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In Situ Template Generation For Zincophosphate Synthesis Leading to $C_2H_7N_4O{\cdot}ZnPO_4$ Containing Template-to-template N–H···O Hydrogen Bonds

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Abstract

The synthesis, structure and some properties of $C_2H_7N_4O{\cdot}ZnPO_4$ (guanylurea zinc phosphate) are reported. The cationic template was prepared *in situ* by partial hydrolysis of the neutral 2-cyanoguanidine starting material. The resulting structure contains a new, unprotonated, zincophosphate layer topology as well as unusual N–H···O template-to-template hydrogen bonds which help to stabilise a "double sandwich" of templating cations between the inorganic sheets. Crystal data: $C_2H_7N_4O{\cdot}ZnPO_4$, $M_r = 229.44$, monoclinic, $P2_1/c$, $a = 13.6453$ (9) Å, $b = 5.0716$ (3) Å, $c = 10.6005$ (7) Å, $\beta = 95.918$ (2)°, V = 729.7 (1) Å^3, $R(F) = 0.034$, $wR(F) = 0.034$.

Introduction

Organically-templated zincophosphate frameworks (ZnPOs) built up from vertex-linked ZnO_4 and PO_4 tetrahedra show considerable structural diversity with some 30 examples characterised so far.[1] In an *ex post facto* sense, a particular ZnPO structure can be correlated with the conformation and H-bonding properties of the organic species.[2] For ZnPOs this is invariably a cation (usually a protonated amine), and template-to-framework N–H···O interactions are assumed to have a strong structure-directing effect.[3] However, structure *prediction* for a particular set of starting materials, based on the ideas of crystal engineering *via* H bonding networks,[4] remains an elusive concept, although some trends are beginning to become more apparent.[5]

Here, we report the solution-mediated synthesis, single-crystal structure, and some properties of guanylurea (**2**) zinc phosphate, $C_2H_7N_4O{\cdot}ZnPO_4$. The cationic template was prepared by the slow, partial hydrolysis of neutral 2-cyanoguanidine (**1**). As expected, the neutral molecule **1** has no templating effect for ZnPOs, although it strongly interacts with zincophosphite ($Zn–HPO_3$) networks by way of Zn–N bonds.[6]

[scheme 1 near here]

Experimental Section

Synthesis: 2.52 g (30 mmol) $C_2N_4H_4$ (2-cyanoguanidine, Aldrich), 0.81 g (10 mmol) ZnO (Spectrum), 1.70 g (20 mmol) H_3PO_3, 97% (Aesar), and 18.0 g (1 mol) deionized water were

combined in a HDPE bottle. This was shaken well and placed in a 70 °C oven for 3 days, after which the contents were filtered hot. The *p*H of the mother liquors was 5. The solid product was washed with water, then methanol, and dried at 70 °C. The yield was xxx (xx% based on Zn) of transparent plates and needles of the title compound. An X-ray powder pattern indicated phase purity and high crystallinity.

Crystal structure determination: A transparent rod of $C_2H_7N_4O{\cdot}ZnPO_4$, dimensions ~0.05 × 0.06 × 0.43 mm, was mounted on a Bruker SMART 1000 CCD diffractometer (Mo Kα radiation, λ = 0.71073 Å).[7] Frames were collected in narrow-slice ω-scan mode for $2° \leq 2\theta \leq 65°$. An empirical absorption correction (correction factor range = 0.569–0.802) was applied with SADABS, resulting in 7305 scanned reflections. After merging to 2575 unique data (R_{Int} = 0.019), 2222 reflections were considered observed with $I > \sigma(I)$. The starting atomic parameters were established by direct methods,[8] and full-matrix least-squares refinement was carried out with CRYSTALS[9] (calculated weighting scheme[10]). All the H atoms were located from difference maps and their positional and isotropic thermal factors were refined without constraints. Crystallographic parameters are summarised in Table 1.

Results and Discussion

The crystal structure (Figure 1 and 2) of $C_2H_7N_4O{\cdot}ZnPO_4$ is built up from alternating inorganic and organic layers. Selected geometrical data are presented in Table 2. The anionic $[ZnPO_4]^-$ sheets, which propagate normal to [100], are built up from vertex-sharing ZnO_4 and PO_4 tetrahedra. The Zn1 species [d_{av}(Zn–O) = 1.953 (2) Å] makes two Zn–O–P bonds (*via* O1 and O3) and two Zn–O2–(P,Zn') links. The trigonal coordination of O2 results in infinite,

contorted chains of ZnO_4 tetrahedra propagating along [010]. The P1 species [d_{av}(P–O) = 1.541 (2) Å] makes two P–O–Zn bonds, one P–O2–(Zn,Zn') link, and a short, terminal P–O4 vertex. This short bond [d = 1.515 (2) Å] indicates that it is not protonated.[11] The linkage pattern of the tetrahedra leads to sheets of edge-sharing 3- and 4-ring loops (Figure 3). We believe that $C_2H_7N_4O{\cdot}ZnPO_4$ is the first layered ZnPO to contain such an unprotonated tetrahedral sheet.

The essentially flat conformation (maximum atomic deviation from the best least-squares plane < 0.13 Å) of the organic cation is similar to that of the same species in simple salts.[12] The template cations arrange into distinctive double layers between the inorganic sheets (Figure 2). Thus, the topological connectivity is sheet···template···template···sheet, rather than the more commonly seen sheet···template···sheet configuration. Hydrogen bonding (Table 1) appears to be a key factor in stabilising this structure. All seven H atoms are involved in hydrogen bonds of varying strength (two of which are bifurcated), with d(H···O) ranging from 1.98 (5) to 2.42 (5) Å, based on the freely refined H atom positions. As well as the typical N–H···O_f(template-to-framework) interactions,[1–3] novel N1–H1···$O5_t$ (inter-molecular template-to-template) linkages are present. This linkage serves to "dimerise" two template molecules about an inversion centre (Figure 4). There is also an *intra*-molecular N3–H5···O5 interaction (Figure 1). The terminal O4 atom of the ZnPO sheet is the acceptor species for no fewer than four H bonds.

In summary, guanylurea zinc phosphate, $C_2H_7N_4O{\cdot}ZnPO_4$, displays two unusual aspects of open-framework ZnPO chemistry:

- *in situ* generation of a cationic template from a neutral starting material, and

• template-to-template N–H···O hydrogen bonds due to the strong H-bond accepting C=O group of the template molecule.

This second point suggests that templates containing strong H-bond acceptors as well as H bond donors (protonated amide groups) can play a distinctive structure-directing role for templated structures and that the ideas of crystal engineering[4] could be fruitfully applied to this area.

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Figure Captions

Figure 1. Fragment of the $C_2H_7N_4O{\cdot}ZnPO_4$ structure (50% thermal ellipsoids, spheres of arbitrary radius for H) showing the atom labelling scheme. Hydrogen bonds are indicated by dotted lines and symmetry generated atoms are indicated by O1a, *etc.*

Figure 2. The structure of $C_2H_7N_4O{\cdot}ZnPO_4$ viewed down [010], with the ZnPO layer represented by polyhedra (ZnO_4 dark shading, PO_4 light shading).

Figure 3. Detail of the $C_2H_7N_4O{\cdot}ZnPO_4$ structure viewed approximately down [100] showing the tetrahedral connectivity in an infinite $[ZnPO_4]^-$ sheet.

Figure 4. Detail of the $C_2H_7N_4O{\cdot}ZnPO_4$ structure showing a dimerised pair of template molecules.

Table 1: Crystallographic Parameters for $C_2H_7N_4O{\cdot}ZnPO_4$

Empirical formula	$C_2H_7N_4O{\cdot}ZnPO_4$
M_r	263.48
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
a (Å)	13.6453 (9)
b (Å)	5.0716 (3)
c (Å)	10.6005 (7)
β (°)	95.918 (2)
V (Å^3)	729.7 (1)
Z	4
T	298 (2) K
λ (Å)	0.71073
ρ_{calc} (g/cm^3)	2.398
μ (cm^{-1})	35.84
min., max. Δρ (e /Å^3)	–0.60, +0.80
$R(F)^q$	0.034
$wR(F)^b$	0.034

[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 Bond Distances(Å)[a]/Angles(°) for $C_2H_7N_4O{\cdot}ZnPO_4$

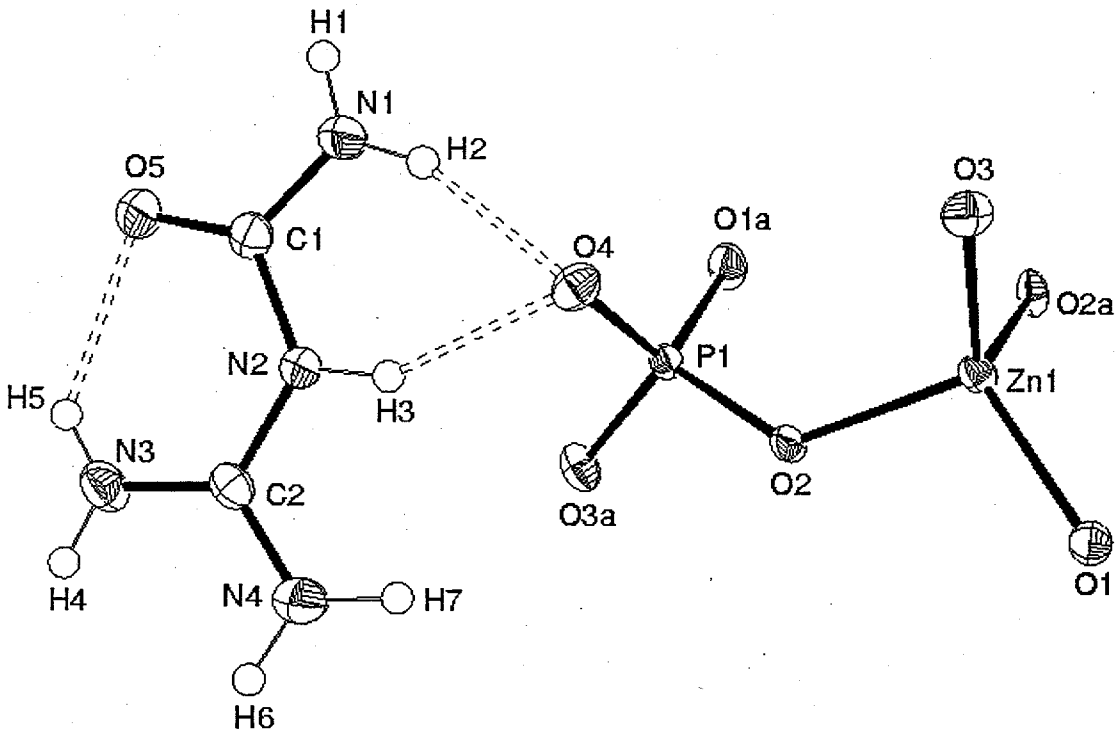
Zn1-O1	1.917(2)	Zn1-O2	1.9789(19)
Zn1-O2	1.9953(19)	Zn1-O3	1.920(2)
P1-O1	1.525(2)	P1-O2	1.5802(19)
P1-O3	1.542(2)	P1-O4	1.515(2)
O5-C1	1.240(3)	C1-N1	1.335(4)
C1-N2	1.395(4)	C2-N2	1.358(4)
C2-N3	1.320(4)	C2-N4	1.315(4)

Zn1-O1-P1	134.20(13)	Zn1-O2-Zn1	118.69(9)
Zn1-O2-P1	128.37(11)	Zn1-O2-P1	112.9(1)
Zn1-O3-P1	128.46(12)		

N1-H1...O5	0.84(4)	2.18(4)	3.014(4)	171(4)
N1-H2...O4	0.86(5)	1.98(5)	2.802(3)	159(5)
N2-H3...O4	0.89(4)	2.12(4)	2.925(4)	150(4)
N2-H3...O3	0.89(4)	2.34(4)	3.031(3)	135(4)
N3-H4...O4	0.87(5)	2.42(5)	3.155(4)	142(4)
N3-H5...O5	0.83(4)	2.12(4)	2.729(4)	130(4)
N4-H6...O4	0.91(5)	2.03(5)	2.900(4)	158(4)
N4-H7...O1	0.96(6)	2.29(6)	3.088(4)	140(4)
N4-H7...O3	0.96(6)	2.38(5)	3.125(4)	134(4)

[a]For the hydrogen bonds, the four values refer to the N–H, H···O, and N···O separations, and the N–H···O bond angle, respectively.

Figure 1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C1
O4
O1a
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O1
H6

Figure 2

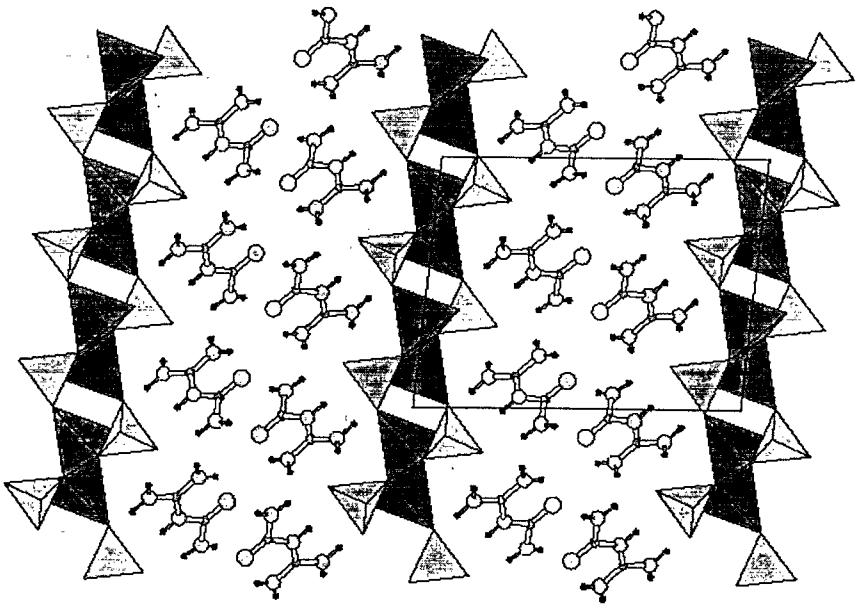

Figure 3

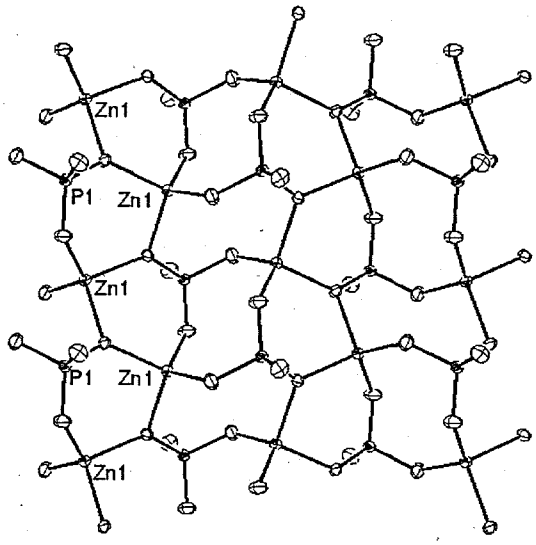

Figure 4