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Open-framework zinc and cobalt phosphates synthesized by the tributylphosphate route†

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By employing tributylphosphate as the source of phosphorus, several open-framework zinc and cobalt phosphates have been prepared hydrothermally. Of the three new zinc phosphates $[C_6N_2H_{18}][Zn(HPO_4)_2]$, **I**, has a linear chain structure while $[C_4N_2H_{14}][Zn_5(PO_4)_4(H_2O)]$, **II**, $[NH_4][H_3O][Zn_4(PO_4)_3]_2{\cdot}H_2O$, **III**, have three-dimensional structures. Of the three new cobalt phosphates described, $[C_5N_2H_{14}][Co(HPO_4)_2]$, **IV**, and $[C_5N_2H_{14}][Co(HPO_4)_2]$, **V**, have linear chain structures, while $[C_4N_2H_{12}]_3\,[Co_2(OH)(HPO_4)_3]_2$, **VI**, has a complex double chain structure. The study shows that the use of the organophosphate yields a variety of architectures of metal phosphates.

Introduction

A large number of open-framework metal phosphates have been discovered in recent years.[1,2] This dramatic expansion has stemmed from their applications to heterogeneous catalysis[3,4] and as sorbents and ion exchangers.[5] For example, nickel phosphates have been studied extensively as hydrogenation/dehydrogenation catalysts,[6] and for hydrogen storage.[7] Group IV and V phosphates have been studied for their ion-exchange properties,[5] and iron phosphates have been extensively researched as potential cathode materials for use in lithium ion batteries.[8] Other transition metal framework phosphates are of special interest due to their potential catalytic, electrical, optical, and magnetic properties, which are inaccessible to zeolites and other frameworks based on main group elements.[9] The synthesis of these materials is generally carried out under hydrothermal conditions by taking a metal salt and phosphoric acid in the presence of an organic amine, which may act as a template or as a structure-directing agent. The formation of open-framework structures is kinetically controlled and can be highly sensitive to the variation in reaction conditions such as the choice of solvent,[10] pH and the nature of the metal source.[11–14] Accordingly, we have shown recently that novel open-framework metal phosphate structures can be obtained by the reaction of metal salts with organophosphate esters[15] and amides.[16] In the present work, we have explored the preparation of metal phosphate open-framework structures using organophosphate esters in order to establish whether this method does indeed give rise to a variety of architectures with novel structural features. The results have been encouraging and in this article we describe three new open-framework zinc phosphates, **I–III**, of which one has a linear chain structure, **I**, and remaining two three-dimensional (3D) structures, **II**, **III**. In addition, we discuss three new cobalt phosphates, with chain structures, **IV–VI**. Considering that a layered and few 3D cobalt phosphates have been reported by us earlier using this method,[15,17] the variety of structures generated in this way is very impressive.

Experimental

Synthesis of zinc phosphates

In a typical synthesis, zinc(II) chloride was dissolved in a butan-2-ol–water mixture. Tributylphosphate (TBP) was added to the solution under constant stirring followed by an organic amine (*N*,*N*′-diethylethylenediamine in the case of **I**, *N*,*N*′-dimethylethylenediamine for **II**, and 4-piperidinopiperidine for **III**). The homogenized gel was sealed in a Parr autoclave and heated at 180 °C for 60 h. The product, consisting of colorless crystals, was filtered off and washed with a minimum quantity of water, and dried at 70 °C. The final compositions and synthesis conditions are listed in Table 1. We also made a piperazine templated zinc phosphate, which has previously been synthesized by another procedure.[18]

Synthesis of cobalt phosphates

In a typical synthesis of a cobalt(II) phosphate, a known amount of $CoCl_2{\cdot}6H_2O$ was dissolved in butan-2-ol. Tributylphosphate was added to the solution followed by an organic amine (2-methylpiperazine in the case of **IV** and **V**, piperazine for **VI**) and the mixture stirred until it became homogeneous. The gels were sealed in Parr autoclaves at 180 °C for 60 h. The products, consisting of deep blue crystals (except in the case of **VI**, which is purple), were filtered off under vacuum and washed with a minimum amount of methanol and dried at 70 °C. The gel compositions and synthesis conditions are listed in Table 1.

Single crystal structure determinations

Suitable single crystals of each of the title compounds were carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (Superglue) adhesive. Crystal structure determination by X-ray diffraction was performed on a Siemens SMART-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with ω scans (width 0.30° and exposure time of 30 s per frame). An empirical correction based on symmetry equivalent reflections was applied using the

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† Electronic supplementary information (ESI) available: Tables S1–16: Atomic coordinates, equivalent isotropic displacement parameters and bond lengths and angles for compounds **I–VII**. See http://www.rsc.org/suppdata/jm/b3/b311529a/

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Table 1 Synthetic conditions and product compositions for new compounds listed in this study

	Gel composition	T/K	Time/h	Product composition
I	$ZnCl_2$:2 TBP:2 N,N'-diethylethylenediamine:80 2-BuOH:20 H_2O	453	60	$[C_6N_2H_{18}][Zn(HPO_4)_2]$
II	$ZnCl_2$:2 TBP:2 N,N'-dimethylethylenediamine:80 2-BuOH:20 H_2O	453	60	$[C_4N_2H_{14}][Zn_5(PO_4)_4(H_2O)]$
III	2 $ZnCl_2$:2 TBP:3 4-piperidinopiperidine:80 2-BuOH:20 H_2O	453	60	$[NH_4][H_3O][Zn_4(PO_4)_3]_2\cdot H_2O$
IV	$CoCl_2\cdot 6H_2O$:2 TBP:2 2-methylpiperazine:100 2-BuOH	453	60	$[C_5N_2H_{14}][Co(HPO_4)_2]$
V	$CoCl_2\cdot 6H_2O$:3 TBP:2 2-methylpiperazine:100 2-BuOH	453	60	$[C_5N_2H_{14}][Co(HPO_4)_2]$
VI	$CoCl_2\cdot 6H_2O$:4 TBP:5 piperazine:100 2-BuOH	453	60	$[C_4N_2H_{12}]_3[Co_2(OH)(HPO_4)_3]_2$

SADABS program.[19] The structures were solved by direct methods using SHELX-97 and difference Fourier syntheses.[20] All the hydrogen positions were located from difference Fourier maps and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The relevant details of the structure determination of the zinc phosphates, **I–III** are given in Table 2 and those of cobalt phosphates **IV–VI** in Table 3. Full matrix least-squares refinement against $|F^2|$ was carried out using the SHELXTL-PLUS package of programs.[21] The last cycles of refinement included atomic positions and anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms.

CCDC reference numbers 220185–220190.

See http://www.rsc.org/suppdata/jm/b3/b311529a/ for crystallographic data in CIF or other electronic format.

Results and discussion

By the reaction of tributylphosphate with metal salts in butan-2-ol–water we have obtained several novel open-framework metal phosphates. These include the one-dimensional chain zinc phosphate $[C_6N_2H_{18}][Zn(HPO_4)_2]$, **I**, two three-dimensional zinc phosphates $[C_4N_2H_{14}][Zn_5(PO_4)_4(H_2O)]$, **II**, and $[NH_4][H_3O][Zn_4(PO_4)_3]_2\cdot H_2O$, **III**, in addition to those reported earlier using this method.[15] Besides the new zinc phosphates, we have obtained three cobalt(II) phosphates, which include those with linear chain structure of compositions $[C_5N_2H_{14}][Co(HPO_4)_2]$, **IV**, $[C_5N_2H_{14}][Co(HPO_4)_2]$, **V**, and a complex double-chain structure with the composition $[C_4N_2H_{12}]_3[Co_2(OH)(HPO_4)_3]_2$, **VI**. Compound **V**, a polymorph of **IV** has already been reported in the literature following a different synthetic route and its structure has not

Table 2 Crystal data and structure refinement parameters for **I–III**

	I	**II**	**III**
Chemical formula	$[C_6N_2H_{18}][Zn(HPO_4)_2]$	$[C_4N_2H_{14}][Zn_5(PO_4)_4(H_2O)]$	$[NH_4][H_3O][Zn_4(PO_4)_3]_2\cdot H_2O$
Formula mass	375.39	814.95	1148.12
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	$Pbca$	$Pna2_1$	$P\bar{1}$
T/K	293	293	293
a/Å	8.0797(18)	20.7603(12)	5.0400(9)
b/Å	14.555(3)	5.2207(3)	9.584(3)
c/Å	28.575(7)	17.9147(10)	13.117(2)
α/°	90	90	101.094(19)
β/°	90	90	100.931(19)
γ/°	90	90	103.598(18)
V/Å^3	3360.4(13)	1941.65(19)	585.7(2)
Z	8	4	2
μ/mm^{-1}	1.695	6.507	8.572
2θ Range data collected/°	2.86–57.68	3.92–56.52	3.26–56.64
Total data collected	18685	10549	3484
Unique data	3986	4153	2529
Observed data ($I > 2\sigma(I)$)	2036	3835	2327
R_1, wR_2 [$I > 2\sigma(I)$]	0.1024, 0.2678	0.0354, 0.0825	0.0456, 0.1204
R_1, wR_2 (all data)	0.1858, 0.3310	0.0391, 0.0840	0.0495, 0.1228

Table 3 Crystal data and structure refinement parameters for **IV–VI**

	IV	**V**	**VI**
Chemical formula	$[C_5N_2H_{14}][Co(HPO_4)_2]$	$[C_5N_2H_{14}][Co(HPO_4)_2]$	$[C_4N_2H_{12}]_3[Co_2(OH)(HPO_4)_3]_2$
Formula mass	352.93	352.93	1109.72
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$	$P2_1/n$
T/K	293	293	293
a/Å	11.939(2)	8.6069(11)	7.2743(18)
b/Å	13.803(3)	13.4487(16)	23.030(6)
c/Å	7.9473(15)	10.8041(13)	9.873(2)
β/°	91.514(3)	95.537(2)	93.131(4)
V/Å^3	1309.2(4)	1244.8(3)	1651.4(7)
Z	8	4	4
μ/mm^{-1}	1.592	1.670	2.377
2θ range data collected/°	4.52–56.54	4.84–56.48	4.50–56.48
Total data collected	3800	7230	10083
Unique data	1515	2867	3857
Observed data ($I > 2\sigma(I)$)	1361	1966	2831
R_1, wR_2 [$I > 2\sigma(I)$]	0.0343, 0.1058	0.0385, 0.0740	0.0501, 0.1348
R_1, wR_2 (all data)	0.0384, 0.1078	0.0692, 0.0806	0.0727, 0.1464

been discussed here.[22] A layered and a few three-dimensional cobalt(II) phosphates prepared by the tributylphosphate route have been reported earlier.[15,17] This method is of general utility for the synthesis of a variety of metal phosphates as demonstrated by the reports of the synthesis of manganese and iron phosphates.[23,24]

Structure of $[C_6N_2H_{18}][Zn(HPO_4)_2]$, I

The asymmetric unit of **I**, shown in Fig. 1(a), consists of 19 non-hydrogen atoms. The structure of **I** is formed of ZnO_4 and PO_4 moieties linked *via* oxygen atoms to form the basic unit of the structure, a four-membered ring. The P–O distances are in the range 1.511–1.552 Å and the O–P–O bond angles are in the range 106.6–111.8°. All the zinc atoms are four-coordinated with respect to oxygen with Zn–O distances in the range 1.915–1.962 Å and O–Zn–O bond angles in the range 99.1–117.0°. The framework structure consists of infinite chains along the *a*-axis, each chain consisting of corner-shared four-membered rings. The anionic chains are held together by strong hydrogen bond interactions between the terminal –OH groups, water molecules and the protonated *N*,*N*′-diethylethylenediamine molecules that are located between the two chains (Fig. 1(b))

Structure of $[C_4N_2H_{14}][Zn_5(PO_4)_4(H_2O)]$, II

Compound **II** possesses a three-dimensional architecture built of ZnO_4 and PO_4 tetrahedra. The asymmetric unit shown in Fig. 2(a) consists of 32 atoms of which 26 belong to the framework and 6 atoms belong to the guest species. There are five crystallographically independent zinc and four phosphorus atoms. Of the 17 oxygen atoms present in the asymmetric unit, four (O(2), O(9), O(14), O(17)) are three-coordinated and the remainder are two-coordinated. The Zn–O distances are in the range 1.880–2.051 Å and the O–Zn–O angles are in the range 97.84–126.27°, which are typical of Zn atoms in a tetrahedral environment. Zn(5) bears a terminal H_2O ligand characterized by a long Zn–O distance of 2.051 Å. All the four P atoms have P–O distances in the range 1.510–1.585 Å and the O–P–O angles are in the range 104.2–113.3°. All the long P–O bonds involve the three-coordinated oxygen atoms.

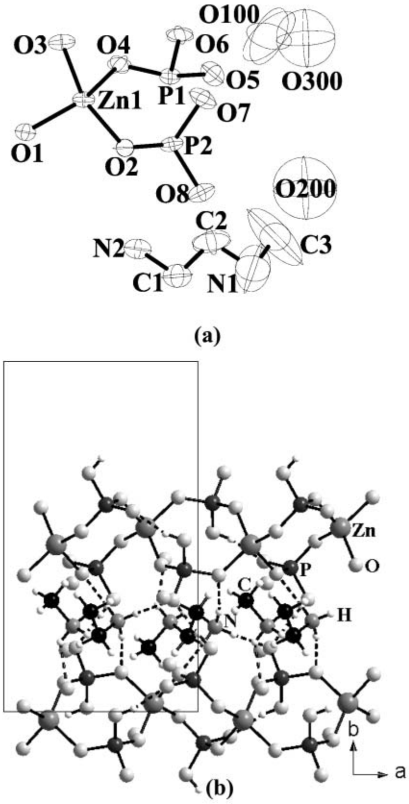

Fig. 1 (a) ORTEP plot of the asymmetric unit of $[C_6N_2H_{18}]$-$[Zn(HPO_4)_2]$, **I**. (b) Structure of **I** when viewing down the *c*-axis showing the corner-sharing chains. Note the hydrogen bonded amine molecules.

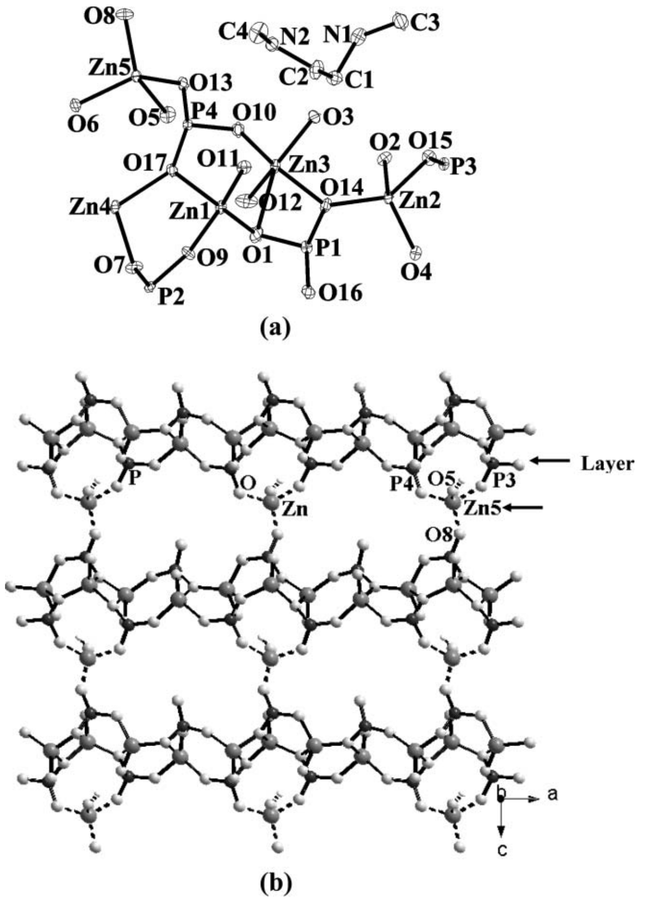

Fig. 2 (a) ORTEP plot of the asymmetric unit of $[C_4N_2H_{14}]$-$[Zn_5(PO_4)_4(H_2O)]$, **II**. (b) Ball-and-stick view of **II** along the *b*-axis. Also marked are the layers and the ZnO_4 (Zn(5)) tetrahedra, which links the layers through the PO_4 tetrahedra (P(3) and P(4)) to form the three-dimensional framework.

Assuming the valences of Zn, P and O to be +2, +5 and −2, respectively, the framework stoichiometry of $Zn_5(PO_4)_4$ creates a framework charge of −2. The negative charge of the framework is balanced by diprotonated *N*,*N*′-dimethylethylenediamine molecules. The bond valence sums calculated using the program VALIST[25] are in accordance with the assignment of the formula.

The three-dimensional structure can be envisaged in many ways. One of the simple ways is to consider it as comprising zinc phosphate layers perpendicular to the *c*-axis (Fig. 2(b)) linked together by ZnO_4 tetrahedra to form the three-dimensional architecture. The connectivity of the ZnO_4 and PO_4 moieties with in the zinc phosphate layer produces four types of chains, labeled as A, B, C and D in Fig. 3(a). The type A chain is made up of only four-membered rings (Zn(1), Zn(3), P(1), P(4)), while type B chain is made up only three-membered rings (Zn(1), Zn(4), P(4); Zn(1), Zn(4), P(2)). The C type chain consists of alternate stacks of three- and four-membered rings (Zn(2), Zn(4), P(2); Zn(2), Zn(4), P(2), P(3)) (Fig. 3(a)). The linking of A and C chains results in chain D which also contains alternate stacks of three- and four-membered rings (Zn(2), Zn(3), P(3); Zn(2), Zn(3), P(1), P(3)). The chains are connected to each another forming the layer as shown in Fig. 3(a) The phosphate tetrahedra P(3) and P(4) of the layer add on another ZnO_4 tetrahedra Zn(5) which links to the phosphate tetrahedra P(2) of another layer through oxygen

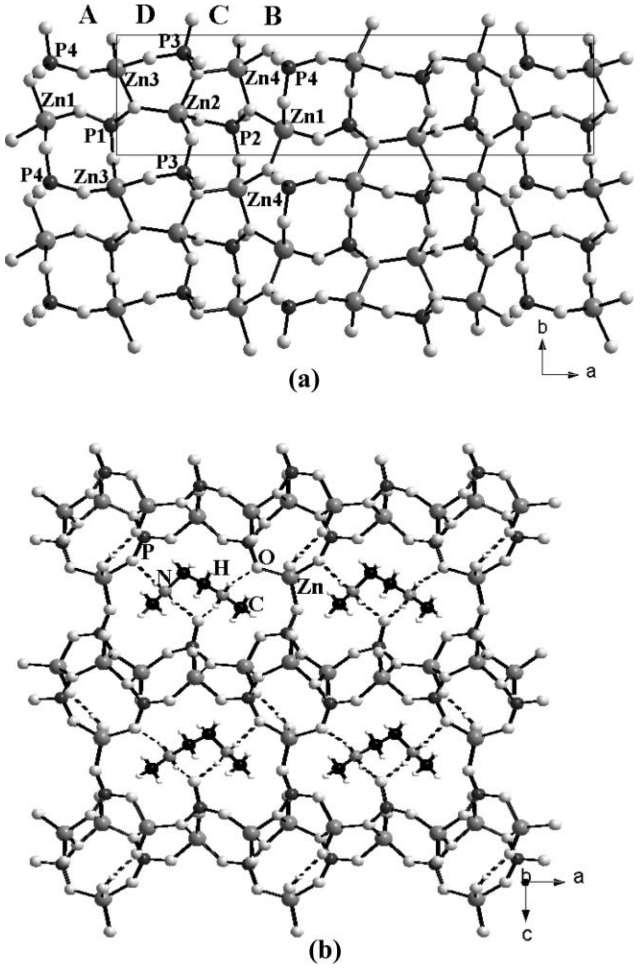

Fig. 3 (a) A section of **II** showing the layer formed from chains A, B, C and D. Also labeled are the zinc and phosphorus atoms involved in forming the various rings, which build these chains. (b) Structure of **II** along the *b*-axis showing the 10-membered channels and the amine molecule. Dotted lines represent the hydrogen bond interactions.

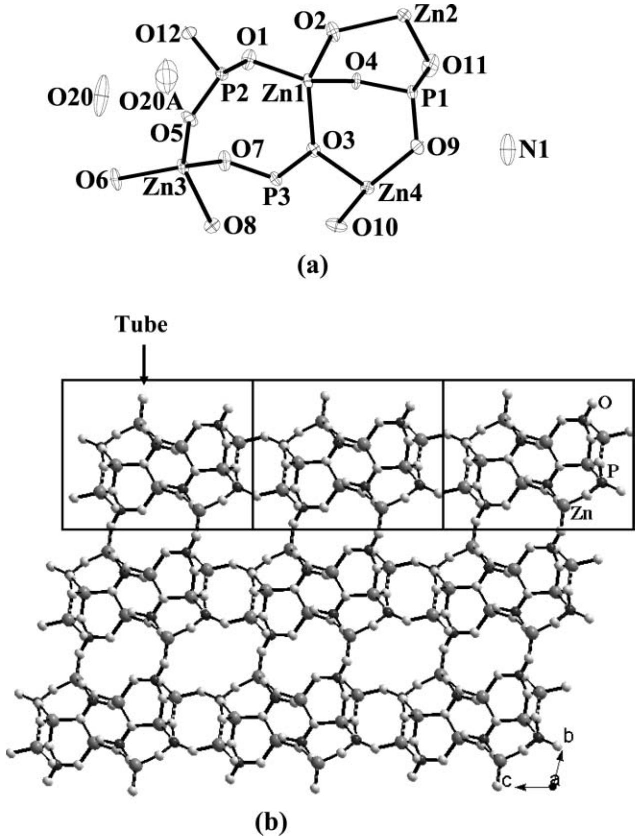

Fig. 4 (a) ORTEP plot of the asymmetric unit of $[NH_4][H_3O][Zn_4(PO_4)_3]_2\cdot H_2O$, **III**. (b) Ball-and-stick view of **III** along the *a*-axis. Also marked in boxes are 'tube' like features which link together to form the structure.

O(8) to form the three-dimensional architecture containing 10-membered channels along the *b*-axis (Fig. 2(b), 3(b)). The diprotonated *N*,*N*′-dimethylethylenediamine molecules are present in the middle of 10-membered channels (10.42 × 4.72 Å; oxygen-to-oxygen contact distance excluding the van der Waals radii) and interact with the framework oxygen *via* hydrogen-bonding (Fig. 3(b)). The Zn(5) atom bears a terminal oxygen O(5) which has been assigned as a water molecule. The presence of the ABCCABCC repeat unit along the *ab* plane gives rise to the repeat ring sequences of 43444333 and 43334344 along the *a*-axis. The framework of the **II** is also characterized by the presence of infinite Zn–O–Zn chains formed by Zn(1) and Zn(4) atoms. The short Zn–O–Zn branches emerging from the main chain involve Zn(2) and Zn(3) tetrahedra. Zn–O–Zn linkage is accompanied by the trigonal coordination of the bridging oxygen atoms, the third coordination being always to a P atom.

Structure of $[NH_4][H_3O][Zn_4(PO_4)_3]_2\cdot H_2O$, III

Compound **III** possesses a three-dimensional architecture built of ZnO_4 and PO_4 tetrahedra. The asymmetric unit shown in Fig. 4(a) consists of 21 atoms of which 19 belong to the framework and 2 atoms belong to the guest species. There are four crystallographically independent zinc and three phosphorus atoms. Of the 12 oxygen atoms present in the asymmetric unit, four (O(2), O(3), O(4), O(8)) are three-coordinated and the remainder are two-coordinated. The Zn–O distances are in the range 1.893–2.046 Å and the O–Zn–O angles are in the range 99.28–118.6°, which are typical of Zn atoms in a tetrahedral environment. All the three P atoms have P–O distances in the range 1.508–1.573 Å and the O–P–O angles are in the range 105.2–113.3°. All the long P–O and Zn–O bonds involve the three-coordinated oxygen atoms.

Assuming the valences of Zn, P and O to be +2, +5 and −2, respectively, the framework stoichiometry of $Zn_4(PO_4)_3$ creates a framework charge of −1. The negative charge of the framework is balanced by 0.5 molecules of ammonium ion (formed by decomposition of 4-piperidinopiperidine). The remaining half charge is balanced by a proton, which may be present on the water molecule located in the channel.

The three-dimensional structure can be envisaged to be built of linkage of zinc phosphate tubes, which can viewed along the *a*-axis (Fig. 4(b)). The structure of the zinc phosphate tubes can be understood by complex linking of a core zinc phosphate chain with two identical peripheral zinc phosphate chains (Fig. 5(a)). The core is formed by linking of two three-membered chains (type A) linked in an inverted fashion (see Fig. 5(b)), where as the peripheral zinc phosphate chains, which are also comprised of three-membered rings, involve a different connectivity (type B). The type A chain involves Zn(3), Zn(4) and P(3) tetrahedra, whereas the type B chain involves Zn(1), Zn(2), P(1) and Zn(1), Zn(2), P(2) tetrahedra (Fig. 6(a)–(c)). The linking of these chains results in the zinc phosphate tube, which are linked with each other along the *a*-axis to result in eight-membered channels formed along the *a*-axis (Fig. 6(d)). The channels are alternately occupied by water and ammonium molecules (Fig. 6(d)). The water molecules are crystallographically disordered. The channel like features are evident when the structure is viewed along the *c*-axis.

The framework of **III** is also characterized by the presence of infinite Zn–O–Zn chains formed by Zn(1) and Zn(2) atoms. The short Zn–O–Zn branches emerging from the main chain

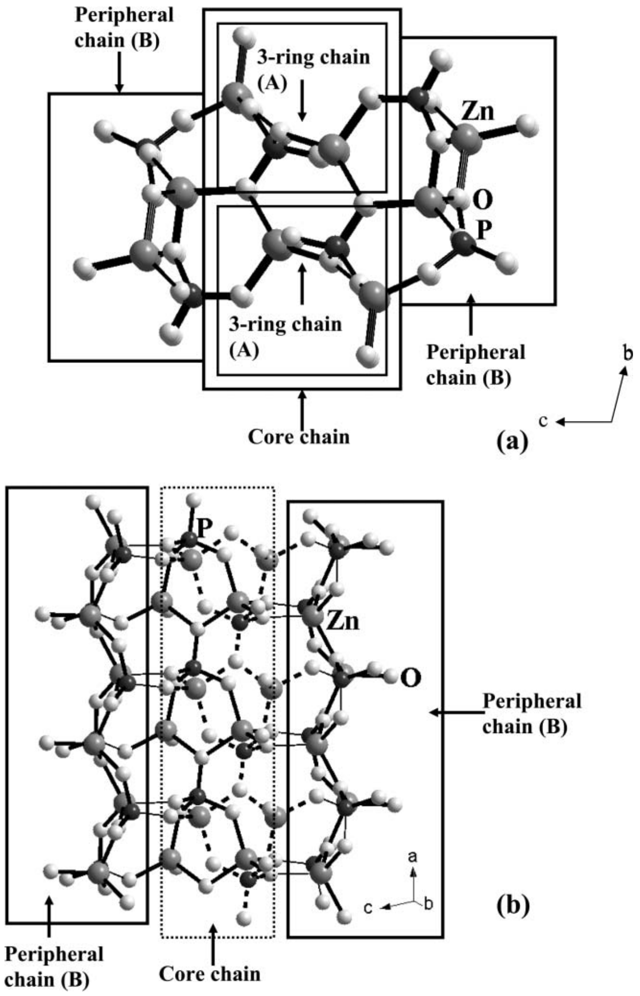

Fig. 5 (a) Top view of a single 'tube' taken from a section of **III** along the *a*-axis. The core and peripheral chains (B) are labeled and marked in separate boxes. Note that core chains are formed by linking of two three-ring chains (A). (b) Side view of a single 'tube' of **III**. The core chain is marked in the dotted box whereas the peripheral chains are marked in solid boxes.

involve Zn(3) and Zn(4) tetrahedra. Zn–O–Zn linkage is accompanied by the trigonal coordination of the bridging oxygen atoms, the third coordination being always to a P atom.

Structure of $[C_5N_2H_{14}][Co(HPO_4)_2]$, IV

The asymmetric unit of **IV**, shown in Fig. 7(a), consists of 10 non-hydrogen atoms. The structure of **IV** is formed of CoO_4 and PO_4 moieties linked *via* oxygen atoms to form the basic unit of the structure, a four-membered ring. The P–O distances are in the range 1.514–1.569 Å and the O–P–O bond angles are in the range 105.51–112.05°. All the cobalt atoms are four-coordinated with respect to oxygen with Co–O distances in the range 1.929–1.968 Å and O–Co–O bond angles in the range 94.92–116.38°. The blue colour is consistent with the tetrahedral coordination of cobalt. The framework structure consists of infinite chains along the *c*-axis, each chain consisting of corner-shared four-membered rings. The anionic chains are held together by strong hydrogen bond interactions between the terminal –OH groups, water molecules and the protonated 2-methylpiperazine molecules that are located between the two chains (Fig. 7(b)). The 2-methylpiperazine molecule appears as 2,4-dimethylpiperazine due to its statistical distribution on two sites.

Structure of $[C_4N_2H_{12}]_3[Co_2(OH)(HPO_4)_3]_2$, VI

The asymmetric unit of **VI**, shown in Fig. 8(a), consists of 27 non-hydrogen atoms. The structure of **VI** is formed of CoO_5 and PO_4 moieties linked *via* oxygen atoms to form a complex double chain structure. The P–O distances are in the range 1.504–1.585 Å and the O–P–O bond angles are in the range 104.51–115.47°. All the cobalt atoms are five-coordinated with respect to oxygens with Co–O distances in the range 1.969–2.179 Å and O–Co–O bond angles in the range 83.95–177.73°. Unlike the tetrahedrally coordinated systems, **VI**, **V** and **VII**, this material is purple rather than blue. On taking into account the interaction between the Co(2) and O(3) oxygen atoms of $Co(1)O_5$ polyhedra, which are at a distance of 2.417 Å from Co(2), the cobalt atom Co(2) becomes six-coordinated. All the oxygen atoms are two connected except for three (O(2), O(3) and O(5)) which are three-connected. The framework consists of two identical chains linked together by HPO_4 moieties to yield a complex double chain structure. Each individual chain is built up of linking of corner-shared three-rings (Co(2), P(1), Co(1); Co(1), P(2), Co(2)) with Co(1) being the vertex atom (Fig. 8(b)). Two of these chains are linked together by HPO_4 (P(3)) tetrahedra (O4, O9, O13) to form the complex double chain (Fig. 8(c)). The cobalt–oxygen connectivity leads to the formation of a one-dimensional cobalt–oxygen ladder (Fig. 9(a)). The bond valence calculations performed using VALIST[25] confirm that the cobalt atoms are in the +2 oxidation state and oxygen atom O(2) is a hydroxyl group. The anionic chains are held together by diprotonated piperazinium cations, which interact with the terminal –OH groups of the chains *via* strong hydrogen bonding (Fig. 9(b)).

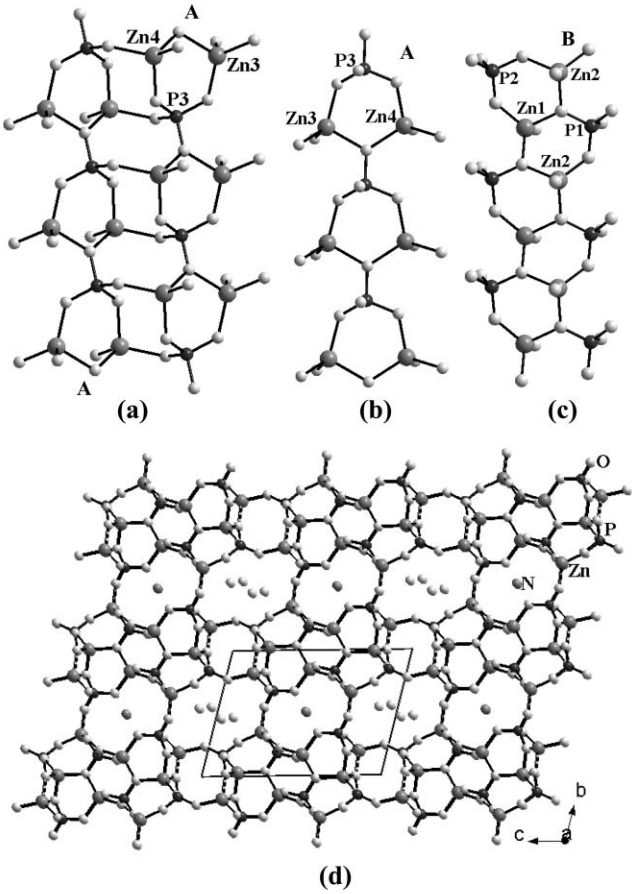

Fig. 6 (a) A section of tube showing the linkage of two three-ring chains (A) in a core chain. (b) Ball-and-stick view showing the three-ring connectivity in a type A chain in **III**. (c) Ball-and-stick view showing the three-ring connectivity in a type B chain in **III**. (d) Structure of **III** along the *a*-axis showing the six- and eight-membered channels containing ammonium ions and water molecules.

A large number of open-framework zinc, cobalt, and iron phosphates have been synthesized using the new synthetic route wherein an organophosphate, tributylphosphate, is used as the

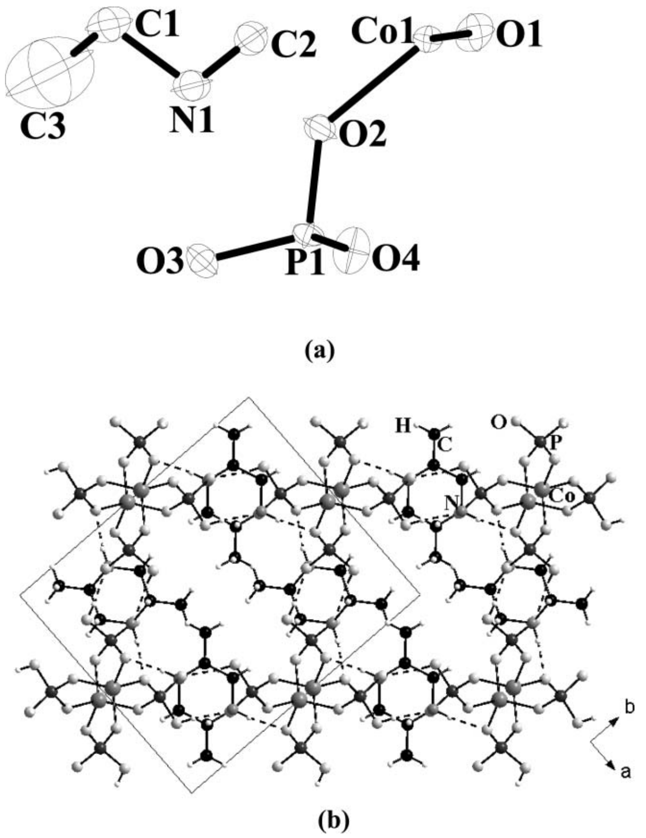

Fig. 7 (a) ORTEP plot of the asymmetric unit of $[C_5N_2H_{14}][Co(HPO_4)_2]$, **IV**. (b) Structure of **IV** when viewing along the *c*-axis showing the corner-sharing chains and the hydrogen bonded amine molecules. Dotted lines represent the hydrogen bond interactions. Also note the disorder of the methyl group of the amine molecule.

source of phosphorus. Among the zinc phosphates, **I**, exhibits one-dimensional chain topology, whereas **II** and **III** exhibit three-dimensional architectures. The framework of **I** is made up of corner-shared four-membered Zn_2P_2 rings. These chains have been proposed to be the significant building block in the case of aluminium, zinc and gallium phosphates and have been known to transform to result in complex three-dimensional architectures.[26–28] The framework of **II** is comprised of zinc phosphate layers perpendicular to the *c*-axis linked together by ZnO_4 tetrahedra to form the three-dimensional architecture. Compound **III** is isostructural with a material reported by Stucky and coworkers.[29] The framework of **III** can be envisaged to be built of linking of zinc phosphate tubes viewed along the *a*-axis. The structures of both **II** and **III** are primarily characterized by infinite Zn–O–Zn chains, with short Zn–O–Zn branches emanating from the chains. Compound **II** has an inorganic framework identical to that of a zinc phosphate obtained with diethylenetriamine reported in the literature, except that one of the nitrogen atoms of the amine in the latter is coordinated to the zinc center.[30] Both **II** and the zinc phosphate reported earlier possess one-dimensional 10-membered channels, akin to that of aluminosilicates.[2] Surprisingly, these are the only cases where the existence of 10-membered channels has been observed in zinc phosphates, although they are commonly found in other open-framework systems.

The corner-sharing (CS) chains of cobalt phosphates **IV** and **V**, is a key structural element of the sodalite structure.[17] Compound **IV** obtained with 2-methylpiperazine has similar unit cell parameters and is isostructural to a linear chain cobalt phosphate reported in the literature obtained with a different amine, *N*,*N*′-dimethylpiperazine. Such four-ring CS chains have been isolated in zinc, aluminium and gallium phosphates.[26–28] The complex double-chain structure in cobalt(II) phosphate, **VI** containing five- and six-coordinated cobalt atoms has been observed for the first time, however, a three-dimensional cobalt phosphate with four-, five- and six-coordinated cobalt atoms has already been reported in the literature.[14] We had earlier reported two- and three-dimensional cobalt phosphates synthesized *via* the tributylphosphate route.[15,17] The layered cobalt phosphate has chains formed from vertex connected cobalt–oxygen tetrahedra, similar to that reported in a layered cobalt phosphate.[31] Of the three-dimensional cobalt phosphates two of these have interrupted sodalite-type structures resulting from the removal of Co^{2+} atoms from sites related by two-fold axes passing through the four-rings of the normal sodalite cage structure.[17]

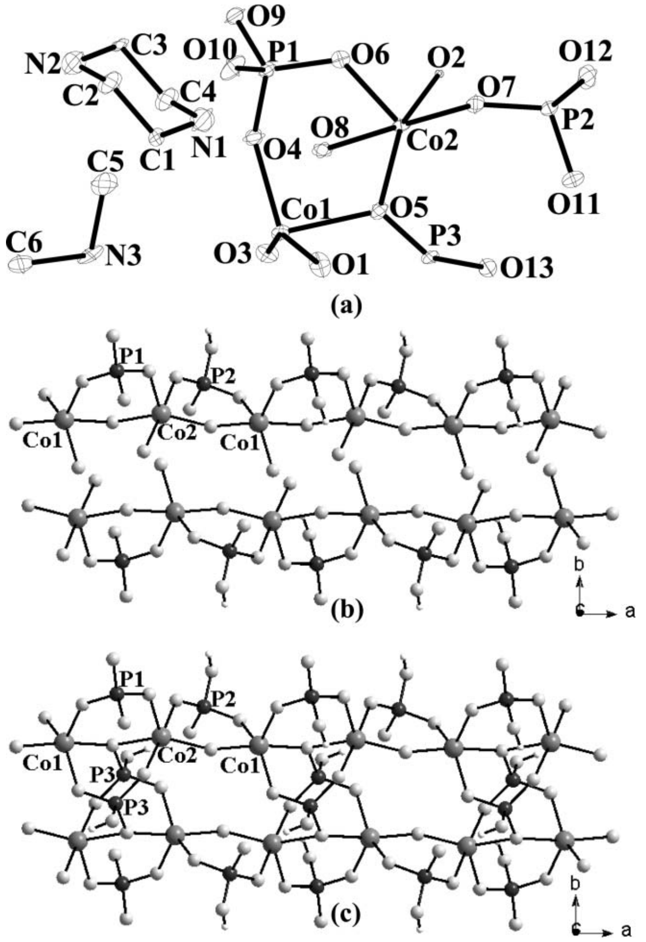

Fig. 8 (a) ORTEP plot of the asymmetric unit of $[C_4N_2H_{12}]_3[Co_2(OH)(HPO_4)_3]_2$, **VI**. (b) A section of **VI** showing the two three-ring chains. (c) The linking of two three-ring chains *via* HPO_4 (P(3)) groups to yield the complex double chain of **VI**. Also labeled are the cobalt and phosphorus atom involved in the formation of the complex chains.

The present study clearly demonstrates that the tributylphosphate route yields a large variety of open-framework zinc and cobalt phosphates. Apart from the zinc and cobalt phosphates, described in the present study and elsewhere,[15,17] manganese and iron phosphates have also been prepared by using the tributylphosphate route.[23,24] The isolation of these framework solids shows that by choosing the appropriate reactant, one can alter the kinetics of the hydrothermal reaction, which can help in the isolation of new frameworks. The choice of organophosphate as a phosphorylating agent is very crucial to these syntheses as it allows the reaction media to be altered from aqueous to completely non-aqueous by varying the size of the alkyl group of the phosphate ester. Non-aqueous conditions, as with TBP, have been especially useful in the synthesis of open-framework cobalt(II) and manganese(II) phosphates. Use of phosphorus pentaoxide or phosphoric acid often leads to the

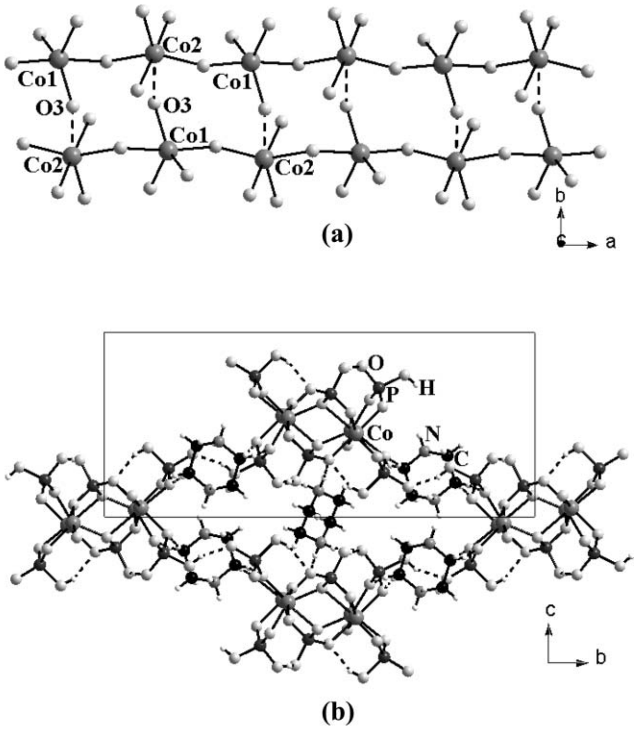

Fig. 9 (a) Infinite one-dimensional cobalt–oxygen ladders observed in complex double chains in **VI**. The dotted lines show the Co(2)–O(3) bond at a distance of 2.417 Å. (b) Structure of **VI** along the *a*-axis showing the chains and the hydrogen bonded amine molecules. The hydrogen bond interactions are shown as dotted lines.

formation of dense zinc and cobalt phosphates. This is because tetrahedral cobalt species form in non-aqueous (alcoholic) conditions, whereas when other sources of phosphorus are used cobalt tends to be octahedral and often ends up forming dense phases. The slow hydrolysis of tributylphosphate ester also influences the kinetics of the reaction by controlling the release of phosphate ions in solution. The non-aqeuous solvent and the organophosphate ester also influence the polarity and viscosity of the medium thereby affecting the mass transfer in addition to the kinetics. Our recent experiments with phosphite esters have also yielded zinc and cobalt phosphates.

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