4598 *Inorg. Chem.* **2009,** *48,* 4598–4600
DOI:10.1021/ic900107p

Inorganic Chemistry
Communication

New Crystalline Layered Zinc Phosphate with 10-Membered-Ring Channels Perpendicular to Layers

Lei Liu,[†] Stanislav Ferdov,[‡,§] Cristina Coelho,[‡] Ying Kong,[†] Luís Mafra,[‡] Jin P. Li,[†] Jin X. Dong,[†] Uwe Kolitsch,[⊥] Rute A. Sá Ferreira,[¶] Ekkehart Tillmanns,[#] João Rocha,[‡] and Zhi Lin*[,‡]

[†]*Research Institute of Special Chemicals, Taiyuan University of Technology, 030024 Taiyuan, People's Republic of China,* [‡]*Department of Chemistry, CICECO, University of Aveiro, Aveiro 3810-193, Portugal,* [§]*Department of Physics, University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal,* [⊥]*Mineralogisch-Petrographische Abteilung, Naturhistorisches Museum, Burgring 7, A-1010 Wien, Austria,* [¶]*Department of Physics, CICECO, University of Aveiro, Aveiro 3810-193, Portugal and* [#]*Institut für Mineralogie and Kristallographie, Universität Wien, Geozentrum, Althanstrasse 14, A-1090 Wien, Austria*

Received January 19, 2009

A novel layered zinc phosphate, $[N_2C_6H_{12}]_2[Zn_7H_3(HPO_{4-x})_5(PO_4)_3]$ H_2O, with unique 10-membered-ring ellipsoidal channels running perpendicularly to ladder-shaped tetrahedral layers, has been synthesized ionothermally via in situ generation of 1,4-diazabicyclo[2.2.2]octane.

Layered materials have versatile applications in catalysis, adsorption, and ion exchange.[1] Recently, layered materials have been used as precursors in the preparation of nanocomposites.[2] Layered materials with perforated sheets are particularly interesting[3] and have been used as selectivity-enhancing additives in polymer membranes.[2]

Zincophosphates are an important subset of the large phosphate family. Although over 20 different zincophosphates with various structural dimensionalities and stoichiometries have been synthesized and characterized,[4−8] the preparation of zinc phosphates with novel structures is still possible.[9−11] Most of these structures are built up from vertex-linked ZnO_4 and PO_4 tetrahedra, and connectivity between two or more ZnO_4 tetrahedra through Zn−O−Zn linkages is rare.[12] These materials are typically synthesized hydrothermally using a zinc salt and phosphoric acid, together with an organic amine acting as a template or structure-directing agent.

Recently, ionothermal synthesis has been used in the preparation of aluminophosphate molecular sieves, among other materials.[13] The term "ionothermal synthesis" was proposed to describe a reaction using ionic liquids or eutectic mixtures as solvents to distinguish it from hydrothermal synthesis.[13] One class of deep eutectic solvents (DESs), formed between a variety of quaternary ammonium salts and carboxylic acids or urea-based amines,[14,15] exhibits unusual solvent properties that are very similar to those of ionic liquids and can be used in ionothermal syntheses as an alternative to ionic liquids.[13,16] Among these DESs, the carboxylic acid/quaternary ammonium salt DESs seem to be stable and usually do not contribute decomposition products as templates to the reactions,[16] while the ionic liquid acts as both a solvent and a template provider in ionothermal syntheses. Quaternary ammonium salts, such as TMABr, TEABr, TPABr, TBABr, and choline chloride, have been much used as structure-directing agents in the hydrothermal synthesis of molecular sieves. Different quaternary ammonium cations may template dissimilar frameworks. The above-mentioned quaternary ammonium salts may be mixed with oxalic acid to form DES, with melting points

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*To whom correspondence should be addressed. E-mail: zlin@ua.pt.

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below 150 °C, making these mixtures particularly useful solvents in ionothermal synthesis.

Harrison prepared $C_5H_{14}NO \cdot ZnCl(HPO_3)$ by reacting a zinc precursor with a mixture of choline chloride and urea at 25 °C for several weeks, where choline chloride acted as a templating agent.[17] This is the only example of a zincophosphate molecular sieve synthesized using DES. To the best of our knowledge, the synthesis of novel zincophosphate frameworks using the ionothermal approach has not been reported.

Here, we report a new crystalline layered zinc phosphate, $[N_2C_6H_{12}]_2[Zn_7H_3(HPO_{4-x})_5(PO_4)_3] \cdot H_2O$ (denoted as ZnPO-DES1), with 10-membered-ring channels perpendicular to layers. This material was prepared by ionothermal synthesis from a mixture of DES [made from $(CH_3CH_2CH_2)_4NBr$ (TPABr) and oxalic acid], zinc acetate, H_3PO_4, and triethanolamine (TEA) at 150−180 °C for 3 days, with 65% yield based on zinc (see the Supporting Information). The structure of ZnPO-DES1 was solved by combining single-crystal X-ray diffraction (XRD) and solid-state ^{13}C and ^{31}P NMR spectroscopy.

ZnPO-DES1 is a two-dimensional (2D) zinc phosphate with a novel structure type, and it crystallizes in the triclinic space group $P\bar{1}$. The ladder-shaped layers (Figure 1a) consist of simple four-membered-ring secondary building units (Figure 1b) composed of alternating zinc- (ZnO_4) and phosphorus-centered tetrahedra (PO_4 and HPO_4) whose interconnection results in the formation of large 10-membered-ring ellipsoidal channels running perpendicularly to tetrahedral layers (Figure 1c). The free diameters of these rings are ca. 7.3 × 5.1 Å, based on the van der Waals diameter of the O atom, 2.7 Å (Figure S1 in the Supporting Information). It should be pointed out that the minimum distances between O atoms in adjacent layers are very short, viz., 2.674 and 3.000 Å for O11−O21 and O20−O23, respectively. Therefore, this material possesses a pseudo-three-dimensional framework. The "ladder" channel along the *a* axis consists of interconnected elongated voids, with their largest dimension being 21.6 Å. In the interlayer space and within the 10-membered-ring units reside two distinct 1,4-diazabicyclo[2.2.2]octane (DABCO) molecules and a water molecule (Figure 1a,c). To the best of our knowledge, this is the first layered zinc phosphate with 10-membered-ring channels perpendicular to their layers.

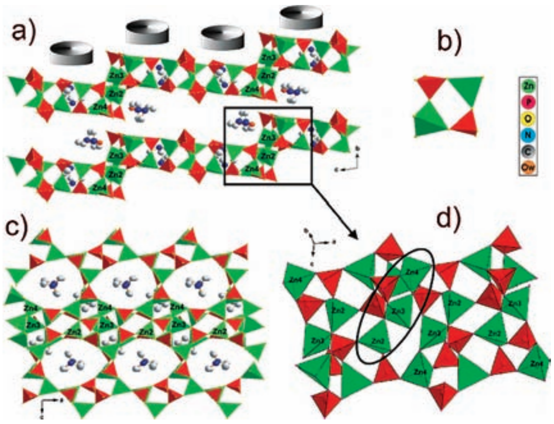

Figure 1. (a) Polyhedral representation of ZnPO-DES1 in a view along the [100] direction, showing ladder-shaped layers. The circle marks indicate the position of 10-membered-ring channels running perpendicularly to layers. (b) Main secondary building unit. (c) Two DABCO molecules residing in the interlayer space and within the 10-membered rings (H atoms are omitted for clarity). (d) Representation of Zn−O−Zn linkages.

The thermogravimetric analysis (TGA) curve of ZnPO-DES1 consists of three main steps showing a total mass loss of 21.5% up to about 450 °C (Figure S2 in the Supporting Information). The first step corresponds to ca. 2% (between room temperature and 300 °C), the second to 6.0% (between 300 and 380 °C), and the third to 12.5% (between 380 and 450 °C) mass loss. The first step is attributed to the loss of surface and structural water. The second and third steps are assigned to the loss of DABCO and residues of organic fragments of TEA and DABCO (see the Supporting Information). The mass loss above 450 °C may result from thermal decomposition of the material. The structure is stable at least up to 230 °C (Figure S3 in the Supporting Information). After having been heated at 230 °C for 20 h, single crystals still diffract well. Single crystals heated at 280 or 320 °C for 90 min, however, do not give XRD reflections anymore, although the crystal habit is well preserved (Figure S4 in the Supporting Information).

In the structure of ZnPO-DES1, there are seven crystallographically distinct Zn atoms in an asymmetric unit. The Zn2, Zn3, and Zn4 atoms share one (Zn2 and Zn4) or two (Zn3) of their tetrahedral corners together with Zn and P atoms (Zn−O−Zn and Zn−O−P linkages in Figure 1d). Therefore, the structure has three-coordinated O atoms, a feature that has seldom been observed in other open-framework zincophosphates.[12] The remaining Zn atoms are only bonded to P atoms via single Zn−O−P links, with bond lengths (Zn−O ranging from 1.902 to 2.017 Å; P−O and P−OH ranging from 1.448 to 1.611 Å) typical for this class of materials.[11,18−23] The P atoms are in the centers of isolated PO_4 and HPO_4 groups connected via ZnO_4 tetrahedra. Five of them (P3, P5, P6, P7, and P8) share three of their corners with Zn atoms (P−O−Zn links), with the fourth one being a terminal hydroxyl group, as indicated by ^{31}P NMR. A complex disorder involving the phosphate groups is also observed. The P8 atom position is split over sites P8A (50% refined occupancy) and P8B (50% occupancy). Among the O atoms (O25, O26, and O27) coordinating P8, the O27 atom is disordered over sites O27A (two half-occupied sites), O27B (50% occupancy), and O27C (50% occupancy) (Figure 2). Apart from the three H atoms connected to O12, O23, and O27, which could be located and refined, the rest of the hydroxyl groups were determined by calculations of bond valence sums (BVS; Table S3 in the Supporting Information). A small excess negative charge suggested by the calculated formula may be explained by the additional presence of disordered positively charged residues of organic fragments

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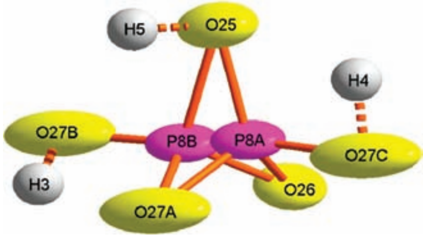

Figure 2. View of the disorder in the $HP8O_4$ tetrahedron (50% probability displacement ellipsoids).

of TEA and DABCO that can contribute to the charge compensation.

The BVS calculations[24] (Table S3 in the Supporting Information) show that the average BVSs of Zn, P, and O are 2.03, 5.09, and 2.18 valence units (vu), in fair agreement with the expected values of 2.00, 5.00, and 2.00 vu, respectively.

NMR spectroscopy complements the XRD evidence because of its ability to probe, in particular, the ^1H nuclei. The high-resolution 2D $^1H-^{31}P$ HETCOR NMR spectrum (Figure 3a) reveals the nuclear proximities between the different ^{31}P sites and the various ^1H environments. This spectrum shows a clear distinction between ^1H environments present in the inorganic (POH groups) and organic ($-NCH_2$ groups) moieties. The former appear at considerably larger ^1H NMR chemical shifts (δ_{1H}) of ca. 10 ppm, while the latter typically resonate at 3−5 ppm. The ^{31}P nuclei, which have cross-peaks with ^1H nuclei at δ_{1H} of ca. 10 ppm, are easily identified as POH groups involved in PO$\cdots$H$\cdots$OP hydrogen bonding, as shown by the short O$\cdots$O bond lengths present in the crystal structure. At least two ^{31}P NMR resonances at ca. 4.0 and 6.3 ppm, correlated with ^1H NMR peaks at $\delta_{1H} \sim 10$ ppm, are observed in Figure 3a. Deconvolution of the ^{31}P MAS NMR spectrum (Figure 3b) allows the quantification and assignment of all resonances. The spectrum (Figure 3c) was deconvoluted with five Lorentzian/Gaussian peaks, yielding the populations 1:1.5:1.5:3:1, for P_5:(P_3 + $P_{8A/B}$):(P_7 + $P_{8A/B}$):(P_1 + P_2 + P_4):P_6, respectively. This deconvolution shows that the P8 site is disordered over two different crystallographic positions, each with 50% occupancy. Moreover, P_7 and P_3 share a ^1H nucleus with $P_{8A/B}$, establishing the hydrogen bonds $P_{8A/B}O\cdots H\cdots OP_7$ and $P_{8A/B}O\cdots H\cdots OP_3$, respectively. The pairs $P_{8A/B}/P_7$ and $P_{8A/B}/P_3$ are assigned to the peaks resonating at ca. 4 and 6.3 ppm, respectively. From the structure model and BVS, P_5 and P_6 may be assigned to POH groups. The peak with the largest area (38%) is assigned to the three internal {PO_4} sites, P_1, P_2, and P_4. It is worth noting that all P sites are equally correlated with protons at $\delta_{1H} \sim 3-5$ ppm because they are close to the organic guests. The assignment of the P_1, P_2, and P_4 sites (peak at ca. 2 ppm) to ^{31}P nuclei without ^1H nuclei in their neighborhood may be further confirmed by comparing the ^{31}P MAS and ^{31}P CPMAS NMR spectra (Figure S5a in the Supporting Information). The latter discriminates in favor of P sites close to protons. The peak given by the three {PO_4} groups (P_1, P_2, and P_4), at ca. 2 ppm, becomes less intense in the CPMAS NMR spectrum (Figure S5 in the Supporting Information).

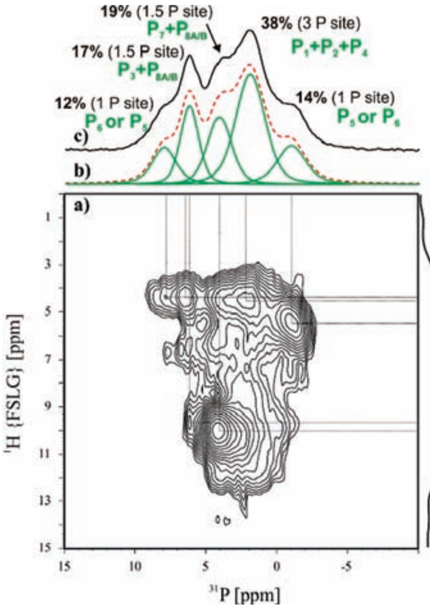

Figure 3. 2D $^1H\{FS\text{-}LG\}-^{31}P$ HETCOR NMR spectrum of ZnPO-DES1 recorded with a contact time of 100 μs (a). Individual deconvolution peaks (green lines) and simulated (dashed red lines) (b) and experimental (c) ^{31}P MAS NMR spectra.

DABCO has been used previously as a structure-directing agent in the hydrothermal synthesis of zincophosphates, and nine different compounds have been obtained.[11] Although DABCO was not added to our precursor mixture, the structure determination and solid-state NMR studies clearly attest to its presence. This is not surprising because TEA may be converted to DABCO under certain conditions.[25] Because the structure determination showed the presence of DABCO, additional syntheses were also carried out by replacing TEA with DABCO. However, a different, unidentified phase was obtained.

In summary, a novel layered zinc phosphate with Zn−O−Zn linkages, $[N_2C_6H_{12}]_2[Zn_7H_3(HPO_{4-x})_5(PO_4)_3]\cdot H_2O$, has been synthesized and characterized. Its structure consists of unique 10-membered-ring ellipsoidal channels running perpendicularly to ladder-shaped layers. In order to obtain this material, DABCO needs be generated in the process of synthesis. Our results also show that novel zinc phosphate structures may be obtained via ionothermal synthesis using DESs.

Acknowledgment. The Chinese group was financially supported by the National Natural Science Foundation of China (Grant 20573077) and the Special Program for Key Basic Research of the Ministry of Science and Technology, China (Grant 2007CB616914). The Portuguese group was financially supported by FCT, POCI2010, PTDC, FSE, and FEDER.

Supporting Information Available: Experimental details, TGA, powder XRD, SEM images, additional NMR data, and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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