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Triethanolamine Zinc Phosphite, $(C_6H_{13}NO_3)Zn_2(HPO_3)$: A Templated Network or a Network of Clusters?

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$(C_6H_{13}NO_3)Zn_2(HPO_3)$ (**I**) displays an extended hybrid organic/inorganic structure in which the triethanolamine organic species acts as an anionic tetradentate ligand, rather than a typical protonated cationic template. Crystal data for **I**: $M_r = 357.89$, monoclinic, $P2_1/c$ (no. 14), $a = 8.4216(4)$ Å, $b = 9.9262(5)$ Å, $c = 12.8494(6)$ Å, $\beta = 91.824(1)°$, $V = 1073.6(1)$ Å^3, $Z = 4$.

Organically templated zinc phosphates (ZnPOs) now form an extensive family of compounds, with at least 100 well-characterized phases known.[1] A key idea[2] in rationalizing the structural diversity of these phases is that the organic species, typically a protonated bi- or polyfunctional amine, can be considered as a separate entity from the inorganic network. The organic component directs the synthesis to a low-density (i.e., noncondensed) network by *templating*,[3] and usually, N−H···O hydrogen bonds are a key feature of the resulting structure.[4]

More recently, organically templated zinc phosphites (ZnHPOs), which display broadly similar features to ZnPOs, have been prepared and characterized.[5−7] Here, we describe the unusual ZnHPO phase $(C_6H_{13}NO_3)Zn_2(HPO_3)$, which results from the combination of triethanolamine [$C_6H_{15}NO_3$ or $N(CH_2CH_2OH)_3$], zinc oxide, and phosphorus acid. It shows a new type of extended structure in which the nominal template acts as a tetradentate anionic ligand, resulting in a layered structure. It is also unique among ZnHPOs characterized so far in being zinc-rich with a Zn/P ratio of 2:1. A few other hybrid inorganic/organic network solids in which the template is covalently bonded to a metal center have been reported, including $(Hdab)Zn_3(PO_4)(HPO_4)_2$ (dab = $C_6H_{12}N_2$)[8] and $(H_3NCH_2CH_2NH_2)(VO)Al(PO_4)_2$,[9] both with monodentate ligands. In $(H_2dach)Ga_2(dach)(HPO_4)(PO_4)_2$ [10] (dach = 1*S*,2*S*-dianinocyclohexane), the ligand is bidentate, and in $Ga_2(deta)(PO_4)_2\cdot 2H_2O$[11] (deta = diethylenetriamine), it is tridentate. In all of these phases, ligand−N−M bonds occur.

The title compound was prepared by a typical solution-mediated reaction: 1.01 g of ZnO, 2.02 g of H_3PO_3, 1.88 g of $C_6H_{15}NO_3$ (Zn/P/template molar ratio = 1:2:1), and 10 mL of water were mixed in a plastic bottle and heated to 80 °C for 3 days. Product recovery by vacuum filtration yielded 0.997 g (yield based on Zn = 46%) of colorless blocks of $(C_6H_{13}NO_3)Zn_2(HPO_3)$. Powder diffraction (Bruker D8 diffractometer) indicated that the product was almost phase-pure, accompanied by trace amounts of ZnO. Under the heating conditions used here, essentially pure (trace impurities only) $(C_6H_{13}NO_3)Zn_2(HPO_3)$ was recovered from Zn/H_3PO_3/TEA starting ratios of 1:1:1, 1:2:1, 2:2:3, and 2:1:3. Starting compositions richer in zinc lead to increasing amounts of unreacted ZnO in the product, and compositions richer in phosphite lead to as yet unidentified polycrystalline phases.

The crystal structure[12] of $(C_6H_{13}NO_3)Zn_2(HPO_3)$ shows that the Zn1 species has trigonal bipyramidal coordination

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[12] $(C_6H_{13}NO_3)Zn_2(HPO_3)$, $M_r = 357.89$, monoclinic, $P2_1/c$ (no. 14), $a = 8.4216(4)$ Å, $b = 9.9262(5)$ Å, $c = 12.8494(6)$ Å, $\beta = 91.824(1)°$, $V = 1073.6(1)$ Å^3, $Z = 4$, $\mu = 46.3$ cm^{-1}, $\rho_{calc} = 2.214$ g cm^{-3}, $F(000) = 720$, $R(F) = 0.024$, $R_w(F) = 0.048$. Bruker SMART 1000 CCD diffractometer (graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, $T = 295$ K): the O−H hydrogen atom was located from a difference map and freely refined; the C−H hydrogen atoms were refined by riding on their carrier atoms in idealized positions.

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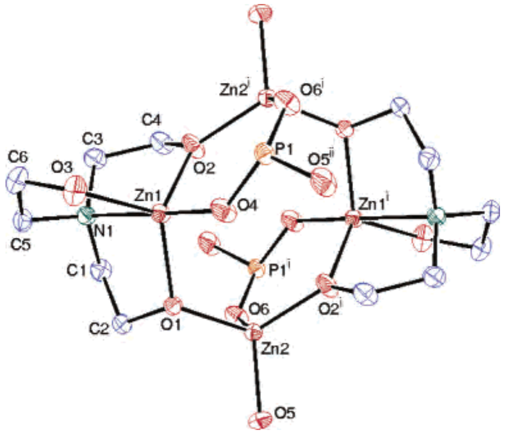

Figure 1. Cluster motif in $(C_6H_{13}NO_3)Zn_2(HPO_3)$ showing the connectivity of the $Zn1O_4N$, $Zn2O_4$, and HPO_3 building units (50% thermal ellipsoids). Hydrogen atoms omitted for clarity. Selected bond length data (Å): Zn1−O4 1.9457(12), Zn1−O2 1.9682(12), Zn1−O1 2.0478(11), Zn1−O3 2.1394(14), Zn1−N1 2.1708(14), Zn2−O2^i 1.9171(12), Zn2−O5 1.9241(13), Zn2−O6 1.9469(12), Zn2−O1 2.0055(11), P1−O5^{ii} 1.5095(13), P1−O4 1.5125(13), P1−O6^i 1.5157(13). Symmetry codes: (i) $1 - x, -y, -z$; (ii) $x, -y - {}^1/_2, z + {}^1/_2$.

to four O atoms and one N atom [$d_{av}(Zn1-O) = 2.052(2)$ Å]. The three equatorial O atoms and the N atom belong to the triethanolamine molecule, which is thus acting as a tetradentate ligand (Figure 1). The remaining oxygen atom (O4) forms a bridge to P1. Zn2 is tetrahedrally coordinated to four O atoms with $d_{av}(Zn2-O) = 1.948(2)$ Å. Two of these O atoms (O1 and O2) are part of the organic molecule, and two (O5 and O6) bridge to adjacent phosphorus atoms. The hydrogen phosphite P atom shows its usual coordination to three O atoms in pyramidal geometry [$d_{av}(P1-O) = 1.513(2)$ Å] and a P−H bond in the fourth tetrahedral position. The O atoms divide into O1 and O2 (bonded to two Zn + C); O3 (bonded to one Zn + one H + one C); and O4, O5, and O6 (bonded to one Zn + one P; $\theta_{av} = 136.5°$).

To encompass Zn1 in tetradentate (*N*, *O*, *O′*, *O″*) coordination, the geometry of the organic species is claw-like. The individual bond lengths and angles are unexceptional [$d_{av}(N-C) = 1.477(2)$ Å, $d_{av}(C-C) = 1.519(2)$ Å, $d_{av}(C-O) = 1.430(2)$ Å]. The X-ray diffraction results clearly show that only one of the three hydroxyl protons of the free $C_6H_{15}NO_3$ molecule (that attached to O3) remains; thus this species has a formal charge of −2, which is consistent with the overall charge-balancing criterion, assuming the usual charges for two Zn^{2+} and one $[HPO_3]^{2-}$. This is supported by the IR spectrum of the title compound, which shows a strong band at ∼2900 cm^{-1} indicating a hydrogen-bonded O−H moiety. Thus, rather than being protonated, as we initially assumed for the low-pH reaction conditions (starting pH ≈ 2) used here, the N atom participates in a Zn−N bond by formal donation of its lone pair of electrons, i.e., as a Lewis base.[5b] This slightly surprising result correlates with the observation of other metalation/deprotonation reactions of TEA with metal ions in acidic conditions.[13] In simple molecular coordination compounds containing TEA and Zn^{2+}, the organic moiety has been seen in tridentate[14] (*N*, *O*, *O′*), tetradentate[15] (as here), and nonbonded[16] configurations. The connectivity of the building units in the title compound results in a layered structure composed of novel cluster-like entities (Figure 1). Each cluster, which is generated by inversion symmetry from the asymmetric atoms, has the formulation $[(C_6H_{13}NO_3)_2Zn_4(HPO_3)_2]$. The nodal zinc atoms form a 4-ring (or square) built up from alternating ZnO_4N and ZnO_4 moieties, and the P atoms are grafted onto two edges, resulting in polyhedral 3-rings (nodal atoms Zn1, Zn2, P1) built up from the unusual combination of trigonal bipyramidal ZnO_4N, tetrahedral ZnO_4, and pseudo-pyramidal HPO_3 units.

The clusters are linked into a two-dimensional network by way of Zn1−O5−P1 bonds. These bonds link the clusters into infinite neutral corrugated sheets that propagate in the (100) plane (Figure 2). Intersheet connectivity (Figure 3) is

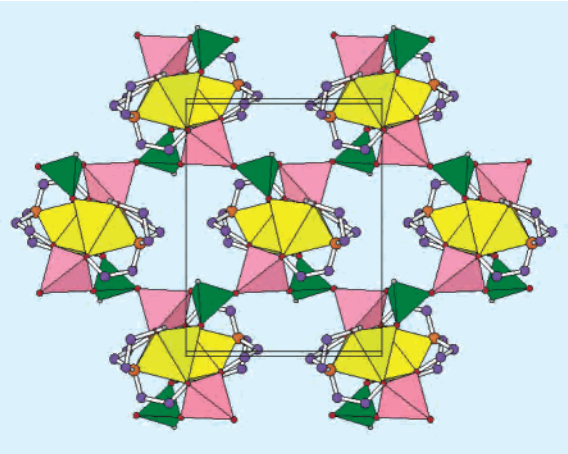

Figure 2. View approximately normal to (100) of the sheet structure of $(C_6H_{13}NO_3)Zn_2(HPO_3)$ showing the connectivity of the $Zn1O_4N$ (yellow), $Zn2O_4$ (pink), and HPO_3 (green) polyhedra. C atoms blue, N atoms orange. C−H hydrogen atoms omitted for clarity.

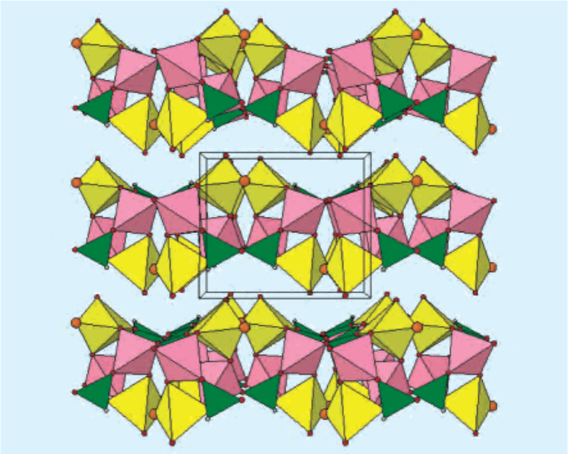

Figure 3. View approximately down [001] of the layer structure of $(C_6H_{13}NO_3)Zn_2(HPO_3)$. Color key as in Figure 2 with C and H atoms omitted for clarity.

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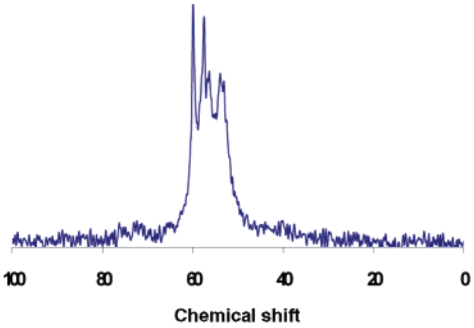

Figure 4. ^{13}C CP-MAS NMR spectrum of $(C_6H_{13}NO_3)Zn_2(HPO_3)$. Varian UNITY/Inova spectrometer; spinning speed = 4 kHz, magnetic field strength = 7.05 T.

maintained by van der Waals' contacts and O3−H3···O1 hydrogen bonds [d(O−H) = 0.81(2) Å, d(H···O) = 1.82(2) Å, d(O···O) = 2.6209(18) Å, (O−H···O) = 175(2)°]. This is the only H bond in the structure. The (100) layers stack in *AAA* configuration, resulting in *psuedo*-10-ring channels propagating along [100], although most if not all of the apparent channel space is probably taken up by the methylene groups of the template.

The ^{31}P MAS NMR spectrum of $(C_6H_{13}NO_3)Zn_2(HPO_3)$ showed a single sharp resonance at $\delta = 0.65$ ppm (standard 85% H_3PO_4), which is consistent with the crystal structure and typical for phosphite P.[6] The ^{13}C MAS NMR spectrum (Figure 4) showed a number of partially resolved peaks around $\delta = 50-60$ ppm (standard TMS), corresponding to the six distinct CH_2 groups in the template.

This unusual phase indicates that anionic as well cationic organic templates can help to generate extended hybrid inorganic/organic structures. This means of course, that if it can be considered in isolation, the inorganic $[Zn_2(HPO_3)]^{2+}$ component of the title compound is cationic, in contrast to the normal situation for organically templated networks, in which the framework is anionic.[3] However, an alternative view of this structure would be as an extended network of covalently interlinked neutral clusters.

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Supporting Information Available: CIF file for the title compound. This material is available free of charge via the Internet at http://pubs.acs.org.

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