metal-organic compounds

Poly[diaqua-μ_4-oxalato-di-μ_6-phosphato-tetrazinc]

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The structure of the title compound, $[Zn_4(C_2O_4)(PO_4)_2(H_2O)_2]_n$, which was synthesized under hydrothermal conditions, consists of zinc phosphate layers joined by bridging oxalate ligands to generate a three-dimensional framework. An extended zinc phosphate layer lies parallel to the ab plane and within this layer there are helical chains, composed of ZnO_6 octahedra and ZnO_5 square pyramids, that run parallel to the b axis and coincide with the 2_1 screw element. The oxalate groups sit on crystallographic inversion centers.

Comment

Inorganic–organic hybrid materials based on phosphate and oxalate ligands are of considerable interest because of the rich structural chemistry of these materials and their established or potential applications in sorption and separation, heterogeneous catalysis and ion exchange (Cheetham *et al.*, 1999; Ekambaram & Sevov, 2000; Halasyamani *et al.*, 1997; Lin *et al.*, 2001). Research into metal–phosphate–oxalate systems has generated numerous structures containing $C_2O_4^{2-}$ and PO_4^{3-} ions, including the phosphato–oxalates of vanadium (Do *et al.*, 2000, 2001; Tsai *et al.*, 1999), manganese (Lethbridge *et al.*, 2000, 2004), iron (Choudhury *et al.*, 2000, 1999; Lethbridge & Lightfoot, 2000), aluminium (Kedarnath *et al.*, 2000; Lightfoot & Lethbridge, 1999; Rajic *et al.*, 2003), gallium (Choi & Lachgar, 2002; Lii & Chen, 2000), indium (Huang & Lii, 1998), molybdenum (Lee & Wang, 1999) and zinc (Fu *et al.*, 2003; Neeraj *et al.*, 2001). The aim of our work is to pursue new open frameworks that combine the rigidity of the oxalate ligand with the thermal stability of the phosphate group. In the course of this work, we have isolated a new zinc phosphato–oxalate, $[Zn_4(C_2O_4)(PO_4)_2(H_2O)_2]$, (I), the structure of which is reported here. The two zinc phosphato–oxalates cited above, *viz.* $[NH_3(CH_2)_3NH_3][Zn_6(PO_4)_4(C_2O_4)]$ (Neeraj *et al.*, 2001) and $\{Na_2[Zn(C_2O_4)_{1.5}H_2PO_4]\cdot2(H_2O)\}_n$ (Fu *et al.*, 2003), possess different structure-directing entities. These two compounds consist of macro-anionic frameworks, with the guest templating agents intercalated between the inorganic layers or located within channels in the structure. The structure of the title compound provides an interesting example of a three-dimensional zinc phosphato–oxalate with a neutral framework.


(I)
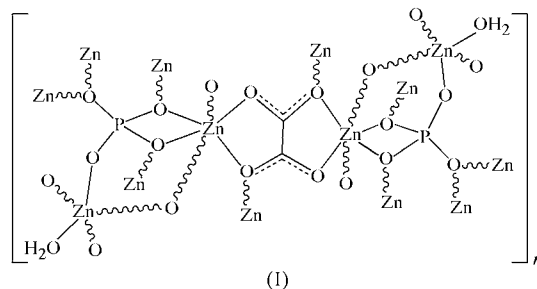
The structure of (I) (Fig. 1) has two crystallographically independent zinc sites within a zinc phosphate layer. Atom Zn1 is surrounded by a distorted octahedron formed by one doubly bridging O atom and five μ_3-O atoms, with Zn1—O bond distances in the range 1.994 (2)–2.320 (2) Å and *cis*-O—Zn1—O bond angles in the range 65.72 (8)–97.01 (9)°. Atom Zn2 is five-coordinated by three μ_3-O atoms, one doubly bridging O atom and one terminal water molecule, with Zn2—O bond distances in the range 1.947 (2)–2.346 (2) Å and *cis*-O—Zn2—O bond angles in the range 84.24 (9)–107.18 (10)°. The PO_4 tetrahedron acts as a multiple bridge, with three μ_3-O atoms and one doubly bridging O atom, and with P1—O bond distances in the range 1.530 (2)–1.552 (2) Å and O—P1—O bond angles in the range 102.81 (12)–113.44 (13)° (Table 1). The linkage of ZnO_6, ZnO_5 and PO_4 polyhedra generates two-dimensional zinc phosphate layers parallel to the ab plane. The PO_4 tetrahedron shares a common edge with the ZnO_6 octahedron.

The oxalate molecule sits on an inversion center and possesses unexceptional geometrical parameters. It exhibits bis-bidentate coordination to atom Zn1 – that is, it chelates two symmetry-related congeners of Zn1 – and bis-monodentate coordination to atom Zn2. The oxalate ligand thus acts as a spacer, or short pillar, between adjacent two-
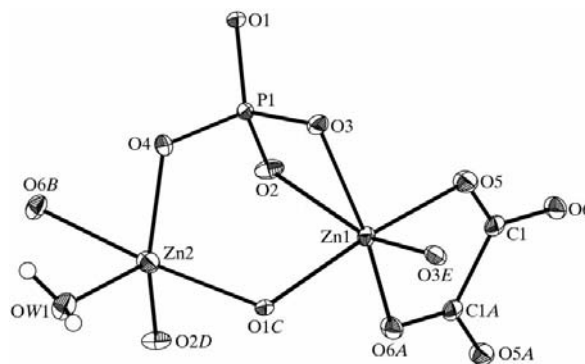
Figure 1
A view of the coordination environments of the Zn and P atoms in (I). [Symmetry codes: (A) $1-x$, $-y$, $1-z$; (B) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (C) x, $-1+y$, z; (D) $\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$; (E) $\frac{3}{2}-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$.]
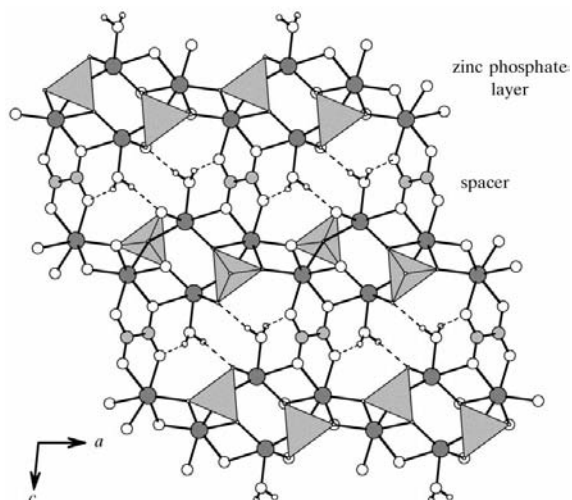
Figure 2
A view along the *b* axis, showing the zinc phosphate layers separated by oxalate ligands. Key: Zn atoms: medium gray; PO_4 groups: tetrahedra; C atoms: light gray; O atoms: white; H atoms: small white.
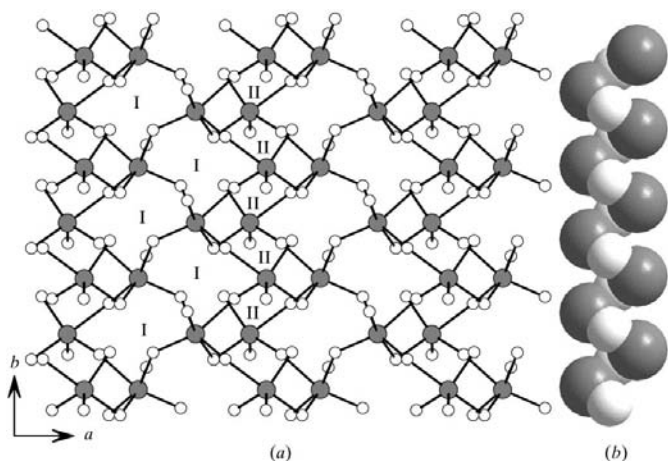
Figure 3
(*a*) A ball-and-stick view of the two-dimensional Zn—O—Zn connectivity in the *ab* plane. (*b*) A space-filling plot of the helical chains composed of ZnO_6 octahedra and ZnO_5 square pyramids along the *c* axis. Key: Zn atoms: medium gray; O atoms: white.

dimensional zinc phosphate layers, thus linking the latter into a three-dimensional architecture (Fig. 2). The *ac* projection of the structure reveals a small amount of space between the oxalate moieties. Small channels along *b* accommodate the $ZnOH_2$ groups. Hydrogen bonding is present between the water molecules and the framework O atoms [H1···O4^i = 1.85 (5) Å and H2···O5^{ii} = 1.91 (5) Å; see Table 2 for further details and symmetry codes].

One unique structural feature of the title compound is the presence of an extended two-dimensional Zn—O—Zn net, in which two distinct types of rings, labelled I and II in Fig. 3(*a*), each with four metal atoms, share edges. Interestingly, the layer is further characterized by the presence of helical Zn—O chains composed of ZnO_6 octahedra and ZnO_5 square pyra-

mids (Fig. 3*b*). The central axis of each helical chain is a twofold screw axis along the crystallographic *b* axis.

Experimental

In a typical synthesis, a mixture of ZnO (0.16 g), H_3PO_4 (0.2 ml, 85 wt%), $H_2C_2O_4$·$2H_2O$ (0.606 g) and H_2O (5.0 ml) in a molar ratio of 1.0:1.5:2.4:141 was sealed in a Teflon-lined steel autoclave, heated at 433 K for 3 d and then cooled to room temperature. The resulting plate-like crystals were recovered by filtration, washed with distilled water and dried in air (72% yield based on zinc). The elemental analysis of the bulk product is consistent with the reported stoichiometry. Analysis found: C 4.08%, H 0.62%; calculated: C 4.17%, H 0.70%. IR (KBr pellet, cm^{-1}): 3395 (*s*), 1644 (*s*), 1364 (*m*), 1320 (*s*), 1158 (*m*), 1052 (*s*), 1004 (*s*), 955 (*m*), 822 (*m*), 625 (*m*), 497 (*m*). The initial thermogravimetric analysis, performed under a flowing N_2 atmosphere in the range 313–873 K with a heating rate of 10 K min^{-1}, shows a two-step weight loss for the sample. The initial weight loss, between 393 and 443 K, corresponds to the release of water ligands (observed: 6.18%; expected: 6.26%). The second step, occurring between 503 and 743 K, is assigned to the removal of oxalate ligands. The weight loss (12.29%) is slightly less than the calculated value (12.52%). The title compound exhibits intense photoluminescence upon photoexcitation at 310 nm. The intense emissions shown at 470 nm may be assigned as ligand-to-metal charge transfer (LMCT).

Crystal data

$[Zn_4(C_2O_4)(PO_4)_2(H_2O)_2]$	Mo $K\alpha$ radiation
$M_r = 575.47$	Cell parameters from 1080
Monoclinic, $P2_1/n$	reflections
$a = 7.8752$ (6) Å	$\theta = 2.6–25.0°$
$b = 4.7971$ (2) Å	$\mu = 9.36$ mm^{-1}
$c = 14.0735$ (6) Å	$T = 293$ (2) K
$\beta = 95.835$ (7)°	Plate, colorless
$V = 528.92$ (5) Å^3	$0.15 \times 0.10 \times 0.10$ mm
$Z = 2$	
$D_x = 3.613$ Mg m^{-3}	

Data collection

Rigaku Mercury CCD	932 independent reflections
diffractometer	860 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.024$
Absorption correction: multi-scan	$\theta_{max} = 25.0°$
(*CrystalClear*; Rigaku, 2000)	$h = -9 \rightarrow 9$
$T_{min} = 0.338$, $T_{max} = 0.392$	$k = -5 \rightarrow 5$
2971 measured reflections	$l = -11 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.047P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.023$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.066$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.01$	$\Delta\rho_{max} = 0.49$ e Å^{-3}
932 reflections	$\Delta\rho_{min} = -0.85$ e Å^{-3}
108 parameters	
All H-atom parameters refined	

The two water H atoms were clearly visible in difference density maps. They were refined freely [OW1—H1 = 0.87 (5) Å and OW1—H2 = 0.85 (6) Å] with individual isotropic displacement parameters.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXTL*.

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Table 1
Selected geometric parameters (Å, °).

Zn1—O3^i	1.994 (2)	Zn2—O1^{ii}	2.169 (2)
Zn1—O1^{ii}	2.087 (2)	Zn2—O6^v	2.346 (2)
Zn1—O5	2.100 (2)	P1—O4	1.530 (2)
Zn1—O3	2.128 (2)	P1—O1	1.533 (2)
Zn1—O6^{iii}	2.129 (2)	P1—O3	1.543 (2)
Zn1—O2	2.320 (2)	P1—O2	1.552 (2)
Zn2—O2^{iv}	1.947 (2)	O5—C1	1.250 (4)
Zn2—OW1	1.981 (2)	O6—C1	1.261 (4)
Zn2—O4	1.994 (2)		
O3^i—Zn1—O1^{ii}	96.22 (9)	O2^{iv}—Zn2—O4	147.03 (10)
O3^i—Zn1—O5	93.18 (9)	OW1—Zn2—O4	103.05 (10)
O1^{ii}—Zn1—O5	165.87 (9)	O2^{iv}—Zn2—O1^{ii}	90.60 (9)
O3^i—Zn1—O3	90.63 (6)	OW1—Zn2—O1^{ii}	102.86 (10)
O1^{ii}—Zn1—O3	93.43 (9)	O4—Zn2—O1^{ii}	95.30 (9)
O5—Zn1—O3	97.01 (9)	O2^{iv}—Zn2—O6^v	84.24 (9)
O3^i—Zn1—O6^{iii}	111.01 (9)	OW1—Zn2—O6^v	86.97 (10)
O1^{ii}—Zn1—O6^{iii}	88.76 (9)	O4—Zn2—O6^v	84.52 (8)
O5—Zn1—O6^{iii}	78.00 (8)	O1^{ii}—Zn2—O6^v	169.92 (8)
O3—Zn1—O6^{iii}	157.90 (9)	O4—P1—O1	111.03 (13)
O3^i—Zn1—O2	156.30 (9)	O4—P1—O3	110.58 (13)
O1^{ii}—Zn1—O2	84.36 (9)	O1—P1—O3	112.10 (13)
O5—Zn1—O2	91.26 (9)	O4—P1—O2	106.48 (14)
O3—Zn1—O2	65.72 (8)	O1—P1—O2	113.44 (13)
O6^{iii}—Zn1—O2	92.68 (8)	O3—P1—O2	102.81 (12)
O2^{iv}—Zn2—OW1	107.18 (10)	O5—C1—O6	126.6 (3)

Symmetry codes: (i) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $x, y - 1, z$; (iii) $1 - x, -y, 1 - z$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (v) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
OW1—H1$\cdots$O4^i	0.87 (5)	1.85 (5)	2.698 (3)	164 (4)
OW1—H2$\cdots$O5^{ii}	0.85 (6)	1.91 (5)	2.676 (4)	149 (6)

Symmetry codes: (i) $1 - x, -y, 2 - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$.

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