DALTON
FULL PAPER

$(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$: An open-framework zincophosphite built up from polyhedral 12-rings

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Received 2nd March 2001, Accepted 9th July 2001
First published as an Advance Article on the web 9th August 2001

The solution-mediated synthesis and single crystal structure of $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$ are reported. This phase is built up from a three-dimensional framework of vertex-linked ZnO_4 and HPO_3 building units encapsulating the extra-framework guanidinium cations. The structure is stabilised by template-to-framework hydrogen bonding. The inorganic framework contains polyhedral 12-rings and shows a surprising similarity to those of some known organically-templated zinc phosphates.

Introduction

Organically-templated zincophosphates (ZnPOs), which are mostly built up from vertex-linked ZnO_4 and PO_4 tetrahedra, show great structural diversity, with at least 30 examples known.[1] We have recently begun to explore[2–4] the chemistry of organically-templated zincophosphites containing networks of ZnO_4 tetrahedra and pseudo pyramidal $[HPO_3]^{2-}$ building units. Interesting features such as Zn–N (zinc-to-template) bonds in the polymorphic α- and β-$ZnHPO_3{\cdot}N_4C_2H_4$ phases[2] and polyhedral 16-ring windows in $(NC_5H_{12})_2{\cdot}Zn_3(HPO_3)_4$[3] have been observed. $[H_2N(CH_2)_2NH_2]_{0.5}{\cdot}ZnHPO_3$ combines the structural features of templated networks and coordination polymers in terms of its unprecedented architecture of two interpenetrated, independent mixed inorganic–organic networks.[4]

In this paper we describe the synthesis, structure and some properties of $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$, a new framework zincophosphite templated by guanidinium cations. The resulting crystal structure shows surprising similarities to that of the guanidinium-templated zinc *phosphate* $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$.[5]

Experimental

Synthesis and characterisation

4.50 g (25 mmol) guanidinium carbonate (Fluka), 2.54 g (30 mmol) H_3PO_3 (Alfa/Aesar), and 18.0 g (1 mol) deionised water were combined in a HDPE bottle, which was heated open in a 70 °C oven while CO_2 was evolved. Then, 0.81 g (10 mmol) ZnO (Spectrum) was added to yield a starting stoichiometry of guanidine: Zn : P : H_2O of 5 : 1 : 3 : 100. The bottle was capped, shaken, and installed in a 90 °C oven for 5 days. The solid product was recovered by vacuum filtration from the pH ≈ 9.5 mother liquors. The yield of large, transparent, faceted octahedral chunks of the title compound was 0.21 g (61% based on Zn).

Powder X-ray diffraction data for well-ground crystals of $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$ were collected on a Siemens D500 diffractometer (Cu-Kα radiation, $\lambda = 1.5418$ Å, $T = 25 \pm 2$ °C). The resulting pattern was in excellent agreement with a simulation based on the single-crystal parameters, indicating phase purity and a high degree of crystallinity. The cross-polarised ^{31}P MAS NMR spectrum of $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$ was collected on a Varian spectrometer and chemical shifts were referenced to a standard of 85% H_3PO_4.

Single-crystal structure study

A chunky, well faceted octahedral lump (≈ 0.34 × 0.36 × 0.36 mm) of $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$ was glued to a thin glass fibre and mounted on a Bruker SMART 1000 CCD area detector diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å, $T = 25 \pm 2$ °C). After preliminary scans indicated good crystal quality and a face-centred orthorhombic unit cell, a hemisphere of intensity data was collected (ω scan width = 0.3°) and processed with the aid of the SMART, SAINT, and SADABS software packages[6] (absorption correction factor range = 0.809–0.962). Data merging of the 6402 measured intensities with $2\theta_{max} = 65°$ resulted in 2223 unique reflections (R_{int} = 0.027) of which 2131 were considered observed according to the criterion $I > \sigma(I)$. The systematic absences indicated space group *Fdd*2 (no. 43).

Approximate positional parameters for the non-hydrogen atoms were located by direct methods.[7] The P–H (phosphite) hydrogen atom was found in a difference map and freely refined (isotropic thermal factor). The H atoms associated with the organic entity were positioned geometrically [d(N–H) = 1.001 Å] and refined by riding on their appropriate N atoms. The final cycles of full-matrix least-squares refinement with CRYSTALS[8] included positional and anisotropic thermal factors for all the non-hydrogen atoms, a Larson-type secondary extinction correction, and the Flack absolute structure parameter.[9] Refinement of this latter parameter to 0.037(7) indicated that the absolute structure of the crystal studied was well defined and is as presented in the results section. A calculated weighting scheme was applied.[10] Crystallographic parameters are summarised in Table 1.

CCDC reference number 160990.

See http://www.rsc.org/suppdata/dt/b1/b102007m/ for crystallographic data in CIF or other electronic format.

DOI: 10.1039/b102007m

Table 1 Crystallographic parameters for $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$

Empirical formula	$ZnP_2O_6N_6C_2H_{14}$
M_r	345.50
Crystal system	Orthorhombic
Space group	*Fdd*2 (no. 43)
a/Å	15.2109(6)
b/Å	11.7281(5)
c/Å	14.1821(6)
V/Å^3	2530.0
Z	8
T/K	298
λ/Å	0.71073
ρ_{calc}/g cm^{-3}	1.81
μ/cm^{-1}	22.21
Min., max. $\Delta\rho$/e Å^{-3}	−0.52, +0.75
$R(F)$ [a]	0.020
$wR(F)$ [b]	0.025

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 2 Selected geometrical data for $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$[a]

Zn1–O1 (×2)	1.9370(11)	Zn1–O2 (×2)	1.952(1)
P1–O1	1.5198(11)	P1–O2	1.5358(11)
P1–O3	1.4935(13)	P1–H1	1.32(3)
C1–N1	1.313(2)	C1–N2	1.319(2)
C1–N3	1.327(2)		
Zn1–O1–P1	129.77(8)	Zn1–O2–P1	126.33(6)
N1–H11 · · · O1	1.97	2.964(2)	177
N1–H12 · · · O3	2.06	2.983(3)	153
N2–H21 · · · O2	1.91	2.906(2)	175
N2–H22 · · · O3	2.02	2.915(2)	148
N3–H31 · · · O3	2.48	3.120(3)	121
N3–H31 · · · O3	2.33	3.148(3)	138
N3–H32 · · · O2	2.14	3.099(2)	159

[a] For the N–H · · · O hydrogen bonds [*d*(N–H) fixed at 1.00 Å in each case], the three values refer to the H · · · O and N · · · O separations (Å), and the N–H · · · O bond angle (°), respectively. H31 is involved in a bifurcated H bond.

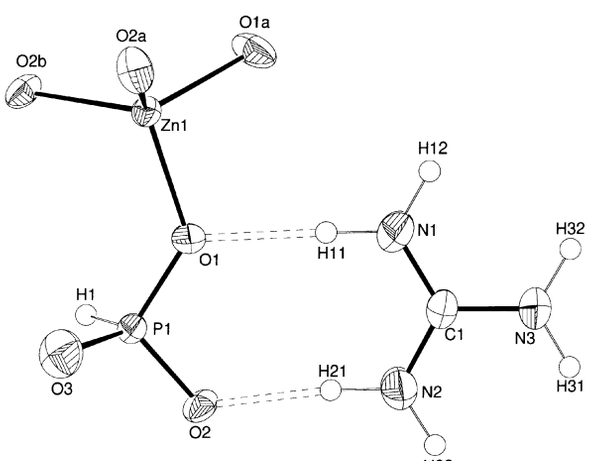

Fig. 1 Fragment of $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$ showing the atom labelling scheme (50% thermal ellipsoids). Symmetry-generated atoms are indicated by *e.g.*, O1a.

Results

Selected geometrical data are listed in Table 2. The $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$ structure is illustrated in Fig. 1 and 2. The single distinct zinc atom (site symmetry 2) adopts tetrahedral coordination with geometrical parameters typical[1] of related materials [d_{av}(Zn1–O) = 1.945(1) Å]. It makes four bonds to nearby P atoms *via* Zn–O–P links. The P atom has three O atom neighbours [d_{av}(P1–O) = 1.516(1) Å], and a P–H bond occupying the fourth tetrahedral vertex, which is completely characteristic[11] of phosphorus(III), as used in the synthesis. In $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$, two P–O–Zn links ($\theta_{av}$ = 128.1°) and a terminal P–O3 bond are formed. The anionic $[Zn(HPO_3)_2]^-$ component of the structure is charge balanced by a guanidinium cation which has typical[5] C–N geometrical parameters.

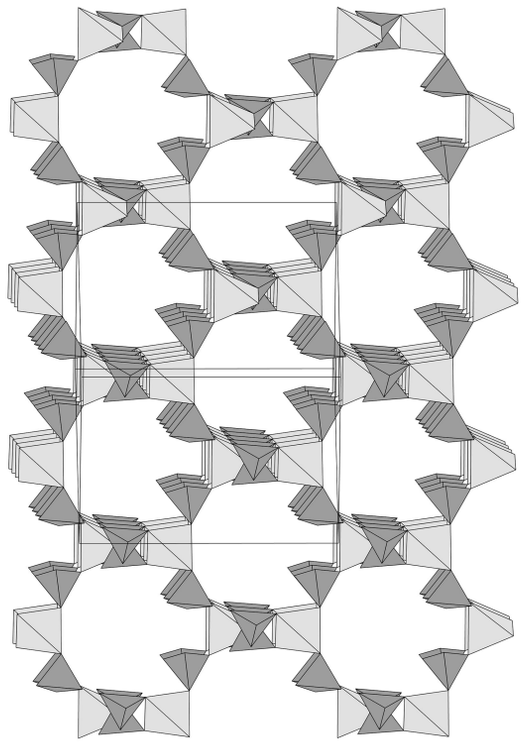

Fig. 2 Polyhedral view down [110] of the framework of $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$ (ZnO_4 tetrahedra light shading, HPO_3 pseudo tetrahedra dark shading, template species omitted for clarity).

The polyhedral connectivity of the strictly alternating ZnO_4 and HPO_3 nodes in $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$ results in an infinite, anionic, three-dimensional network. The smallest identifiable out-and-back loop from each zinc centre is a polyhedral 12-ring, built up from six ZnO_4 and six HPO_3 units. Thus, there are no polyhedral 4-rings, as commonly seen in zincophosphate networks.[12] This network encapsulates a two-dimensional system of intersecting channels propagating along [$\bar{1}$10] and [110]. Conversely, there are no channels apparent in the [001] direction. The atom-to-atom dimensions of the framework 12-ring are approximately 7.7 × 8.9 Å.

The well-ordered, essentially rigid, guanidinium cations occupy all of the 12-ring windows (Fig. 3), and interact with the zincophosphite framework by way of N–H · · · O hydrogen bonds.[5] Based on the geometrical placement of the hydrogen atoms described above, all of the N–H moieties are involved in H bonding. There are five simple N–H · · · O interactions with *d*(H · · · O) ranging between 1.91 and 2.141 Å (Table 2). H31 is involved in a bifurcated link to two O atom acceptors, although these bonds are both long.

The amount of void space[13] encapsulated by the zincophosphite framework in $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$ is 1442.6 Å^3 (57.0% of the unit cell volume) and the framework density[14] is 9.49 nodal framework atoms (*i.e.*, Zn and P)/1000 Å^3.

The ^{31}P MAS NMR spectrum of $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$ showed a single, sharp line at δ = 5.094, relative to a standard of 85% H_3PO_4, which is consistent with the crystal structure results (one distinct P species).

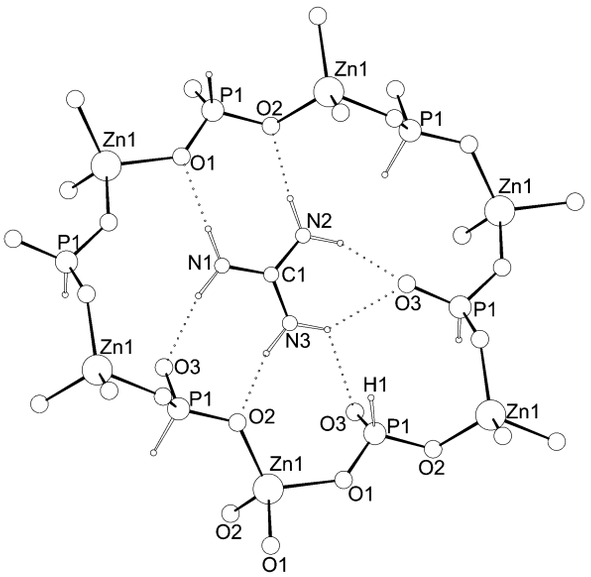

Fig. 3 Detail of $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$ showing a framework 12-ring window, with N–H · · · O hydrogen bonds indicated by dotted lines.

Discussion

The new phase $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$, which is built up from a three-dimensional network of vertex-linked ZnO_4 and HPO_3 building units, has been prepared hydrothermally and structurally characterised. It complements the organically-templated zincophosphites[2–4] noted in the introduction, but shares few overall structural characteristics with them. This type of behaviour is broadly similar to that of zincophosphate frameworks, where the overall structure strongly depends on the nature of the template, above all its hydrogen bonding capability.[15]

Interestingly, $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$ has a very similar structure to the guanidinium-templated zinco*phosphate* $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$.[5] These two phases contain equivalent 12-ring polyhedral networks, encapsulating the same organic species, which is templating in essentially the same way in each case, in terms of N–H · · · O hydrogen bonds. Hence, in this case, although the precise crystallographic details for these two phases differ, we may regard $[HP^{III}O_3]^{2-}$ and $[HP^{V}O_4]^{2-}$ as structurally equivalent species. Each anion makes two links to nearby Zn atoms (as P–O–Zn bonds); in addition, the former group has $P^{III}–O_T$ (T = terminal) and P^{III}–H bonds, whereas the latter group has $P^{V}–O_T$ and P^{V}–OH links. However, a very important distinction for the phosphate arises from the presence of *intra*-framework $P^{V}–OH \cdots O_T–P^{V}$ hydrogen bonds,[5] which are not seen in the phosphite. As expected, the H atom of the P^{III}–H unit is not acidic, and does not participate in H bonds.

The similarity between $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$ and $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ is further emphasised by the exceptionally open nature of this type of phosphorus-rich framework (the Zn : P ratio of 1 : 2 is fixed). The zincophosphate network in $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ surrounds void space amounting to some 55% of its unit cell volume, and has a framework density of 9.1 nodal atoms/1000 Å^3. These values compare very closely to the equivalent values for the title compound noted above. When the topological connectivity of the $(CN_3H_6)_2{\cdot}Zn(HPO_3)_2$ and $(CN_3H_6)_2{\cdot}Zn(HPO_4)_2$ frameworks are considered, they are both "metastructures"[16] of the α-cristobalite (SiO_2) framework. Thus, Zn corresponds to Si and HPO_4/HPO_3 corresponds to O in the SiO_2 phase, with an approximate magnification (scale factor) of 1.9.

The guanidinium cation seems to have a strong templating influence on polyhedral 12-rings. Thus, the first organically-templated selenite, $(CN_3H_6)_4{\cdot}Zn_3(SeO_3)_5$[17] contains 12-ring apertures (six ZnO_4 tetrahedra and six SeO_3 pyramids) although the overall structure is layered in this case. Even more striking is $(CN_3H_6)_2{\cdot}Zn(CO_3)_2$,[18] the first organically-templated carbonate framework. This structure is topologically equivalent to its phosphate and phosphite congeners and contains a 12-ring network of alternating ZnO_4 tetrahedra and CO_3 triangles templated by guanidinium cations.

Acknowledgements

We thank David Apperley (EPSRC National Solid State NMR Service, University of Durham, UK) for collecting the NMR data. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

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