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The synthesis and crystal structure of UiO-19; an organically templated layered titanium phosphate with the ULM-11 topology

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An organically templated layered titanium phosphate, $[TiOPO_4]^-[NH_3(CH_2)_2NH_2]^+$, has been synthesised under hydrothermal conditions. The crystal structure was determined from single-crystal X-ray diffraction. The layers of the two-dimensional structure consist of infinite corner-sharing chains of TiO_5N octahedra cross linked by PO_4 tetrahedra. The bonds to oxygen along the chain of titanium octahedra alternate between a short bond (1.719(1) Å) and a long bond (2.150(1) Å). One nitrogen of the diamine is directly coordinated to titanium while the other participates in hydrogen bonding to the subsequent anionic layer. The presence of Ti^{IV} in the compound is consistent with bond valence analysis, the observation of diamagnetic susceptibility and sharp signals in the solid state ^{31}P NMR measurements. The compound is isostructural to the ULM-11 type of Fe-, Al-, V-fluorophoshates and identical to a titanium phosphate which had been assumed to contain Ti^{III}.

Introduction

Titanium phosphates are of considerable interest since a number of these show interesting properties leading to potential applications. Potassium titanium oxide phosphate, $KTiOPO_4$, has a three-dimensional structure and shows remarkable highly non-linear optical properties,[1,2] whereas high ionic conductivity is observed in NASICON-type phosphates like $MTi_2(PO_4)_3$ ($M = Li^+$, Na^+, *etc.*).[3] Many layered and framework titanium phosphates show promising ion exchange properties.[4] Catalytic properties have furthermore been probed both for titanium phosphate compounds[5] and for aluminophosphate compounds with small amounts of incorporated titanium.[6]

The chemistry of layered titanium phosphates has been investigated for decades. The well known α-$Ti(HPO_4)_2\cdot H_2O$ (α-TiP) and γ-$Ti(PO_4)(H_2PO_4)_2\cdot H_2O$ (γ-TiP) were synthesised in the 1960–1970s, and later characterised.[7,8] Yet, the anhydrous form of γ-TiP, β-$Ti(PO_4)(H_2PO_4)_2$ was only recently structurally characterised.[9] Other compounds like $TiO(OH)(H_2PO_4)_2\cdot H_2O$[10] and $Ti_2O_3(H_2PO_4)_2\cdot H_2O$[11] have been reported as layered materials, although no structure determinations are at hand. Recently the first two organically templated layered titanium phosphates were reported.[12] Their structures were solved from powder diffraction data, however, strong preferred orientation prevented accurate structure determination. Both these structures are monoclinic distorted variants of the $VO(PO_4)\cdot 2H_2O$ structure type with TiO_4F_2 octahedra being linked by PO_4 tetrahedra. The layers are held together by hydrogen bonding between interlamellar amine molecules and fluorine. Also several open framework titanium phosphates with tetravalent[13,14] or mixed tri/tetravalent titanium have been reported.[15,16]

During the preparation of the present paper, a publication on $Ti(OH)PO_4\cdot N_2C_2H_9$ with the ULM-11 two-dimensional topology appeared.[17] That lamellar material is probably identical to UiO-19 reported here. However, the structure determination was obviously hampered by the poor quality of the powder diffraction data, yielding unlikely P–O bond lengths. Furthermore, there are open questions regarding the oxidation state of titanium which calls for a more detailed study. The present paper is based on high quality single-crystal X-ray data which facilitate description and discussion of interesting aspects of the lamellar structure of the organically templated layered titanium phosphate, $[TiOPO_4]^-[NH_3(CH_2)_2NH_2]^+$, here termed UiO-19. The compound is in addition characterised by solid state NMR spectroscopy, thermogravimetric analysis and magnetic measurements.

Experimental

Synthesis

The layered titanium phosphate $[TiOPO_4]^-[NH_3(CH_2)_2NH_2]^+$ was synthesised using titanium(IV) butoxide ($Ti[O(CH_2)_3CH_3]_4$, Aldrich, 97%), phosphoric acid (Merck, 85%) and ethylenediamine (Fluka, 97%) as starting reactants. The molar composition of the starting gel was 1.0 Ti-butoxide : 2.0 H_3PO_4 : 3.0 ethylenediamine : 50 H_2O. Crystallisation was carried out in a Teflon-lined steel autoclave at 200 °C for 2 days. The pH at the end of the reaction was 10.55. The crystalline product was filtered off, washed with water and dried in air. The yield based on Ti was 70%.

Single-crystal structure determination

The obtained product of $[TiOPO_4]^-[NH_3(CH_2)_2NH_2]^+$ has a light blue colour, and the powder contained platelets of a size suitable for single-crystal analysis. Data were collected on a Siemens Smart four-circle diffractometer equipped with a CCD detector. Integration and data reduction were carried out using the SAINT program.[18] An empirical absorption correction was applied by means of the SADABS program.[19] The structure was solved and refined using the SHELXTL program package.[20] The last cycles of least squares refinement included atomic coordinates for all atoms, anisotropic displacement parameters for all non-hydrogen atoms and a common, constant isotropic displacement parameter for all the hydrogen atoms. Unit cell data and parameters relevant for the data collection and the refinements are given in Table 1. Selected bond distances and angles are listed in Table 2.

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See http://www.rsc.org/suppdata/dt/a9/a908051a/ for crystallographic files in .cif format.

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Table 1 Crystal data and relevant parameters for the structure refinement of UiO-19

Empirical formula	$TiPO_5N_2C_2H_9$
Formula weight	219.98
Temperature/K	150
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a/Å	9.2650(2)
b/Å	7.35460(10)
c/Å	9.91780(10)
β/°	100.6130(10)
V/Å^3	664.242(18)
Z	4
μ/mm^{-1}	1.506
Reflections collected	9127
Independent reflections	2015 [R(int) = 0.0343]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0315$, $wR_2 = 0.0774$
R indices (all data)	$R_1 = 0.0367$, $wR_2 = 0.0805$

Table 2 Bond lengths [Å] and selected bond angles [°] for UiO-19. Calculated standard deviations in parentheses

Ti–O(5)	1.719(1)	Ti–O(3)	1.976(1)
Ti–O(4)	1.970(1)	Ti–O(5′)	2.150(1)
Ti–O(2)	1.975(1)	Ti–N(1)	2.219(2)
P–O(1)	1.537(1)	P–O(3)	1.539(1)
P–O(2)	1.538(1)	P–O(4)	1.542(1)
N(1)–C(2)	1.472(2)	C(1)–C(2)	1.528(3)
N(2)–C(1)	1.498(2)		
O(5)–Ti–O(4)	95.43(6)	O(2)–Ti–N(1)	169.44(6)
O(5)–Ti–O(2)	99.09(6)	O(3)–Ti–N(1)	87.49(6)
O(4)–Ti–O(2)	89.48(6)	O(5)–Ti–N(1)	78.88(6)
O(5)–Ti–O(3)	94.69(6)	O(1)–P–O(2)	107.87(8)
O(4)–Ti–O(3)	167.77(5)	O(1)–P–O(3)	110.24(7)
O(2)–Ti–O(3)	95.69(6)	O(2)–P–O(3)	109.60(7)
O(5)–Ti–O(5)	169.55(2)	O(1)–P–O(4)	108.65(7)
O(4)–Ti–O(5)	83.88(5)	O(2)–P–O(4)	108.62(7)
O(2)–Ti–O(5)	91.34(5)	O(3)–P–O(4)	111.77(7)
O(3)–Ti–O(5)	84.92(5)	N(2)–C(1)–C(2)	111.23(15)
O(5)–Ti–N(1)	90.67(6)	N(1)–C(2)–C(1)	111.00(14)
O(4)–Ti–N(1)	85.54(6)		

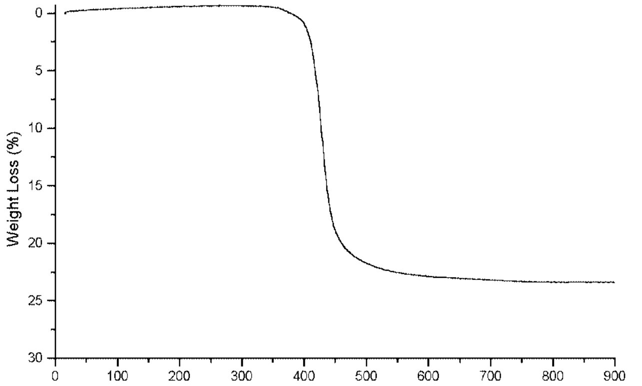

Fig. 1 TGA data for UiO-19 on heating to 900 °C in nitrogen at a rate of 5 K min^{-1}.

Thermogravimetric analysis (TGA)

TGA was performed with a Scientific Rheometric STA 1500 in a flow of nitrogen gas. The powder sample (20 mg) was heated from room temperature to 900 °C at a rate of 5 K min^{-1}. The TG curve (Fig. 1) reveals a single weight loss of 23.60% above 400 °C corresponding to the loss of the amine. The loss is, however, somewhat less than the theoretical weight loss of 27.78%, and this discrepancy is considered to indicate the presence of impurity phases in the synthesis batch. However, several attempts to obtain phase pure UiO-19 according to the TGA criterion by optimising the synthesis parameters (time, temperature, gel molar composition) were unsuccessful.

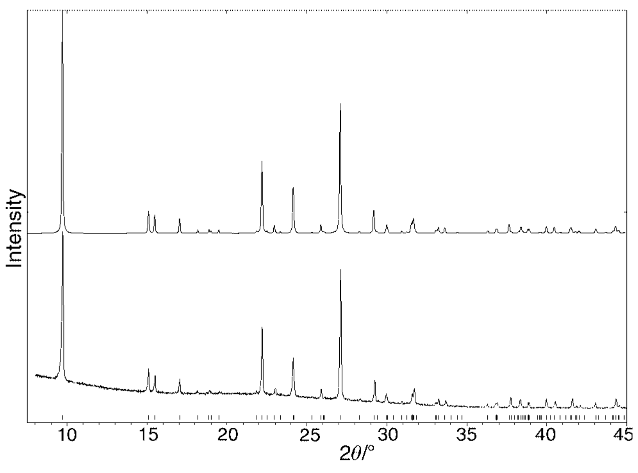

Fig. 2 Simulated (top) and experimental (bottom) powder X-ray diffraction patterns of UiO-19.

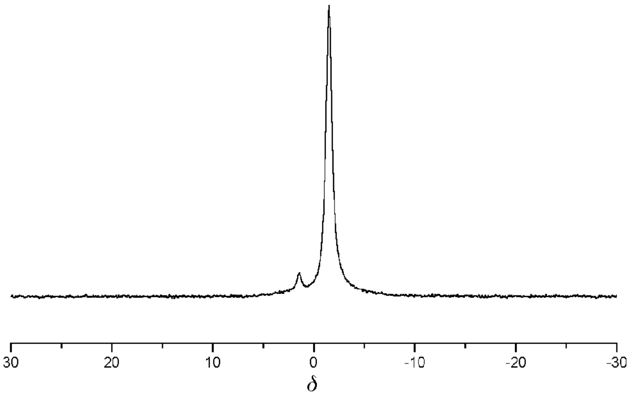

Fig. 3 Solid state ^{31}P MAS NMR spectrum of UiO-19.

Powder X-ray diffraction

X-Ray powder diffraction data were recorded in capillary geometry using a Siemens D5000 diffractometer equipped with a primary germanium monochromator and position sensitive detector (PSD). The pattern was recorded from 8 to 90° in 2θ with a nominal step length of 0.015552° (defined by the PSD) and a counting time of 15 s per step. Fig. 2 reveals a close correspondence between the experimental powder pattern and that simulated on the basis of the single-crystal structure determination. This proves that the crystallite chosen for the single crystal analysis was representative for the bulk sample. The impurity phase(s) indicated by TGA must therefore be amorphous.

Solid state ^{31}P MAS NMR spectroscopy

NMR measurements were performed with a Bruker DMX-200 spectrometer. The ^{31}P high power ^{1}H decoupled solid state MAS NMR spectra were recorded at 81 MHz at a spinning frequency of 8.0 kHz. The repetition time was 100 s. The ^{31}P chemical shifts were defined relative to an 85% H_3PO_4 standard. The spectrum (Fig. 3) shows a single resonance at δ −1.88 consistent with the findings of one single crystallographically distinct P position in the structure determination. The small, additional peak at δ 1.74 is ascribed to the amorphous impurity phase.

Magnetic properties

The light blue colour of the compound could indicate the presence of titanium in a valence state lower than 4. Magnetic susceptibility data were therefore measured by an MPMS (Quantum Design; SQUID-sensor) in the temperature range

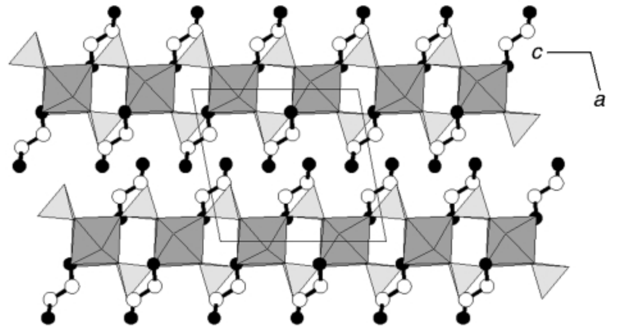

Fig. 4 Polyhedral representation of UiO-19 as seen along [010]. Ti octahedra with darker shading, PO_4 tetrahedra with lighter shading, C atoms with open circles and N atoms with filled circles.

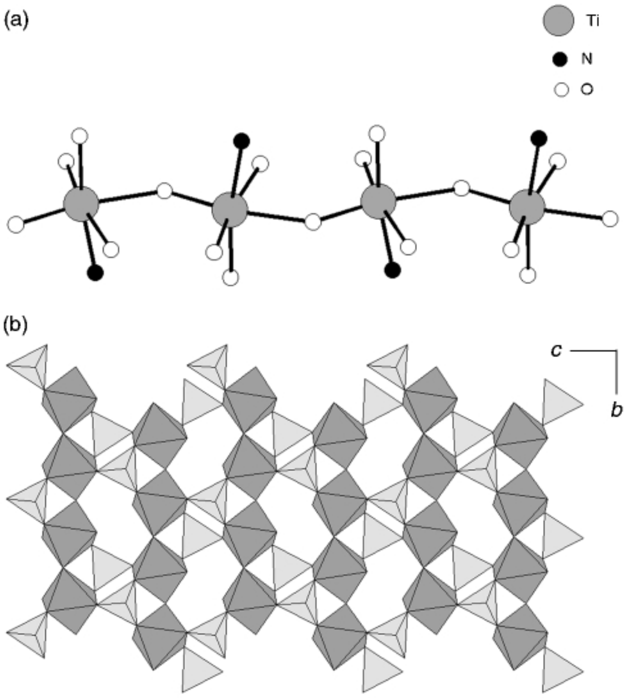

Fig. 5 (a) TiO_5N octahedral chain. (b) Polyhedral representation of UiO-19 as seen along [100]. Ti octahedra with darker shading and PO_4 tetrahedra with lighter shading.

5–300 K and a magnetic field $H = 10$ kOe. Diamagnetic behaviour was observed, which is consistent with tetravalent titanium. It is considered likely that the colour is caused by charge transfer, possibly related to the existence of TiO_5N octahedra, see below.

Discussion

The layered compound UiO-19, $[TiOPO_4]^-[NH_3(CH_2)_2NH_2]^+$, is structurally related to many organically templated layered materials[21–24] where anionic inorganic layers are separated by protonated amine molecules, through which hydrogen bonding facilitates cohesion of the structure. UiO-19 is identical to the ULM-11 variant recently described by Riou-Cavellec *et al.*[17] UiO-19 differs in one interesting way from most of the other layered compounds since the nitrogen of the amine is directly coordinated to titanium. A similar situation is found for the Al, Fe and V related compounds $AlF(HPO_4)(NH_2(CH_2)_2NH_2)$,[25] $FeF(HPO_4)(NH_2(CH_2)_2NH_2)$[26] and $[VF(PO_4)][NH_2(CH_2)_2NH_3]$,[17] which also can be considered as isostructural to UiO-19.

The two-dimensional nature of UiO-19 is illustrated in Fig. 4 where layers are seen to be stacked along [100]. The layers are built of infinite corner-sharing chains of TiO_5N octahedra along [010] (Fig. 5(a)), that are cross linked by phosphate tetrahedra (Fig. 5(b)). This is a structural motif present in many compounds.[27–29]

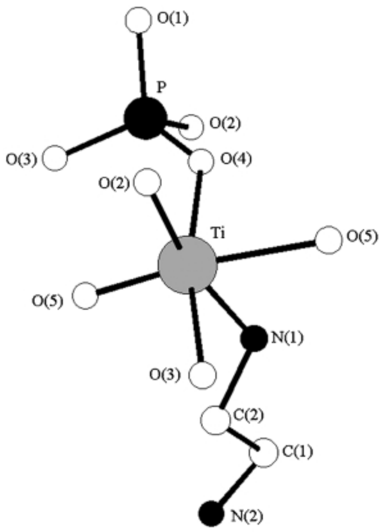

Fig. 6 Coordination environment of Ti and P in UiO-19.

Table 3 Bond valence analysis for UiO-19

	P	Ti	C	H	Σ
O(1)	1.242				1.242
O(2)	1.238	0.650			1.888
O(3)	1.233	0.647			1.880
O(4)	1.226	0.658			1.884
O(5)		1.296 0.404			1.700
N(1)		0.458	0.995	3.434	4.886
Σ	4.939	4.113			

Table 4 Hydrogen bonding interactions in UiO-19

Interaction	Distance/Å
O(5)···H(1)	2.49(3)
O(1)···H(3)	1.96(3)
O(1)···H(4)	1.91(3)
O(1)···H(5)	2.08(3)

The coordination environments of Ti and P are illustrated in Fig. 6. The P atom is coordinated *via* three bridging oxygens to titanium [O(2), O(3) and O(4)] with normal bond distances between 1.538(1) and 1.542(1) Å. The fourth oxygen of the phosphate group is terminal. A bond valence analysis[30] (Table 3) shows that O(1) is underbonded. The single-crystal analysis did not reveal any residual electron density in the difference Fourier map close to O(1). The $[TiOPO_4]^-$ anionic layer is charge balanced by the protonated $[NH_3(CH_2)_2NH_2]^+$. The proton is located at the nitrogen of the ethylenediamine not coordinating titanium, *i.e.* N(2). The valence of O(1) is fulfilled by being an acceptor of three hydrogen bonding interactions (Table 4). It is interesting to note the structure stabilising role of the ethylenediammonium ion, by at one end donating an N-ligand to titanium whereas at the other end it is involved in hydrogen bonding towards the subsequent anionic layer. The organic unit is hence an integrated part of the inorganic structure.

The titanium TiO_5N octahedron is very distorted. The bond distances to the bridging oxygens [O(2), O(3) and O(4)] of 1.970(1)–1.976(1) Å are normal, and the calculated bond valences for these oxygen atoms are close to the expected value of two (Table 3). The Ti–N(1) bond is 2.219(2) Å, and the calculated valence of nitrogen is close to the expected value of five. The bonds to O(5) along the chain of titanium octahedra alternate between a short bond (1.719(1) Å) and a long bond (2.150(1) Å). This type of octahedral distortion for titanium is observed in many other compounds, *e.g.* $KTiOPO_4$,[1] $TiOSO_4$ and $TiOSO_4 \cdot H_2O$.[31]

The calculated valence of O(5) is rather low, 1.70 valence units. The only additional stabilising interaction for O(5) is a very weak hydrogen bond (Table 4) from a proton attached to N(1), however, this is apparently sufficient to stabilise the structure. In other structures with similar types of distorted titanium octahedra the bridging oxygen is involved in quite strong interactions with alkali or alkaline-earth cations. In the three isostructural Fe-, Al- and V-fluorophosphates, the corresponding bridge between the octahedra is made up of a fluorine atom, and the distortions of the (Fe, Al, V)-O_3F_2N octahedra are modest compared with those of the TiO_5N octahedra in UiO-19. Another main difference between UiO-19 and the related Al- and Fe-compounds, is the monoprotonation of the amine in UiO-19. In the Al- and Fe-compounds the amine is not protonated, instead the terminal oxygen of the phosphate group is protonated, and the inorganic sheets are neutral.

UiO-19 has interesting structural motifs with 1D-chains of corner sharing octahedral groups cross linked by phosphate groups, and the characteristic short–long alternation of the Ti–O bonds. These motifs are also present in $KTiOPO_4$ and isostructural compounds, which all exhibit technologically very interesting non-linear optical properties. Especially, the short Ti–O bonds are believed to play a key role in the non-linear optical properties. UiO-19 is however not a potential non-linear optical medium since it crystallises in a centrosymmetric space group, $P2_1/c$. The short titanyl bond has further been related to another optical property, luminescence,[32] and in this area UiO-19 may be a candidate for examination.

The recent paper by Riou-Cavellec *et al.*[17] describes a material which based on comparison between the powder diffraction patterns is identical to UiO-19. Our single-crystal structure detemination is however superior to the powder structure determination offered by Riou-Cavellec *et al.* The proposed chemical formula for their material is $Ti(OH)PO_4 \cdot N_2C_2H_9$ implying trivalent titanium. Nevertheless, the present study strongly suggests the presence of Ti^{IV}. First, the magnetic susceptibility shows diamagnetic behaviour consistent with a d^0 electron configuration. Second, the presence of paramagnetic Ti^{III} would make ^{31}P NMR experiments impossible, *cf.* the collected high quality data in Fig. 3. Third, the calculated bond valence sum for titanium is 4.11 (Table 3), in good accordance with Ti^{IV}. Finally, the chosen reactants and synthesis conditions appear not to favour reduction of titanium from the Ti^{IV} state in the reactants. The present study shows furthermore that the O-atom bridging the TiO_5N-octahedra is not directly protonated, but is rather stabilised *via* a weak H-bond.

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