Hydrothermal Synthesis and Characterization of an Ethylenediamine-Templated Mixed-Valence Titanium Phosphate

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The mixed-valence compound $Ti^{III}Ti^{IV}(HPO_4)_4{\cdot}C_2N_2H_9{\cdot}H_2O$ (**1**) is synthesized hydrothermally from titanium powder, phosphoric and boric acids, and ethylenediamine. The compound is structurally stable up to 650 °C. It loses the template and the water molecule above 250 °C, all titanium becomes Ti^{IV} at 600 °C, and the result is the new compound $Ti^{IV}Ti^{IV}(HPO_4)_4$ (**2**). The structures of the two compounds were determined ab initio from powder diffraction data. Crystal data: $Ti^{III}Ti^{IV}(HPO_4)_4{\cdot}C_2N_2H_9{\cdot}H_2O$, $I4_1$, $a = 6.371(2)$, $c = 16.571(1)$ Å, $V = 672.5(1)$ Å^3, $Z = 2$; $Ti^{IV}Ti^{IV}(HPO_4)_4$, $I4_1/a$, $a = 6.335(2)$, $c = 16.389(1)$ Å, $V = 657.7(1)$ Å^3, $Z = 2$. Both structures are of the open type, and the frameworks are nearly identical. Compound **2**, τ-$Ti(HPO_4)_2$, is the first three-dimensional titanium hydrogen phosphate. Results of magnetization, TGA, BET, X-ray thermodiffractometry, and density measurements are also presented.

Introduction

The synthesis of new microporous materials containing transition metals in the framework is of growing interest due to the expected catalytic redox properties.[1,2] The recently discovered microporous titanium(IV) silicates, ETS-4, ETS-10, and others,[3] have already proven the concept by showing very good catalytic activities and are widely used nowdays.[4] Similarly, hydrothermally synthesized titanium phosphates with open-framework or layered structures attract attention as potential materials with similar properties.[5] Of even greater interest for redox applications would be microporous materials that contain reduced or mixed-valence transition metals. Such compounds with open frameworks are known for a variety of organically templated phosphates and fluorophosphates of molybdenum,[6] vanadium,[7] and iron,[8] for example, but until recently none was known for titanium. Two of these recently synthesized reduced titanium phosphates contain mixed-valence Ti^{III} and Ti^{IV},[9] and one is with Ti^{III} only.[10] Here we report the synthesis and structure of another mixed-valence phosphate of titanium, $Ti^{III}Ti^{IV}(HPO_4)_4{\cdot}C_2N_2H_9{\cdot}H_2O$ **(1)**, and

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(1) Arends, I. W. C. E.; Sheldon, R. A.; Wallau, M.; Schuchardt, U. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1145, and references therein.

(2) Hartmann, M.; Kevan, L. *Chem. Rev.* **1999**, *99*, 635, and references therein.

(3) (a) Kuznicki, S. M. U.S. Patent 4853202, 1989. (b) Kuznicki, S. M. U.S. Patent 4938989, 1990. (c) Chapman, D. M.; Roe, A. L. *Zeolites* **1990**, *10*, 730. (d) Chapman, D. M. U.S. Patent 5015453, 1991. (e) Kuznicki, S. M.; Thrush, K. A.; Allen, F. M.; Levine, S. M.; Hamil, M. M.; Hayhurst, D. T.; Mansour, M. In *Molecular Sieves*; Occelli, M. L., Robson, H., Eds.; Van Nostrand Reinhold: New York, 1992; Vol. 1, pp 427−453. (f) Poojari, D. M.; Cahill, R. A.; Clearfield, A. *Chem. Mater.* **1994**, *6*, 2364. (g) Anderson, M. W.; Terasaki, O.; Ohsuna, T.; Philippou, A.; MacKay, S. P.; Ferreira, A.; Rocha, J.; Lidin, S. *Nature* **1994**, *367*, 347. (h) Harrison, W. T. A.; Gier, T. E.; Stucky, G. D. *Zeolites* **1995**, *15*, 408. (i) Sankar, G.; Bell, R. G.; Thomas, J. M.; Anderson, M. W.; Wright, P. A.; Rocha, J. *J. Phys. Chem.* **1996**, *100*, 449.

(4) (a) Tatsumi, T.; Nakamura, M.; Negishi, S.; Tominaga, H. *J. Chem. Soc., Chem. Commun.* **1990**, 476. (b) Reddy, J. S.; Khire, U. R.; Ratnasamy, P.; Mitra, R. B. *J. Chem. Soc., Chem. Commun.* **1992**, 1234. (c) Clerici, M. G.; Ingallina, P. *J. Catal.* **1993**, *140*, 71. (d) Robert, R.; Rajamohanan, P. R.; Ratnasamy, P. *J. Catal.* **1995**, *155*, 345. (e) Kumar, R.; Pais, G. C. G.; Pandey, B.; Kumar, P. *J. Chem. Soc. Chem. Comm.* **1995**, 1315. (f) Sasidharan, M.; Raju, S. V. N.; Srinivasan, K. V.; Paul, V.; Kumar, R. *J. Chem. Soc., Chem. Commun.* **1996**, 129. (g) Das, T. K.; Chandwadkar, A. J.; Sivasanker, S. *J. Mol. Catal. A* **1996**, *107*, 199. (h) Bianchi, C. L.; Ragaini, V. *J. Catal.* **1997**, *168*, 70. (i) Das, T. K.; Chandwadkar, A. J.; Sivasanker, S. *Catal. Lett.* **1997**, *44*, 113.

(5) (a) Serre, C.; Ferey, G. *J. Mater. Chem.* **1999**, *9*, 579. (b) Serre, C.; Ferey, G. *C. R. Acad. Sci., Ser. IIc* **1999**, *2*, 85. (c) Clearfield, A.; Stynes, J. A. *J. Inorg. Nucl. Chem.* **1964**, *26*, 117. (d) Poojary, D. M.; Bortun, A. I.; Bortun, L. N.; Clearfield, A. *J. Solid State Chem.* **1997**, *132*, 213. (e) Bortun, A. I.; Bortun, L. N.; Clearfield, A. *J. Mater. Res.* **1996**, *11*, 2490. (f) Bortun, A. I.; Khainakov, S. A.; Bortun, L. N.; Poojary, D. M.; Rodriguez, J.; Garcia, J. R.; Clearfield, A. *Chem. Mater.* **1997**, *9*, 1805. (g) Li, Y. J.; Whittingham, M. S. *Solid State Ionics* **1993**, *63−65*, 391. (h) Krogh Andersen, A. M.; Norby, P. *Inorg. Chem.* **1998**, *37*, 4313. (i) Krogh Andersen, A. M.; Norby, P.; Vogt, T. *J. Solid State Chem.* **1998**, *140*, 266.

(6) Haushalter, R. C.; Mundi, L. A. *Chem. Mater.* **1992**, *4*, 31, and references therein.

(7) (a) Khan, M. I.; Meyer, L. M.; Haushalter, R. C.; Schweitzer, A. L.; Zubieta, J.; Dye, J. L. *Chem. Mater.* **1996**, *8*, 43. (b) Harrison, W. T. A.; Hsu, K.; Jacobson, A. J. *Chem. Mater.* **1995**, *7*, 2004. (c) Soghomonian, V.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1995**, *7*, 1648.

(8) (a) Cavellec, M.; Ferey, G.; Greneche, J. M. *J. Magn. Magn. Mater.* **1997**, *174*, 109. (b) Cavellec, M.; Riou, D.; Ferey, G. *J. Solid State Chem.* **1994**, *112*, 441. (c) Korzenski, M. B.; Schimek, G. L.; Kolis, J. W. *J. Solid State Chem.* **1998**, *139*, 152. (d) Zima, V.; Lii, K. H.; Nguyen, N.; Ducouret, A. *Chem. Mater.* **1998**, *10*, 1914. (e) DeBord, J. R. D.; Reiff, W. M.; Warren, C. J.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1997**, *9*, 1994.

(9) (a) Ekambaram, S.; Sevov, S. C. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 372. (b) Serre, C.; Guillou, N.; Ferey, G. *J. Mater. Chem.* **1999**, *9*, 1185.

(10) Riou-Cavellec, M.; Serre, C.; Ferey, G. *C. R. Acad. Sci., Ser. IIc* **1999**, *2*, 147.

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Table 1. The Powder Patterns of (a) 1 and (b) 2

(a) **1** indexed in $I4_1$ with $a = 6.372(2)$ and $c = 16.564(1)$ Å					(b) **2** indexed in $I4_1/a$ with $a = 6.332(2)$, $c = 16.354(1)$				
h k l	$2\theta_{obs}$	$2\theta_{calc}$	d_{hkl} (Å)	intensity	h k l	$2\theta_{obs}$	$2\theta_{calc}$	d_{hkl} (Å)	intensity
0 1 1	14.90	14.90	5.945	69	0 1 1	14.97	14.96	5.918	100
0 1 3	21.27	21.28	4.172	10	0 1 3	21.43	21.44	4.137	2
0 0 4	21.44	21.45	4.140	55	0 0 4	21.67	21.69	4.094	33
0 2 0	27.98	27.99	3.186	100	1 1 2	22.56	22.59	3.933	1
0 2 2	30.04	30.03	2.973	4	0 2 0	28.14	28.13	3.170	58
0 1 5	30.38	30.39	2.939	40	0 2 2	30.24	30.21	2.956	2
1 2 1	31.83	31.84	2.808	8	0 1 5	30.69	30.71	2.909	21
1 2 3	35.43	35.42	2.532	7	1 2 1	32.02	32.02	2.793	9
0 2 4	35.53	35.53	2.525	5	0 1 6	35.79	35.81	2.506	5
2 2 0	40.01	39.99	2.253	2	1 2 4	38.64	38.61	2.330	1
0 1 7	40.63	40.64	2.218	2	2 2 0	40.26	40.21	2.241	2
0 3 1	42.90	42.89	2.107	10	0 1 7	41.13	41.12	2.194	1
0 2 6	43.32	43.33	2.086	2	0 3 1	43.16	43.14	2.095	24
0 0 8	43.71	43.69	2.070	1	0 2 6	43.74	43.76	2.067	1
2 2 4	45.86	45.81	1.979	1	0 0 8	44.22	44.24	2.046	1
1 3 2	46.34	46.33	1.958	3	0 3 3	46.06	46.04	1.970	1
0 3 5	51.04	51.04	1.788	6	1 3 2	46.64	46.63	1.946	3
0 1 9	51.63	51.66	1.768	8	0 3 5	51.43	51.45	1.775	6
2 3 1	52.00	51.99	1.757	4	2 3 1	52.32	52.31	1.747	7
0 2 8	52.67	52.68	1.736	1	0 2 8	53.21	53.26	1.718	1

its calcined product of fully oxidized $Ti^{IV}Ti^{IV}(HPO_4)_4$ **(2)**. Compound **1** was synthesized in an attempt to make a reduced titanium borophosphate analogous to the known ethylenediamine-templated borophosphates $M^{II}B_2P_3O_{12}(OH)(H_2en)$ where M^{II} = Co, Fe, Ni, Zn, Mg, or Mn.[11] In analogy with high-temperature chemistry of reduced transition metal compounds the source of titanium was titanium metal itself rather than a salt. This approach has proven to be successful in the synthesis of another organically templated mixed-valence titanium phosphate, that of $Ti^{III}Ti^{IV}(PO_4)(HPO_4)_2(H_2O)_2 \cdot 0.5dap$.[9a]

Experimental Section

Synthesis. The reaction mixture for the synthesis of **1** contains titanium, phosphoric acid, boric acid (initially aimed to produce a borophosphate), ethylenediamine, and water in molar ratio 1:15:6.5:4:600, respectively. The resulting pH is lower than 2. The mixture is loaded in a Teflon-lined stainless steel autoclave (23 mL) and heated at 225 °C for 2 days.

The resulting blue powder is filtered, washed with water, ethanol, and acetone, and dried at room temperature under vacuum. The intensive coloring is the first indication of the presence of Ti(III) in the compound. Changing reaction conditions resulted in producing very tiny crystals. A few of them were inspected on a CAD4 diffractometer, and others on a Siemens diffractometer with a CCD plate. None showed satisfactory diffraction intensity. All subsequent numerous attempts involving different reaction temperatures, concentrations, molar ratios, etc., did not produce better crystals. Formation of the compound was not affected by adding HCl, 1,4-butanediol, or HF in the reaction mixture. However, boric acid seems to be essential for obtaining the compound although boron is not present in the product according to the elemental analysis which showed only traces of it. Calcination of **1** at 600 °C for 10 h in the flow of air resulted in formation of **2**. This phase is white in color.

Phase Identification, and Magnetic, Thermal, and Spectroscopic Measurements. Phase identification was done with X-ray powder diffraction on an Enraf-Nonius Guinier camera with Cu $K\alpha_1$ radiation and Si as an internal standard. Perkin-Elmer FTIR (400−4000 nm) was utilized for monitoring the presence or lack of ethylenediamine in the compound before and after heat treatments. The latter were carried out on a CAHN TG-131 under different gases, flow and heating rates, and temperatures. The magnetization of 43 mg of **1** was measured at 3 T over the temperature range 10−300 K with a step of 10 K on a Quantum Design MPMS SQUID magnetometer. X-ray thermodiffractometry was performed under air on a D5000 Siemens diffractometer equipped with a high-temperature stage ($\theta - \theta$ mode, Co Kα radiation with $\lambda = 1.7903$ Å, temperature range 50−1000 °C with scans at every 25 °C).

Structure Determination. An ab initio structure determination from X-ray powder data was performed. To minimize the preferred orientation effect, the powders were pulverized with a "Mac Crone" grinder in ethanol, dried, and then side loaded in the holder.

Powder X-ray diffraction data were recorded on a D5000 Siemens diffractometer. The patterns were indexed with the aid of the Ito program.[12] Tetragonal body-centered solutions were found with satisfactory figures of merit ($M(20) = 34$ and zeroshift = 0.0037) for **1**, $M(20) = 24$ and zeroshift = −0.032 for **2**). The observed systematic absences were consistent with space groups I_1 for **1** and I_1/a for **2**. The indexed powder patterns are reported in Table 1. The matching of the powder patterns was performed with the aid of EXTRACT,[13] and the structures were solved by direct methods using SIRPOW97.[13] For both phases, the phosphorus atoms were found to occupy positions that are very close to symmetry elements and to each other. This suggests that they are with half-occupancies, and this is how they were refined. The same half-occupancy was assigned also to the corresponding terminal oxygens bonded to the phosphorus atoms, i.e., the OH groups. The atoms of the ethylenediamine template and the water molecule of phase **1** were also refined with half occupancy since they clearly must alternate with the occupancy of the phosphorus positions. All attempts to use lower symmetry space groups or doubled unit cell did not lead to a better refinement or to removal of the statistic disorder. The final Rietveld refinements using 182 and 170 F_{obs} for **1** and **2**, respectively, were carried out with the aid of Fullprof97 in the angular 2θ range of 17−100°.[14] Due to relatively strong preferred orientation, the first reflection of each pattern was excluded from the refinement. The following parameters were refined: 1 scale factor, 28 and 11 atomic coordinates for **1** and **2**, respectively, 1 overall isotropic temperature factor, 1 zero-point and 4 cell parameters, 3 half-

(11) Sevov, S. C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2630.

(12) Visser, J. W. *J. Appl. Crystallogr.* **1969**, *2*, 89.

(13) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(14) Rodriguez-Carvajal, J. In *Collected Abstracts of Powder Diffraction Meetings*; Toulouse, France; International Union of Crystallography: Chester, England, 1990; p 127.

Table 2. Crystallographic Data for 1 and 2

phase	**1**	**2**
formula	$Ti^{III}Ti^{IV}(HPO_4)_4$·Henxe1 H_2O	$Ti^{IV}Ti^{IV}(HPO_4)_4$
molar weight ($g \cdot mol^{-1}$)	558.6	479.6
calculated density ($g \cdot cm^{-3}$)	2.76	2.42
symmetry	tetragonal	tetragonal
space group, Z	$I4_1$ (no.80), 2	$I4_1/a$ (no.88), 2
a (Å)	6.371(2)	6.335(2)
c (Å)	16.571(1)	16.389(1)
V (Å^3)	672.5(1)	657.7(1)
λ for Cu Kα_1/Cu Kα_2 (Å)	1.54059/1.54439	1.54059/1.54439
ranges (deg 2θ)	13−45 and 45.02−100	13−45 and 45.02−100
Time/step (s)	30 for range 1 60 for range 2	30 for range 1 60 for range 2
step size (deg)	0.02	0.02
excluded area (deg 2θ)	13.00−16.00	13.00−16.00
total no. of reflections	182	170
total no. points	4351	4351
no. structural parameters	28	10
no. profile parameters	19	20
no. atoms refined	12	5
no. distance constraints	13	6
R_p (%)	12.1	11.7
R_{wp} (%)	16.8	14.6
R_{Bragg} (%)	12.5	12.2

width parameters, 4 asymmetry factors, 2 parameters to define the θ-dependent pseudo-Voigt profile shape function, 4 and 5 coefficients to describe the functional dependence of the background for **1** and **2**, respectively, and 1 preferred orientation factor. Soft distance constraints were applied for the Ti−O and P−O interatomic distances. Details of the structure determination are summarized in Table 2 and the Rietveld plots are shown in Figure 1. The final agreement factors for the two phases are: $R_p = 12.3\%$, $R_{wp} = 16.1\%$ and $R_{Bragg} = 12.5\%$ for **1** and $R_p = 11.7\%$, $R_{wp} = 14.8\%$ and $R_{Bragg} = 12.2\%$ for **2**. Positional parameters and essential distances and angles are listed in Tables3 and 4, respectively.

The calculated densities of the refined structures, 2.76 and 2.42 $g \cdot cm^{-1}$ for **1** and **2**, respectively, are in a good agreement with the measured numbers, 2.842 $g \cdot cm^{-1}$ for **1** and 2.208 $g \cdot cm^{-1}$ for **2**. Elemental analysis was carried out for **1** only (Galbraith Laboratories, Inc.), and the results are also in good agreement with the composition derived from the structure refinement. The measured and theoretical values (in parentheses) are as follows: Ti, 18.25 (17.14); P, 22.68 (22.18); C, 4.01 (4.30); N, 4.73 (5.01); H, 2.26 (2.68; and O (by difference), 48.07 (48.69). Also, the results from both IR and TGA measurements corroborate the formulas derived from the structure determination (below).

Results and Discussion

The structures of both **1** and **2** are of the open-framework type, and the framework is essentially the same in both compounds. It is made of corner-sharing octahedra and tetrahedra of oxygen centered by titanium and phosphorus, respectively. There is no Ti−O−Ti or P−O−P bonding in the structures. Figure 2 shows the connectivity between the polyhedra in the structures where rings of two different sizes are formed. The rings made of two tetrahedra and two octahedra are too small to be of any interest and will not be discussed further. The larger ones, on the other hand, are large enough to accommodate ethylenediamine and water molecules in **1**. Because of the observed disorder and half-occupancy of the phosphate tetrahedra, half of the rings have all HPO_4 groups pointing inward and do not contain guest molecules, and the other half are open and contain them. For clarity these two types of rings are shown in Figures2 and 3 as strictly alternating but this is not the case in the real structure where they are truly disordered and no superstructure is observed. Had they been ordered with the open rings stacked on top of each other, channels would have been created. Nevertheless, this is not the case here and although the rings are of appropriate size no porosity is possible after the removal of the templates and water molecules.

The ethylenediamine templates are singly protonated and in syn conformation. Both ends are hydrogen-bonded with very short distances of 2.72 Å to oxygen atoms (O1) of the framework.

Crystallographically there is only one type of titanium, and it is coordinated octahedrally by oxygen atoms. The distances range from 1.94 to 1.98 Å in **1**, and are somewhat shorter in **2** where they range from 1.94 to 1.95 Å (Table 4). From magnetic measurements, color, and valence sum calculations it is clear that the titanium in **1** is of mixed valence. The magnetic susceptibility dependence of the temperature (Figure 4) indicates a simple Curie type behavior with an effective magnetic moment of 1.23 μ_B. This is consistent with one unpaired electron per formula unit, and therefore with equimolar ratio of Ti^{III} and Ti^{IV} in the compound. The valence sum for the titanium position in **1** is 3.80 while this number for **2** is 4.20.[15] Since all titanium in **2** is clearly Ti^{IV} (see below) the calculated valence sums must be somewhat exaggerated. The same problem was encountered in another templated titanium phosphate where the valence sums for the Ti^{III} and Ti^{IV} sites were calculated to be 3.17 and 4.32, respectively.[9a] Thus, the number 3.80 for **1** indicates that there is nearly equimolar ratio of Ti^{III} and Ti^{IV} disordered at the titanium position.

All phosphate groups are actually hydrogen phosphates since one of the four vertexes is an OH group. They are bonded to three different octahedra via the three nonprotonated oxygen vertexes (Figure 3). The oxygen atoms of the hydroxyl groups are refined half occupied together with the phosphorus. Their occupancy alternates with the occupancy of the ethylenediamine (and water) site since otherwise the distances between them would be too short. The observed P−O distances in the hydro-phosphate groups, 1.44−1.59 Å in **1** and 1.49−1.64 Å in **2**, are quite typical.

As mentioned above when phase **1** is calcined at 600 °C for 10 h in a flow of air the product is white powder of phase **2**. In this compound the positive charge from the ethylenediamine monocation is replaced by the extra positive charge of the fully oxidized titanium, Ti^{IV}, compared to Ti^{III} in **1**. The formal process can be written as $Ti^{III}Ti^{IV}(HPO_4)_4 \cdot Hen \cdot H_2O + nO_2 \rightarrow Ti^{IV}Ti^{IV}(HPO_4)_4 + 2CO_2 + 5.5H_2O + 2NO_x$. The process is accompanied by a weight loss of 14.3 wt % (from the TGA measurements), and this is in perfect agreement with the calculated percentage for the loss of one ethylenedi-

(15) Brese, N. E.; O'Keefe, M. *Acta Crystallogr. Sect. B* **1991**, *47*, 192.

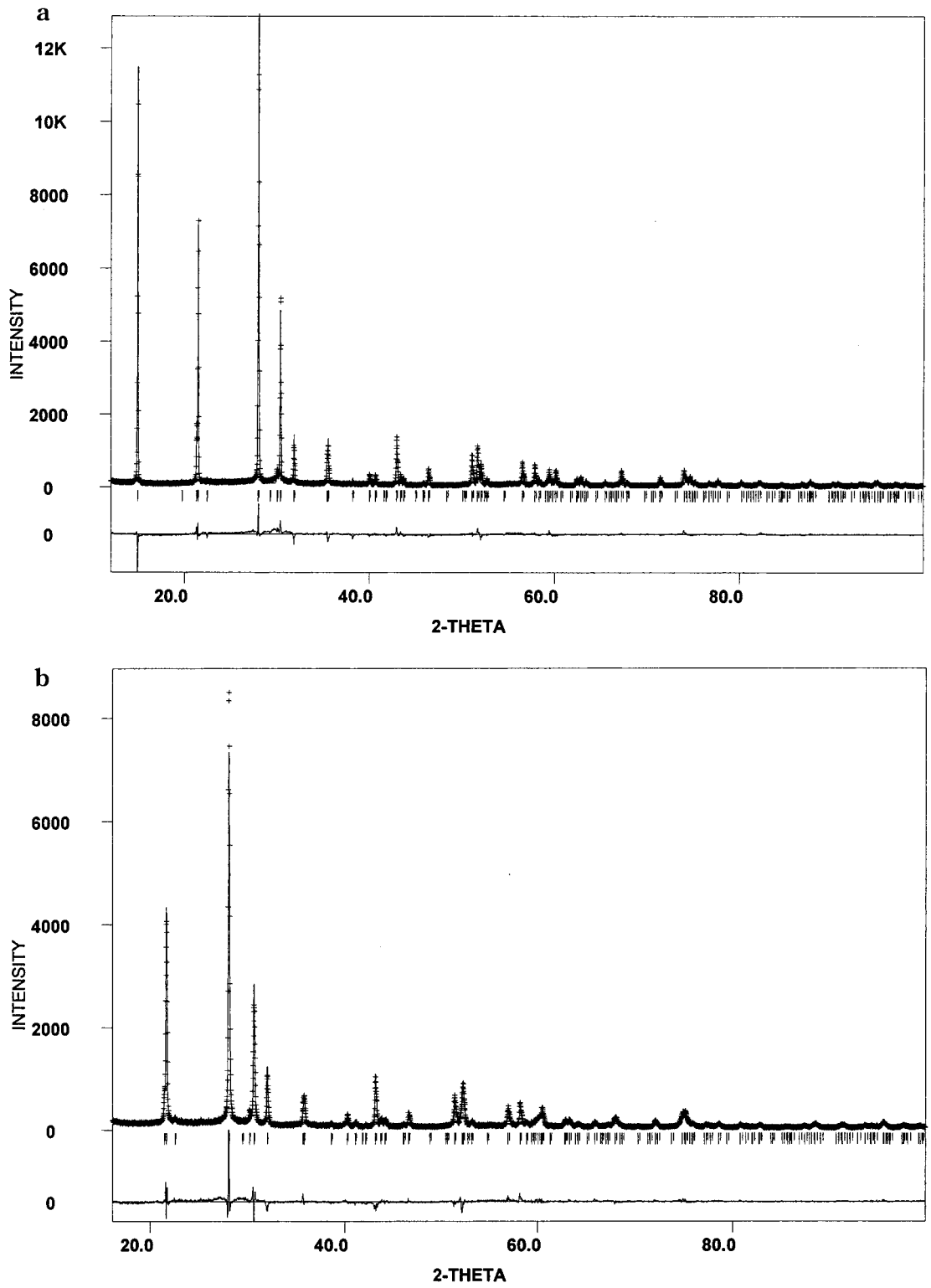

Figure 1. Final Rietveld and difference plots for: (a) $Ti^{III}Ti^{IV}(HPO_4)_4 \cdot C_2N_2H_9 \cdot H_2O$ and (b) $Ti^{IV}Ti^{IV}(HPO_4)_4$.

amine and one water molecules, 14.15 wt %. Clearly the presence of reduced titanium(III) in **1** and its ability to easily oxidize to titanium(IV) in **2** preserve the crystallinity of the material at as high temperatures as 600 °C. Above this temperature the compound recrystallizes into titanium pyrophosphate with additional loss of 5.9% of the weight which corresponds to a loss of the hydroxyl groups. The majority of open-framework cation-templated compounds of the transition metals collapse structurally after the removal of the guests due to charge disbalance. Phase **2** in this case retains exactly the same framework as that of **1**. While that framework is negatively charged and involves a mixed-valence Ti^{III}/Ti^{IV} site in **1** it is neutral and built only of Ti^{IV} in **2**. The structure of **2** was refined in a higher symmetry space group, $I4_1/a$ instead of $I4_1$. The lower symmetry of **1** is clearly due to the presence of ethylenediamine and water molecules. Nevertheless, the disorder of the phosphate groups is present even without the guest molecules in the structure. Because of this disorder the

Table 3. Atomic Coordinates for (a) 1 and (b) 2

(a) Atomic Coordinates for **1**.
Overall Thermal Isotropic Factor Is 0.95(1) Å^2

atom	*x*	*y*	*z*	occupancy
Ti	0	0.5	0.079 (1)	1.0
P(1)	0.503 (4)	−0.418 (2)	0.126 (1)	0.5
P(2)	0.071 (2)	0.008 (4)	0.031 (1)	0.5
O(1)	0.698 (2)	0.520 (6)	0.089 (2)	1.0
O(2)	0	0.5	0.196 (1)	1.0
O(3)	−0.007 (3)	0.189 (2)	0.084 (2)	1.0
O(4)	0	0.5	−0.040 (1)	1.0
O(5)	0.537 (5)	0.192 (3)	0.145 (3)	0.5
O(6)	0.312 (4)	0.028 (9)	0.025 (5)	0.5
Ow	0.5	0	0.137 (2)	0.5
N	0.560 (5)	−0.147 (4)	0.004 (1)	0.5
C	0.533 (11)	−0.119 (2)	0.098 (1)	0.5

(b) Atomic Coordinates for **2**.
Overall Thermal Isotropic Factor Is 0.86(1) Å^2

atom	*x*	*y*	*z*	occupancy
Ti	0	0.250	0.125	1.0
P	0.497 (2)	0.1745 (1)	0.1707 (2)	0.5
O(1)	0.307 (1)	0.262 (2)	0.1262 (3)	1.0
O(2)	0	0.250	0.2432 (4)	1.0
O(3)	0.468 (1)	−0.083 (1)	0.1764 (5)	0.5

Table 4. Interatomic Distances (Å) and Angles (deg) in (a) 1 and (b) 2

(a) **1**

Ti−O(1)	1.94 (1) × 2	Ti−O(2)	1.95 (3)
Ti−O(3)	1.98 (1) × 2	Ti−O(4)	1.97 (3)
P(1)−O(1)	1.44 (3)	P(1)−O(1)	1.56 (3)
P(1)−O(4)	1.48 (2)	P(1)−O(5)	1.49 (3)
P(2)−O(2)	1.47 (2)	P(2)−O(3)	1.59 (3)
P(2)−O(3)	1.53 (3)	P(2)−O(6)	1.54 (3)
C−C	1.57 (3)	C−N	1.57 (3)
O(1)−Ti−O(1)	170 (1)	O(1)−Ti−O(2)	85 (1)
O(1)−Ti−O(3)	87 (2)	O(1)−Ti−O(3)	92 (2)
O(1)−Ti−O(4)	95 (1)	O(1)−Ti−O(4)	95 (1)
O(2)−Ti−O(3)	87 (1)	O(2)−Ti−O(4)	180 (2)
O(3)−Ti−O(3)	175 (1)	O(3)−Ti−O(4)	93 (1)
O(1)−P(1)−O(1)	115 (2)	O(1)−P(1)−O(4)	108 (2)
O(1)−P(1)−O(5)	120 (3)	O(3)−P(1)−O(4)	102 (2)
O(1)−P(1)−O(5)	110 (3)	O(4)−P(1)−O(5)	98 (2)
O(2)−P(2)−O(3)	118 (2)	O(2)−P(2)−O(3)	115 (2)
O(2)−P(2)−O(6)	104 (2)	O(3)−P(2)−O(3)	101 (2)
O(3)−P(2)−O(6)	108 (3)	O(3)−P(2)−O(6)	111 (3)
N−C−C	98 (2)		

(b) **2**

Ti−O(1)	1.95 (1) × 4	Ti−O(2)	1.94 (1) × 2
P−O(1)	1.51 (1)	P−O(1)	1.50 (1)
P−O(2)	1.49 (1)	P−O(3)	1.64 (1)
O(1)−Ti−O(1)	179 (1)	O(1)−Ti−O(1)	90 (1)
O(1)−Ti−O(2)	89 (1)	O(1)−Ti−O(2)	91 (1)
O(2)−Ti−O(2)	180		
O(1)−P−O(1)	109 (1)	O(1)−P−O(2)	110 (1)
O(1)−P−O(2)	111 (1)	O(1)−P−O(3)	108 (1)
O(1)−P−O(3)	113 (1)	O(2)−P−O(3)	105 (1)

structure lacks channels and is nonporous even after the removal of the templates (see above). This was proven by surface area measurements by the BET method which showed a very low number that is typical for nonporous powders, 2.57 $m^2 \cdot g^{-1}$. The only small differences in the frameworks of **1** and **2** are the distances. As expected, the Ti−O bonds are shorter in **2** (Table 4) as it should be for Ti^{IV} compared to those of the mixed-valence site in **1**.

The results of X-ray powder thermodiffractometry of compound **1** are shown in Figure 5. They are in perfect agreement with the results from the TGA and indicate

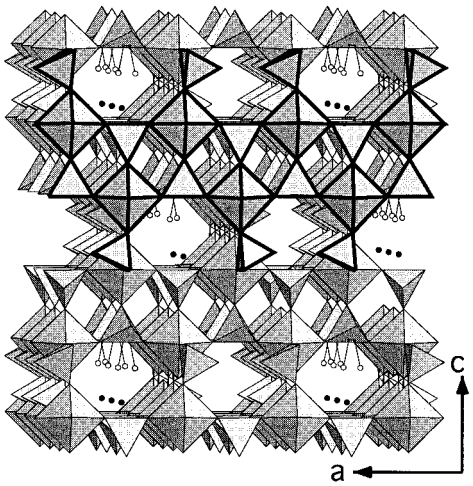

Figure 2. A polyhedral view along *b* of the structure of the body-centered tetragonal ($I4_1$) $Ti^{III}Ti^{IV}(HPO_4)_4 \cdot C_2N_2H_9 \cdot H_2O$ where the tetrahedra and octahedra are centered by P and Ti, respectively. The terminal vertexes of the tetrahedra are the OH groups. The ethylenediamine and water molecules (isolated filled circles) are shown as well. The framework part is identical to that of the calcined phase, $Ti^{IV}Ti^{IV}(HPO_4)_4$. Outlined with thicker polyhedral edges is the repeating building unit, a "double" chain along both *a* and *b* axes.

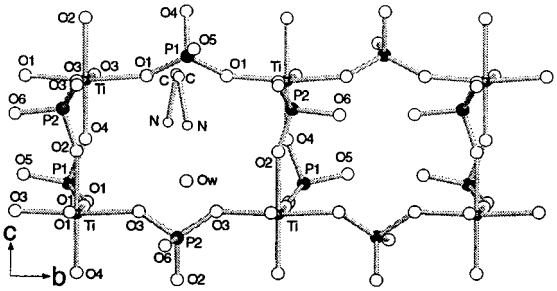

Figure 3. A closer view of the structure of **1** (with the atoms labeled) showing two crystallographically equivalent rings. Because of the disorder of the phosphorus and O5 and O6 positions the rings can be occupied differently (see text). The left ring is shown as occupied by the ethylenediamine and water molecules, and the right one has the hydroxyl groups of the four HPO_4 pointing inward.

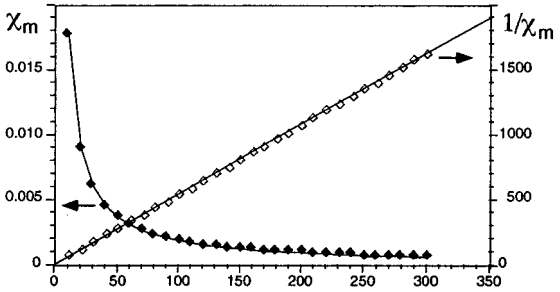

Figure 4. Plot of the molar magnetic susceptibility, χ_m, and its inverse, $1/\chi_m$, of **1** versus the temperature. The straight line through the $1/\chi$ data is a linear fit which provides effective magnetic moment of 1.23 μ_B.

that the transformation from compound **1** into **2** starts at around 350−400 °C. This can be seen most clearly in the change of intensity of the peak at the lowest angle. Actually, when plotted the intensity of this peak follows exactly the shape of the TGA curve up to 600 °C when they both reach a maximum. In addition to the intensity changes the transformation from **1** to **2** can be observed in the slight shift to the right (higher

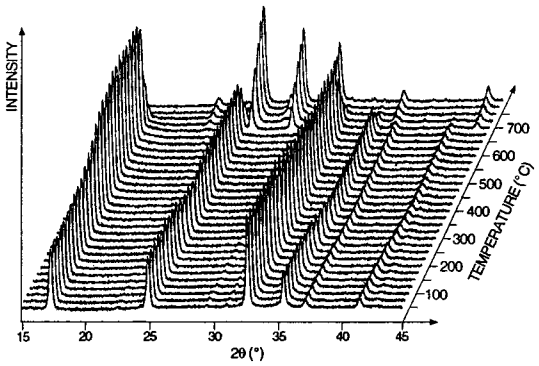

Figure 5. Evolution of X-ray powder diffractograms of compound **1** upon heating from 50 to 1000 °C (Co Kα radiation, $\lambda = 1.7903$ Å). Two transitions, one at around 350 °C to compound **2** and one at 700 °C to TiP_2O_7, are clearly visible. The first one is accompanied by change of intensity (best seen in the low-angle peak) and smooth shift of all peaks to higher 2θ angle (better seen in the high-angle peaks).

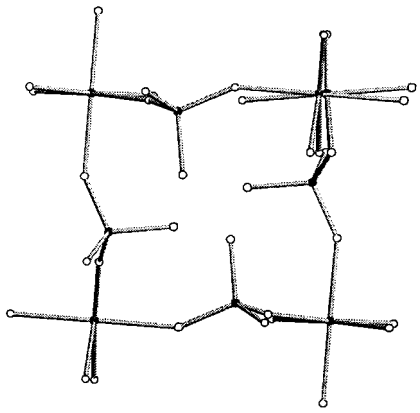

Figure 6. A view of the structure of the first three-dimensional zirconium hydrogen phosphate, τ-$Zr(HPO_4)_2$.[16] All hydroxyl groups of the O_3P-OH tetrahedra point into a channel. The arrangement resembles that found in compounds **1** and **2** (Figure 3) where all OH groups also point into channels of similar dimensions.

angle) of all diffraction peaks at around the same temperature of 350 °C. This is most clearly noticeable for the three peaks at the highest angle. The dehydroxylation of compound **2** and the transformation into titanium pyrophosphate, TiP_2O_7, clearly takes place at around 700 °C. The change in the diffraction pattern at around this temperature is easily distinguishable.

Compound **2** is the first three-dimensional titanium hydrogen phosphate. The structure can be viewed in light of the structure of the first three-dimensional zirconium analogue, τ-$Zr(HPO_4)_2$, that has been recently characterized.[16] Since the layered isostructural hydrogen phosphates of titanium and zirconium are labeled with the same Greek symbols, α and γ, perhaps we should use also use τ for compound **2**, i.e., τ-$Ti(HPO_4)_2$. The two structures, the τ-$Ti(HPO_4)_2$ and τ-$Zr(HPO_4)_2$, are different as a whole but have one very similar building motif. In both structures, the terminal hydroxyl groups of the phosphorus-centered tetrahedra, O_3P-OH, point into channels with similar dimensions and are hydrogen-bonded to each other (compare Figure 6 and the right-hand side of Figure 3). Also, both structures exhibit a 4_1 axis although the channels in τ-$Zr(HPO_4)_2$ are along that axis while they are perpendicular to it in τ-$Ti(HPO_4)_2$. There is also similarities between this titanium hydrogen phosphate and the recently characterized β-$Ti(PO_4)(H_2PO_4)$.[5i] The repeating building unit in both structures is the same type "double" chain outlined in Figures2 and 7. The chain is made of interconnected alternating octahedra and tetrahedra in the middle and terminal tetrahedra on the sides. In the structure of β-$Ti(PO_4)(H_2PO_4)$, the middle tetrahedra, PO_4, are connected to octahedra of another such chain and form layers. The side tetrahedra, H_2PO_4, are only two-bonded and diprotonated. In the present structure all tetrahedra are similarly bonded, i.e., those in the middle of a chain along *b* are the side tetrahedra of the same type of chains but along *a*. Thus, all of them are HPO_4 and are three-bonded.

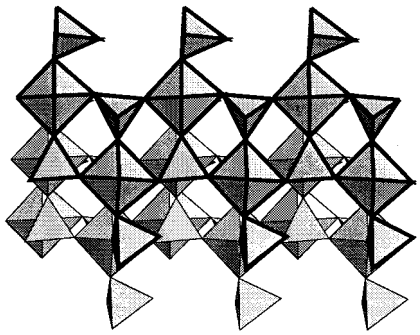

Figure 7. Polyhedral view of the structure of the recently characterized β-$Ti(PO_4)(H_2PO_4)$.[5i] Outlined with thicker polyhedral edges is the repeating building unit, the same "double" chain as that found in compound **2** and shown in Figure 2. The connectivity of the chain in this structure is such that rather layers are formed.

The IR spectrum of **1** shows bands characteristic of ethylenediamine molecules, phosphate groups, and water/OH. Thus, bands observed at 3430, 3250, and 3030 cm^{-1} are characteristic of N−H and/or O−H and C−H stretching, respectively. The corresponding bending vibrational modes were identified at 1600 and 1520 cm^{-1}. Compound **2** does not exhibit, of course, the vibrational modes corresponding to ethylenediamine molecules and water. The phosphate groups in both **1** and **2** show their characteristic bands at around 1000 cm^{-1}.

In conclusion, the mixed-valence $Ti^{III}Ti^{IV}(HPO_4)_4 \cdot (Hen) \cdot H_2O$ is the first templated titanium phosphate that is thermally stable up to 600 °C and remains crystalline, after the removal of the guest molecules. Similar reduced and mixed-valence templated transition metal phosphates and perhaps other salts and oxides, in general, should be accessible using the transition metal itself as a starting material. This approach, coupled with the use of a different amine or diamine from the available variety of templates, can provide many novel compounds, some of them will hopefully combine reduced transition metals with porosity and thermal stability.

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(16) Krogh Andersen, A. M.; Norby, P.; Hanson, J. C.; Vogt, T. *Inorg. Chem.* **1998**, *37*, 876.