the two Ti-O-Ti angles are $130.7(4)^\circ$ (Ti1-O17-Ti2) and $128.4(5)^\circ$ (Ti1-O18-Ti3). The average value of the bond angles in the Ti-O-P links is about 129° and is comparable to that found for compounds (1) and (2). Among the four independent phosphate groups, two (P1 and P4) are present as PO_4^{3-} and the other two (P2 and P3) as HPO_4^{2-} . The two oxygens of the P-OH groups in P2 and P3 phosphate groups are O8 and O12, respectively. These hydroxyl oxygens are not involved in metal binding.

A polyhedral representation of the structure viewed down the c -axis is shown in Fig. 8. As in the case of compounds (1)

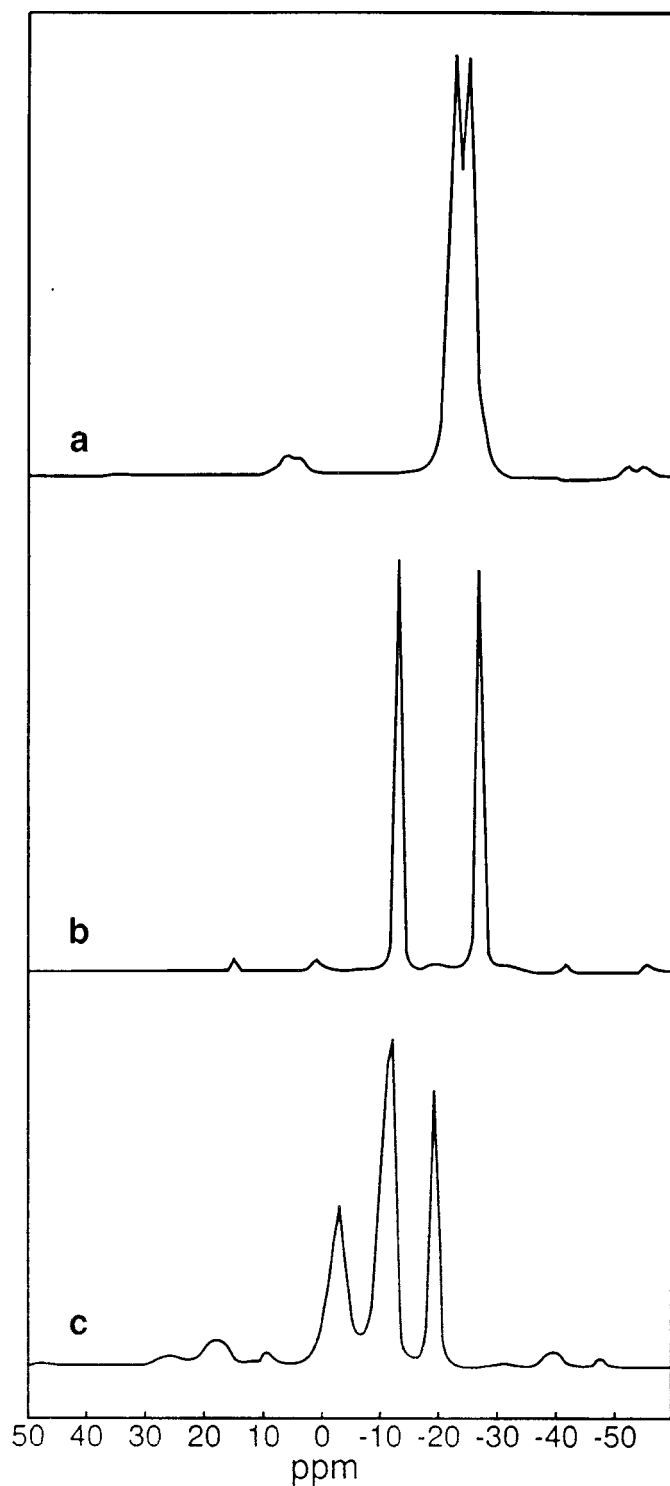


FIG. 2. ^{31}P magic angle spinning NMR spectra for (a) compound (1), (b) compound (2), and (c) compound (3).

and (2), the structure consists of large one-dimensional channels along the smallest cell dimension (c -axis). The channel in this case is larger than that found for compounds (1) and (2) as it has a 24-membered ring opening consisting

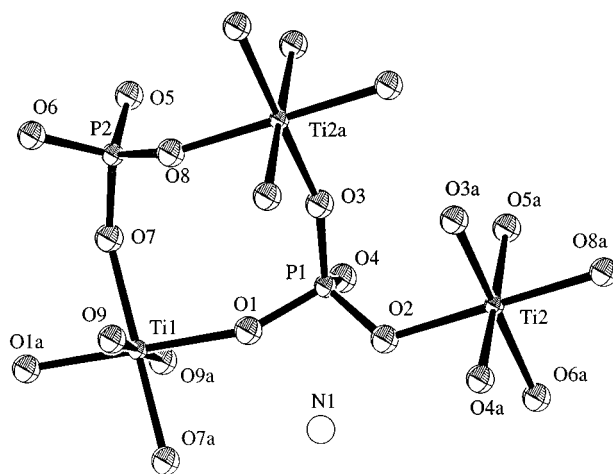


FIG. 3. A section of the structure of compound (1) showing the atom labeling and coordination about the two independent titanium atoms. The water molecules are coordinated to only Ti1.

of six titanium octahedra and six phosphate groups. The open space in this channel is substantially reduced by the monohydrogen phosphate groups P2 and P3. The hydroxyls of these phosphates project into the center of the channel resulting in partitioning of the large channel into two parts as shown in Fig. 8. The oxygen atoms of the Ti–O–P linkages on the walls of the channel are at about

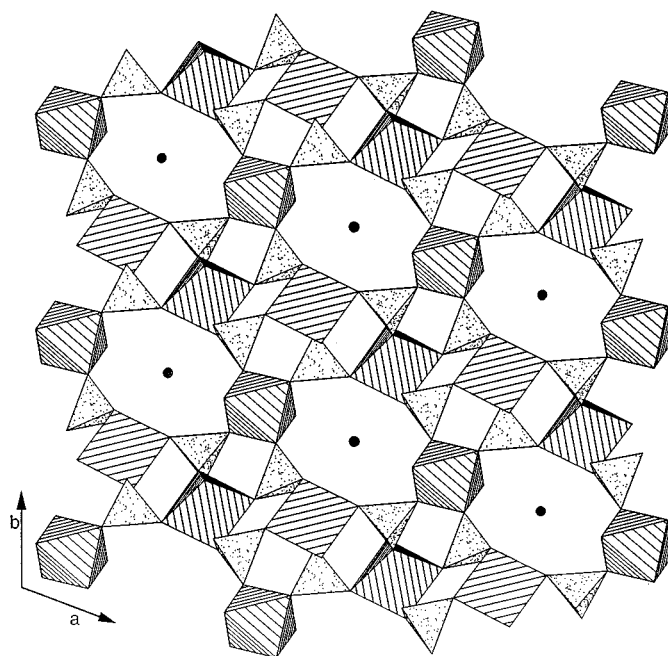


FIG. 4. A polyhedral representation of the structure of compound (1) down the c -axis. Solid lines depict titanium octahedra and the phosphate groups are represented by dots. The ammonia molecules are located in the channels.

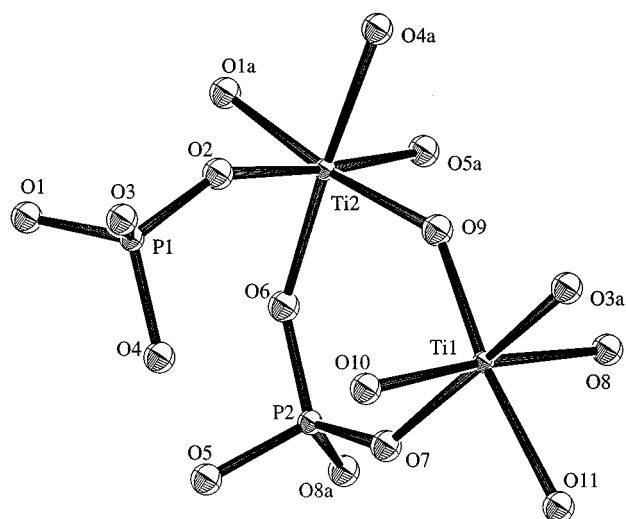


FIG. 5. A portion of the structure of compound (2) showing the coordination of the Ti_2O group.

3.7 \AA from the hydroxyl oxygen atoms and as a result of this arrangement cavities are formed in the channels. The ammonium ions are trapped inside these cavities and since the opening of the cavity is only on the order of 3.7 \AA , these ions are difficult to remove from the structure. The result is in good agreement to the TGA result which shows remarkable stability of the compound up to 415°C . The ammonium ions are released only at higher temperature ($415\text{--}725^\circ\text{C}$).

The ammonium ions in the cavities do not seem to interact very strongly with the framework oxygens. Some of the possible hydrogen bonding contacts are $\text{N1---O5} =$

$2.86(3) \text{ \AA}$, $\text{N1---O3} = 2.89(3) \text{ \AA}$, $\text{N2---O6} = 2.77(3) \text{ \AA}$, and $\text{N2---O9} = 2.97(3) \text{ \AA}$; all other contacts are above 3 \AA . The ammonium ions are also hydrogen bonded to the hydroxyl oxygens ($\text{N1---O12} = 3.07(3) \text{ \AA}$; $\text{N2---O8} = 2.88(3) \text{ \AA}$) of the HPO_4^{2-} groups. The two hydroxyl groups that are projected into the channel are strongly hydrogen bonded to each other with an O8-O12 distance of $2.48(2) \text{ \AA}$.

DISCUSSION

Compounds (1), (2), and (3) contain monomeric, dimeric, and trimeric TiO_6 groups, respectively. These compounds possess unidimensional channels with large pore openings. Compounds (1) and (2) contain 16-membered pores while compound (3) has a 24-membered pore opening. Only compound (3) has charge neutralizing cations while the other two possess neutral frameworks. In the case of compound (1) the channel is occupied by ammonia molecules. The compound begins to lose the coordinated water molecules and the ammonia molecules at around 225°C . To understand the affect of these groups on the three-dimensional structure, the compound was heated to temperatures of 330°C and its XRD pattern was recorded. The pattern is totally different from the unheated sample indicating that on losing water the compound has undergone a phase change. Accordingly, the heated sample does not pick up water molecules since the original structure has changed and the thermal conversion is not reversible. In the case of compound (2), the presence of coordinated water molecules prevents the diffusion of any guest molecules into the channel. The compound loses these water molecules on heating, and interestingly removal of only up to 50% of the water

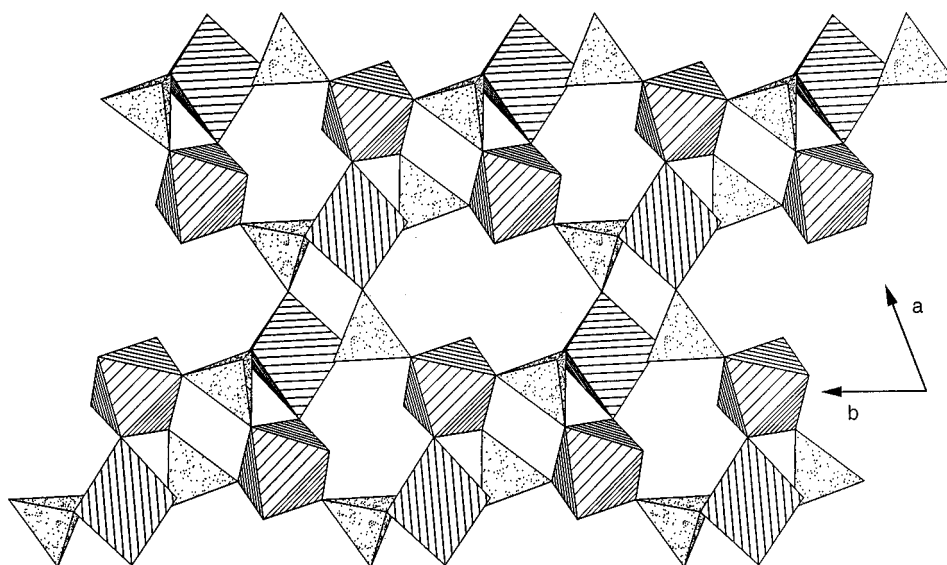


FIG. 6. Plot of the titanophosphate structure (compound (2)) down the c -axis showing the pores in the structure. The representation of polyhedra is the same as that in Fig. 4.

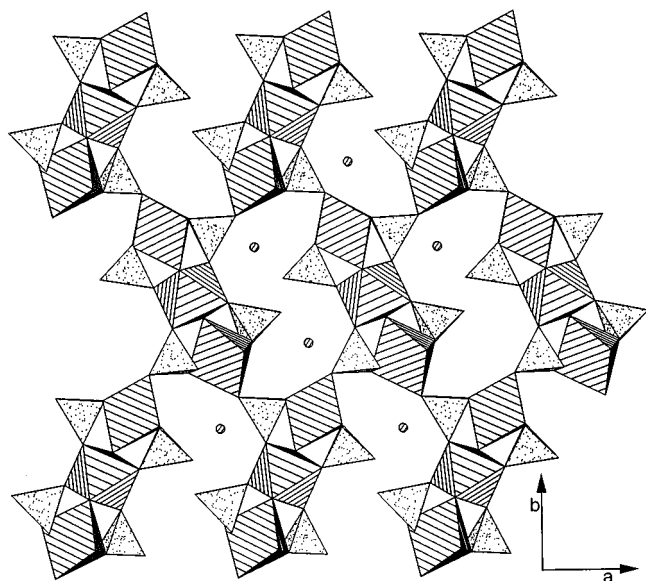


FIG. 8. Polyhedral representation of the structure of compound (3) as viewed down the c -axis. The ammonium ions occupy the cavities and are represented by unconnected circles. The representation of polyhedra is the same as that in Fig. 4.

reasonably good diffraction data up to at least 100° in 2θ Å (for $\text{CuK}\alpha$). Our earlier studies were mostly concentrated on metal phosphonates (26–35). These compounds normally precipitate in poorly crystalline form and their diffraction patterns extend only up to about 60 – 80° in 2θ . In most cases their structures were solved by a combination of Patterson and Fourier methods while in some cases direct methods provided starting models for Rietveld refinement and subsequent structure completion. These studies collectively provide confidence in the use of conventional X-ray powder diffraction data for the solution of simple to complex structures in a manner similar to that used for single crystal methods. However, it should be pointed out that the powder methods are only in the development stage and they require the use of efficient methods by an experienced crystallographer.

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