

Isolation of a monomeric hybrid zinc phosphate and its one-dimensional relative

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Received 29th April 2003, Accepted 25th June 2003

First published as an Advance Article on the web 9th July 2003

Two hybrid zinc phosphates, $[\text{Zn}(\text{phen})]_2(\text{H}_{1.5}\text{PO}_4)_2(\text{H}_2\text{PO}_4)$ (**1**) and $[\text{Zn}(\text{phen})]_2(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ ($x \approx 0.5$) (**2**), have been synthesized under hydrothermal conditions in the presence of 1,10-phenanthroline (phen) ligands. They are the first members in the zinc–phosphate–phen system. The structure of **1** consists of two ZnO_3N_2 trigonal bipyramids bridged by three P-centered tetrahedra. **1** is novel in the sense that it provides the first example of a monomeric zinc phosphate crystallized in a non-centrosymmetric space group. The one-dimensional structure of **2** consists of a network of strictly alternating ZnO_3N_2 trigonal bipyramids, HPO_4 and H_2PO_4 tetrahedra by sharing vertices. Interestingly, the chain-like structure of **2** can be generated from **1** by a shifting of Zn–O–P bonds.

Introduction

The design and synthesis of open-framework transition metal phosphates are of great interest due to their intriguing architecture and appealing catalytic, optical, electrical, and magnetic properties which are not accessible to the main group systems of tetrahedral framework zeolites.¹ A large number of novel metal phosphates with one-dimensional (1D) chains or ladders, two dimensional (2D) layers, and three-dimensional (3D) open structures have been reported in the past two decades.² One useful approach to the synthesis of these materials is the hydrothermal crystallization in the presence of organic amines, which are used as templates or structure-directing agents to facilitate the formation of various networks.

Recently, many research interests have been focused on the fabrication of inorganic–organic hybrid frameworks incorporating organic ligands. Compared with inorganic ligands, the organic molecules possess more rich coordination sites and a wide variety of shapes. This suggests to us that the rational design of crystalline solids with complex structures may be realized through a shrewd choice of organic species. One class of hybrid metal phosphates is obtained by the combination of the oxalate and the phosphate group in the same crystalline material.³ Most of these compounds possess an anionic framework templated by protonated organic amines. Another class of hybrid materials in this system is based on organonitrogen ligands and phosphate groups.^{4,5} Generally, organonitrogen ligands are incorporated in the skeletons and result in neutral frameworks. The most extensively studied organonitrogen ligand is 4,4'-bipyridine. Many new compounds in the phosphate–4,4'-bipyridine system have been synthesized and characterized.⁵

The aim of our work is to synthesize new metal phosphates with novel topology in the presence of 2,2'-bipyridine or 1,10-phenanthroline ligands, and have now isolated several new phases with a hybrid framework. Here we report the syntheses, structures and some properties of two novel inorganic–organic hybrid zinc phosphates grafted with phen ligands, $[\text{Zn}(\text{phen})]_2(\text{H}_{1.5}\text{PO}_4)_2(\text{H}_2\text{PO}_4)$ (**1**) and $[\text{Zn}(\text{phen})]_2(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ ($x \approx 0.5$) (**2**). To our knowledge, the two hybrid solids are the only known compounds in the zinc–phosphate–phen system

and **1** is the first example of a zinc phosphate cluster crystallized in a non-centrosymmetric space group.

Experimental

Materials and methods

Reagents were purchased commercially and used without further purification. Elemental analyses were carried out on a Elementar Vario EL III analyzer and the inductively coupled plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300 DV spectrometer. IR spectrum (KBr pellets) was recorded on ABB Bomen MB 102 spectrometer. Powder X-ray diffraction (XRD) data were obtained using a Philips X'Pert-MPD diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). The thermogravimetric analysis was performed on a Netzsch STA 449c analyzer in air atmosphere with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. Fluorescent spectra were measured on a Perkin-Elmer LS 55 luminescence spectrometer, equipped with a 20 kW xenon lamp.

Synthesis of compounds

[Zn(phen)]₂(H_{1.5}PO₄)₂(H₂PO₄) 1. In a typical synthesis for **1**, a mixture of ZnO (0.36 g), H₃PO₄ (0.45 ml, 85 wt%), phen·H₂O (0.871 g) and H₂O (6 ml) in a molar ratio of 1 : 1.5 : 1 : 77 was stirred under ambient conditions. The resulting gel, with a pH of 5, was sealed in a Teflon-lined steel autoclave and heated at 150 °C for 5 days and then cooled to room temperature. The resulting product was recovered by filtration, washed with distilled water and dried in air (80% yield based on zinc). The pH of the solution remained at 5 during crystallization. The X-ray powder diffraction pattern for the bulk product is in good agreement with the pattern based on single-crystal X-ray solution, indicating the phase purity. ICP analysis gave the contents of Zn (16.38 wt%, calc. 16.74 wt%) and P (11.45 wt%, calc. 11.90 wt%), indicating a Zn : P ratio of 2 : 3. Elemental analysis showed that the sample contains 36.18, 2.65 and 7.13 wt% of C, H and N, respectively, in good accord with the expected values of 36.9, 2.71 and 7.17 wt% of C, H and N on the basis of the empirical formula given by the single-crystal structure analysis.

Table 1 Crystal data and structure refinement for compounds **1** and **2**

	1	2
Empirical formula	C ₂₄ H ₂₁ N ₄ O ₁₂ P ₃ Zn ₂	C ₂₄ H ₂₂ N ₄ O _{12.5} P ₃ Zn ₂
Formula weight	781.10	790.11
Crystal system	Orthorhombic	Triclinic
Space group	<i>Fdd2</i> (no. 43)	<i>P1</i> (no. 2)
<i>a</i> /Å	40.391(3)	10.3179(2)
<i>b</i> /Å	7.4568(4)	12.4168(2)
<i>c</i> /Å	17.4247(8)	12.9696(2)
<i>a</i> ^o	90	65.057(2)
<i>β</i> ^o	90	74.625(2)
<i>γ</i> ^o	90	71.593(2)
<i>V</i> /Å ³	5248.1(5)	1412.62(4)
<i>Z</i>	8	2
<i>D_c</i> /g cm ⁻³	1.977	1.858
<i>μ</i> (Mo-Kα)/mm ⁻¹	2.090	1.943
Reflections collected	3813	7199
Independent reflections	2024	4868
Absolute structure parameter	0.031(18)	
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0335, 0.0800	0.0454, 0.1100

IR (KBr, cm⁻¹) for **1**: 3077w, 2924w, 2855w, 1628m, 1587m, 1577m, 1515s, 1495m, 1426s, 1321w, 1228vs, 1151m, 1139m, 1104m, 1022vs, 956m, 892m, 866m, 849vs, 729vs, 639m, 562m, 529m, 505s, 422m.

[Zn(phen)]₂(HPO₄)(H₂PO₄)₂·*x*H₂O **2.** In a typical synthesis for **2**, a mixture of ZnO (0.36 g), H₃PO₄ (0.95 ml, 85 wt%), phen·H₂O (1.225 g) and H₂O (6.7 ml) in a molar ratio of 1 : 3.2 : 1.4 : 87 was stirred under ambient conditions. The resulting gel, with a pH of 3, was sealed in a Teflon-lined steel autoclave and heated at 160 °C for 3 days and then cooled to room temperature. Rod-like crystals were obtained which were recovered by filtration, washed with distilled water and dried in air (75% yield based on zinc). The pH of the solution remained at 3 during crystallization. The X-ray powder diffraction pattern for the bulk product is in good agreement with the pattern based on single crystal X-ray solution, proving the phase purity. ICP analysis gave the contents of Zn (16.41 wt%, calc. 16.55 wt%) and P (11.43 wt%, calc. 11.76 wt%), indicating a Zn : P ratio of 2 : 3. Elemental analysis showed that the sample contains 36.58, 2.81 and 7.00 wt% of C, H and N, respectively, in good accord with the expected values of 36.48, 2.81 and 7.09 wt% of C, H and N on the basis of the empirical formula given by the single-crystal structure analysis. IR (KBr, cm⁻¹) for **2**: 3745w, 3592w, 3069w, 1623w, 1581m, 1558w, 1541w, 1518s, 1495w, 1426s, 1279m, 1217m, 1100vs, 1049m, 983m, 943m, 887m, 867m, 849s, 778m, 726vs, 643m, 568m, 532s, 497m, 423m.

X-Ray crystallography

Suitable single crystals of the as-synthesized compounds with dimensions of 0.46 × 0.30 × 0.14 mm³ for **1** and 0.52 × 0.12 × 0.10 mm³ for **2** were carefully selected under an optical microscope and glued to a thin glass fiber with epoxy resin. Crystal structure determination by X-ray diffraction was performed on a Siemens SMART CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) in the ω and φ scanning mode at room temperature. An empirical absorption correction was applied using the SADABS program.⁶ The structure was solved using direct methods. The zinc and phosphorus atoms were first located, and the carbon, nitrogen and oxygen atoms were found in the final difference Fourier map. Hydrogen atoms in **1** were geometrically placed, except the hydrogen attached to the O(4) atom. In the case of **2**, the H atom attached to O(10) was placed geometrically and the remaining H atoms (except hydrogens of the water molecules) were found in the difference Fourier maps. The structure was refined on *F*² by full-matrix least-squares methods using the SHELX97 program package.^{7,8} All non-hydrogen atoms were refined anisotropically. Experimental details for the structural determin-

ations of **1** and **2** are presented in Table 1. Selected bond distances and angles for **1** and **2** are listed in Tables 2 and 3, respectively.

CCDC reference numbers 208837 and 208838.

See <http://www.rsc.org/suppdata/dt/b3/b304778d/> for crystallographic data in CIF or other electronic format.

Results and discussion

Compound **1** has a zero-dimensional structure built up of ZnO₃N₂ trigonal bipyramids, H_{1.5}PO₄ tetrahedra and H₂PO₄ tetrahedra sharing their vertices. The asymmetric unit consists of one unique Zn²⁺ atom and two unique P⁵⁺ atoms, as shown in Fig. 1. The zinc atom is coordinated by two nitrogen atoms from a 1,10-phenanthroline ligand and three oxygen atoms to form a distorted trigonal bipyramidal geometry. The Zn–O(N) bond distances are in the range of 1.958(4)–2.199(5) Å, with an average value of 2.066 Å. The zinc atom is connected to three P atoms *via* Zn–O–P links. Of the two independent P atoms, P(1) is located at a general position and makes two P–O–Zn linkages. P(2) is located on the crystallographic two-fold axis and also makes two P–O–Zn linkages. The P–O bond distances are in the range 1.491(4)–1.575(4) Å (av. P(1)–O = 1.538 Å and P(2)–O = 1.529 Å). The framework stoichiometry of Zn₁P_{1.5}O₆ creates a net charge of –2.5, which is needed to be balanced. Bond valence sum values clearly indicate that P(1)–O(4), P(1)–O(5), P(2)–O(6) with distances of 1.554(4), 1.575(4) and 1.560(4) are formally hydroxyl groups.⁹ The hydrogen atom attached to the O(4) atom is shared by two symmetry related H_{1.5}P(1)O₄ groups in the monomeric unit. Such O–H–O linkages are also found in a chain-like gallophosphate.¹⁰

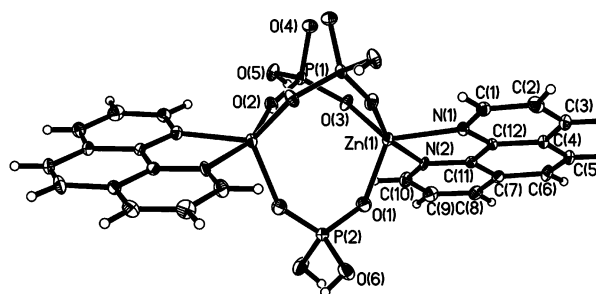


Fig. 1 The zero-dimensional structure of **1**, with 30% thermal ellipsoids, and the atom-labeling scheme.

It is well known that multipoint hydrogen bond interactions are necessary in the formation and stability of low-dimensional structures. In the present instance, the framework is stabilized by the extensive multi-point hydrogen bonds involving the

Table 2 Selected bond lengths (Å) and angles (°) for **1**^a

Zn(1)–O(1)	1.958(4)	P(1)–O(4)	1.554(4)
Zn(1)–O(2)#1	2.010(4)	P(1)–O(5)	1.575(4)
Zn(1)–O(3)	2.014(4)	P(2)–O(1)#1	1.498(4)
Zn(1)–N(1)	2.149(4)	P(2)–O(1)	1.498(4)
Zn(1)–N(2)	2.199(5)	P(2)–O(6)#1	1.560(4)
P(1)–O(2)	1.491(4)	P(2)–O(6)	1.560(4)
P(1)–O(3)	1.530(3)		
O(1)–Zn(1)–O(2)#1	102.51(17)	O(2)–P(1)–O(4)	110.9(2)
O(1)–Zn(1)–O(3)	113.57(17)	O(3)–P(1)–O(4)	111.2(2)
O(2)#1–Zn(1)–O(3)	97.41(15)	O(2)–P(1)–O(5)	109.3(2)
O(1)–Zn(1)–N(1)	114.01(17)	O(3)–P(1)–O(5)	107.2(2)
O(2)#1–Zn(1)–N(1)	87.94(16)	O(4)–P(1)–O(5)	104.2(2)
O(3)–Zn(1)–N(1)	129.55(16)	O(1)#1–P(2)–O(1)	116.8(3)
O(1)–Zn(1)–N(2)	91.75(17)	O(1)#1–P(2)–O(6)#1	104.6(2)
O(2)#1–Zn(1)–N(2)	161.70(16)	O(1)–P(2)–O(6)#1	112.2(3)
O(3)–Zn(1)–N(2)	87.12(15)	O(1)#1–P(2)–O(6)	112.2(3)
N(1)–Zn(1)–N(2)	75.68(16)	O(1)–P(2)–O(6)	104.6(2)
O(2)–P(1)–O(3)	113.5(2)	O(6)#1–P(2)–O(6)	106.1(4)

^a Symmetry transformations used to generate equivalent atoms: #1 $-x + 3/2, -y + 3/2, z$.

Table 3 Selected bond lengths (Å) and angles (°) for **2**^a

Zn(1)–O(5)#1	1.953(3)	P(1)–O(2)	1.528(4)
Zn(1)–O(2)	1.990(3)	P(1)–O(8)	1.542(4)
Zn(1)–O(6)	2.065(3)	P(1)–O(7)	1.556(4)
Zn(1)–N(1)	2.118(4)	P(2)–O(4)	1.483(4)
Zn(1)–N(2)	2.192(4)	P(2)–O(3)	1.508(4)
Zn(2)–O(4)#2	1.936(4)	P(2)–O(10)	1.565(4)
Zn(2)–O(1)	1.996(3)	P(2)–O(9)	1.575(4)
Zn(2)–O(3)	2.103(3)	P(3)–O(12)	1.498(4)
Zn(2)–N(3)	2.127(4)	P(3)–O(6)	1.528(4)
Zn(2)–N(4)	2.178(4)	P(3)–O(5)	1.540(4)
P(1)–O(1)	1.499(4)	P(3)–O(11)	1.593(4)
O(5)#1–Zn(1)–O(2)	114.28(14)	N(3)–Zn(2)–N(4)	76.64(16)
O(5)#1–Zn(1)–O(6)	100.54(14)	O(1)–P(1)–O(2)	112.7(2)
O(2)–Zn(1)–O(6)	91.63(14)	O(1)–P(1)–O(8)	107.3(2)
O(5)#1–Zn(1)–N(1)	111.84(16)	O(2)–P(1)–O(8)	111.7(2)
O(2)–Zn(1)–N(1)	133.01(15)	O(1)–P(1)–O(7)	108.7(2)
O(6)–Zn(1)–N(1)	88.49(15)	O(2)–P(1)–O(7)	108.8(2)
O(5)#1–Zn(1)–N(2)	97.88(15)	O(8)–P(1)–O(7)	107.4(3)
O(2)–Zn(1)–N(2)	88.69(15)	O(4)–P(2)–O(3)	117.1(2)
O(6)–Zn(1)–N(2)	159.61(15)	O(4)–P(2)–O(10)	106.2(2)
N(1)–Zn(1)–N(2)	76.55(16)	O(3)–P(2)–O(10)	108.45(19)
O(4)#2–Zn(2)–O(1)	103.96(15)	O(4)–P(2)–O(9)	108.4(2)
O(4)#2–Zn(2)–O(3)	101.33(15)	O(3)–P(2)–O(9)	109.3(2)
O(1)–Zn(2)–O(3)	95.77(14)	O(10)–P(2)–O(9)	106.9(2)
O(4)#2–Zn(2)–N(3)	112.74(16)	O(12)–P(3)–O(6)	114.5(2)
O(1)–Zn(2)–N(3)	141.85(16)	O(12)–P(3)–O(5)	112.6(2)
O(3)–Zn(2)–N(3)	87.18(15)	O(6)–P(3)–O(5)	109.5(2)
O(4)#2–Zn(2)–N(4)	99.45(17)	O(12)–P(3)–O(11)	106.8(2)
O(1)–Zn(2)–N(4)	87.72(15)	O(6)–P(3)–O(11)	106.6(2)
O(3)–Zn(2)–N(4)	157.40(16)	O(5)–P(3)–O(11)	106.2(2)

^a Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y, -z + 1$. #2 $-x + 1, -y + 1, -z$.

phosphate groups, forming a sheet-like structure parallel to the *bc* plane: O(5)–H(1) \cdots O(3) ($d = 1.82$ Å), O(6)–H(2) \cdots O(4) ($d = 1.95$ Å) (Fig. 2). These adjacent layers are further connected with each other through strong π – π interactions of the phen ligand, as reflected in close (<3.3 Å) intermolecular contacts. So far, reports of 0D zinc phosphate clusters are still very rare. To our knowledge, only five organically templated zincophosphate clusters have been reported.¹¹ Interestingly, all of them crystallized in a centrosymmetric space group ($P\bar{1}$). **1** is the first example of a monomeric phase crystallized in a non-centrosymmetric space group.

Compound **2** is a one-dimensional framework constructed from ZnO_3N_2 , HPO_4 and H_2PO_4 polyhedra and phen ligands. The asymmetric unit of **2** contains two unique Zn sites and three unique P sites (Fig. 3). Both the zinc sites are coordinated

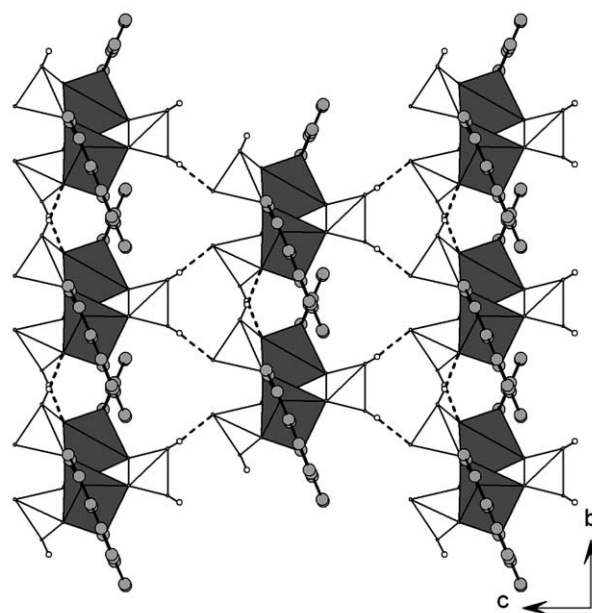


Fig. 2 Packing drawing of the unit cell of **1** viewed along the $[100]$ direction. Hydrogen bonds between the monomers are shown as dotted lines. Medium gray, Zn-centered polyhedra; white, P-centered tetrahedra.

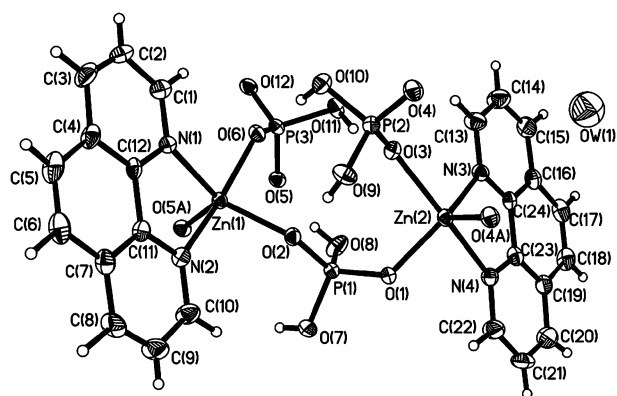


Fig. 3 View of the coordination environments of the zinc and phosphorus atoms in **2**, showing the atom labeling scheme, and with 30% thermal ellipsoids.

by three oxygen atoms and as well as two nitrogen atoms from a phen ligand. The ZnO_3N_2 trigonal bipyramids are highly distorted due to the μ_2 coordination by the phen ligands, as indicated by the wide range of Zn–O(N) distances [1.953(3)–2.192(4) Å] and the small N–Zn–N angles [76.55(16) and 76.64(16)°]. All three P atoms are tetrahedrally coordinated, with $d_{av}[P(1)–O] = 1.531$ Å, $d_{av}[P(2)–O] = 1.551$ Å and $d_{av}[P(3)–O] = 1.540$ Å. The three independent P atoms represent two chemically distinct types of site. The first phosphorus atom, P(3), makes two bonds to neighboring Zn(1) atoms, leaving the other two oxygen-atom vertices as a terminal –OH group and an “unsaturated” =O atom, respectively. For P(2) or P(3), two of the four oxygen coordinating atoms are bonded to zinc atoms and these P–O bond lengths range from 1.483(4) to 1.528(4) Å. The remaining bound oxygen atoms (P(1)–O(7), P(1)–O(8), P(2)–O(9) and P(2)–O(10) with distances of 1.556(4), 1.542(4), 1.575(4) and 1.565(4) Å) are formally hydroxyl groups.

There are two different single four-membered rings in the chains, one made up of two $H_2P(2)O_4$ and two $Zn(2)O_3N_2$ groups and the other made up of two $HP(3)O_4$ and two $Zn(1)O_3N_2$ groups (Fig. 4(a)). The two motifs are repeated alternating in the one-dimensional structure with $H_2P(1)O_4$ tetrahedra as the bridges to link them together *via* –Zn–O–P(1)–O–Zn– linkages. The adjacent chains are connected with

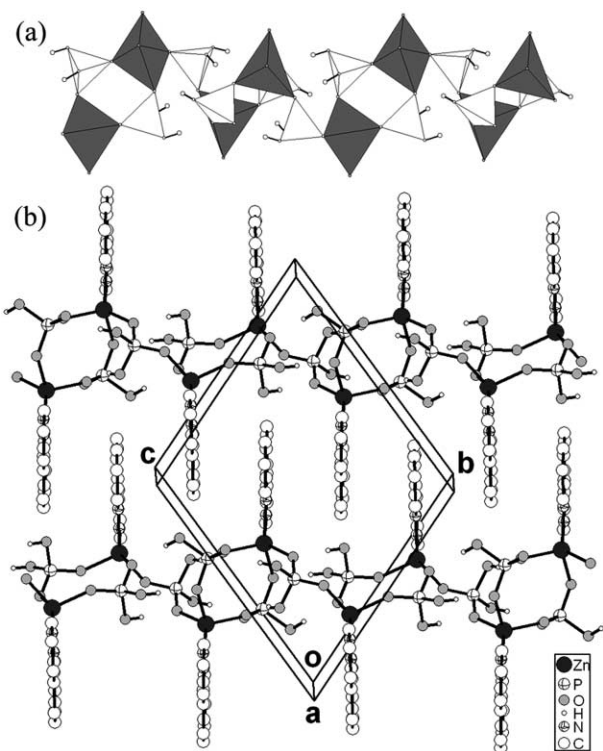


Fig. 4 (a) Polyhedral view of the chain-like structure of **2**. Medium gray, Zn-centered polyhedra; white, P-centered tetrahedra. (b) The structure of **2** along the [100] direction. All the water molecules are omitted for clarity.

each other through strong π - π interactions of the phen ligands that are grafted onto the chains, as reflected in close (<3.5 Å) intermolecular contacts (Fig. 4(b)).

Careful analysis of the structures of **1** and **2** reveals a close relationship between them. Both the compounds have the same Zn : P : phen ratio and similar coordination environments for the Zn and P centers. The chain-like structure of **2** can be generated from **1** by mere shifting of Zn-O-P bonds, as shown in Fig. 5. According to the *aufbau* principle of building higher-dimensional structures from that of the lower-dimensional ones,¹² it is conceivable that the isolation of **1** may give rise to other open architectures.

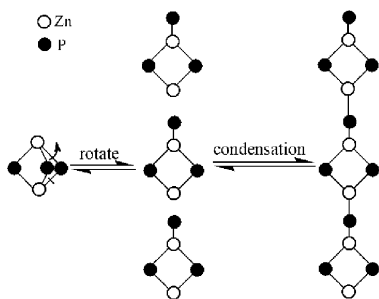


Fig. 5 Schematic representation of the possible pathway in the monomer-to-chain transformation.

Thermogravimetric analysis of **1** and **2** was carried out under air atmosphere from 50 to 1250 °C with a heating rate of 10 °C min⁻¹. The TG curve of **1** shows a two-step weight loss between 280 and 1060 °C. The initial weight loss between 280 and 400 °C corresponds to the dehydration process (observed, 5.77%; expected, 5.76%). The second step occurring between 400 and 1060 °C is assigned to the departure of organic molecules (observed, 45.33%; expected, 46.14%). The TG curve of **2** shows a three-stage weight loss over the range 300–1100 °C. The initial weight loss between 300 and 360 °C is attributed to the loss of occluded water molecules. However, the observed mass

loss (4.69%) was much higher than the expected value (calc. 1.14%). This likely is due to the presence of water molecules absorbed on the surface of the compound. The next two stages correspond to the dehydration of HPO₄²⁻ and H₂PO₄⁻ groups (observed, 5.73%; expected, 5.70%) and the removal of organic molecules (observed, 47.11%; expected, 45.62%). In both cases, the loss of the amine molecule resulted in the collapse of the framework structure, as indicated by powder X-ray diffraction analysis.

The photoluminescent spectra of **1** and **2** were measured in the solid state at room temperature. The emissive spectrum of **1** is composed of two strong bands at 376 and 395 nm, one shoulder at 415 nm and one broad band at 523 nm ($\lambda_{\text{ex}} = 330$ nm). These emissions may be assigned to intraligand fluorescent emission (for $\lambda_{\text{max}} = 376, 395$ and 415 nm) and ligand-to-metal charge transfer (LMCT) (for $\lambda_{\text{max}} = 523$ nm). Upon excitation at 412 nm, **2** gives a strong emission band at $\lambda_{\text{max}} = 530$ nm, assigned as LMCT. It can be expected that by varying the topologies and compositions of metal phosphates, photoluminescent materials with a wide range of emission characteristics may be developed.

Conclusions

In summary, this work describes the syntheses, structures and some properties of two novel inorganic-organic hybrid zinc phosphates with neutral frameworks. Compound **1** provides the first example of a non-centrosymmetric zinc phosphate monomer. It is also clearly illustrated that the one-dimensional structure of **2** may be generated from the monomeric phase by a shifting of Zn-O-P bonds. They are the first members in the zinc-phosphate-phen system. Given the large variety of organic ligands that can be used in the synthesis, it can be expected that many other novel inorganic-organic hybrid materials will be realized.

Acknowledgements

This work was supported by the NSF of China (Grant No. 20271050 and 20171045), the SRF for ROCS of State Education Ministry, the Ministry of Finance of China and the Talents Program of the Chinese Academy of Sciences, and State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University.

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