A two-dimensional cationic lattice built from $[Zn_6(HPO_4)_2(PO_4)_2]^{2+}$ clusters

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A unique cationic zinc phosphate cluster linked by neutral bifunctional rigid ligands to form a two dimensional framework was synthesized and structurally characterized.

Since the first synthesis of aluminium phosphate zeolites in 1982,[1] considerable interest has been focused on various metal phosphate materials due to their structural features that lead to potential applications in the areas of ion-exchange, coatings, membranes, absorbents and catalysis.[2] Zinc phosphates, in particular, have proven to be very versatile in the formation of hybrid inorganic/ organic materials.[3,4] Frameworks built from metal ions and oxoanion units generally, and zinc and phosphate tetrahedral units specifically, are anionic and thus require extra framework cations to balance the framework charge, and to act as structure-directing agents to fill the void space. Notably, Clearfield and co-workers have introduced organophosphates to synthesize hybrid metal phosphate materials with neutral frameworks.[5] Hybrid zinc phosphate and phosphite frameworks are also often neutral.[3f] Recently, a neutral framework built from $[Zn_4(HPO_3)_2]^{4+}$ cations and the dianionic ligand, $(N(C_2H_4OH)(C_2H_4O)_2)^{2-}$, has been reported.[6] In this case, extra framework ions are not needed to balance the charge. So far, no cationic zinc phosphate clusters have been reported.

Here we report the first cationic zinc phosphate cluster, namely, $[Zn_6(HPO_4)_2(PO_4)_2]^{2+}$ which is linked by the neutral ligand, 4,4′-bisimidazolylbiphenyl (L1),† to form an extended cationic framework. Furthermore, although metal–organic frameworks based on metal ion and neutral organic linking units are abundant,[7] frameworks that have large cationic clusters as nodes are rare.[8] The overall cationic charge of the lattice is balanced by extra framework $H_2PO_4^-$ anions. It appears that the growth of a continuous zinc phosphate phase is frustrated by the presence of the large, rigid, bifunctional ligand which causes the inorganic phase to terminate into islands, or clusters, of zinc-phosphate aggregate.

The reaction of 4,4′-bisimidazolylbiphenyl with zinc acetate and phosphoric acid was accomplished in a sealed heavy walled glass tube at 130 °C to give the two-dimensional framework solid: $[Zn_6(HPO_4)_2(PO_4)_2(L1)_5)](H_2PO_4)_2\cdot4H_2O$ (1).‡ The structure of compound **1** is revealed by X-ray analysis.§ In **1**, six zinc atoms, two phosphate anions and two monohydrogen phosphate anions form a unique cationic zinc phosphate cluster. To the best of our knowledge, no cationic zinc phosphate clusters have been reported, and very few anionic or neutral zinc phosphate clusters are known.[6,9] The arrangement of six zinc ions in **1** is best described as

a tetragonally distorted octahedron in which the tetragonal axis is severely compressed. A view of the cluster is given in Fig. 1. The four equatorial zinc atoms (Zn2, Zn3, Zn2A and Zn3A) are coordinated by two phosphate oxygens and two imidazole nitrogens, and the two axial zinc atoms (Zn1 and Zn1A) are bonded to three phosphate oxygens and one nitrogen donor atom. Within a cluster, the axial–axial Zn1–Zn1A distance is only 3.731 Å; in the equatorial plane the *trans* Zn3–Zn3A distance is 8.679 Å and the *trans* Zn2–Zn2A distance is 8.122 Å. Two phosphate anions are located just inside the equatorial plane and two monohydrogen phosphate anions lie just above and below the equatorial plane of the zinc atoms. This arrangement eliminates 2-fold rotational symmetry but retains inversion symmetry in the cluster, as required by the space group. Each monohydrogen phosphate anion is coordinated to three zinc atoms with the terminal –OH group extending to the outside of the cluster.

The asymmetric unit of **1** contains three crystallographically independent L1 ligands; two ligands occupy general positions and one ligand lies on the inversion center. The L1 ligands that coordinate the equatorial zinc atoms form an interesting array of four parallel chains, cross-linked by the zinc clusters. Thus, four ligands and two clusters are knitted together to form a cuboid of dimension 5.94 × 5.95 × 17.20 Å. A modified view of the cationic framework is shown in Fig. 2a. In addition to the arrangement of four rigid bis-imidazolyl ligands along one axis, a fifth ligand interpenetrates the cuboidal network along a diagonal to generate a two-dimensional network structure. The interstitial space within each cuboid is filled by two dihydrogen phosphate anions and four lattice water molecules, which is connected to the framework *via*
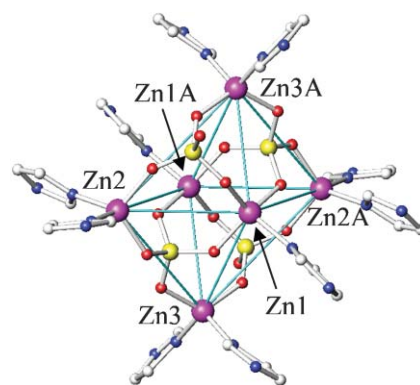
Fig. 1 A ball and stick representation of the zinc phosphate cluster of **1**. Hydrogen atoms and the benzene rings of the organic ligand are omitted (Zn, pink; P, yellow; O, red; N, blue and C, white). For clarity the view is perpendicular to the equatorial plane.

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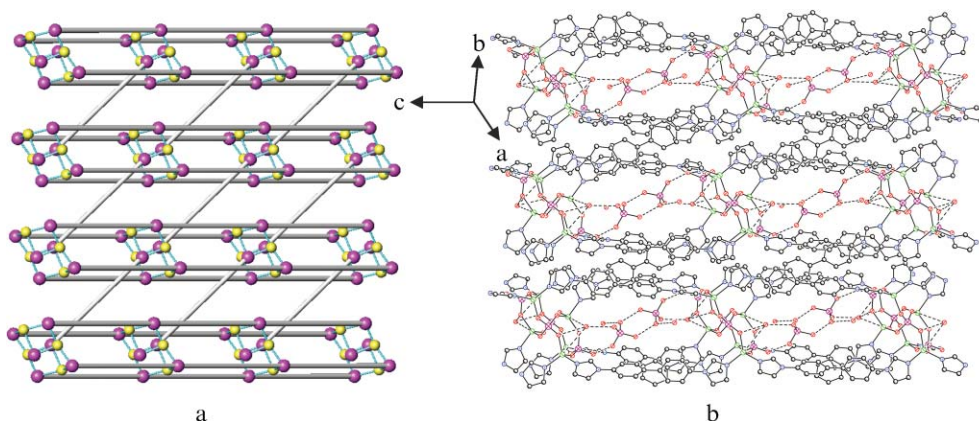
Fig. 2 (a) Schematic representation of the cationic 2D network of **1**. The Zn–O–P linkages are drawn as green lines and the organic ligands are simplified as bars to connect zinc atoms (Zn, pink; P, yellow). (b) A complete representation of the 2D structure of **1** showing the dihydrogen phosphate anion located within the cuboids. Hydrogen bonding interactions are indicated by dashed lines. Hydrogen atoms are omitted for clarity.

hydrogen bonding. The hydrogen bond interactions between dihydrogen phosphate, water and the zinc clusters are shown in Fig. 2b. There are two types of apparent interstitial spaces within the 2D structure; one is defined by four parallel ligands and two clusters and is filled with hydrophilic groups, and the other is a hydrophobic space defined by parallel ligands from adjacent chains and the diagonal ligands that link chains. These are evident in Fig. 2b. Although there are ten organic linking units coming out of each cluster, the topology of the framework can be regarded as a 2D rhombus grid due to the pairing of the organic linking units.

Two types of π–π interactions are observed in **1**, as illustrated in Fig. 3. The first occurs within sheets; specifically, the diagonal ligand is held by the parallel ligands *via* π–π interactions with a centroid–centroid distance of 3.671 Å. The second occurs between parallel ligands from adjacent sheets with a centroid–centroid distance of 3.774 Å. The inter-layer π–π interactions are responsible, in part, for an *AAA* model of layer stacking to form the 3D structure.
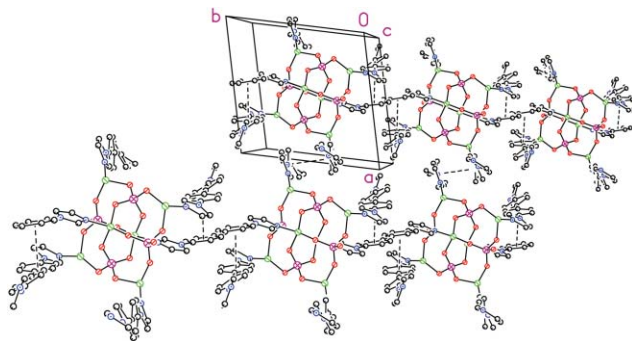
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Notes and references

† Synthesis of ligand L1: 4,4′-dibromobiphenyl (6.24 g, 20 mmol), imidazole (5.76 g, 84 mmol), K_2CO_3 (8.78 g, 63 mmol) and $CuSO_4$ (0.064 g, 0.4 mmol) were mixed and heated at 180 °C for 12 h. under an argon atmosphere. The mixture was cooled to room temperature, washed with water and the residue extracted with ethanol (30 ml) three times. The organic layer was separated and evaporated to dryness to give crude product L1, which was recrystallized from methanol and water. Yield: 73%. ^{1}H NMR (400 MHz; solvent CDCl$_3$) δ 7.26 (2H, s), 7.35 (2H, s), 7.49–7.51 (4H, m), 7.70–7.72 (4H, m), 7.93 (2H, m).

‡ Hydrothermal treatment of zinc acetate dihydrate (219.5 mg, 1.0 mmol), phosphoric acid (85 wt%, 230.6 mg, 2.0 mmol), L1 (427.6 mg, 1.5 mmol), and water (6 ml) for 10 days at 130 °C yields a crystalline product. Yield 78%, based on zinc. Elemental analysis: Found C, 44.42; H, 3.62; N, 11.40. $C_{45}H_{42}N_{10}O_{14}P_3Zn_3$ requires C, 43.73; H, 3.42; N, 11.33%. Full occupancy for the water molecules is also confirmed by TGA. Heating **1** under nitrogen to 200 °C, the weight loss corresponds to loss of water molecules (3.1%, $2H_2O$, calc. 2.9%). The ^{31}P CPMAS NMR spectrum of **1** shows three peaks at δ 10.4, 1.9 and −0.9 ($H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} respectively) with a relative intensity ratio of 1:1:1. These assignments are in agreement with the structure derived by X-ray analysis.

§ Crystallographic data for **1**: $[Zn_6(HPO_4)_2(PO_4)_2(L1)_5](H_2PO_4)_2\cdot4H_2O$, $M_r = 1235.91$. Triclinic, space group P-1, $a = 11.7616(12)$, $b = 11.8456(12)$, $c = 17.1991(15)$ Å, $\alpha = 93.140(8)$, $\beta = 91.869(8)$, $\gamma = 103.343(9)°$, $V = 2325.5(4)$ Å^3, $Z = 2$, $\mu = 1.720$ mm^{-1}, $\rho = 1.765$ g cm^{-3}; 13255 reflections collected, 8015 unique ($R_{int} = 0.0769$) $R = 0.0658$ [$I > 2\sigma(I)$], and $Rw = 0.0887$ (all data). CCDC deposition number: CCDC 262049. An electronic crystallographic data file in .cif format can be found at http://www.rsc.org/suppdata/cc/b5/b501221j/.

1 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigan, *J. Am. Chem. Soc.*, 1982, **104**, 1146.

2 (*a*) T. E. Gier and G. D. Stucky, *Nature*, 1991, **349**, 508; (*b*) J. Yu and R. Xu, *Acc. Chem. Res.*, 2003, **36**, 481; (*c*) A. K. Cheetham, G. Férey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268; (*d*) S. Natarajan, L. V. Wullen, W. Klein and M. Jansen, *Inorg. Chem.*, 2003, **42**, 6265; (*e*) A. Hu, H. L. Ngo and W. Lin, *Angew. Chem., Int. Ed.*, 2004, **43**, 2501; (*f*) Z. Yin, Y. Sakamoto, J. Yu, S. Sun, O. Kerasaki and R. Xu, *J. Am. Chem. Soc.*, 2004, **126**, 8882; (*g*) W. K. Chang, R. K. Chiang, Y. C. Jiang, S. L. Wang, S. F. Lee and K. H. Lii, *Inorg. Chem.*, 2004, **43**, 2564.

Fig. 3 A partial packing diagram of **1**, viewed approximately down the *c*-axis to emphasize π–π interactions (indicated by dashed lines) described in the text.

3 (*a*) R. C. Finn, J. Zubieta and R. C. Haushalter, in *Progress in Inorganic Chemistry*, ed. K. D. Karlin, John Wiley, New York, 2003, vol. 51, p. 421 and references therein; (*b*) C. N. R. Rao, S. Natarajan, A. Choudhury, S. Neeraj and A. A. Ayi, *Acc. Chem. Res.*, 2001, **34**, 80 and references therein; (*c*) P. Feng, X. Bu and G. D. Stucky, *Angew, Chem., Int. Ed. Engl.*, 1995, **34**, 1745; (*d*) X. Shi, G. Zhu, S. Qiu, K. Huang, J. Yu and R. Xu, *Angew. Chem., Int. Ed.*, 2004, **43**, 6482; (*e*) G.-Y. Yang and S. C. Sevov, *J. Am. Chem. Soc.*, 1999, **121**, 8389; (*f*) J. A. Rodgers and W. T. A. Harrison, *Chem. Commun.*, 2000, 2385.

4 D. Hagrman, P. J. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 3165.

5 (*a*) B. Zhang, D. M. Poojary and A. Clearfield, *Inorg. Chem.*, 1998, **37**, 1844; (*b*) Z. Wang, J. M. Heising and A. Clearfield, *J. Am. Chem. Soc.*, 2003, **125**, 10375; (*c*) M. M. Gómez-Alcántara, A. Cabeza, M. Martínez-Lara, M. A. G. Aranda, R. Suau, N. Bhuvanesh and A. Clearfield, *Inorg. Chem.*, 2004, **43**, 5283.

6 J. A. Johnstone and W. T. A. Harrison, *Inorg. Chem.*, 2004, **43**, 4567.

7 (*a*) D. L. Caulder and K. N. Raymond, *Acc. Chem. Res.*, 1999, **32**, 975; (*b*) O. Ohmori, M. Kawano and M. Fujita, *J. Am. Chem. Soc.*, 2004, **126**, 16292; (*c*) A. Lützen, *Angew. Chem., Int. Ed.*, 2005, **44**, 1000 and references therein.

8 (*a*) S. Y. Yang, L. S. Long, Y. B. Jiang, R. B. Huang and L. S. Zheng, *Chem. Mater.*, 2002, **14**, 3229; (*b*) B. Q. Ma, D. S. Zhang, S. Gao, T. Z. Jin, C. H. Yan and G. X. Xu, *Angew, Chem., Int. Ed*, 2000, **39**, 3644.

9 (*a*) W. T. A. Harrison and L. Hannooman, *J. Solid State Chem.*, 1997, **131**, 363; (*b*) C. N. R. Cao, S. Natarajan and S. Neeraj, *J. Solid State Chem.*, 2000, **152**, 302; (*c*) I. Macdonald and W. T. A. Harrison, *Inorg. Chem.*, 2002, **41**, 6184.