Ethylenediamine zinc hydrogen phosphite, $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$, containing two independent, interpenetrating, mixed inorganic/organic networks

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$[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$ combines the structural features of templated networks and coordination polymers.

A vast number of inorganic networks templated by organic species have been reported over the last 10 years.[1] The possibilities of incorporating the phosphorus(III) containing, pseudo-pyramidal $[HPO_3]^{2-}$ hydrogen phosphite group into extended structures templated by *inorganic*, alkaline earth cations was explored a few years ago.[2] We have recently described two polymorphs of $ZnHPO_3\cdot N_4C_2H_4$, the first network hydrogen phosphite templated by an organic species (2-cyanoguanidine).[3] Here, we report the synthesis,† crystal structure,‡ and some properties of ethylenediamine (en) zinc hydrogen phosphite, $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$, which shows a new type of structure combining the features of templated networks and coordination polymers.

A simulation based on the $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$ single crystal structure was in excellent agreement with X-ray powder data, indicating phase purity and high crystallinity. TGA (ramp at 10 °C min^{-1} to 900 °C) for $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$ revealed the onset of a 17% weight loss at *ca*. 200 °C, which was complete by *ca*. 700 °C. This is in good agreement (calc. weight loss = 17.1%) with a process involving the loss of all the organic species to result in a residue of nominal stoichiometry '$ZnHPO_3$.' ^{31}P MAS NMR for $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$ showed a sharp resonance at δ -1.18 (relative to 85% H_3PO_4). There were strong spinning side bands, consistent with the inherently asymmetric environment of the P atom in the $[H_3PO_3]^{2-}$ grouping. The ^{13}C spectrum consisted of a single line at δ = 42.30 relative to $SiMe_4$.

$[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$, which is built up from seven framework atoms (Fig. 1), contains ZnO_3N tetrahedra and HPO_3 pseudo-pyramids as the polyhedral building units. The Zn–N bond corresponds to a direct link between zinc and the en template. The Zn species makes three Zn–O–P links to nearby P atoms [d_{av}(Zn–O) = 1.934(1) Å]. P1 makes three bonds to Zn neighbors [d_{av}(P–O) = 1.516(1) Å], with the expected[4] terminal P–H bond as its fourth vertex. The average Zn–O–P bond angle of the three bridging O atoms is 142.08°. The geometrical parameters of the organic component of $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$ are typical. Fourier difference maps clearly located two H atoms attached to the N atom, thus the en "template" (if the term is still appropriate for this structure) is neutral, in accordance with the charge balancing requirement. Crystallographic symmetry generates the complete en template, which is therefore bonding to Zn from both its terminal N atoms, as Zn–N–C–C–N–Zn, or Zn–en–Zn (H atoms omitted). This linkage forms the connection between *next*-nearest neighbor sheets (*vide infra*).

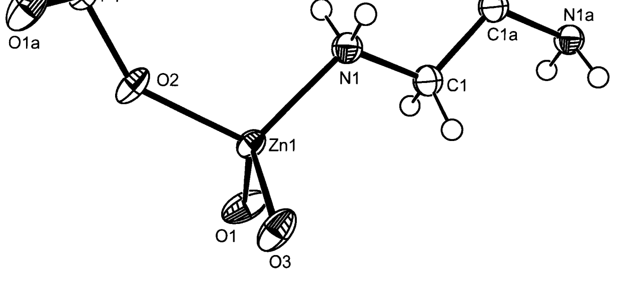

Fig. 1 Detail of the $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$ structure (50% thermal ellipsoids) showing the atom labeling scheme. Symmetry generated atoms are indicated by, *e.g.*, O1a.

The connectivity of the strictly alternating ZnO_3N and HPO_3 units in $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$ results in infinite layers (Fig. 2) propagating normal to [101]. Polyhedral 4-rings and 8-rings are apparent in these formally neutral sheets, and this topology can be described in terms of a 4.8^2 network (*i.e.*, each nodal Zn or P atom participates in one 4-ring and two 8-rings), which forms a characteristic part of feldspar (*e.g.*, $KAlSi_3O_8$) like phases[5] and various aluminosilicate zeolite structures,[6] although the 8-rings maybe subject to various degrees of distortion. The atom-to-atom dimensions of the $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$ 8-ring are approximately 6.51 × 7.14 Å. Each 4-ring has two 'up' (approximately along [101]) and two 'down' vertices, thus both the Zn–N and P–H bonds point into the inter-sheet region.

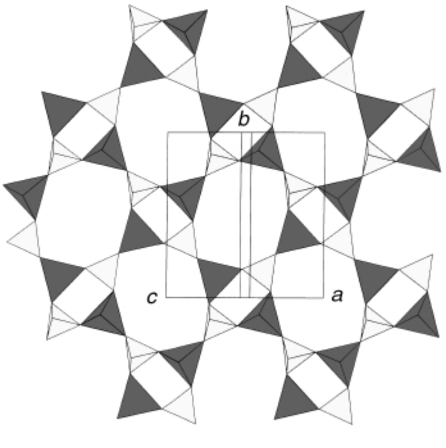

Fig. 2 Polyhedral view approximately down [101] of the 4.8^2 sheet topology of $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$ (dark shading for the ZnO_3N groups, light shading for the HPO_3 groups).

An unusual templating effect occurs in $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$, with the sheet-to-sheet Zn–en–Zn chain sticking *through* an 8-ring in an intermediate zincophosphite layer (Fig. 3). A somewhat similar effect through-the-ring effect involving a protonated template not bound to the inorganic network (and a totally different overall structure) has been seen in the gallofluorophospahte ULM-18.[7] In $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$, every 8-ring is templated in the same way, thus, two completely independent but interpenetrating sets of inorganic sheets (Fig. 4) are 'knitted

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together' by a covalent bonding network *via* zinc and the template rather than by H bonds or van der Waals's forces. This configuration has clear parallels with the structures of interpenetrating coordination polymers.[8,9] However, N–H···O hydrogen bonds, as commonly seen in organically-templated zinc phosphates,[10] are also important in $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$, with N1–H2···O1 [$d$(N1–H2) = 0.85(3) Å, d(H···O) = 2.22(3) Å, d(N···O) = 2.998 (2) Å, θ(N–H···O) = 152(2)°] and N1–H3···O3 bonds [0.90(2), 2.04(2), 2.931(2) Å. 169(3)°] occurring, the latter of these evidently somewhat stronger. Each 8-ring is stabilized by four N–H···O links (two from below, two from above), with all four associated with the same ethylenediamine grouping.

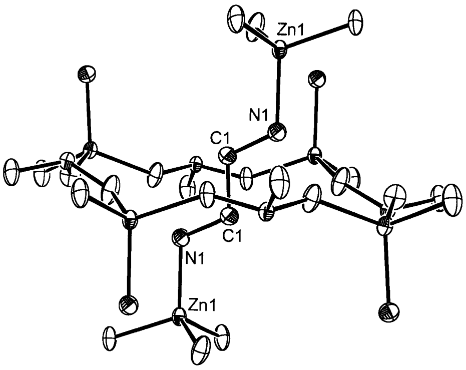

Fig. 3 Side-on view of an 8-ring window in one layer of $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$ showing the Zn–en–Zn grouping passing through it. For the central 8-ring shown, Zn–en links are terminated at N, and all H atoms are omitted for clarity.

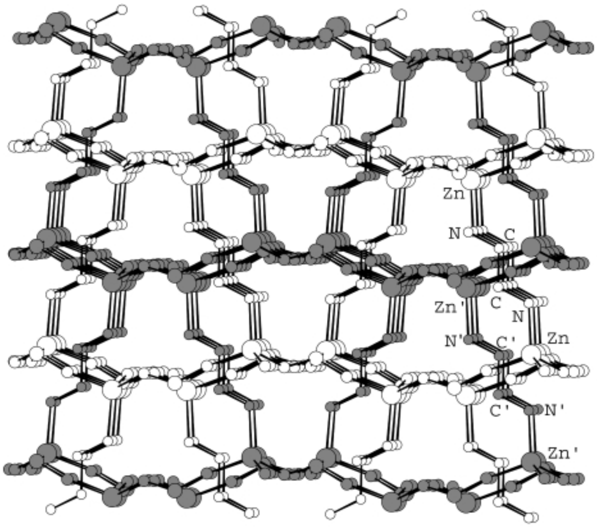

Fig. 4 Side on view approximately down $[10\bar{1}]$ of a set of layers in $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$. The unshaded atoms (unprimed labels) and shaded atoms (primed labels) form separate interpenetrating networks. For clarity, all H atoms are omitted.

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Notes and references

† *Synthesis*: 0.814 g ZnO, 0.824 g H_3PO_3, 0.602 g ethylenediamine (molar ratio of Zn : HPO_3^{2-} : en = 1 : 1 : 1) and 18 g of H_2O were added to a PTFE bottle and shaken well. The mixture was transferred to a Teflon-lined, 23 ml hydrothermal bomb, sealed, and heated to 150 °C for two days. The bomb was left to cool for 24 h, and the solid product, consisting of large (up to 2 mm) transparent lumps of the title compound was recovered by vacuum filtration and rinsing with water and methanol.

‡ *Crystal data*: $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$, M_r = 175.42, monoclinic, space group $P2_1/n$ (no. 14), a = 5.9335(3), b = 10.8863(5), c = 7.7611(4) Å, β = 102.066(1)°, V = 490.25(7) Å^3, Z = 4, μ = 52.2 cm^{-1}, D_c = 2.377 g cm^{-3}, $F(000)$ = 348, $R(F)$ = 0.022, $R_w(F)$ = 0.026. Data collection using a Bruker SMART 1000 CCD diffractometer (graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, T = 300 K): monoclinic cell parameters from 3479 reflections (6.5 < 2θ < 65.0°), 4999 reflections scanned (2 < 2θ < 65°). After merging (R_{Int} = 0.018), 1649 of the 1752 unique reflections were considered observed [$I > \sigma(I)$]. An absorption correction was applied with SADABS (min., max. equivalent transmission factors = 0.543, 0.928). Hydrogen atoms were located from difference maps and their positions and isotropic thermal factors were refined without constraints.

CCDC 182/1831. See http://www.rsc.org/suppdata/cc/b0/b007268k/ for crystallographic files in .cif format.

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