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Synthesis and structure of a layered zinc phosphate–acetate, $[C_5H_{10}NH_2]_2[Zn(ZnO_2CCH_3)(PO_4)(HPO_4)]$

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The solution-mediated synthesis and single crystal structure of an inorganic–organic hybrid solid $[C_5H_{10}NH_2]_2$-$[Zn(ZnO_2CCH_3)(PO_4)(HPO_4)]$, **I**, is presented. The structure of **I** is built up from a network of ZnO_4, $ZnO_3(OAc)$ and $PO_3(OH)$ tetrahedral units, connected through their vertices, forming macroanionic two-dimensional sheets with four- and eight-membered apertures. The acetate groups are perpendicular to the plane of the layers and project from the Zn center into the inter-lamellar region. The charge compensating organic cations, piperidinium, are also located in between the layers. The connectivity within the layers shows close similarity to the three-dimensional zinc phosphate with gismondine topology.

Introduction

Open-framework metal phosphates have grown to be one of the largest family of inorganic solids synthesized during the last decade or so.[1] Of the many materials that have been synthesized and characterized, those of zinc occupy an important position.[2–5] Of these, the zinc phosphate, ND-1, is prominent for the extra-large one-dimensional channels bound by 24-T atoms (T = Zn, P).[5] It has been established that the bis-bidentate oxalates readily substitute for phosphates in some of the open-framework structures forming inorganic–organic hybrid structures. Thus, phosphate–oxalate solids with open architectures have been reported for V,[6] Mn,[7,8] Fe,[9–11] Co,[12] Zn,[13] Al,[14,15] Ga,[16] In[17] and Sn.[18] Unlike the phosphate–oxalates, hybrid structures based on phosphate–acetates have been rare. A zinc phosphate–acetate, $[CH_3CH_2CH_2NH_3]_4[Zn_3Zn(O_2CCH_3)(PO_4)(HPO_4)_3(H_2PO_4)(CH_3CO_2)]$, has been synthesized and characterized recently.[19] During a program of investigations on the formation of inorganic–organic hybrid structures, we have now discovered the second member in the family of zinc phosphate–acetates, **I**, $[C_5H_{10}NH_2]_2[Zn(ZnO_2CCH_3)(PO_4)(HPO_4)]$, prepared under mild conditions in the presence of piperidine. The structure of **I** consists of macroanionic inorganic zinc phosphate layers with the acetate group attached to the Zn center projecting in to the inter-lamellar region. A careful examination of the layer architecture of **I** shows close similarity to the three-dimensional zinc phosphate with gismondine topology.[20]

Experimental

Synthesis of $[C_5H_{10}NH_2]_2[Zn(ZnO_2CCH_3)(PO_4)(HPO_4)]$, I

The zinc phosphate–acetate, $[C_5H_{10}NH_2]_2[Zn(ZnO_2CCH_3)(PO_4)(HPO_4)]$, **I**, was synthesized under non-hydrothermal conditions starting from a mixture containing piperidine. In a typical synthesis, 0.6 ml of piperidine was added to a mixture of 0.75 ml THF and 0.25 ml H_2O, followed by the addition of 0.441 g of zinc acetate tetrahydrate ($Zn(OAc)_2{\cdot}4H_2O$) under continuous stirring. To this mixture 0.3 ml of phosphoric acid (85 wt%) was added slowly (dropwise) and the mixture was homogenized for 30 min at room temperature. The final mixture with the composition, $Zn(OAc)_2{\cdot}4H_2O : 2.35H_3PO_4 : 3.6C_5N_1H_{11} : (4.7THF + 7H_2O)$, was sealed in a 7 ml PTFE-lined acid digestion bomb and heated at 100 °C for 48 h under autogenous pressure. The resulting product, a mixture of powder and a few needle-like single crystals, was filtered under vacuum and dried at ambient temperature. The yield of **I** was very low (≈10%) and any modification in the composition or reaction conditions neither produced a pure phase nor improved the yield. The single crystals were easily separated from the mixture under a polarizing microscope. The powder was found to be a condensed zinc phosphate with very sharp XRD lines that correspond to the mineral hoepite, $Zn_3(PO_4)_2{\cdot}4H_2O$.[21] EDAX analysis gave a Zn : P ratio of 1 : 1 which agrees with the composition obtained from the single-crystal X-ray study. The synthesis of **I** appears to be sensitive to the sequence of addition as condensed zinc phosphates result with changes in the mode of addition, for the same reaction composition and conditions.

Thermogravimetric analysis (TGA) has been carried out on **I** in an oxygen atmosphere in the temperature range 25 to 700 °C. The studies show two distinct mass losses. The mass loss of 33.2% in the range 250–325 °C corresponds well with the loss of some adsorbed water and amine (calc. 31.1%) and the second loss of 14.1% in the range 350–400 °C corresponds to the loss of the bonded acetate groups and hydroxyls of the $PO_3(OH)$ units (calc. 13.7%). The calcined sample is poorly crystalline and corresponds to the condensed zinc phosphate, $Zn_2P_2O_7$ (JCPDS: 11-0026).

X-Ray crystallography

A suitable single crystal of compound **I** (0.12 × 0.16 × 0.20 mm) was carefully selected under a polarizing microscope and glued to a thin glass fiber. Crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å) operating at 40 kV and 40 mA. Pertinent details for the structure determinations are presented in Table 1. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS program.[22] Other effects, such as absorption by glass fiber *etc.* were simultaneously corrected. The structure was

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Table 1 Crystal data and structure refinement parameters for **I**, $[C_5H_{10}NH_2]_2[Zn(ZnO_2CCH_3)(PO_4)(HPO_4)]$

Empirical formula	$Zn_2P_2O_{10}N_2C_{12}H_{28}$
Formula mass	553.04
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	9.1374(10)
b/Å	9.1963(11)
c/Å	12.991(2)
α/°	91.421(2)
β/°	104.988(2)
γ/°	110.162(2)
V/Å^3	982.1(2)
Z	2
T/K	293
μ/mm^{-1}	2.660
Reflections: total, observed	4129, 2767
R indexes $[I > 2\sigma(I)]$	$R_1 = 0.0450^a$, $wR_2 = 0.0917^b$

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; ^{b} $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2(F_c)^2]/3$, where $a = 0.0383$ and $b = 0.0$.

solved and refined using the SHELXTL-PLUS suite of programs.[23] The direct methods solution readily established all the heavy atom positions (Zn and P) and facilitated the identification of most of the other fragments (O, C, N and H) from the difference Fourier maps. All the hydrogen atoms were initially located in the difference Fourier maps and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions for all the atoms and anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares refinement against $|F^2|$ was carried out using the SHELXTL-PLUS[23] suite of programs. Details of the final refinements are given in Table 1. The selected bond distances and angles for **I** are listed in Tables 2 and 3.

CCDC reference number 177858.

See http://www.rsc.org/suppdata/dt/b2/b200642c/ for crystallographic data in CIF or other electronic format.

Results and discussion

The asymmetric unit of **I** contains 28 non-hydrogen atoms as shown in Fig. 1, of which 16 atoms belong to the 'framework' and 12 atoms to two 'guest' molecules. There are two crystallographically distinct Zn and P atoms. The zinc atoms are tetrahedrally coordinated by their O atom neighbors with Zn–O bond lengths in the range 1.894(5)–1.982(4) Å (av. Zn(1)–O = 1.937, Zn(2)–O = 1.947 Å, see Table 2) and O–Zn–O bond angles are in the range 104.2(2)–124.2(2)° (av. O–Zn(1)–O = 109.3, O–Zn(2)–O = 109.6°, see Table 3). Of the two zinc atoms, Zn(1) makes four Zn–O–P bonds and Zn(2) makes only three such bonds, and posseses a terminal acetate group. The Zn–O–P bond angles are fairly widespread with an average of 136.8°. Of the two phosphorus atoms, P(1) makes three and possesses one terminal linkage whilst P(2) makes four P–O–Zn bonds. The P–O distances are in the range 1.497(5)–1.577(5) Å (av. P(1)–O = 1.537 and P(2)–O = 1.532 Å) and O–P–O bond angles have an average value of 109.5°. The terminal P(1)–O(9) linkage with a distance of 1.577(5) is an –OH group. The total negative charge on the framework of −2 is balanced by the presence of two protonated piperidine molecules. Bond valence sum calculations[24] on the framework agree with the above results.

Table 2 Selected bond distances (Å) in **I**, $[C_5H_{10}NH_2]_2[Zn(ZnO_2CCH_3)(PO_4)(HPO_4)]^a$

Zn(1)–O(1)	1.918(5) [0.561]	P(1)–O(4)	1.497(5) [1.383]
Zn(1)–O(2)	1.949(5) [0.516]	P(1)–O(8)	1.530(5) [1.265]
Zn(1)–O(3)	1.940(5) [0.528]	P(1)–O(2)#1	1.542(5) [1.225]
Zn(1)–O(4)	1.941(5) [0.527]	P(1)–O(9)	1.577(5) [1.114]
Σ (Zn–O)	**2.132**	**Σ (P–O)**	**4.987**
Zn(2)–O(5)	1.894(5) [0.598]	P(2)–O(5)#2	1.508(5) [1.343]
Zn(2)–O(6)	1.943(5) [0.524]	P(2)–O(1)#3	1.535(5) [1.248]
Zn(2)–O(7)	1.969(5) [0.489]	P(2)–O(6)#1	1.536(5) [1.245]
Zn(2)–O(8)	1.982(4) [0.472]	P(2)–O(3)	1.548(5) [1.205]
Σ (Zn–O)	**2.083**	**Σ (P–O)**	**5.041**
C(1)–O(7)	1.255(10)	C(1)–O(10)	1.248(10)
C(1)–C(2)	1.512(10)		
		Organic amine	
$(N–C)_{av.}$	1.473	$(C–C)_{av.}$	1.498

#1 $-x + 1, -y + 1, -z + 1$; #2 $x - 1, y - 1, z$; #3 $-x, -y + 1, -z + 1$. ^{a} [BVS] = Bond Valence Sum.

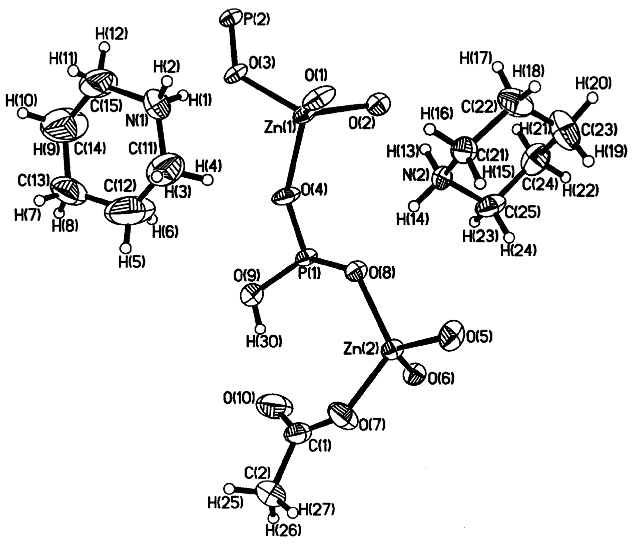

Fig. 1 ORTEP[32] plot showing the asymmetric unit in **I**, $[C_5H_{10}NH_2]_2[Zn(ZnO_2CCH_3)(PO_4)(HPO_4)]$. Thermal ellipsoids are given at 50% probability.

Table 3 Selected bond angles (°) in **I**, $[C_5H_{10}NH_2]_2[Zn(ZnO_2CCH_3)(PO_4)(HPO_4)]$

O(1)–Zn(1)–O(3)	109.7(2)	O(4)–P(1)–O(8)	112.5(3)
O(1)–Zn(1)–O(4)	107.1(2)	O(4)–P(1)–O(2)#1	111.6(3)
O(3)–Zn(1)–O(4)	104.2(2)	O(8)–P(1)–O(2)#1	111.2(3)
O(1)–Zn(1)–O(2)	104.8(2)	O(4)–P(1)–O(9)	104.8(3)
O(3)–Zn(1)–O(2)	124.4(2)	O(8)–P(1)–O(9)	109.4(3)
O(4)–Zn(1)–O(2)	105.7(2)	O(2)#1–P(1)–O(9)	106.9(3)
O(5)–Zn(2)–O(6)	121.9(2)	O(5)#2–P(2)–O(1)#3	108.5(3)
O(5)–Zn(2)–O(7)	103.7(2)	O(5)#2–P(2)–O(6)#1	110.7(3)
O(6)–Zn(2)–O(7)	104.8(2)	O(1)#3–P(2)–O(6)#1	108.6(3)
O(5)–Zn(2)–O(8)	101.9(2)	O(5)#2–P(2)–O(3)	110.8(3)
O(6)–Zn(2)–O(8)	107.0(2)	O(1)#3–P(2)–O(3)	109.5(3)
O(7)–Zn(2)–O(8)	118.4(2)	O(6)#1–P(2)–O(3)	108.7(3)
Zn(1)–O(1)–P(2)#3	134.9(3)	Zn(2)–O(5)–P(2)#4	166.6(4)
Zn(1)–O(2)–P(1)#1	125.8(3)	Zn(2)–O(6)–P(2)#1	125.9(3)
Zn(1)–O(3)–P(2)	129.2(3)	Zn(2)–O(7)–C(1)	123.1(6)
Zn(1)–O(4)–P(1)	148.2(3)	Zn(2)–O(8)–P(1)	126.6(3)
O(7)–C(1)–O(10)	125.7(8)	O(7)–C(1)–C(2)	117.7(8)
O(10)–C(1)–C(2)	116.6(9)		
		Organic amine	
$(N–C–C)_{av.}$	114.6	$(C–C–C)_{av.}$	113.5

#1 $-x + 1, -y + 1, -z + 1$; #2 $x - 1, y - 1, z$; #3 $-x, -y + 1, -z + 1$; #4 $x + 1, y + 1, z$.

The framework structure of **I** is built from strictly alternating ZnO_4, $ZnO_3(OAc)$ and $(H)PO_4$ tetrahedra that are linked through their vertices forming macroanionic layers. The connectivity between the tetrahedra results in four-membered rings, of which there are two types. The first type is made from $Zn(1)O_4$ and $P(2)O_4$ tetrahedra and possesses no terminal linkages whilst the second is constructed from $Zn(2)O_3(OAc)$

Table 4 Important hydrogen bond interactions in **I**, $[C_5H_{10}NH_2]_2[Zn(ZnO_2CCH_3)(PO_4)(HPO_4)]$

D–H ··· A	D–H/Å	H ··· A/Å	D ··· A/Å	D–H ··· A/°
N(1)–H(1) ··· O(3)	0.90	1.90	2.802(6)	177
N(1)–H(2) ··· O(6)	0.90	2.16	2.954(7)	147
N(2)–H(13) ··· O(2)	0.90	2.06	2.941(1)	165
N(2)–H(14) ··· O(8)	0.90	2.04	2.879(8)	156
O(9)–H(30) ··· O(10)[a]	0.82	1.82	2.635(9)	173
C(11)–H(3) ··· O(4)	0.97	2.56	3.419(8)	147
C(14)–H(9) ··· O(7)	0.97	2.53	3.493(3)	172
C(15)–H(11) ··· O(10)	0.97	2.42	3.188(9)	136
C(21)–H(15) ··· O(1)	0.97	2.57	3.529(4)	168
C(25)–H(23) ··· O(3)	0.97	2.55	3.441(3)	152
C(25)–H(23) ··· O(4)	0.97	2.52	3.258(1)	133

[a] Intra-framework.

and P(1)O_3(OH) each possessing a terminal acetate and an –OH group, respectively. The connectivity between the four-membered rings results in a zig-zag ladder-type arrangement, and two such ladders are connected *via* oxygen atoms forming a layer with an eight-membered aperture as shown in Fig. 2. The layer arrangement can also be visualized to result from a connectivity involving the double crankshaft chains. The double crankshaft chains, employing Liebau notation,[25] are useful in describing the zeolitic structures.[20] The terminal acetate groups project in a direction perpendicular to the plane of this layer on either side from the Zn center. The protonated amine molecules are located in between the layers. The relative position of the layers along with the hanging acetate groups appears to be forming pseudo 14-membered channels along the *a* direction.

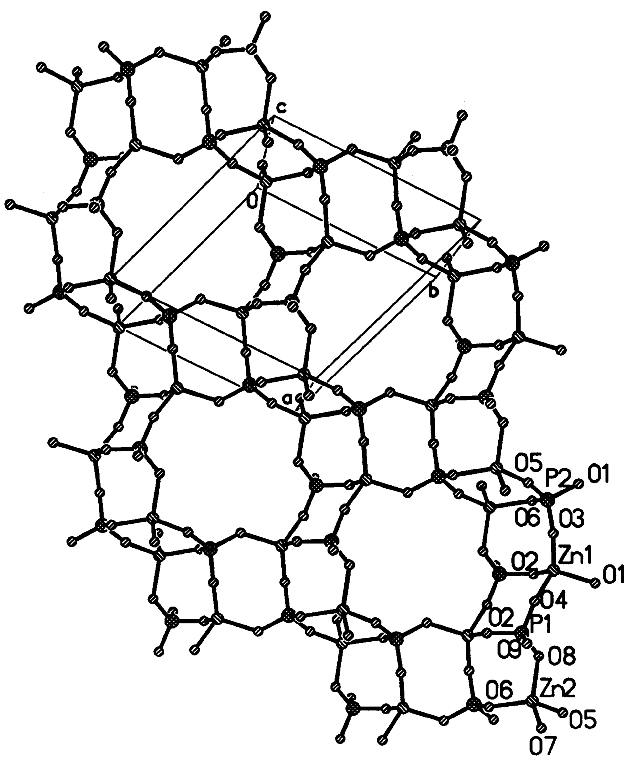

Fig. 2 Structure of **I** in the *ab* plane showing a single layer. Acetate groups are not shown for clarity. Note the crankshaft chains (see text).

The structure of **I** possesses a large number of hydrogen bond interactions involving the framework oxygen and hydrogen atoms of the amine molecule. Thus, strong N–H ··· O (av. H ··· O = 2.041 Å) and C–H ··· O (av. H ··· O = 2.526 Å) interactions are observed in **I**. These values are typical of strong hydrogen bond interactions.[26] In addition, strong *intra-layer* hydrogen bond interaction between the free acetate oxygen atom (non-bonded) and the terminal –OH group (H ··· O = 1.820 Å and O–H ··· O = 173.1°) are also observed. It appears that these hydrogen bond interactions are necessary for the stability of the lower-dimensional solids. The complete list of the hydrogen bond interactions observed in **I** is presented in Table 4.

Comparing the structure of **I** with the previously known zinc phosphate–acetate, $[CH_3CH_2CH_2NH_3]_4[Zn_3Zn(O_2CCH_3)(PO_4)(HPO_4)_3(H_2PO_4)(CH_3CO_2)]$, reveals some interesting features.[19] Both the structures possess typical layered architecture with the acetate groups projecting from the plane of the layer into the inter-lamellar region and are synthesized in the presence of a monoamine, piperidine in **I** and propylamine in the earlier case. It is of interest to note that there are only a few zinc phosphates that have been prepared using a monoamine, under hydrothermal conditions.[27,28] The macroanionic layers in the case of $[CH_3CH_2CH_2NH_3]_4[Zn_3Zn(O_2CCH_3)(PO_4)(HPO_4)_3(H_2PO_4)(CH_3CO_2)]$, are made from a vertex linkage of ZnO_4, ZnO_3(OAc) and $(H/H_2)PO_4$ tetrahedra, forming four-, six- and eight-membered apertures. The inter-lamellar space contains, in addition to the protonated propylamine molecules, free acetate groups as well. In **I**, the layers are made from ZnO_4, ZnO_3(OAc) and (H)PO_4 tetrahedral units forming four- and eight-membered apertures. There are, however, no free acetate groups in the inter-lamellar region in **I**. In the earlier phosphate–acetate, the hanging acetate groups interact with those from a neighboring layer to form unusual C–H ··· O hydrogen bonded acetate dimers. In **I**, no acetate dimers are observed.

The layered architecture of **I** appears to have some clues towards our understanding of the formation of these solids. Recently an Aufbau principle for the building up of three-dimensional structures from structures of lower dimensionalities has been proposed for open-framework zinc phosphates.[29] A careful examination of the layers in **I** reveals some structural similarities between the aluminosilicate gismondine,[15] especially with respect to the connectivity within the layers. As mentioned earlier, the acetate groups project from the Zn center in a perpendicular direction to the plane of the layers. The layers can be joined together, when the acetate group leaves the Zn center, *via* the terminal Zn–O and P–O(H) linkage giving rise to the gismondine structure. Zinc phosphates with gismondine structures have been synthesized before, but in the presence of different amine molecules.[4,30,31]

In summary, a new inorganic–organic hybrid material, $[C_5H_{10}NH_2]_2[Zn(ZnO_2CCH_3)(PO_4)(HPO_4)]$, **I**, has been synthesized, employing ordinary conditions, and characterized. In addition to being only the second member of a potentially large family of such compounds, **I** also holds some clues for our understanding of the formation of these solids. We are currently pursuing this theme to prepare more hybrid solids.

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