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The *cyclo*-propylammonium cation as a templating agent for inorganic networks: synthesis and structure of $(C_3H_8N)_2{\cdot}Zn_3(HPO_3)_4$

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The hydrothermal synthesis and single crystal structure of $(C_3H_8N)_2{\cdot}Zn_3(HPO_3)_4$ are described. This compound is built up from ZnO_4 tetrahedra and HPO_3 pyramids sharing vertices to generate a three-dimensional 4:3 network containing 8-ring channels. The protonated organic cations occupy the channels in a head-to-tail arrangement and interact with the framework by way of N–H···O hydrogen bonds. Crystal data: $C_6H_{20}N_2O_{12}P_4Zn_3$, $M_r = 632.23$, monoclinic, $P2_1/n$ (No. 14), $Z = 4$, $a = 9.6773$ (2) Å, $b = 13.8676$ (2) Å, $c = 15.4482$ (3) Å, $\beta = 90.039$ (1)°, $V = 2073.16$ (7) Å^3, $R(F) = 0.028$, $wR(F^2) = 0.062$.

Keywords: zinc, $[HPO_3]^{2-}$, $C_3H_8N^+$, X-ray structure

A key challenge in materials chemistry is the rational design and synthesis of inorganic open-frameworks templated by organic cations.[1] Such a task is difficult because the mechanism of formation of most frameworks is obscure or unknown and kinetic control plays a key role in the synthesis.[2,3] Many organically-templated frameworks containing zinc cations and $[HPO_3]^{2-}$ (hydrogen) phosphate anions (ZnPOs) have prepared and characterised.[4,5] A number of different templates have been used to form these phases, with a particular focus on doubly-protonated, bifunctional, linear-chain diamines, $H_3N^+(CH_2)_nN^+H_3$ (n = 2–6), which invariably interact with the anionic zincophosphite framework by way of N–H···O hydrogen bonds.[6,7] Conversely, templates with a single $-N^+H_3$ "head group" have been less explored, although their potential to generate new frameworks has been shown by the use of the *cyclo*-pentylammonium cation to form $(C_5H_{12}N)_2{\cdot}Zn_3(HPO_3)_4$,[8] which features clusters of organic cations occupying extra-large 24-ring channels delineated by the inorganic framework. We now report the synthesis and characterisation of $(C_3H_8N)_2{\cdot}Zn_3(HPO_3)_4$ (**1**), the first framework ZnPO phase to be templated by the simple *cyclo*-propylammonium cation, $C_3H_8N^+$. Just one other inorganic framework has been templated by the *cyclo*-propylammonium cation, namely $C_3H_8N.PbI_2$,[9] which adopts a layered structure related to perovskites containing PbI_6 octahedra.

Results and discussion

1 is a new organically templated open-framework zinc phosphate prepared by a typical mild-condition hydrothermal reaction. IR assignments were made by comparison with literature data;[10] the characteristic P–H stretch at 2391 cm^{-1} and the PO_3 asymmetric stretch at 1116 cm^{-1} confirm the presence of the phosphite ion.

The crystal structure of **1** shows the presence of a three-dimensional anionic $[Zn_3(HPO_3)_4]^{2-}$ framework and two *cyclo*-propylammonium $C_3H_8N^+$ templating cations. The three Zn atoms adopt their typical[6] tetrahedral ZnO_4 geometries, with mean Zn–O distances of 1.937 Å, 1.941 Å, and 1.934 Å for Zn1, Zn2 and Zn3, respectively. The environment of Zn3 is significantly distorted in terms of its O–Zn–O bond angles [range of values = 100.52 (11)°–124.83 (11)°], which may correlate with its role in the structure (see below). The four phosphorus atoms all adopt HPO_3 pseudo pyramidal[5] geometries, with unexceptional mean P–O bond lengths of 1.516 Å, 1.518 Å, 1.523 Å and 1.522 Å for P1, P2, P3 and P4, respectively. The 3:4 ratio[6] of Zn to P combined with the four vertices of the ZnO_4 groups and three vertices of the HPO_3 groups leads to a perfect alternation of Zn and P nodes in the crystal structure, and the mean Zn–O–P bond angle for the 12 O atoms is 130.3°, based on a rather narrow spread of values [119.93 (15)°–135.12 (16)°]. In terms of the connectivity of the nodal (Zn and P) atoms, the resulting three-dimensional 4:3 network[11] in **1** may be visualised as follows: Zn1, Zn2 and the four P atoms link together to form corner-linked 4-ring (four nodes) chains propagating in the *b* direction (Fig. 1). Each 4-ring loop is almost perpendicular to its two neighbours, and a zigzag chain motif results. The Zn3 nodes (at the centres of the most distorted ZnO_4 tetrahedra) play a key role in cross-linking the [010] chains to generate a three-dimensional network containing 4-, 6- and 8-ring windows. The organic cations occupy corrugated channels delineated by 8-rings propagating in [100] and interact with the anionic framework by way of N–H···O hydrogen bonds, such that each ammonium ($-NH_3^+$) group makes three of these bonds with N–H···O bond angles in the range 159–176°. Both the N1- and N2-containing cations template 8-rings in the zincophosphite framework (Figs. 2 and 3) in a similar way and they occupy the [100] channels in a head-to-tail fashion, such that the $-NH_3^+$

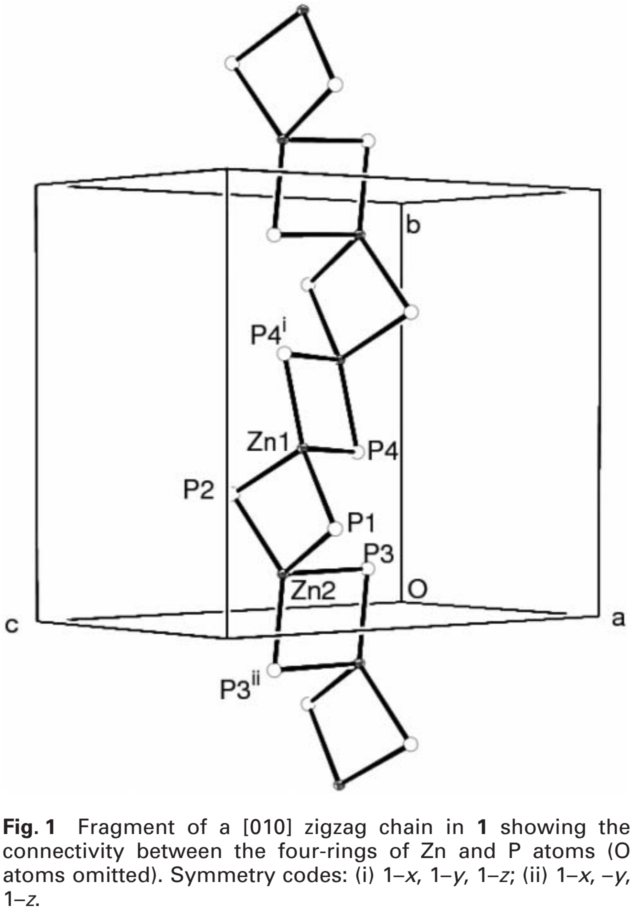

Fig. 1 Fragment of a [010] zigzag chain in **1** showing the connectivity between the four-rings of Zn and P atoms (O atoms omitted). Symmetry codes: (i) 1–*x*, 1–*y*, 1–*z*; (ii) 1–*x*, –*y*, 1–*z*.

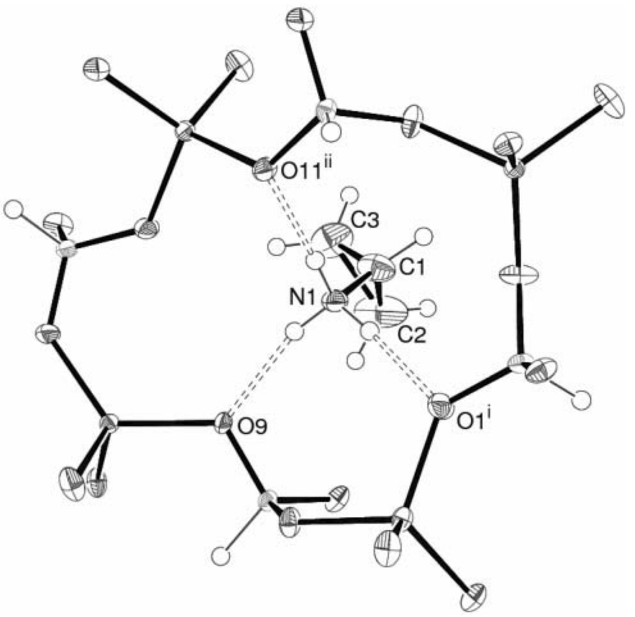

Fig. 2 Fragment of the structure of **1** showing the N–H···O hydrogen-bonding interactions between the N1-containing cation and a framework 8-ring of ZnO_4 and HPO_3 units. Symmetry codes: (i) 1–*x*, –*y*, 1–*z*; (ii) ½–*x*, *y*–½ ½–*z*.

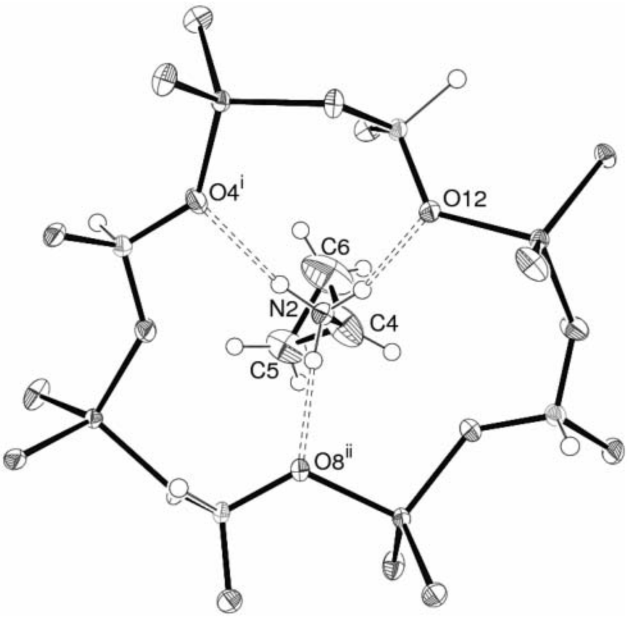

Fig. 3 Fragment of the structure of **1** showing the N–H···O hydrogen-bonding interactions between the N2-containing cation and a framework 8-ring. Symmetry codes: (i) 1–*x*, 1–*y*, 1–*z*; (ii) 3/2–*x*, ½+*y*, ½–*z*.

head group of one cation points towards one of the CH_2 groups of the *cyclo*-propane ring in the adjacent cation. The free volume of **1** calculated using PLATON[12] and expressed as a percentage of the total unit-cell volume is 43.2% and the number of framework nodal atoms (Zn and P) per 1000 Å^3 is 13.5; the latter value is comparable to that of aluminosilicate zeolite rho.[13]

Although the detailed mechanism of formation of **1** is unknown, the cation appears to exert a distinctive templating effect, with the –NH_3^+ head group making three strong and near linear N–H···O hydrogen bonds to a framework 8-ring. However, compared to $(C_5H_{12}N)_2 \cdot Zn_3(HPO_3)_4$,[8] the *template–template* interactions are quite different: in **1**, the cations adopt a head-to-tail arrangement as described above, whereas in $(C_5H_{12}N)_2 \cdot Zn_3(HPO_3)_4$ (containing the same inorganic polyhedra in the same ratio) they adopt a side-by-side arrangement.

Experimental

0.81 g ZnO, 0.97 g H_3PO_3, 0.57 g *cyclo*-propylamine and 20 mL water were placed in a sealed 60-mL HDPE bottle and vigorously shaken, to give a milky suspension. Then, the bottle was placed in a 90 °C oven for 24 hours. After cooling, product recovery by vacuum filtration and rinsing with water yielded 1.79 g (yield based on zinc = 85%) of colourless blocks of **1**. A comparison of the powder pattern of **1** with a simulation of the single-crystal structure indicated phase purity. IR (Nujol mull, cm^{-1}): 2924, 2854, 2391, 1728, 1629, 1535, 1462, 1377, 1116, 1071, 945. Intensity data for a colourless block (0.18 × 0.12 × 0.11 mm) of **1** were collected on a Nonius KappaCCD diffractometer (Mo Kα radiation, λ = 0.71073 Å) at *T* = 120 K. The data set appeared to be satisfactory, but structure solution with SHELXS-97[14] was non-trivial: the initial metrical unit cell and merging-R-factor in *mmm* Laue symmetry of 0.038 seemed to indicate orthorhombic crystal symmetry but the systematic absences did not conform to any known space group. Attempts at solving the structure in various orthorhombic space groups appeared to give partial solutions or fragments but they could not be developed. Lower symmetry models were then tried and a chemically plausible solution for the non-hydrogen atoms was developed in space group $P2_1/n$, although the residuals, following refinement against $|F^2|$ with SHELXL-97,[14] were very high [$wR(F^2) >$ 0.6]. A pseudo-merohedral twinning model was introduced [reflection in (100) represented by the 3 × 3 matrix –1 0 0 / 0 1 0 / 0 0 1], and the refinement rapidly converged to a solution with satisfactory residuals (two C–C bond lengths in the *cyclo*-propane rings are slightly short, perhaps due to un-modelled disorder). No "missed" (additional) symmetry was indicated in a PLATON analysis. All the H atoms were positioned geometrically (C–H = 0.99–1.00 Å, N–H = 0.91 Å, P–H = 1.32 Å) and refined as riding atoms; a rotating rigid-group model was used for the terminal –NH_3 atoms. Crystal data: $C_6H_{20}N_2O_{12}P_4Zn_3$, M_r = 632.23, monoclinic, $P2_1/n$ (No. 14), Z = 4, a = 9.6773 (2) Å, b = 13.8676 (2) Å, c = 15.4482 (3) Å, β = 90.039 (1)°, V = 2073.16 (7) Å^3, $F(000)$ = 1264, ρ_{calc} = 2.026 g cm^{-3}, μ = 3.81 mm^{-1}, min, max Δρ = –0.47, +0.99 e Å^{-3}, twin domain ratio = 0.5036 (9): 0.4964 (9), $R(F)$ = 0.028 [4496 reflections with $I > 2\sigma(I)$], $wR(F^2)$ = 0.062 (4714 reflections), CCDC deposition number: CSD-800077.

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