

A zinc phosphate oxalate with phosphate layers pillared by the oxalate units

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An open-framework phosphate oxalate of zinc, of composition $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Zn}_6(\text{PO}_4)_4(\text{C}_2\text{O}_4)]$, **1**, has been synthesized, for the first time, employing hydrothermal methods in the presence of ethylenediamine. The structure comprises a network of $\text{Zn}(1)\text{O}_5$, $\text{Zn}(2)\text{O}_4$, $\text{Zn}(3)\text{O}_5$ polyhedra and PO_4 tetrahedra connected through their vertices forming neutral layers bridged by the oxalate units, giving one-dimensional channels. The presence of Zn in tetrahedral, trigonal-bipyramidal and square-pyramidal coordinations, and the formation of neutral layers, are noteworthy features.

Introduction

Metal phosphate oxalates constitute an interesting class of inorganic-organic hybrid structure. These compounds generally contain simple sheet-like metal phosphate layers connected by oxalate bridges.^{1,2} The open-framework phosphate oxalates reported so far include those of V,³ Mn,⁴ Fe,⁵ Co,⁶ Al,⁶ Ga,⁷ In⁸ and Sn.⁹ Recently, phosphate oxalates of Fe and Ga in which the oxalate unit not only acts as a bridge between the layers but is also a constituent of the layer have been reported.^{1,7} We have isolated an open-framework phosphate oxalate of zinc, for the first time, which has several structural features, different from those of the other phosphate oxalates. This material with the composition $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Zn}_6(\text{PO}_4)_4(\text{C}_2\text{O}_4)]$, **1**, has Zn in tetrahedral, trigonal-bipyramidal and square-pyramidal coordinations, and comprises two-dimensional, zinc phosphate layers connected by oxalate units. One-dimensional channels result from such bonding. In this paper the synthesis and structure of **1** are presented.

Experimental

The zinc phosphate oxalate, **1**, was synthesized under hydrothermal conditions starting with the tris(1,3-diaminopropane)-zinc complex $\{\text{Zn}[\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_2]_3\}\text{Cl}_2$ (Zn-DAP) which was prepared and characterized using a standard procedure.¹⁰ In a typical synthesis 0.5 g of Zn-DAP was dispersed in 1.2 ml of water. 0.21 g of oxalic acid and 0.03 ml of H_3PO_4 (85 wt%) were added and the mixture stirred until homogeneous. The mixture with composition Zn-DAP: $2.5\text{H}_2\text{C}_2\text{O}_4 \cdot 0.5\text{H}_3\text{PO}_4 \cdot 100\text{H}_2\text{O}$ was transferred to a 7 ml acid digestion bomb and heated at 170 °C for 24 h under autogenous pressure. The resulting product containing large colorless rod-like crystals along with some white powder was filtered off, washed with water and dried under ambient conditions. The single crystals were separated easily from the bulk by ultrasonication. Powder X-ray diffraction of the white powder indicated that it is a zinc phosphate, $[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}_4(\text{PO}_4)_2(\text{HPO}_4)_2]$, reported recently.¹¹ The yield of **1** was about 35%. An EDXA (energy dispersive X-ray analysis) indicated a Zn:P ratio of 3:2, consistent with the single crystal data.

A suitable single crystal of compound **1** was carefully selected under a polarizing microscope and glued to a thin glass fiber. Crystal structure determination by X-ray diffraction at 298 K was performed on a Siemen's Smart-CCD diffractometer

(Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$). Pertinent details for the structure determination are presented in Table 1. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS program.¹² Other effects, such as absorption by glass fiber *etc.*, were simultaneously corrected. The structure was solved by direct methods using SHELXS 86,¹³ which readily established all the heavy atom positions (Zn and P) and facilitated identification of most of the other fragments (O, C, N and H) from Fourier difference maps. One of the carbon atoms of the amine molecule was disordered with a SOF (site occupation factor) of 0.5. The hydrogens, though found in the Fourier difference maps, were not included in the final refinement, due to disorder of the carbon atom. The last cycles of refinement included atomic positions for all the atoms and anisotropic thermal parameters for all non-hydrogen atoms. Full-matrix least-squares refinement against $|F^2|$ was carried out using the SHELXTL PLUS¹⁴ suite of programs. Details of the final refinements are given in Table 1. Selected bond distances and angles are given in Tables 2 and 3.

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See <http://www.rsc.org/suppdata/dt/b0/b007980o/> for crystallographic files in .cif format.

Results and discussion

The asymmetric unit of compound **1** contains 20 non-hydrogen atoms, of which 15 belong to the framework and 5 to the guest (Fig. 1). There are three crystallographically distinct Zn and two P atoms in the asymmetric unit. Of the 10 oxygen atoms in the asymmetric unit, 4 are three-coordinated connecting two Zn and one P atoms (40%). This is rather high for an

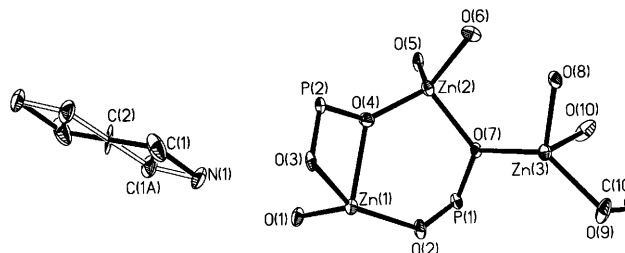
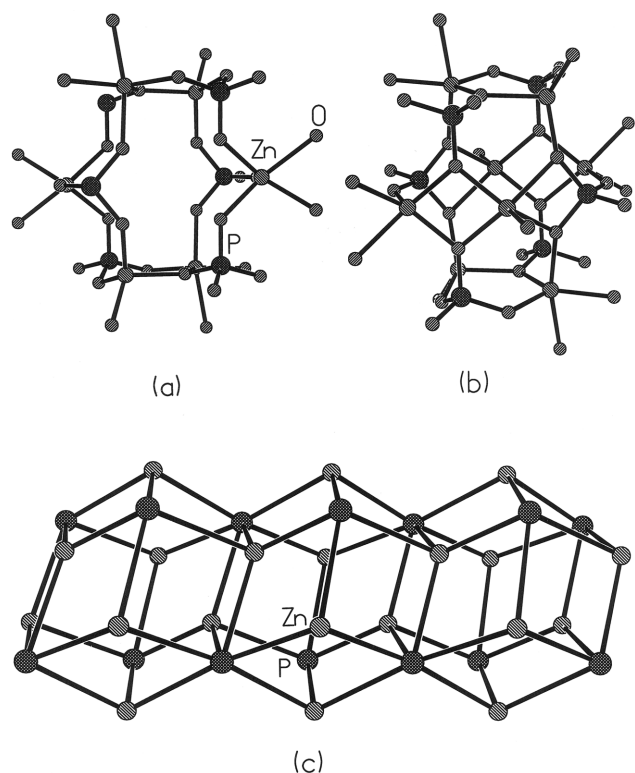


Fig. 1 An ORTEP¹⁵ plot of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Zn}_6(\text{PO}_4)_4(\text{C}_2\text{O}_4)]$. Thermal ellipsoids are given at 50% probability.

Table 1 Crystal data and structural refinement parameters for $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Zn}_6(\text{PO}_4)_4(\text{C}_2\text{O}_4)] \mathbf{1}$

Empirical formula	$\text{C}_{15}\text{H}_6\text{NO}_{10}\text{P}_2\text{Zn}_3$
Formula mass	456.12
Crystal system	Triclinic
Space group	$P\bar{1}$
$a/\text{\AA}$	5.00300(10)
$b/\text{\AA}$	8.5434(3)
$c/\text{\AA}$	12.4336(5)
$\alpha/^\circ$	92.99
$\beta/^\circ$	97.132(2)
$\gamma/^\circ$	91.465(2)
$V/\text{\AA}^3$	526.33(3)
Z	2
μ/mm^{-1}	7.131
Total data collected	2197
Unique data	1476
Observed data [$I > 2\sigma(I)$]	1185
R_{int}	0.030
$R1, wR2$ [$I > 2\sigma(I)$]	0.053, 0.129
(all data)	0.070, 0.142

**Fig. 2** (a) The double-six ring in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Zn}_6(\text{PO}_4)_4(\text{C}_2\text{O}_4)]$. (b) The basic building unit formed by capping of the double-six ring. (c) One-dimensional tubes formed by face sharing of the 3-membered rings. Only the T-atom (T = Zn or P) connectivity is shown.

open-framework material and gives rise to unusual structural features. Thus, **1** comprises a network of $\text{Zn}(2)\text{O}_4$, $\text{Zn}(1)\text{O}_5$, $\text{Zn}(3)\text{O}_5$ and PO_4 units connected through their vertices forming neutral layers. The oxalate unit connects these layers in an out-of-plane manner acting as a pillar, and charge neutrality is achieved by the incorporation of the diprotonated amine.

Of the three distinct Zn atoms, two are five-coordinated [$\text{Zn}(1)$ and $\text{Zn}(3)$] with square-pyramidal and trigonal bipyramidal arrangements and the other [$\text{Zn}(2)$] is tetrahedrally coordinated with oxygen atoms. The Zn–O bond distances are in the range 1.924(6)–2.242(7) Å [average Zn(1)–O_{av} 2.053, Zn(2)–O 1.955 and Zn(3)–O 2.052 Å] and O–Zn–O angles in the range 68.1(3)–166.7(3)° [average O–Zn(1)–O 117.9, O–Zn(2)–O 109.4, O–Zn(3)–O 106.9°]. The Zn atoms are connected to P atoms *via* oxygen links with average Zn–O–P bond angle of 122.7°. The two independent P atoms are tetrahedrally coordinated with oxygens with average P–O distance

Table 2 Selected bond distances (Å) in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Zn}_6(\text{PO}_4)_4(\text{C}_2\text{O}_4)]$

Zn(1)–O(1)	1.930(7)	Zn(3)–O(9)	2.040(7)
Zn(1)–O(2)	1.994(7)	Zn(3)–O(3) ^{#3}	2.064(6)
Zn(1)–O(2) ^{#2}	2.027(7)	Zn(3)–O(10)	2.160(7)
Zn(1)–O(3)	2.073(7)	P(1)–O(8) ^{#4}	1.520(8)
Zn(1)–O(4)	2.242(7)	P(1)–O(6) ^{#4}	1.529(7)
Zn(2)–O(5)	1.924(6)	P(1)–O(2)	1.534(7)
Zn(2)–O(4)	1.928(7)	P(1)–O(7)	1.551(7)
Zn(2)–O(6)	1.937(7)	P(2)–O(1) ^{#5}	1.495(8)
Zn(2)–O(7)	2.030(7)	P(2)–O(5) ^{#6}	1.531(7)
Zn(3)–O(8)	1.965(7)	P(2)–O(3)	1.556(7)
Zn(3)–O(7)	2.033(6)	P(2)–O(4)	1.559(7)
C(10) ^{#1} –O(10)	1.243(14)	C(10)–C(10) ^{#1}	1.52(2)
C(10)–O(9)	1.269(13)		

Organic moiety

C(1)–N(1)	1.41(3)	C(1)–C(2)	1.33(3)
C(1A)–N(1)	1.39(3)	C(1A)–C(2)	1.33(2)

Symmetry operations used to generate equivalent atoms: #1 $-x, -y + 2, -z - 1$; #2 $-x + 1, -y + 2, -z$; #3 $-x, -y + 2, -z$; #4 $x + 1, y, z$; #5 $x - 1, y, z$; #6 $-x, -y + 1, -z$.

Table 3 Selected bond angles (°) in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Zn}_6(\text{PO}_4)_4(\text{C}_2\text{O}_4)]$

O(1)–Zn(1)–O(2)	112.0(3)	O(8) ^{#4} –P(1)–O(2)	109.5(4)
O(1)–Zn(1)–O(2) ^{#2}	107.3(3)	O(6) ^{#4} –P(1)–O(2)	107.4(4)
O(2)–Zn(1)–O(2) ^{#2}	80.6(3)	O(8) ^{#4} –P(1)–O(7)	108.6(4)
O(1)–Zn(1)–O(3)	101.4(3)	O(6) ^{#4} –P(1)–O(7)	108.5(4)
O(2)–Zn(1)–O(3)	145.3(3)	O(2)–P(1)–O(7)	108.6(4)
O(2) ^{#2} –Zn(1)–O(3)	98.9(3)	O(1) ^{#5} –P(2)–O(5) ^{#5}	108.4(4)
O(1)–Zn(1)–O(4)	101.4(3)	O(1) ^{#5} –P(2)–O(3)	112.7(4)
O(2)–Zn(1)–O(4)	95.3(3)	O(5) ^{#6} –P(2)–O(3)	109.1(4)
O(2) ^{#2} –Zn(1)–O(4)	150.4(3)	O(1) ^{#5} –P(2)–O(4)	113.6(4)
O(3)–Zn(1)–O(4)	68.1(3)	O(5) ^{#6} –P(2)–O(4)	111.0(4)
O(5)–Zn(2)–O(4)	115.1(3)	O(3)–P(2)–O(4)	102.0(4)
O(5)–Zn(2)–O(6)	103.1(3)	P(2) ^{#4} –O(1)–Zn(1)	134.6(5)
O(4)–Zn(2)–O(6)	123.6(3)	P(1)–O(2)–Zn(1)	131.7(5)
O(5)–Zn(2)–O(7)	112.1(3)	P(1)–O(2)–Zn(1) ^{#2}	128.5(4)
O(4)–Zn(2)–O(7)	100.2(3)	Zn(1)–O(2)–Zn(1) ^{#2}	99.4(3)
O(6)–Zn(2)–O(7)	102.0(3)	P(2)–O(3)–Zn(3) ³	142.7(4)
O(8)–Zn(3)–O(7)	107.5(3)	P(2)–O(3)–Zn(1)	96.3(3)
O(8)–Zn(3)–O(9)	123.9(3)	Zn(3) ^{#3} –O(3)–Zn(1)	120.9(3)
O(7)–Zn(3)–O(9)	127.8(3)	P(2)–O(4)–Zn(2)	138.8(4)
O(8)–Zn(3)–O(3) ^{#3}	93.1(3)	P(2)–O(4)–Zn(1)	89.8(3)
O(7)–Zn(3)–O(3) ^{#3}	99.2(3)	Zn(2)–O(4)–Zn(1)	127.3(3)
O(9)–Zn(3)–O(3) ^{#3}	87.5(3)	P(2) ^{#6} –O(5)–Zn(2)	128.3(4)
O(8)–Zn(3)–O(10)	93.8(3)	P(1) ^{#5} –O(6)–Zn(2)	123.2(4)
O(7)–Zn(3)–O(10)	89.6(3)	P(1)–O(7)–Zn(2)	119.9(4)
O(9)–Zn(3)–O(10)	79.2(3)	P(1)–O(7)–Zn(3)	117.6(4)
O(3) ^{#3} –Zn(3)–O(10)	166.7(3)	Zn(2)–O(7)–Zn(3)	120.3(3)
O(8) ^{#4} –P(1)–O(6) ^{#4}	114.2(4)	P(1) ^{#5} –O(8)–Zn(3)	121.7(4)
O(10) ^{#1} –C(10)–O(9)	125.2(11)	O(10) ^{#1} –C(10)–O(10) ^{#1}	117.0(12)

Organic moiety

C(2)–C(1)–N(1)	130(2)	C(2)–C(1A)–N(1)	131(2)
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Symmetry operations used to generate equivalent atoms: #1 $-x, -y + 2, -z - 1$; #2 $-x + 1, -y + 2, -z$; #3 $-x, -y + 2, -z$; #4 $x + 1, y, z$; #5 $x - 1, y, z$; #6 $-x, -y + 1, -z$.

of 1.534 Å and O–P–O angle of 109.5°. These are typical values observed in zinc phosphates.^{16,17} The C–O bond distances and O–C–O angles are as expected for this type of bonding (Tables 2 and 3).

The basic building unit of compound **1**, shown in Fig. 2(a), is a double-six ring formed by four 4-membered rings and two 3-membered rings. The double-six rings present in zeolites are generally formed by six 4-membered rings alone.¹⁸ A square-pyramidal Zn ($\text{Zn}(1)\text{O}_5$) caps the six-membered ring through 3-coordinated oxygen atoms forming 2-membered Zn_2O_2 and ZnPO_2 units along with a 3-membered Zn_2PO_3 unit (Fig. 2b). The 3-membered rings are joined through their faces forming a pearl bead like arrangement as shown in Fig. 2(c). These

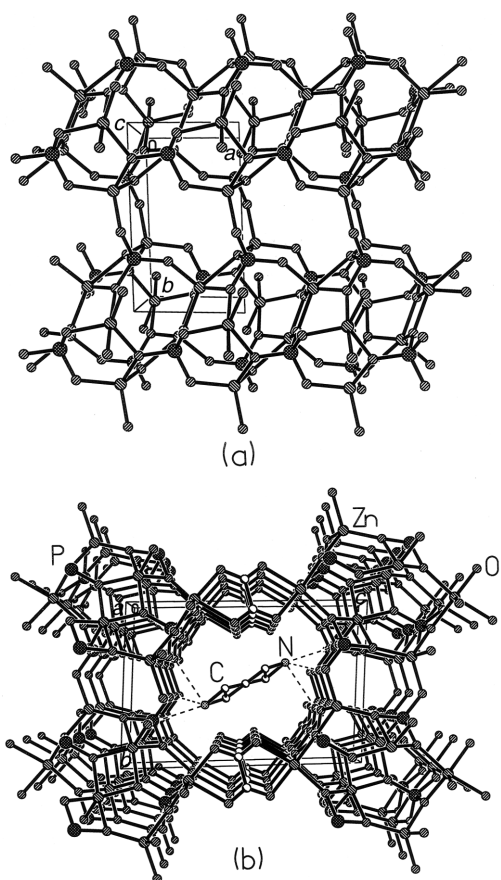


Fig. 3 (a) The metal phosphate layer in compound **1**. Note the formation of a double-six ring by the connectivity between two tubes. (b) The connectivity between the inorganic phosphate layers and the oxalate units. The amine molecule occupies the one-dimensional channels.

units are further connected to one another by the oxygens of the $\text{Zn}(\text{2})\text{O}_4$ tetrahedra *via* another double-six ring, forming the two-dimensional arrangement shown in Fig. 3(a). This is the first instance of the formation of such layers in open-framework structures. The layers are bridged by the oxalate units giving rise to one-dimensional channels ($6.1 \times 7.9 \text{ \AA}$, shortest atom–atom contacts not including the van der Waals radii) along the *a* axis as revealed in Fig. 3(b). The connectivity between the oxalates and the layers occurs through the $\text{Zn}(\text{3})\text{O}_5$

trigonal bipyramidal units. The diprotonated 1,3-diaminopropane molecules located within the channels are disordered (Fig. 3(b)).

It is instructive to compare the structural features of compound **1** with other phosphate oxalates reported.^{1–9} **1** is composed of neutral $\text{Zn}_6(\text{PO}_4)_4$ layers pillared by oxalate units, just as in the iron phosphate oxalates.¹ The Zn atoms are 4- or 5-coordinated unlike the metal atoms in most other phosphate oxalates which are 6-coordinated. The reduced coordination of Zn in **1** is primarily because 40% of the oxygens are 3-coordinated, a feature common in zinc phosphates.^{16,17} It is possible that some of the structural features of **1** also arise because of the use of the zinc amine complex as the starting material.

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