DALTON
FULL PAPER

Simple linear-chain cobalt phosphates

Amitava Choudhury,[ab] **Srinivasan Natarajan**[a] **and C. N. R. Rao** *[ab]

[a] *Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India. E-mail: cnrrao@jncasr.ac.in*
[b] *Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India*

Received 4th April 2000, Accepted 13th June 2000
Published on the Web 13th July 2000

Two simple one-dimensional cobalt phosphates containing linear chains of corner-shared 4-membered rings have been synthesized hydrothermally by the reaction between amine phosphates and cobalt(II) ions under non-aqueous conditions. The linear chains are held together by hydrogen bond interactions involving the hydrogens of the amine and the framework oxygens. The two cobalt phosphates reported are the first linear chain compounds discovered in the family of open-framework transition metal phosphates.

Introduction

Open-framework metal phosphates, by and large, exhibit three-dimensional structures.[1] Several metal phosphates with two-dimensional layer structures have been reported, but only a few one-dimensional structures are known.[2] The one-dimensional structures occur either as edge-shared ladders or corner-shared linear chains, made-up of 4-membered rings, the ladders being more common. Surprisingly, of the few linear chain structures reported, none is that of a transition metal phosphate. Interest in these linear chain structures arises partly because of the crucial step these structures are expected to play, as precursors, in the formation of the complex two- and three-dimensional open-framework structures.[3] In order to prepare linear chain metal phosphates, we have sought to exploit the recent finding that the reaction of amine phosphates with metal ions provides a facile means of producing metal phosphates.[4] In this context, it is noteworthy that the not so common, two- and three-dimensional cobalt(II) phosphates were recently synthesized by the amine phosphate route.[5,6] We have been able to synthesize, for the first time, two new linear chain cobalt phosphates, **I**, $[C_5N_2H_{14}][Co(HPO_4)_2]$, and **II**, $[C_6N_2H_{16}][Co(HPO_4)_2]$, by the reaction of 2-methylpiperazinedium phosphate (MPIP-P) and *N*,*N'*-dimethylpiperazinedium phosphate (DPIP-P) with Co^{2+} ions. The amine phosphates themselves had to be prepared and characterized for this purpose. The compounds, **I** and **II**, possess 4-membered rings linked through their corners and stabilized by hydrogen bond interactions.

Experimental

The amine phosphates, MPIP-P and DPIP-P, were prepared employing standard synthetic procedures. Typically, for MPIP-P, 6 g of 2-methylpiperazine were dissolved in 6.5 ml of water. 5 ml of H_3PO_4 (85 wt%) were added dropwise under constant stirring. The mixture was heated in a polypropylene bottle at 110 °C for 20 h and allowed to crystallize at room temperature. A similar procedure was adopted for the preparation of DPIP-P. Large colorless rod-like crystals were obtained for both amine phosphates. The crystals of MPIP-P and DPIP-P were subjected to X-ray diffraction studies. Crystal data (298 K): $[C_5N_2H_{14}]_{0.5}[H_2PO_4]$ (MPIP-P), $M = 148.1$, space group = $P2_1/n$, $a = 6.680(6)$, $b = 7.962(6)$, $c = 12.218(8)$ Å, $\beta = 103.4(1)°$, $V = 632.1(8)$ Å^3, $Z = 4$, $\mu(\mathrm{MoK}\alpha) = 0.376$ mm^{-1}, $R1 = 0.1$, total data collected 2586, unique data 910, data $[I > 2\sigma(I)]$ 788; $[C_6N_2H_{16}]_{0.5}[H_2PO_4]$ (DPIP-P), $M = 155.1$, space group = $P2_1/c$, $a = 6.623(1)$, $b = 14.445(1)$, $c = 7.129(1)$ Å, $\beta = 104.9(1)°$, $V = 659.2(1)$ Å^3, $Z = 4$, $\mu(\mathrm{MoK}\alpha) = 0.364$ mm^{-1}; $R1 = 0.05$, total data collected 2665, unique data 946, data $[I > 2\sigma(I)]$ 721. The amine phosphates are similar to the many amine phosphates that have been reported recently.[7]

Compounds **I** and **II** were synthesized hydrothermally by treating the amine phosphates with Co^{2+} ions employing non-aqueous conditions. Thus, for **I**, 0.357 g of $CoCl_2 \cdot 6H_2O$ was dispersed in 3 ml of THF resulting in a clear blue solution. To this, 0.666 g of MPIP-P was added under continuous stirring, followed by 0.63 ml of triethylamine (TEA) to obtain a basic pH of 8. The final mixture with the composition $CoCl_2 \cdot 6H_2O$: 3MPIP-P : 3TEA : 25 THF was sealed in a poly(tetrafluoroethylene) (PTFE)-lined stainless-steel autoclave and heated at 180 °C for 40 h, to yield a crop of deep blue rod-like crystals. The crystals were vacuum filtered, washed with ethanol and dried under ambient conditions. A similar procedure employing DPIP-P with the starting composition $CoCl_2 \cdot 6H_2O$: 3DPIP-P : 3TEA : 25 THF gave a monophasic product **II**. Unlike **II**, **I** could be synthesized without the addition of TEA. The yields of the products were 55 and 70% for **I** and **II** respectively. An EDAX analysis indicated a Co : P ratio of 1 : 2 consistent with the single crystal data. The as-prepared compounds were stable in air, although finely ground samples absorbed water (changed from deep blue to pink) forming amorphous gelatinous solids. Attempts thermally to characterize **I** and **II** using thermogravimetric analysis (TGA) were not successful, since the removal of the amine and subsequent decomposition of the sample tended to be somewhat violent.

Suitable single crystals of compounds **I** and **II** were carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (super glue) adhesive. Single 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 (298 K). Pertinent experimental details are presented in Table 1. The structure was solved by direct methods using SHELXS 86[8] and Fourier difference syntheses. An empirical absorption correction based on symmetry equivalent reflections was applied for all the compounds using the SADABS[9] program. All the hydrogen positions were initially located in the Fourier difference maps, and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen

DOI: 10.1039/b002653k

Table 1 Crystal data and structure refinement parameters for compounds **I**, $[C_5N_2H_{14}][Co(HPO_4)_2]$, and **II**, $[C_6N_2H_{16}][Co(HPO_4)_2]$

	I	II
Formula mass	353.0	367.1
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	*Pccn*
a/Å	8.614(1)	11.879(1)
b/Å	13.456(1)	13.507(1)
c/Å	10.816(1)	8.168(1)
β/°	95.4(1)	
V/Å^3	1248.0(1)	1310.7(1)
Z	4	4
μ/mm^{-1}	1.666	1.590
Total data collected	5019	4929
Unique data	1788	938
Data $[I > 2\sigma(I)]$	1468	758
R_{int}	0.05	0.04
$R1$, $wR2$ $[I > 2\sigma(I)]$	0.03, 0.10	0.02, 0.06
(all data)	0.05, 0.11	0.04, 0.06

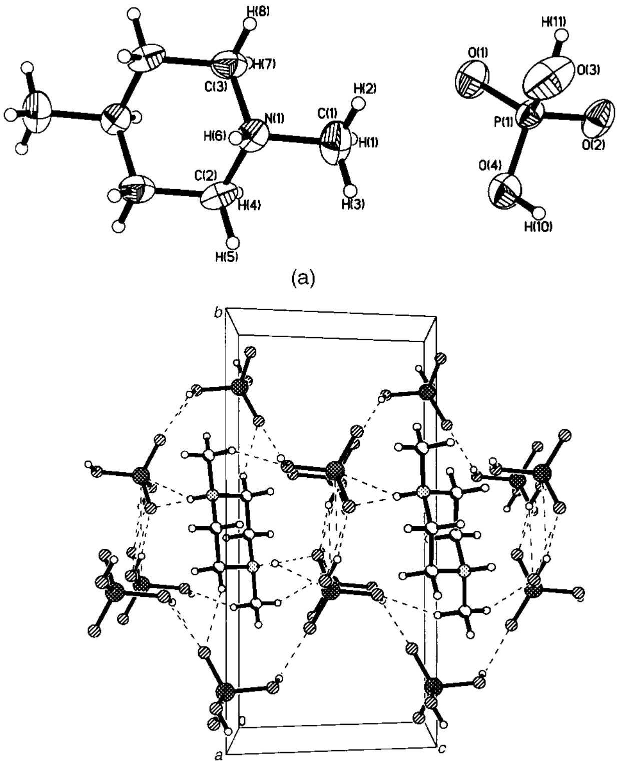

Fig. 1 (a) An ORTEP[11] plot of the amine phosphate DPIP-P. Thermal ellipsoids are given at 50% probability. (b) The packing diagram showing the arrangement of H_2PO_4 units and the amine molecules. Note that a layer-like arrangement with apertures is formed by the non-covalent interactions.

atoms. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL PLUS[10] package of programs.

CCDC reference number 186/2032.

See http://www.rsc.org/suppdata/dt/b0/b002653k/ for crystallographic files in .cif format.

Results and discussion

The structures of MPIP-P and DPIP-P are shown in Figs. 1 and 2. The tetrahedra of the dihydrogenphosphate units interact with each other *via* non-covalent interactions, forming layer like arrangements with apertures. The amine molecule sits in the middle of the apertures (Fig. 1b and 2b) and interacts with the phosphate moieties. Similar amine phosphate structures have been reported recently.[7] As mentioned earlier, compounds **I** and **II** are formed by the reaction between the amine phosphate and cobalt(II) ions.

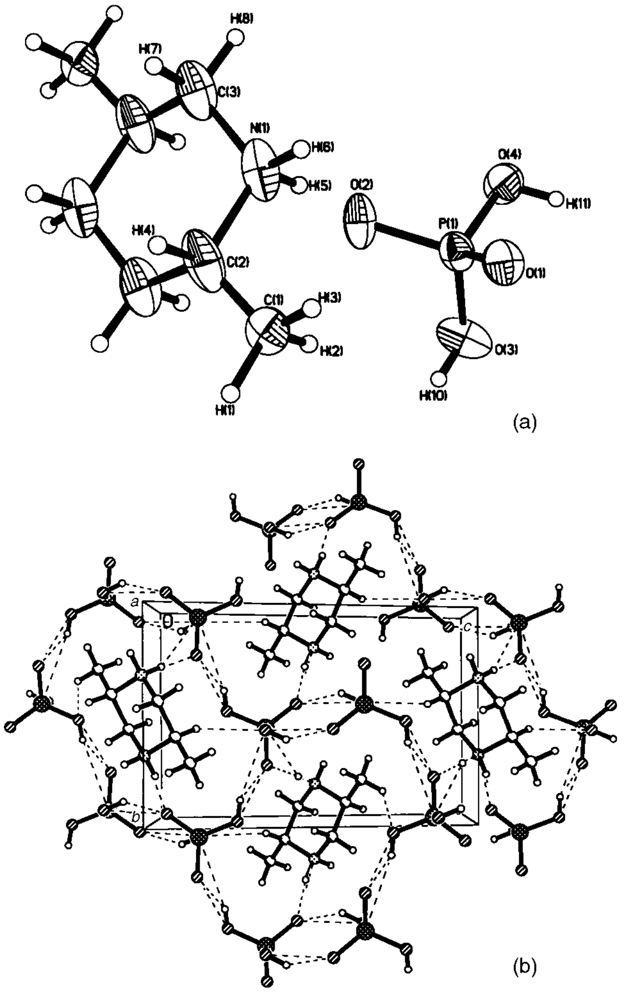

Fig. 2 (a) An ORTEP plot of the amine phosphate MPIP-P. (b) The packing diagram. Note that the non-covalent interaction forms a layer-like arrangement. Other details as in Fig. 1. There is a disorder found in the CH_3 (C1) site with an occupancy of 0.5.

The asymmetric units of compounds **I** and **II** contain 10 and 18 non-hydrogen atoms respectively as shown in Fig. 3(a) and 3(b). The structures consist of polymeric one-dimensional cobalt hydrogenphosphate anions of formula $[Co(HPO_4)_2]$, shown in Fig. 4. The cobalt atoms in both **I** and **II** are tetrahedrally co-ordinated by four oxygen atoms, consistent with the deep blue color of the compounds. The Co–O bond lengths (av. 1.963 Å for **I** and 1.954 Å for **II**) are similar to those observed in other cobalt phosphates, such as in the ladder compound, $[NH_3(CH_2)_3NH_3][Co(HPO_4)_2]$ $(Co–O)_{av}$ = 1.952 Å.[12] The structure of **I** contains two crystallographically distinct P atoms with average P–O distances of 1.535 and 1.542 Å. The distances P(1)–O(6) 1.577 and P(2)–O(8) 1.569 Å suggest that the oxygen atoms are protonated (Table 2). The presence of hydroxyl groups was confirmed by the observation of peaks corresponding to the hydrogen positions in the Fourier difference maps close to these oxygens. The P–O distances of **II** were similar with P(1)–O(4) 1.584 corresponding to the P–OH linkage (Table 3). The P–O distances in **I** and **II** agree well with those reported for similar compounds.[2]

The strictly alternating CoO_4 and HPO_4 units form 4-membered rings, which are linked through their corners giving the one-dimensional chains in **I** and **II** as shown in Fig. 5(a) and 5(b), respectively. The individual chain units are held together by strong hydrogen bond interactions involving the amine. The arrangement of the chains and the amine is shown in the

Table 2 Selected bond distances (Å) and angles (°) in compound **I**, $[C_5N_2H_{14}][Co(HPO_4)_2]$

Co(1)–O(1)	1.941(3)	O(2)–Co(1)–O(4)	96.62(14)
Co(1)–O(2)	1.962(3)	O(3)–Co(1)–O(4)	110.80(13)
Co(1)–O(3)	1.972(3)	O(5)–P(1)–O(4)$^{\#1}$	110.1(2)
Co(1)–O(4)	1.976(3)	O(5)–P(1)–O(2)	111.5(2)
P(1)–O(5)	1.514(3)	O(4)$^{\#1}$–P(1)–O(2)	112.5(2)
P(1)–O(4)$^{\#1}$	1.524(3)	O(5)–P(1)–O(6)	108.6(2)
P(1)–O(2)	1.525(3)	O(4)$^{\#1}$–P(1)–O(6)	106.5(2)
P(1)–O(6)	1.577(3)	O(2)–P(1)–O(6)	107.3(2)
P(2)–O(1)	1.517(3)	O(1)–P(2)–O(7)	114.0(2)
P(2)–O(7)	1.523(3)	O(1)–P(2)–O(3)$^{\#2}$	112.6(2)
P(2)–O(3)$^{\#2}$	1.538(3)	O(7)–P(2)–O(3)$^{\#2}$	108.2(2)
P(2)–O(8)	1.569(3)	O(1)–P(2)–O(8)	108.3(2)
		O(7)–P(2)–O(8)	107.1(2)
O(1)–Co(1)–O(2)	107.87(14)	O(3)$^{\#2}$–P(2)–O(8)	106.2(2)
O(1)–Co(1)–O(3)	114.88(13)	P(2)–O(1)–Co(1)	130.7(2)
O(2)–Co(1)–O(3)	119.18(13)	P(1)–O(2)–Co(1)	127.7(2)
O(1)–Co(1)–O(4)	105.20(14)	P(2)$^{\#2}$–O(3)–Co(1)	113.4(2)
		P(1)$^{\#1}$–O(4)–Co(1)	128.9(2)
Organic moiety			
N(1)–C(1)	1.449(8)	C(1)–N(1)–C(4)	111.9(5)
N(1)–C(4)	1.534(7)	C(2)–C(1)–N(1)	112.6(5)
C(1)–C(2)	1.426(9)	C(1)–C(2)–N(2)	111.8(5)
C(2)–N(2)	1.549(8)	C(3)–N(2)–C(2)	107.4(5)
N(2)–C(3)	1.489(9)	C(4)–C(3)–N(2)	114.3(5)
C(3)–C(4)	1.478(9)	C(3)–C(4)–C(5)	110.4(5)
C(4)–C(5)	1.498(8)	C(3)–C(4)–N(1)	109.0(4)
		C(5)–C(4)–N(1)	113.5(5)

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

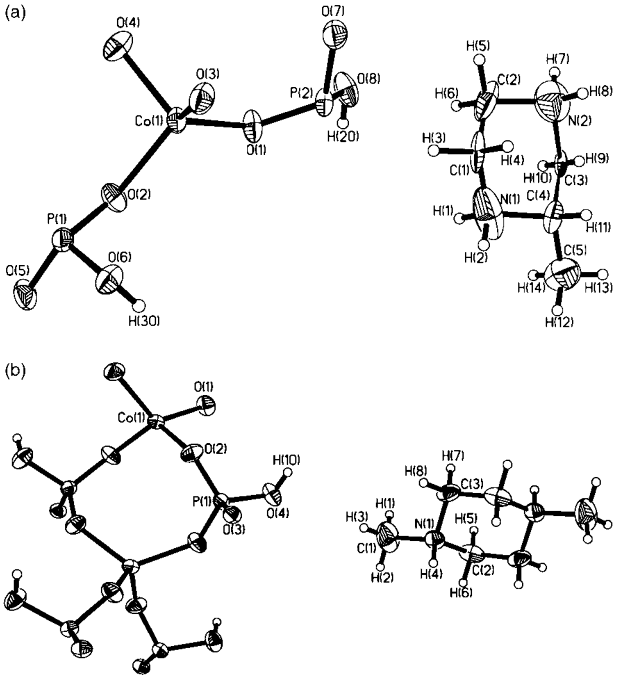

Fig. 3 ORTEP plots of (a) **I**, $[C_5N_2H_{14}][Co(HPO_4)_2]$ and (b) **II**, $[C_6N_2H_{16}][Co(HPO_4)_2]$, with thermal ellipsoids given at 50% probability.

case of **I** in Fig. 4. As can be seen the amine molecules, in the inter-chain positions, are arranged such that the different orientations alternate. The hydrogen bond interactions involving the terminal P–OH linkages form a sheet-like architecture with apertures, wherein the amine molecules reside (Fig. 5a and 5b). Looking down the chain axis, the hydrogen bond interactions between the individual chain units in **I** and **II** resemble organic channel structures formed by non-covalent interactions[13] as can be seen from Fig. 6(a) and 6(b). The differences in the hydrogen bond interactions between **I** and **II** are responsible for the differences in the shapes of the channels.

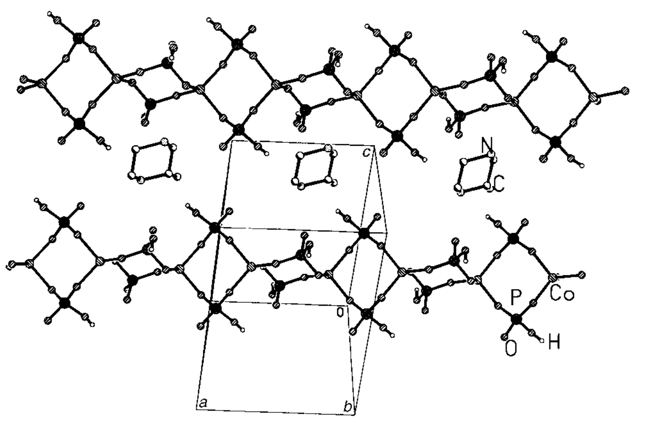

Fig. 4 Structure showing the linear chain arrangement along the [001] direction in compound **I**. Note that the amine molecules separate the linear chains. Hydrogens on the amine molecules are not shown for clarity.

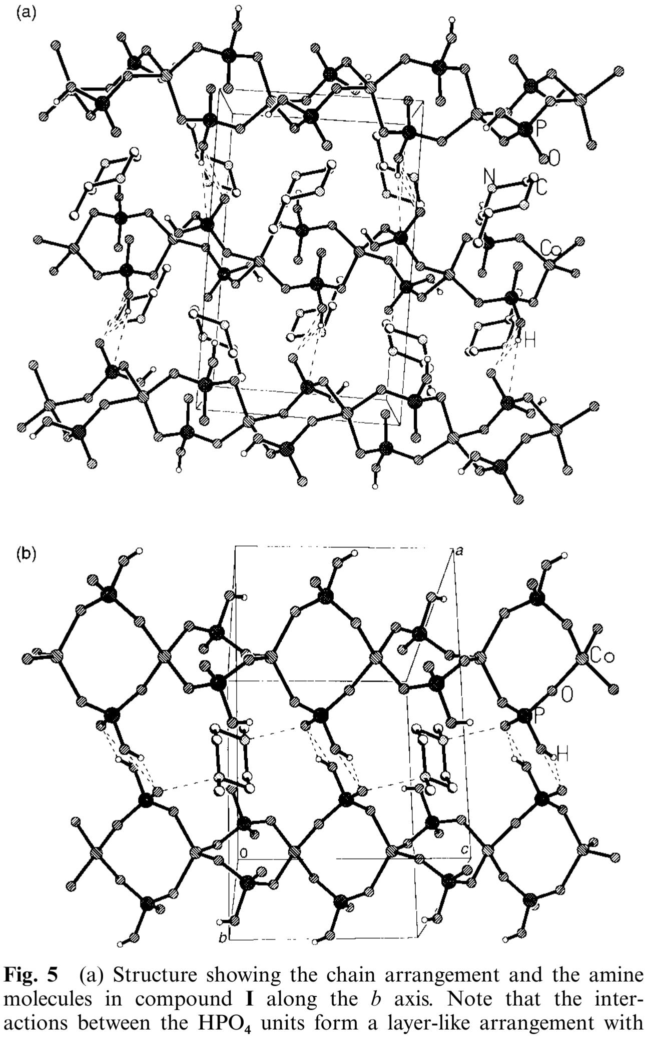

Fig. 5 (a) Structure showing the chain arrangement and the amine molecules in compound **I** along the *b* axis. Note that the interactions between the HPO_4 units form a layer-like arrangement with apertures. (b) Structure showing linear chain and amine molecules in **II**. Hydrogens on the amine molelcules are omitted for clarity.

While compounds **I** and **II** are the first examples of a transition metal phosphate containing corner-shared tetrahedral chains, similar one-dimensional structures of aluminum and gallium phosphates have been reported.[2] The present materials possess the same framework formula as that reported recently by Cowley and Chippindale,[12] but the connectivity resulting from the 4-membered rings is different. In the structure described by Cowley and Chippindale the edge-wise connectivity between the 4-membered rings forms a ladder-like structure with one HPO_4 unit hanging from the Co, while in **I** and **II** the

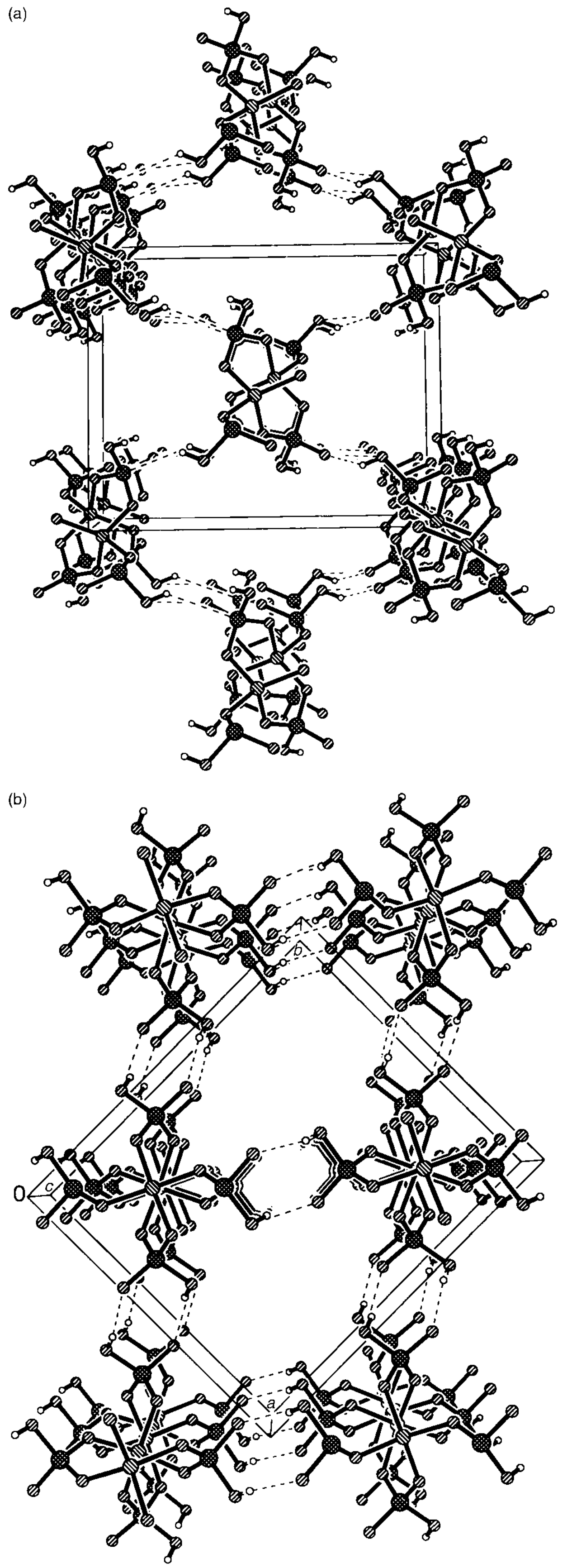

Fig. 6 (a) The structure of compound **I** along chain axis. Note that each HPO_4 unit interacts with two different linear chains forming channels. (b) Structure of **II** along the chain axis. Each HPO_4 unit interacts with only one linear chain.

connectivity is through the corners with no hanging phosphates. Since the linear-chain metal phosphates are so rare, the isolation of two corner-shared chain cobalt(II) phosphates in the present study is of significance. In the mechanism proposed for the formation of open-framework phosphates by Oliver *et al.*[6] the corner-shared chain structure is the primary building unit. One of the reasons that such lower dimensional structures are seldom found under conventional hydrothermal conditions may be because they undergo facile transformations to layer and three-dimensional structures. The use of the organic amine phosphate in the present study may have facilitated the isolation of the one-dimensional corner-shared chains.

Table 3 Selected bond distances and angles in compound **II**, $[C_6N_2H_{16}][Co(HPO_4)_2]$

Co(1)–O(1)	1.955(2)	O(2)$^{\#1}$–Co(1)–O(1)	103.59(9)
Co(1)–O(1)$^{\#1}$	1.955(2)	O(2)–Co(1)–O(1)$^{\#1}$	103.59(9)
Co(1)–O(2)	1.952(2)	O(2)$^{\#1}$–Co(1)–O(1)$^{\#1}$	102.15(9)
Co(1)–O(2)$^{\#1}$	1.952(2)	O(1)–Co(1)–O(1)$^{\#1}$	123.12(14)
P(1)–O(1)$^{\#2}$	1.514(2)	O(1)$^{\#2}$–P(1)–O(2)	112.51(13)
P(1)–O(2)	1.519(2)	0(1)$^{\#2}$–P(1)–O(3)	112.92(13)
P(1)–O(3)	1.525(2)	O(2)–P(1)–O(3)	109.49(13)
P(1)–O(4)	1.584(2)	O(1)$^{\#2}$–P(1)–O(4)	104.21(13)
		O(2)–P(1)–O(4)	109.98(14)
O(2)–Co(1)–O(2)$^{\#1}$	124.25(13)	O(3)–P(1)–O(4)	107.49(12)
O(2)–Co(1)–O(1)	102.15(9)	P(1)$^{\#1}$–O(1)–Co(1)	133.56(14)
		P(1)–O(2)–Co(1)	134.67(14)
Organic moiety			
N(1)–C(2)	1.478(4)	C(2)–N(1)–C(1)	111.8(3)
N(1)–C(1)	1.491(5)	C(2)–N(1)–C(3)	109.6(3)
N(1)–C(3)	1.491(4)	C(1)–N(1)–C(3)	111.8(3)
C(2)–C(3)$^{\#4}$	1.498(5)	N(1)–C(2)–C(3)$^{\#4}$	110.3(3)
C(3)–C(2)$^{\#4}$	1.498(5)	N(1)–C(3)–C(2)$^{\#4}$	110.3(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x + \frac{1}{2}, -y + \frac{1}{2}, z$; #2 $x, -y + \frac{1}{2}, z + \frac{1}{2}$; #3 $x, -y + \frac{1}{2}, z - \frac{1}{2}$; #4 $-x + 2, -y + 1, -z - 1$.

Acknowledgements

A. C. thanks the Council of Scientific and Industrial Research (CSIR), Govt. of India for the award of a research fellowship.

References

1 A. K. Cheetham, T. Loiseau and G. Ferey, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268.
2 R. H. Jones, J. M. Thomas, R. Xu, Q. Huo, Y. Xu, A. K. Cheetham and D. Bieber, *J. Chem. Soc., Chem. Commun.*, 1990, 1170; Q. Gao, J. Chen, S. Li, R. Xu, J. M. Thomas, M. Light and M. B. Hursthouse, *J. Solid State Chem.*, 1996, **127**, 145; I. D. Williams, J. Yu, Q. Gao, J. Chen and R. Xu, *Chem. Commun.*, 1997, 1273; A. M. Chippindale and C. Turner, *J. Solid State Chem.*, 1997, **128**, 318; T. Loiseau, F. Sepaggi and G. Ferey, *Chem. Commun.*, 1997, 1093; A. M. Chippindale, A. D. Bond, A. D. Law and A. R. Cowley, *J. Solid State Chem.*, 1998, **136**, 227.
3 S. Neeraj, S. Natarajan and C. N. R. Rao, *Angew. Chem., Int. Ed.*, 1999, **38**, 3480.
4 C. N. R. Rao, S. Natarajan and S. Neeraj, *J. Am. Chem. Soc.*, 2000, **122**, 2810.
5 S. Natarajan, A. Choudhury, S. Neeraj and C. N. R. Rao, *Inorg. Chem.*, 2000, **39**, 1426.
6 S. Oliver, A. Kuperman, A. Lough and G. A. Ozin, *Chem. Mater.*, 1996, **8**, 2391; S. Oliver, A. Kuperman and G. A. Ozin, *Angew. Chem., Int. Ed.*, 1998, **37**, 46 and references therein.
7 C. N. R. Rao, S. Natarajan and S. Neeraj, *J. Solid State Chem.*, 2000, **153**, 302.
8 G. M. Sheldrick, "SHELXS 86, A program for the solution of crystal structures", University of Göttingen, 1986.
9 G. M. Sheldrick, SADABS, Siemens Area Detector Absorption Correction Program, University of Göttingen, 1994.
10 G. M. Sheldrick, SHELXTL PLUS, Program for Crystal Structure Solution and Refinement, University of Göttingen, 1993.
11 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
12 A. R. Cowley and A. M. Chippindale, *J. Chem. Soc., Dalton Trans.*, 1999, 2147.
13 V. R. Pedireddi, S. Chatterjee, A. Ranganathan and C. N. R. Rao, *J. Am. Chem. Soc.*, 1997, **119**, 10867.