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Communication

$C_4N_3OH_7 \cdot Zn(H_2O)HPO_4$, a Neutral Zincophosphate Cluster

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$C_4N_3OH_7 \cdot Zn(H_2O)HPO_4$, built up from 4-rings of $ZnO_2(H_2O)N$ and HPO_4 tetrahedra, is the first neutral, molecular, zincophosphate cluster. The unit-cell packing involves numerous O–H···O and N–H···O hydrogen bonds and $\pi \cdots \pi$ stacking interactions. Crystal data: $C_4N_3OH_7 \cdot Zn(H_2O)HPO_4$, $M_r = 292.49$, triclinic, $P\bar{1}$ (No. 2), $a = 9.2956(5)$ Å, $b = 11.2077(6)$ Å, $c = 19.8319(12)$ Å, $\alpha = 80.314(1)°$, $\beta = 78.829(1)°$, $\gamma = 89.241(1)°$, $V = 1997.7(2)$ Å^3, $Z = 4$.

A large number of organically templated zincophosphates (ZnPO's) have now been reported.[1] The organic entity, usually a protonated amine cation, is especially important in promoting the formation of new types of networks, although more exotic species have also been used.[2] A fundamental way to classify the resulting phases is in terms of the dimensionality of the inorganic component of the structure, as clusters, chains, layers, or infinite, three-dimensional networks.[3] "Zero-dimensional" clusters are the rarest type of ZnPO, with only two examples reported so far. The phases $N(CH_3)_4 \cdot Zn(H_2PO_4)_3$[4] and $C_6N_2H_{18} \cdot Zn(HPO_4)(H_2PO_4)_2$[5] contain similar inorganic groupings consisting of a central 4-ring of alternating ZnO_4 and $(H_2/H)PO_4$ tetrahedra with additional, terminal, (di)hydrogen phosphate moieties attached to Zn. In each case, the anionic cluster is charge balanced by the organic cation. Interestingly, the cluster charge (−1 and −2, respectively) differs for these phases. In this communication we report the synthesis, crystal structure, and some properties of creatinine zinc phosphate hydrate, $C_4N_3OH_7 \cdot Zn(H_2O)HPO_4$. This novel cluster is neutral and contains direct Zn−N (zinc to template) bonds.[6,7] It is the first example of a creatinine-templated inorganic network.

The title compound was prepared from a mixture of 0.814 g (10 mmol) of ZnO, 20 mL of 1 M (20 mmol) H_3PO_4, and 2.262 g (20 mmol) of creatinine (starting pH < 1). These components were shaken together in a polypropylene bottle and left at room temperature for 72 h. Product recovery by vacuum filtration resulted in 0.987 g of chunky plates of the title compound (yield based on Zn = 34%). The synthesis is easily reproducible and can be carried out at various temperatures.

An X-ray powder pattern (Bruker D8 diffractometer, Cu Kα radiation, $\lambda = 1.5418$ Å) of well-ground crystals of $C_4N_3OH_7 \cdot Zn(H_2O)HPO_4$ showed sharp peaks and was in good agreement with a simulation of the single-crystal structure, indicating phase purity. The infrared spectrum (KBr pellet method) was consistent with the crystal structure and indicated the presence of H bonding.[8] TGA (ramp at 5 °C/min in air) showed weight loss/thermal events at 180−280 °C (−6.1%; endothermic), 285−600 °C (−26.4%; several exotherms), and 600−885 °C (−15.8%; exothermic). The first of these can be ascribed to water loss (calcd 6.2%), and the overall weight loss of 48.2% is in good accord with the calculated loss of 48.1% for the transformation of $C_4N_3OH_7 \cdot Zn(H_2O)HPO_4$ to $^1/_2Zn_2P_2O_7$ and gaseous products.

The crystal structure[9] of $C_4N_3OH_7 \cdot Zn(H_2O)HPO_4$ contains 60 non-H atoms in the asymmetric unit, corresponding to two crystallographically distinct $[C_4N_3OH_7 \cdot Zn(H_2O)HPO_4]_2$ clusters (Figure 1). Each of the four zinc atoms is tetrahedrally coordinated to two O atoms bridging to P, a water molecule, and an N atom of the creatinine molecule. As this species bonds directly to zinc by formal donation of the N lone-pair electrons, it could be described as a Lewis-base

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[8] IR data: 3500−3200 (very strong, very broad), 2365, 1734, 1658, 1505, 1420, 1350, 1241, 1129, 1004, 917, 893, 852, 749, 605, 581 cm^{-1}.

[9] Bruker SMART 1000 CCD diffractometer, Mo Kα radiation, $\lambda = 0.71073$ Å,. $T = 20$ °C. The H atoms were located in difference maps and refined by riding in idealized (C−H, N−H) and as-found (O−H) positions on their parent atoms. Crystal data: $C_4N_3OH_7 \cdot Zn(H_2O)HPO_4$, $M_r = 292.49$, triclinic, $P\bar{1}$ (No. 2), $a = 9.2956(5)$ Å, $b = 11.2077(6)$ Å, $c = 19.8319(12)$ Å, $\alpha = 80.314(1)°$, $\beta = 78.829(1)°$, $\gamma = 89.241(1)°$, $V = 1997.7(2)$ Å^3, $Z = 4$, $R(F) = 0.045$, $R_w(F^2) = 0.098$.

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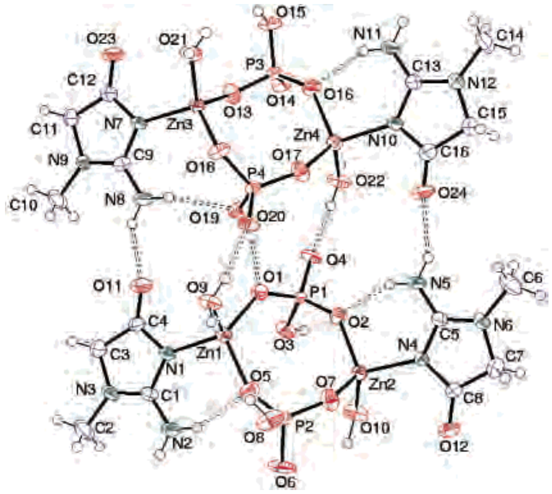

Figure 1. Asymmetric unit of $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_4$ (50% thermal ellipsoids) with hydrogen bonds indicated by dashed lines.

ligand, rather than a template.[10] The Zn−N bonds [$d_{av} = 1.998(2)$ Å] are distinctly longer than the Zn−O [$d_{av} = 1.925(2)$ Å] and Zn−OH_2 links [$d_{av} = 1.962(2)$ Å]. The four distinct tetrahedral P atoms each make two links to Zn via O and possess two terminal P−O vertices, one each of which is protonated [$d_{av}(P-O) = 1.527(2)$ Å]. The variation in individual P−OH bond lengths [e.g., P1−O3 1.576(3) Å; P2−O8 1.550(3) Å] can perhaps be correlated with intercluster H bonding in this phase (see below). The eight bridging O atoms have an average Zn−O−P bond angle of 137.3°.

The four creatinine molecules have typical geometrical parameters,[11] and their non-H atoms are essentially planar. The crystal structure study clearly shows the terminal N atoms (N2, N5, N8, and N11) to be doubly protonated; thus this species is neutral, in accordance with the charge-balancing criterion. The occurrence of a neutral template/ligand in ZnPO's is very unusual, with the recently reported layered phase $(C_3N_2H_4)_3{\cdot}Zn_4P_3O_{11}(OH)$ [$C_3N_2H_4$ = imidazole], which contains both ZnO_3N and ZnO_2N_2 tetrahedra, apparently representing the only other example.[7]

The linkage of the tetrahedra in $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_4$ results in simple, but novel, isolated 4-ring clusters consisting of alternating $ZnO_2(H_2O)N$ and HPO_4 building blocks. A similar entity (but with O−P moieties replacing the N and OH_2 units) occurs in the anionic ZnPO clusters noted above. Interestingly, a 4-ring unit of alternating ZnO_4 and PO_4 nodes has been proposed[12] as the "primary building unit" in ZnPO's, and this represents an unusual variation on this motif.

Hydrogen bonding appears to be a key factor in defining the molecular packing, and numerous intercluster N−H···O and O−H···O links are present, the latter arising from both P−OH groups and the water molecules bound to Zn. These interactions help to define a crystal structure (Figure 2) in which the clusters form distinct sheets arrayed in the (010) plane. The planes of the organic moieties are all arrayed roughly normal to [110], and there are possibly pseudo $\pi\cdots\pi$ like interactions[7] between adjacent molecules, as reflected in close (<3.7 Å) intermolecular contacts in this direction.

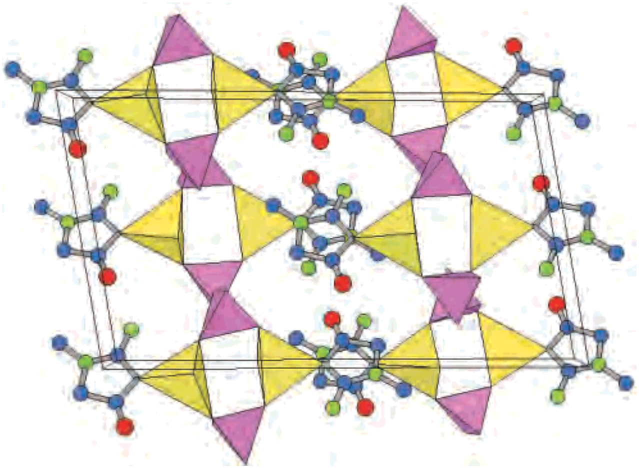

Figure 2. Unit-cell packing in $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_4$ with the $ZnO_2(H_2O)N$ and HPO_4 groups represented by mustard and purple tetrahedra, respectively. View direction: approximately [100].

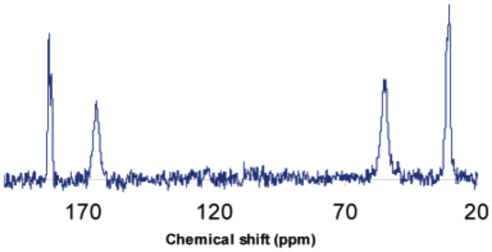

Figure 3. ^{13}C MAS NMR spectrum of $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_4$.

It is notable that the two clusters possess distinctly different *intramolecular* H bonding schemes. In particular, in the cluster containing Zn1, there are two N−H···O links to acceptor O atoms participating in Zn−O−P bridges (O2 and O5), whereas in the Zn3 cluster, one of the N−H···O acceptor species (atom O19) is a terminal P−OH vertex. Despite this, there is no significant difference in the rather acute intramolecular N−H···O bond angles (all lying between 152° and 154°), nor do the Zn−O−P bond angles show any obvious correlation with their H bonding roles.

The ^{31}P CP MAS NMR spectrum of $C_4N_3OH_7{\cdot}Zn(H_2O)HPO_4$ showed four overlapped resonances of approximately equal intensity at $\delta = -1.49, -2.15, -2.67$, and -3.10 (external standard 85% H_3PO_4), which is consistent with the crystal structure results (four independent P atoms in similar chemical environments). Similar ^{31}P chemical shifts have been seen in other zincophosphates.[13] The ^{13}C CP MAS NMR spectrum (Figure 3) showed four resonances of roughly equal intensity at $\delta = 182.5$ (doublet), 164.8 (broad), 55.4 (broad doublet), and 30.5 (doublet) (standard Me_4Si), accompanied by spinning sidebands. On the basis of simple

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chemical shift calculations,[14] we attribute these four signals to the carbonyl (e.g., C4 in Figure 1), guanidinium-like (C1), methylene (C3), and terminal methyl (C2) carbon atoms, respectively. The calculated chemical shifts are 190, 120−160 (uncertain), 56.2, and 30.4 ppm, respectively. The crystal structure indicates that there are four distinct carbon atoms per peak; the doublets and broad peaks may thus represent partial resolution of these signals, although the broadening may also arise from $^{13}C-^{15}N$ coupling.

Gentle hydrothermal treatment of $C_4N_3OH_7 \cdot Zn(H_2O)HPO_4$ single crystals (heat at 80 °C in water for 12 h) resulted in complete amorphization of the crystal structure, although their platy morphology was relatively unaffected. By comparison,[5] $C_6N_2H_{18} \cdot Zn(HPO_4)(H_2PO_4)_2$ showed a facile transformation to a new layered structure under similar conditions, in accordance with the aufbau transformation principle of open-framework structures.[15]

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Supporting Information Available: A 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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