

A new layered zinc phosphate templated by protonated isonicotinate, $[\text{Zn}_2(\text{C}_6\text{H}_5\text{NO}_2)_2(\text{HPO}_4)_2]$

Guang-Sheng Guo,^a Yong-Ge Wei,^b Jing Li,^c Ying Wang^a
and Hong-You Guo^{a*}

^aDepartment of Chemistry, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China, ^bState Key Laboratory for Structural Chemistry of Stable and Unstable Species, Institute of Physical Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China, and ^cDepartment of Chemistry and Chemical Biology, Rutgers University, 610 Taylor Road, Piscataway, New Jersey 08854, USA
Correspondence e-mail: guohy@mail.buct.edu.cn

Received 31 August 2004

Accepted 30 November 2004

Online 15 January 2005

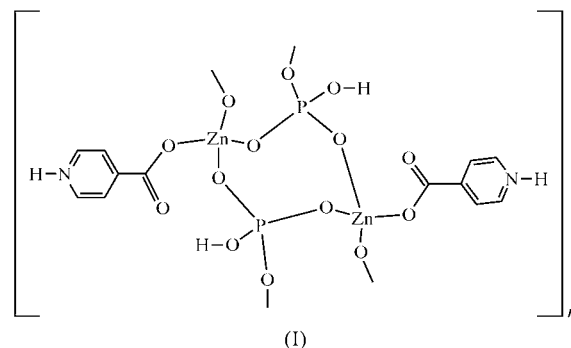
An organic–inorganic hybrid compound, poly[bis[(pyridine-4-carboxylato)zinc(II)]-di- μ_3 -phosphato], $[\text{Zn}_2(\text{C}_6\text{H}_5\text{NO}_2)_2(\text{HPO}_4)_2]$, has been hydrothermally synthesized and structurally characterized. The crystal structure consists of two types of two-dimensional layers of zinc hydrogenphosphate templated by protonated isonicotinate (ina) (or 4-pyridine-carboxylic acid), which contain two crystallographically independent centrosymmetric $[\text{Zn}_2(\text{ina})_2(\text{HPO}_4)_2]$ dimers as basic building units. The layers are interconnected *via* hydrogen-bonding and heterocyclic ring interactions.

Comment

Because of their potential applications in catalysis, medicine and host–guest chemistry, inorganic metal oxides and salts structurally directed by polydentate organic ligands have attracted much attention (Leininger *et al.*, 2000; Hargman *et al.*, 1999; Zhang *et al.*, 2002; Yuan *et al.*, 2002). In recent years, organically templated zinc phosphates have become a focus of much interest as a result of their rich structural and compositional diversity. A number of zinc phosphates with zero-, one-, two- and three-dimensional architectures have been constructed by employing solvothermal methods (Wang *et al.*, 2003; Xing *et al.*, 2004). In this paper, we report the hydrothermal synthesis and structural characterization of $[\text{Zn}_2(\text{C}_6\text{H}_5\text{NO}_2)_2(\text{HPO}_4)_2]$, ($\text{C}_6\text{H}_5\text{NO}_2$ is isonicotinate, ina), a novel organic–inorganic hybrid compound, (I).

The asymmetric unit contains two crystallographically non-equivalent, but chemically identical, $[\text{Zn}(\text{ina})(\text{HPO}_4)]$ groups. Each of these groups is bonded to another *via* a centrosymmetric junction, forming two different dimers that

can be regarded as the secondary building units of the structure (Fig. 1). These secondary building units are bonded to like units to form two distinct inorganic two-dimensional networks,



viz. a Zn1 layer and a Zn2 layer (Fig. 2). The centrosymmetric junctions are eight-membered rings comprising four tetrahedral centres (two Zn and two P) and four corner-shared bridging O atoms (Fig. 1). The Zn_2O_4 unit is considerably distorted from a regular tetrahedral geometry (Table 1). Each dimer is connected to four others in the same layer *via* a bridging O atom of a PO_4 group (O5 for the Zn1 layer and O9 for the Zn2 layer; Fig. 1), forming two-dimensional inorganic networks composed of the eight-membered rings and larger 16-membered rings (four Zn, four P and eight O atoms; Fig. 2). The ina ligands are coordinated to Zn *via* one carboxylate O atom and extend on both sides of the networks (Figs. 2 and 3). There are strong intradimer hydrogen bonds between the HPO_4 units and the free carboxyl O atoms of the ina groups (Table 2). These bonds help control the steric relationship between the pyridine rings and the eight-membered inorganic rings.

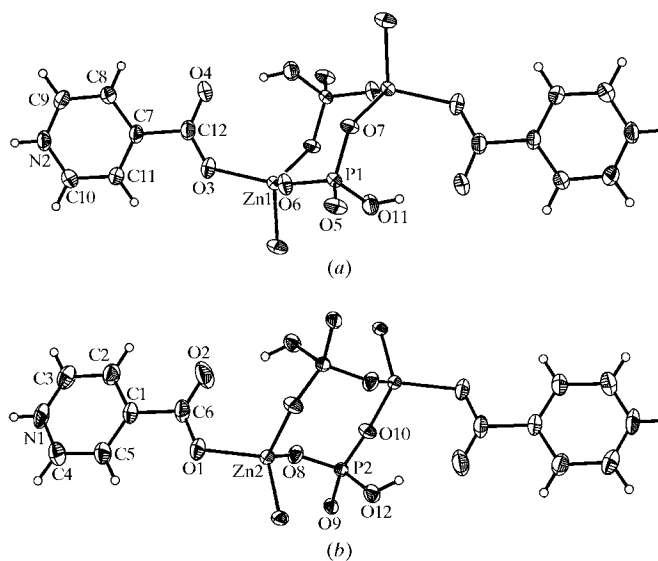


Figure 1

The two centrosymmetric dimers that comprise the secondary building units of the (a) Zn1 and (b) Zn2 layers. Non-labeled atoms are related to the labeled ones by a centre of symmetry within the eight-membered rings. Displacement ellipsoids are shown at the 50% probability level.

The main difference between the two layers is that, in the Zn1 layer, all pyridine rings are parallel to one another (face-to-face arrangement), while in the Zn2 layer, they have two orientations that are perpendicular to one another (face-to-edge arrangement). The Zn1 and Zn2 layers stack alternately in an ...*ABAB*... fashion along the *a* axis, giving rise to a three-dimensional structure (Fig. 3). Adjacent layers are interdigitated through inorganic rings, resulting in a tight packing. The layers are also connected *via* interlayer hydrogen bonding (Table 2).

The title compound contains N-protonated isonicotinate, [(H)NC₅H₄CO₂], which was not a starting reactant. It has been demonstrated that 4-cyanopyridine can be hydrolyzed slowly to yield isonicotinic acid under hydrothermal conditions (Evens *et al.*, 1999). It is therefore very likely that the

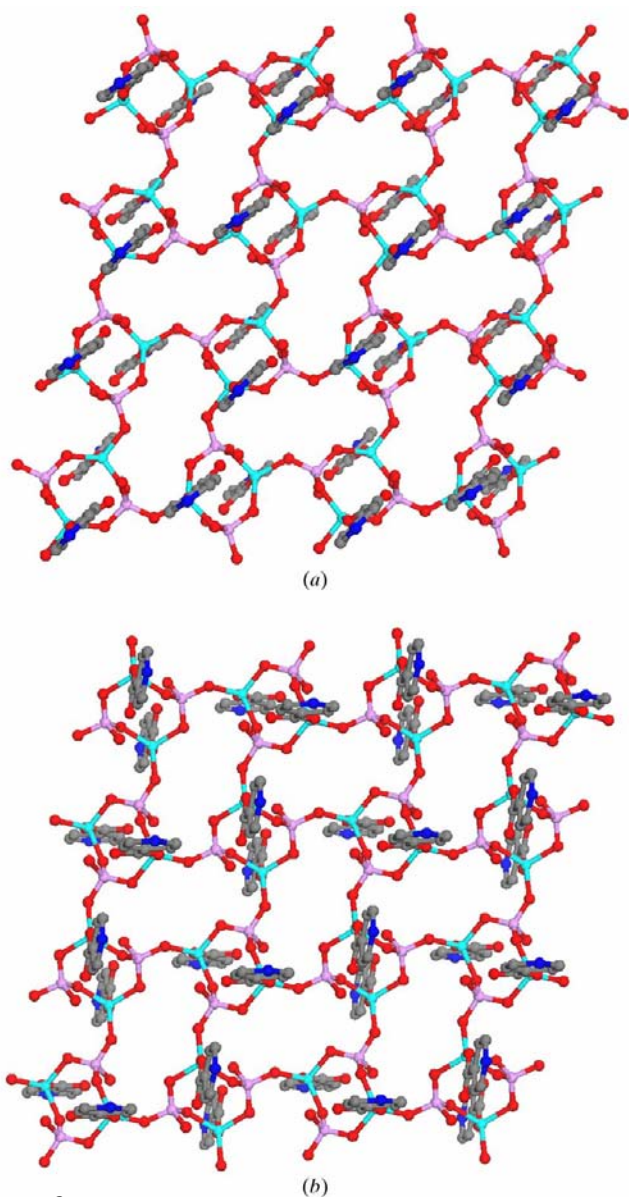


Figure 2
View of the (a) Zn1 and (b) Zn2 layers in the title compound. The pyridine rings are all parallel in (a) but have two perpendicular arrangements in (b).

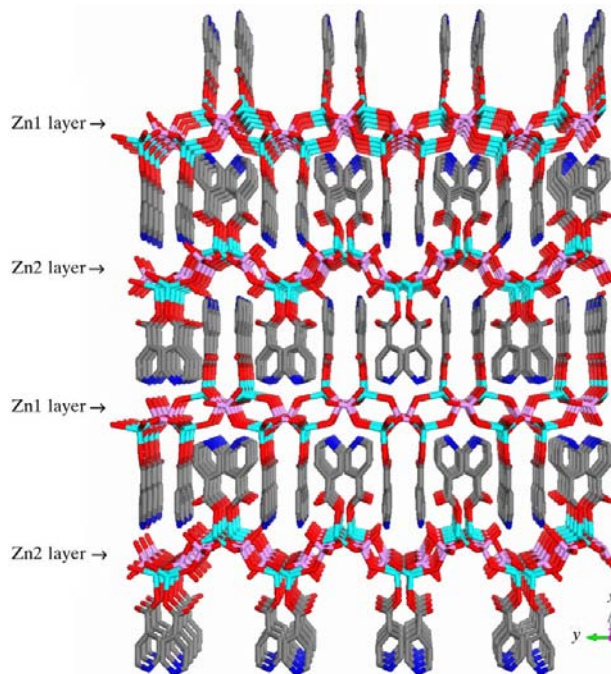


Figure 3
A view of the alternate stacking of the two distinct layers (Zn1 and Zn2). The layers are interdigitated by isonicotinate groups and interconnected by hydrogen bonds (not shown).

formation and crystal growth of the title compound was controlled by the hydrolyzation of 4-cyanopyridine.

Experimental

All chemicals and solvents were of reagent grade and were used without further purification. The title compound was synthesized from a hydrothermal reaction of ZnO (0.600 g), 4-cyanopyridine (0.770 g), H₃PO₄ (85 wt%, 1.00 ml) and H₂O (12.0 ml) in a 25 ml Teflon-lined stainless steel Parr bomb at 413 K for 3 d. Colorless block-like crystals were isolated and washed, in turn, with water, ethanol and anhydrous ether. IR (KBr disc, cm⁻¹): 3253.40 (*w*), 3104.20 (*s*), 2425.06 (*w*), 1609.01 (*s*), 1498.67 (*w*), 1403.81 (*s*), 1247.75 (*m*), 1200.04 (*w*), 1141.98 (*s*), 1072.69 (*s*), 1018.50 (*s*), 911.04 (*m*), 856.05 (*w*), 821.15 (*w*), 752.01 (*m*), 684.01 (*m*), 595.50 (*s*), 573.82 (*m*), 543.86 (*w*), 431.24 (*m*).

Crystal data

[Zn₂(C₆H₅NO₂)₂(HPO₄)₂]
M_r = 568.92
 Monoclinic, *P*2₁/*c*
a = 20.560 (4) Å
b = 8.5138 (17) Å
c = 10.387 (2) Å
 β = 97.46 (3)°
V = 1802.8 (6) Å³
Z = 4

D_x = 2.096 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 4415 reflections
 θ = 2.6–31.9°
 μ = 2.91 mm⁻¹
T = 292 (2) K
 Block, colorless
 0.20 × 0.20 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.564, *T_{max}* = 0.646
 17 073 measured reflections

6748 independent reflections
 5343 reflections with *I* > 2σ(*I*)
R_{int} = 0.033
 θ_{max} = 33.5°
h = -31 → 27
k = -13 → 10
l = -14 → 15

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.040$ $wR(F^2) = 0.097$ $S = 1.02$

6748 reflections

271 parameters

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0485P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.84 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$ **Table 1**Selected geometric parameters (\AA , $^\circ$).

Zn1—O6	1.9222 (16)	Zn2—O8	1.9210 (16)
Zn1—O5 ⁱ	1.9226 (17)	Zn2—O9 ⁱⁱⁱ	1.9255 (15)
Zn1—O7 ⁱⁱ	1.9303 (16)	Zn2—O10 ^{iv}	1.9442 (16)
Zn1—O3	1.9671 (17)	Zn2—O1	1.9656 (16)
O6—Zn1—O5 ⁱ	102.90 (7)	O8—Zn2—O9 ⁱⁱⁱ	114.15 (7)
O6—Zn1—O7 ⁱⁱ	119.02 (7)	O8—Zn2—O10 ^{iv}	111.27 (7)
O5 ⁱ —Zn1—O7 ⁱⁱ	111.97 (7)	O9 ⁱⁱⁱ —Zn2—O10 ^{iv}	104.20 (7)
O6—Zn1—O3	105.05 (8)	O8—Zn2—O1	105.59 (7)
O5 ⁱ —Zn1—O3	104.05 (8)	O9 ⁱⁱⁱ —Zn2—O1	110.38 (7)
O7 ⁱⁱ —Zn1—O3	112.40 (8)	O10 ^{iv} —Zn2—O1	111.40 (8)

Symmetry codes: (i) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $-x, 1 - y, 1 - z$; (iii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $1 - x, 1 - y, -z$.**Table 2**Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O11—H1O \cdots O4 ⁱⁱ	0.85	1.77	2.610 (2)	167
O12—H2O \cdots O2 ^{iv}	0.85	1.81	2.655 (3)	170
N2—H2N \cdots O8	0.86	2.64	3.153 (3)	119

Symmetry codes: (ii) $-x, 1 - y, 1 - z$; (iv) $1 - x, 1 - y, -z$.

H atoms attached to N and O atoms were located from difference Fourier maps, and other H atoms were positioned geometrically. H atoms attached to N and C atoms were refined using a riding model, and those attached to O atoms were refined in fixed positions.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

Financial support from the State Key Laboratory of Structural Chemistry for Unstable and Stable Species, People's Republic of China (2003), is greatly appreciated.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1477). Services for accessing these data are described at the back of the journal.

References

- Bruker (2000). *SMART*. Version 5.618. Bruker AXS Inc., Madison, Wisconsin, USA.
- Evens, O. R., Wang, Z.-Y., Xiong, R.-G., Foxman, B. M. & Lin, W.-B. (1999). *Inorg. Chem.* **38**, 2969–2973.
- Hagrman, P. J., Hagrman, D. & Zubieta, J. (1999). *Angew. Chem. Int. Ed.* **38**, 2639–2684.
- Leininger, S., Olenyuk, B. & Stang, P. J. (2000). *Chem. Rev.* **100**, 853–908.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1990). *XP*. Version 4.2 for MS-DOS. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995). *SAINT*. Version 4.05. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Wang, Y., Yu, J., Li, Y., Du, Y., Xu, R. & Ye, L. (2003). *J. Solid State Chem.* **170**, 303–307.
- Xing, Y., Li, G., Meng, H., Shi, Z., Liu, Y., Wei, X., Yang, Y. & Pang, W. (2004). *Inorg. Chem. Commun.* **7**, 475–477.
- Yuan, M., Li, Y., Wang, E., Lu, Y., Hu, C., Hu, N. & Jia, H. (2002). *J. Chem. Soc. Dalton Trans.* pp. 2916–2920.
- Zhang, X., Tong, M. & Chen, X. (2002). *Angew. Chem. Int. Ed.* **41**, 1029–1031.