Three-Dimensional Open-Framework Cobalt(II) Phosphates by Novel Routes

Srinivasan Natarajan,[†] S. Neeraj,[†] Amitava Choudhury,[†,‡] and C. N. R. Rao*[,†,‡]

Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research,
Jakkur P.O., Bangalore 560 064, India, and Solid State and Structural Chemistry Unit,
Indian Institute of Science, Bangalore 560 012, India

Received October 18, 1999

Two new three-dimensional open-framework cobalt phosphates, $[C_2N_2H_{10}]_2[Co_4(PO_4)_4]H_2O$, **I**, and $[C_4N_3H_{16}]_3[Co_6(PO_4)_5(HPO_4)_3]H_2O$, **II**, have been prepared by the reaction of amine phosphates with Co^{2+} salts. **I** could also be prepared by the reaction of the cobalt tris amine complex with H_3PO_4. The crystal data for **I** and **II** are as follows: phosphate **I**, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 10.277$ (1) Å, $b = 10.302$ (1) Å, $c = 18.836$ (1) Å, $V = 1994.2$ (2) Å^3, $Z = 4$; phosphate **II**, monoclinic, space group $P2_1/c$ (No. 14), $a = 31.950$ (1) Å, $b = 8.360$ (1) Å, $c = 15.920$ (1) Å, $\beta = 96.6$ (1)° $V = 4223.4$ (2) Å^3, $Z = 4$. The structures of both **I** and **II** are constructed from alternating CoO_4 and PO_4 tetrahedra. The connectivity leads to the formation of eight-membered channels in all the crystallographic directions resembling the aluminosilicate zeolite, merlinoite in the case of **I** and to a rather large, one-dimensional 16-membered channel in **II**. Strong hydrogen-bond interactions involving the amine and framework oxygens are present in both **I** and **II**.

Introduction

Among the vast family of open-framework metal phosphates, the transition metal phosphates constitute an important group. The synthesis and structure of several open-framework iron phosphates have been reported in the recent literature.[1−4] However, there are very few reports of open-framework phosphates of cobalt and nickel. A new three-dimensional (3-D) nickel phosphate with an open architecture has just been reported by Guillou et al.[5] Several cobalt phosphates with open-framework structures using alkali and alkaline-earth metals as countercations have been prepared by Feng et al.[6,7] and others.[8] Cobalt phosphate structures stabilized by the incorporation of aluminum as part of the framework have been prepared in the presence of structure-directing amines.[9] A few cobalt phosphates with open architectures are known,[10] but to our knowledge, only one known 3-D open-framework cobalt phosphate appears to have been synthesized to date in the presence of an organic amine.[11] We, therefore, embarked on alternative ways to prepare three-dimensional open-framework cobalt phosphates in the presence of structure-directing amines. An important strategy employed by us uses amine phosphates as the starting materials for the synthesis, since it has been shown recently that amine phosphates could be intermediates in the formation of open-framework metal phosphates.[12,13] It is noteworthy that amine phosphates are stable under hydrothermal conditions. We have also used the Co(II) tris amine complex as the starting material expecting that it may act as an appropriate source of the amine by slowly releasing it, since the complex itself is unstable under hydrothermal conditions. By employing these novel routes, it has been possible to obtain two new 3-D cobalt phosphates, $[C_2N_2H_{10}]_2[Co_4(PO_4)_4]H_2O$, **I**, and $[C_4N_3H_{16}]_3[Co_6(PO_4)_5(HPO_4)_3]H_2O$, **II**, possessing the structure-directing amine molecules within the channels. While **I** possesses interpenetrating channels bound by 8-T atoms (T = Co/P) reminiscent of aluminosilicate zeolites,[14] **II** possesses one-dimensional channels

---

* To whom correspondence should be addressed.

[†] Chemistry and Physics Materials Unit.

[‡] Solid State and Structural Chemistry Unit.

(1) Cavellec, M.; Riou, D.; Ferey, G. *J. Solid State Chem*. **1994**, *112*, 441; Cavellec, M.; Riou, D.; Greneche, J.-M.; Ferey, G. *Zeolites* **1996**, *17*, 252. Cavellec, M.; Egger, C.; Linares, J.; Nogues, M.; Varret, F.; Ferey, G. *J. Solid State Chem*. **1997**, *134*, 349. Cavellec, M. R.; Greneche, J.-M.; Riou, D.; Ferey, G. *Chem. Mater*. **1998**, *10*, 2434. Cavellec, M.; Greneche, J. M.; Riou, D.; Ferey, G. *Microporous Mater*. **1997**, *8*, 103. Cavellec, M.; Riou, D.; Greneche, J. M.; Ferey, G. *J. Magn. Magn. Mater*. **1996**, *163*, 173.

(2) Choudhury, A.; Natarajan, S.; Rao, C. N. R. *Chem. Commun*. **1999**, 1305. Choudhury, A.; Natarajan, S. *Proc. Ind. Acad. Sci. (Chem. Sci.)* **1999**, *111*, 627.

(3) Lethbridge, Z. A. D.; Lightfoot, P.; Morris, R. E.; Wragg, D. S.; Wright, P. A.; Kvick, Å.; Vaughan, G. *J. Solid State Chem*. **1999**, *142*, 455; DeBord, J. R. D.; Reiff, W. M.; Warren, C. J.; Haushalter, R. C.; Zubieta, J. *Chem. Mater*. **1997**, *9*, 1994. Mgaidi, A.; Boughzala, H.; Driss, A.; Clerac, R.; Coulon, C. *J. Solid State Chem*. **1999**, *144*, 163.

(4) Lii, K.-H.; Huang, Y.-F.; Zima, V.; Huang, C.-Y.; Lin, H.-M.; Jiang, Y.-C.; Liao, F.-L.; Wang, S.-L. *Chem. Mater*. **1998**, *10*, 2599 and references therein.

(5) Guillou, N.; Gao, Q.; Nogues, M.; Morris, R. E.; Hervieu, M.; Ferey, G.; Cheetham, A. K. *C. R. Acad. Sci. Paris. Ser. II* **1999**, 387.

(6) Feng, P.; Bu, X.; Tolbert, S. H.; Stucky, G. D. *J. Am. Chem. Soc*. **1997**, *119*, 2497.

(7) Feng, P.; Bu, X.; Stucky, G. D. *J. Solid State Chem*. **1997**, *129*, 328. Feng, P.; Bu, X.; Stucky, G. D. *J. Solid State Chem*. **1997**, *131*, 160. Feng, P.; Bu, X.; Stucky, G. D. *J. Solid State Chem*. **1997**, *131*, 387.

(8) Bu, X.; Feng, P.; Gier, T. E.; Stucky, G. D. *J. Solid State Chem*. **1998**, *136*, 210. Harrison, W. T. A.; Vaughey, J. T.; Dussack, L. L.; Jacobson, A. J.; Martin, T. E.; Stucky, G. D. *J. Solid State Chem*. **1995**, *114*, 151. Bircsak, Z.; Harrison, W. T. A. *Acta Crystallogr., Sect. C*. **1998**, *54*, 1554. Zabukovec, N.; Golic, L.; Fajdiga, P.; Kaucic, P. *Zeolites* **1995**, *15*, 104.

(9) Feng, P.; Bu, X.; Stucky, G. D. *Nature* **1997**, *388*, 735. Bu, X.; Feng, P.; Stucky, G. D. *Science* **1997**, *278*, 2080.

(10) Chippindale, A. M.; Cowley, A. R. *J. Chem. Soc., Dalton Trans*. **1999**, 2147; DeBord, J. R. D.; Haushalter, R. C.; Zubieta, J. *J. Solid State Chem*. **1996**, *125*, 270.

(11) Chen, J.; Jones, R. H.; Natarajan, S.; Hursthouse, M. B.; Thomas, J. M. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 639.

(12) Neeraj, S.; Natarajan, S.; Rao, C. N. R. *Angew. Chem., Int. Ed*. **1999**, *39*, 3480.

(13) Natarajan, S.; Neeraj, S.; Choudhury, A.; Rao, C. N. R. *Solid State Sci*. **2000**. In press.

(14) Meier, W. H., Olson, D. H., Eds. *Atlas of Zeolite Structure Types*; Butterworth-Heinemann: London, 1992.

10.1021/ic991223x CCC: $19.00

Table 1. Crystal Data and Structure Refinement Parameters for Compounds **I**, $[C_2N_2H_{10}]_2[Co_4(PO_4)_4]H_2O$, and **II**, $[C_4N_3H_{16}]_3[Co_6(PO_4)_5(HPO_4)_3]H_2O$

structural parameter	I	II
chemical formula	$Co_4P_4O_{17}C_4N_4H_{22}$	$Co_6P_8O_{32}C_{12}N_9H_{51}$
space group	$P2_12_12_1$ (no. 19)	$P2_1/c$ (no. 14)
T (K)	293(2)	293(2)
a (Å)	10.277(1)	31.950(1)
b (Å)	10.302(1)	8.360(1)
c (Å)	18.836(1)	15.920(1)
α (deg)	90.0	90.0
β (deg)	90.0	96.6(1)
γ (deg)	90.0	90.0
volume (Å^3)	1994.2(2)	4223.4(2)
Z	4	4
formula mass	757.9	1434.9
$\lambda_{MoK\alpha}$ (Å)	0.710 73	0.710 73
ρ_{calc} (g cm^{-3})	1.893	2.254
μ (mm^{-1})	2.764	2.721
R (F_o^2) [$I > 2\sigma(I)$]	$R_1 = 0.020$,[a] $wR_2 = 0.049$[b]	$R_1 = 0.051$,[a] $wR_2 = 0.123$[b]
R (F_o^2) (all data)	$R_1 = 0.020$, $wR_2 = 0.049$	$R_1 = 0.067$, $wR_2 = 0.136$

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max.(F_o^2,0) + 2(F_c)^2]/3$, where $a = 0.0212$ and $b = 0.0$ for **I**, $a = 0.0476$ and $b = 39.228$ for **II**.

bound by 16-T atoms. The observation of a one-dimensional 16-membered channel is significant in that this is the first example of an open-framework cobalt phosphate with such a large channel.

Experimental Section

Synthesis. The synthesis of the cobalt(II) phosphates, **I** and **II**, was facilitated by employing diethyelenetriamine-phosphate (DETAPHOS),[15a] $[C_4N_3H_{15}][HPO_4]H_2O$, as the starting source of phosphorus and amine. DETAPHOS was synthesized at room temperature from an aqueous solution. In a typical preparation, 17.8 mmol of phosphoric acid was mixed with 444 mmol of H_2O and 17.3 mmol of DETA was added to the mixture very slowly dropwise under continuous stirring. After homogenizing for ~30 min, the mixture was transferred into a polyethylene bottle and heated at 110 °C for 10 h. The mixture, cooled to room temperature (RT), was allowed to stay at RT for about 48 h, resulting in the formation of large number of crystals with platelike morphology. The crystals were filtered and washed with a minimum quantity of water and used for all further characterizations. A single-crystal X-ray diffraction study gave the following cell for the DETAPHOS: $a = 6.116(1)$, $b = 10.667(1)$, $c = 17.061(1)$ Å, $V = 1112.3(2)$ Å^3; space group = $P2_12_12_1$, $R_1 = 0.07$. Elemental analysis for $[C_4N_3H_{15}][HPO_4]H_2O$ as follows. Calcd: C, 21.9; H, 8.2; N, 19.2. Found: C, 21.2; H, 7.5; N, 19.0.

The DETAPHOS intermediate, thus prepared, was used for the synthesis of cobalt phosphates **I** and **II**. In a typical preparation, 1 mmol of cobalt chloride was dispersed in 50 mmol of butan-2-ol and 1.36 mmol of DETAPHOS was added to the above mixture, producing a final composition of: $2CoCl_2{\cdot}6H_2O{:}2.75[C_4N_3H_{15}][HPO_4]H_2O{:}100C_4H_8\text{-}OH$. The resulting pH was adjusted to ~7−8 by the addition of 25% aq ammonia solution. The mixtures were stirred until homogeneous, sealed in a 23 mL PTFE-lined stainless steel pressure vessels (Parr Instrument Co., Moline, IL), and heated at 453 K for 40 h. The resulting product contained large quantities of deep blue-colored crystals, suitable for single-crystal X-ray diffraction, was filtered and washed with plenty of water and dried at ambient temperature. A preliminary examination under an optical microscope revealed that the product was a mixture containing more than one type of crystal with similar morphologies. Select crystals from the mixture were isolated and used for structural studies, which revealed that both compound **I** and **II** possess a irregular morphology. **I** contained ethylenediamine in its channels, a product of the decomposition of the DETA during the hydrothermal crystallization, while **II** had the DETA molecules in its channels. To facilitate the formation of **I** in pure form, synthesis was carried out starting from ethylenediamine-phosphate (ENPHOS).[15b] (ENPHOS was synthesized using 60 mmol of H_3PO_4 in 225 mmol of H_2O, and 41.6 mmol of ethylenediamine (en) was added dropwise under constant stirring. The mixture was left to crystallize at room temperature. A single-crystal X-ray diffraction study yielded the following cell: $a = 7.507(1)$, $b = 11.816(1)$, $c = 8.055(1)$ Å, $\beta = 110.1(3)°$; $\upsilon = 670.9(2)$ Å^3, space group = $P2_1/c$ $R_1 = 0.03$. C, H, N analysis yielded the following. Calcd: C, 15.2; H, 6.9; N, 17.7. Found: C, 15.1; H, 6.9; N, 17.5). Again the result was a mixture of products, a big chunky type among them. The chunky type of crystals was identical to that reported by Chen et al.[11] The other crystals were found to be those of the condensed phosphates. Compound **I** was not one of the products obtained with ENPHOS as the starting material.

We sought to synthesize **I** in pure form by employing another route starting with a cobalt(II) tris amine complex. The amine complex was prepared using the standard inorganic synthesis procedures[16] starting from $CoCl_2{\cdot}6H_2O$ and ethylenediamine (en) in water at room temperature. The clear solution thus formed was allowed to undergo areal oxidation over a period of 48 h. The purity of the amine complex was checked using IR, TGA studies and used without further purification. In a typical synthesis, 0.416 g of $Co(en)_3Cl_3{\cdot}2H_2O$ was dissolved in 3 mL of deionized water and 0.15 mL of aq H_3PO_4 (85 wt %) was added to it under continuous stirring. $H_2C_2O_4{\cdot}2H_2O$ (0.138 g) was added to the above, and the mixture was stirred until homogeneous. The final composition of the mixture was $Co(en)_3Cl_3{\cdot}2H_2O$: $2H_3PO_4$: $H_2C_2O_4$: $150H_2O$. The final mixture with a pH of 2, was transferred to a 7 mL Parr-type PTFE-lined stainless steel pressure vessel and heated at 165 °C for 70 h under autogenous pressure. The resulting product was found to be a mixture and contained large quantities of crystals of **I** admixed with another reported cobalt phosphate by Chen et al.[11] and other as yet unidentified phases which are currently being investigated. The crystals were filtered and washed thoroughly with copious quantity of deionized water. The crystals were dried at ambient atmosphere at room temperature. An EDAX analysis gave the Co:P as 51.8:48.2 (Calcd. 50:50) for **I** and 58.6:41.4 (Calcd. 57.2:42.8) and **II**, respectively.

Single-Crystal Structure Determination. A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (superglue) 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. A hemisphere of intensity data was collected at room temperature in 1321 frames with ω scans (width of

---

(15) (a) Kamoun, S.; Jouini, A.; Dasud, A. *Acta Crystallogr., Sect. C.* **1980**, *36*, 1481. (b) Averbuch-Pouchot, M. T.; Durif, A. *Acta Crystallogr., Sect. C.* **1987**, *43*, 1894; Golubav, S. N.; Yu; Kontrashev, D. *Zhr. Strukt. Khim.* **1984**, *25*, 150.

(16) *Inorg. Synth.* **1946**, *2*, 221.

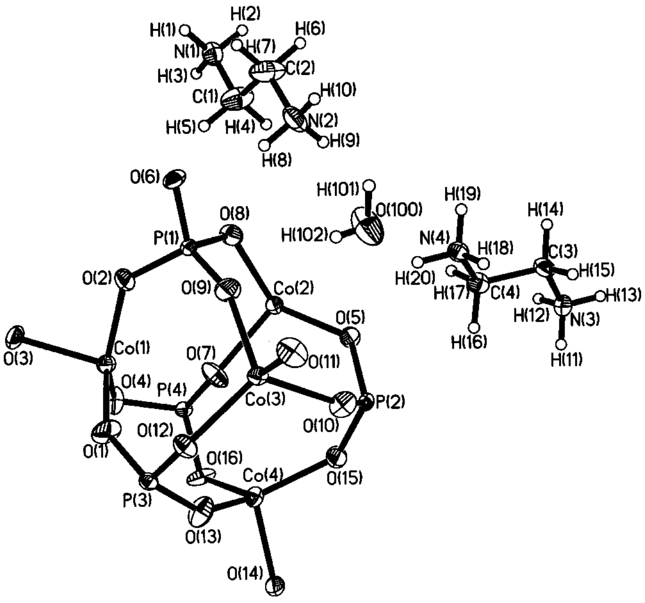

Figure 1. ORTEP plot of **I**, $[C_2N_2H_{10}]_2[Co_4(PO_4)_4]H_2O$. Thermal ellipsoids are given at 50% probability.

Table 2. Atomic Coordinates [×10^4] and Equivalent Isotropic Displacement Parameters [Å^2 × 10^3] for **I**, $[C_2N_2H_{10}]_2[Co_4(PO_4)_4]H_2O$

atom	*x*	*Y*	*Z*	$U_{(eq)}$[a]
Co(1)	5722(1)	8679(1)	606(1)	16(1)
Co(2)	5954(1)	11370(1)	2008(1)	14(1)
Co(3)	9094(1)	8977(1)	1947(1)	14(1)
Co(4)	8484(1)	11653(1)	323(1)	16(1)
P(1)	5943(1)	8479(1)	2315(1)	12(1)
P(2)	8963(1)	12087(1)	2002(1)	13(1)
P(3)	8890(1)	8477(1)	326(1)	13(1)
P(4)	5615(1)	11350(1)	291(1)	13(1)
O(1)	7452(3)	8156(4)	320(2)	29(1)
O(2)	5467(4)	8010(3)	1590(2)	23(1)
O(3)	4542(4)	7276(4)	265(2)	30(1)
O(4)	5024(3)	10106(3)	−20(2)	26(1)
O(5)	7604(3)	12032(3)	2341(2)	20(1)
O(6)	5540(3)	7520(3)	2895(2)	20(1)
O(7)	6208(4)	10908(3)	1007(2)	26(1)
O(8)	5321(4)	9800(3)	2486(2)	22(1)
O(9)	7427(3)	8607(4)	2352(2)	28(1)
O(10)	9663(3)	10780(3)	2079(2)	24(1)
O(11)	10253(4)	8136(4)	2623(2)	26(1)
O(12)	9509(3)	8094(3)	1047(2)	21(1)
O(13)	9147(4)	9916(3)	199(2)	29(1)
O(14)	9599(3)	12590(3)	−381(2)	22(1)
O(15)	8888(4)	12479(3)	1217(2)	25(1)
O(16)	6771(3)	11820(3)	−161(2)	25(1)
O(100)	7854(6)	10245(5)	3675(3)	50(1)
N(1)	910(4)	10355(4)	3581(2)	25(1)
N(2)	4518(5)	10130(5)	3867(2)	36(1)
C(1)	2310(5)	10450(7)	3437(3)	38(2)
C(2)	3126(6)	10002(7)	4010(3)	44(2)
N(3)	7815(4)	16665(4)	3679(2)	22(1)
N(4)	7672(4)	13021(4)	3769(2)	21(1)
C(3)	7808(5)	15369(5)	4021(3)	22(1)
C(4)	7501(5)	14319(5)	3480(3)	22(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Distances in **I**, $[C_2N_2H_{10}]_2[Co_4(PO_4)_4]H_2O$

moiety	distance	moiety	distance
Co(1)−O(1)	1.934(3)	P(1)−O(2)	1.530(3)
Co(1)−O(2)	1.994(3)	P(1)−O(6)	1.530(3)
Co(1)−O(3)	1.993(3)	P(1)−O(8)	1.538(4)
Co(1)−O(4)	2.016(4)	P(1)−O(9)	1.533(3)
Co(2)−O(5)	1.933(3)	P(2)−O(5)	1.536(4)
Co(2)−O(6)[a]	1.948(3)	P(2)−O(10)	1.534(3)
Co(2)−O(7)	1.962(3)	P(2)−O(11)[b]	1.522(4)
Co(2)−O(8)	1.962(3)	P(2)−O(15)	1.534(3)
Co(3)−O(9)	1.913(3)	P(3)−O(1)	1.515(4)
Co(3)−O(10)	1.963(3)	P(3)−O(3)[c]	1.514(3)
Co(3)−O(11)	1.947(3)	P(3)−O(12)	1.551(3)
Co(3)−O(12)	1.970(3)	P(3)−O(13)	1.524(4)
Co(4)−O(13)	1.930(3)	P(4)−O(4)	1.534(4)
Co(4)−O(14)	2.001(3)	P(4)−O(7)	1.548(3)
Co(4)−O(15)	1.931(3)	P(4)−O(14)[d]	1.520(3)
Co(4)−O(16)	1.990(3)	P(4)−O(16)	1.540(3)
	Organic Moiety		
N(1)−C(1)	1.468(7)	N(3)−C(3)	1.482(7)
C(1)−C(2)	1.441(8)	C(3)−C(4)	1.519(8)
N(2)−C(2)	1.462(7)	N(4)−C(4)	1.455(7)

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1, y + {}^1/_2, -z + {}^1/_2$. [b] Symmetry transformations used to generate equivalent atoms: $-x + 2, y + {}^1/_2, -z + {}^1/_2$. [c] Symmetry transformations used to generate equivalent atoms: $x + {}^1/_2, -y + {}^3/_2, -z$. [d] Symmetry transformations used to generate equivalent atoms: $x - {}^1/_2, -y + {}^5/_2, -z$.

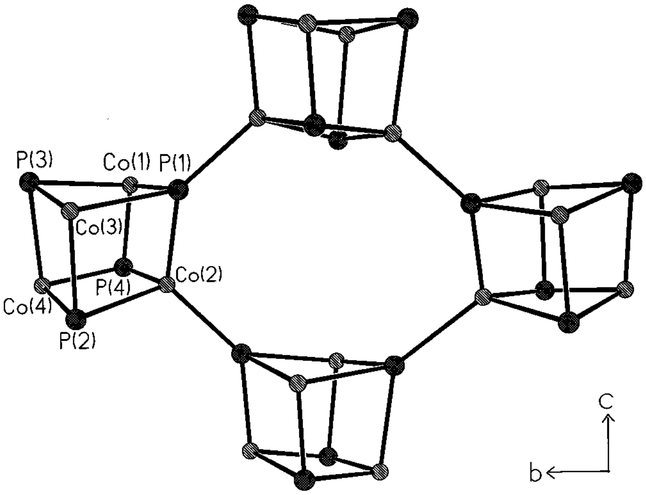

Figure 2. Structure of **I** along the [100] direction showing a single eight-membered channel. Only T-atom (T = Co, P) connectivity is shown.

0.30° and exposure time of 10s per frame). Pertinent experimental details for the structure determinations are presented in Table 1.

The structure was solved by direct methods using SHELXS-86[17] and difference Fourier syntheses. An empirical absorption correction based on symmetry equivalent reflections was applied using SADABS program.[18] Other effects, such as absorption by the glass fiber, were simultaneously corrected. All the hydrogen positions were initially located in the difference Fourier 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 atoms. Full-matrix-least-squares structure refinement against $|F^2|$ was carried out using SHELXTL-PLUS[19] package of programs. Details of the final refinements are given in Table 1. The final atomic coordinates and selected bond distances and angles for **I** are presented in Tables 2−4 and for **II** in Tables 5−7.

---

(17) Sheldrick, G. M. *SHELX-86, Program for Crystal Structure Determination*; University of Göttingen: Germany, 1986.

(18) Sheldrick, G. M. *SADABS User Guide*; University of Göttingen: Germany, 1995.

(19) Sheldrick, G. M. *SHELXL-93, A Program for Crystal Structure Solution and Refinement*; University of Göttingen: Germany, 1993.

Table 4. Selected Bond Angles in **I**, $[C_2N_2H_{10}]_2[Co_4(PO_4)_4]H_2O$

moiety	angle (deg)	moiety	angle, deg
O(1)−Co(1)−O(2)	106.5(2)	O(6)−P(1)−O(2)	110.3(2)
O(1)−Co(1)−O(3)	105.5(2)	O(6)−P(1)−O(9)	107.0(2)
O(1)−Co(1)−O(4)	111.5(2)	O(2)−P(1)−O(8)	109.5(2)
O(2)−Co(1)−O(4)	138.4(2)	O(2)−P(1)−O(9)	112.7(2)
O(3)−Co(1)−O(2)	88.19(1)	O(6)−P(1)−O(8)	109.0(2)
O(3)−Co(1)−O(4)	97.1(2)	O(9)−P(1)−O(8)	109.1(2)
O(5)−Co(2)−O(6)[d]	116.5(2)	O(11)[b]−P(2)−O(15)	106.7(2)
O(5)−Co(2)−O(7)	106.3(2)	O(11)[b]−P(2)−O(10)	109.3(2)
O(5)−Co(2)−O(8)	115.6(2)	O(11)[b]−P(2)−O(5)	108.3(2)
O(6)[d]−Co(2)−O(5)	116.5(2)	O(10)−P(2)−O(5)	110.7(2)
O(6)[d]−Co(2)−O(7)	110.05(1)	O(15)−P(2)−O(10)	110.3(2)
O(6)[d]−Co(2)−O(8)	101.4(2)	O(15)−P(2)−O(5)	111.4(2)
O(9)−Co(3)−O(10)	113.9(2)	O(3)[c]−P(3)−O(1)	108.3(2)
O(9)−Co(3)−O(11)	101.4(2)	O(3)[c]−P(3)−O(13)	107.8(2)
O(9)−Co(3)−O(12)	116.4(2)	O(3)[c]−P(3)−O(12)	109.5(2)
O(10)−Co(3)−O(12)	118.77(1)	O(1)−P(3)−O(12)	110.5(2)
O(11)−Co(3)−O(10)	99.0(2)	O(1)−P(3)−O(13)	112.3(2)
O(11)−Co(3)−O(12)	103.0(2)	O(13)−P(3)−O(12)	108.3(2)
O(13)−Co(4)−O(14)	99.5(2)	O(14)[d]−P(4)−O(4)	111.8(2)
O(13)−Co(4)−O(15)	116.0(2)	O(14)[d]−P(4)−O(16)	111.5(2)
O(13)−Co(4)−O(16)	109.7(2)	O(14)[d]−P(4)−O(7)	112.6(2)
O(15)−Co(4)−O(14)	104.02(1)	O(4)−P(4)−O(16)	110.9(2)
O(15)−Co(4)−O(16)	123.5(2)	O(4)−P(4)−O(7)	104.0(2)
O(16)−Co(4)−O(14)	99.28(1)	O(16)−P(4)−O(7)	105.7(2)
Organic Moiety			
N(1)−C(1)−C(2)	114.3(5)	N(3)−C(3)−C(4)	110.6(4)
C(1)−C(2)−N(2)	113.8(5)	C(3)−C(4)−N(4)	112.3(4)

[a] Symmetry transformations used to generated equivalent atoms: $-x + 1, y + {}^1/_2, -z + {}^1/_2$. [b] Symmetry transformations used to generated equivalent atoms: $-x + 2, y + {}^1/_2, -z + {}^1/_2$. [c] Symmetry transformations used to generated equivalent atoms: $x + {}^1/_2, -y + {}^3/_2, -z$. [d] Symmetry transformations used to generated equivalent atoms: $x - {}^1/_2, -y + {}^5/_2, -z$.

Results

$[C_2N_2H_{10}]_2[Co_4(PO_4)_4]H_2O$, I. The asymmetric unit of **I** consists of 33 non-hydrogen atoms (Figure 1). The structure comprises a network of alternating CoO_4 and PO_4 tetrahedra connected by Co−O−P linkages. The organic amine, en, sits in the middle of the channels formed by these linkages. There are four crystallographically independent cobalt and phosphorus atoms. The cobalt atoms are tetrahedrally coordinated by their oxygen atom neighbors with cobalt−oxygen bond distances in the range 1.913−2.016 Å [$(Co(1)-O)_{av}$ = 1.984, $(Co(2)-O)_{av}$ = 1.951, $(Co(3)-O)_{av}$ = 1.948, $(Co(4)-O)_{av}$ = 1.963 Å]. The cobalt atoms form four Co−O−P bonds with four distinct phosphorus atom neighbors with Co−O−P bond angles over the range 104.2−160.7° (av = 127.6°) (Tables 3 and 4). These geometrical data are in good agreement with those known for similar compounds.[9−11] The four distinct phosphorus atoms are tetrahedrally coordinated to oxygen atoms. The average P−O distances of 1.533, 1.532, 1.526, 1.536 Å result for P(1), P(2), P(3), and P(4), respectively (Table 3). The O−P−O bond angels are in the range 105.7−112.7° (av 109.5°), indicating that the PO_4 tetrahedra are regular. Extensive bond valence sum calculations[20] indicated the valences of Co, P, and O, to be +2, +5, and −2, respectively, and the framework stoichiometry works out to be $Co_4(PO_4)_4$. This results in the framework composition consisting of Co/P ratio of 1.0 and to have a charge of −4. Charge compensation is achieved by extraframework organic cation. Thus, there are two doubly protonated en molecules present in the material and are located in the channels. The water molecule, present in the material, also occupies the same channels.

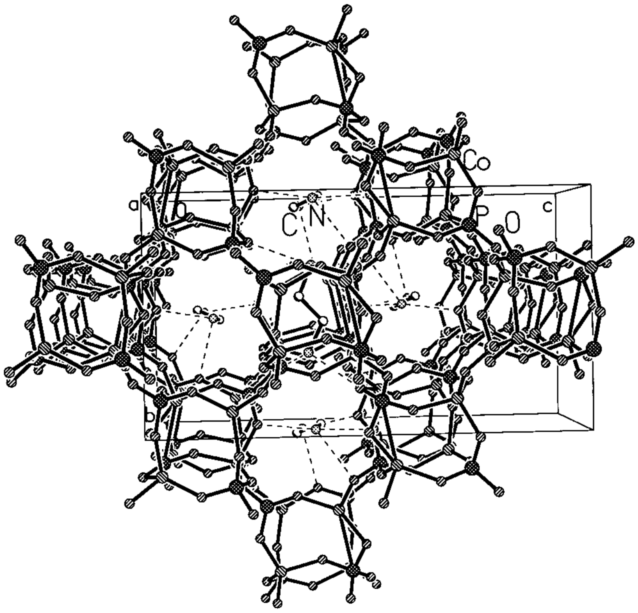

Figure 3. Structure of **I** along the [001] direction. The dotted lines represent hydrogen bond interactions between the framework oxygens and the amine.

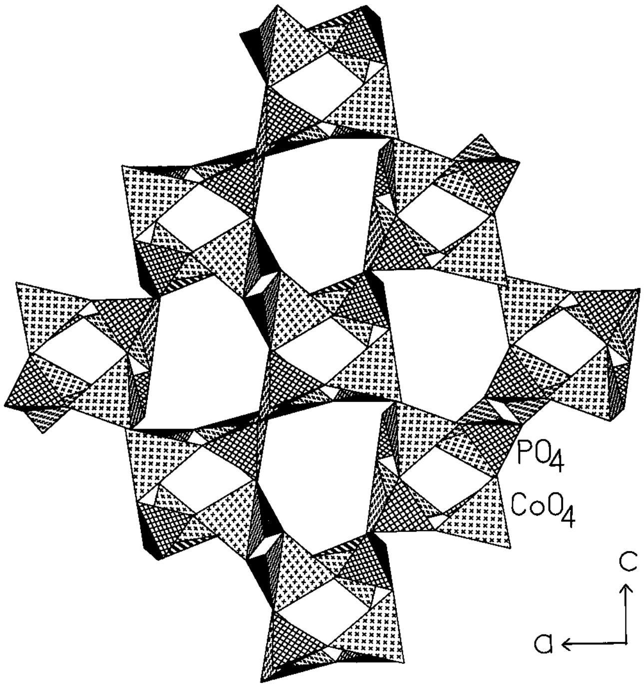

Figure 4. Polyhedral view of **I** along the [010] direction showing the eight-membered channels. Amine molecules are omitted for clarity.

The polyhedral connectivity in **I** leads to the open-framework network as shown in Figure 2. The structure is built from the vertex linkage of the CoO_4 and PO_4 tetrahedra forming double four rings as shown in Figures 2−4. The double 4-rings are linked to each other via an oxygen forming an 8-membred channel, of width 6.7 × 6.6 Å, along the [100] direction. Similar connectivity results in eight-membered channels along the [010] and [001] direction as well. The width of these eight-membered channels are 4.8 × 6.2 ([010]) and 6.6 × 7.2 Å ([001]). The water molecules and the protonated ethylenediamine molecules sit in the middle of these channels. Thus, **I** is a typical zeolite-type three-dimensional open-framework material with the framework resembling very closely to the aluminosilicate, merlinoite.[14]

---

(20) Brown, I. D.; Aldermatt, D. *Acta Crystallogr., Sect. B* **1984**, *41*, 244.

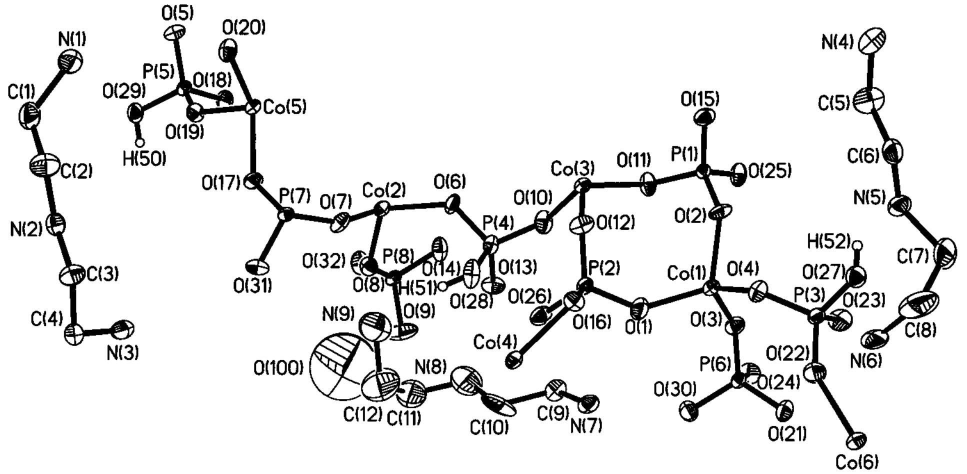

Figure 5. ORTEP plot of **II**, $[C_4N_3H_{16}]_3[Co_6(PO_4)_5(HPO_4)_3]H_2O$. The hydrogens of the amine molecules are not shown. Thermal ellipsoids are given at 50% probability.

$[C_4N_3H_{16}]_3[Co_6(PO_4)_5(HPO_4)_3]H_2O$, II. The structure of **II** contains 67 non-hydrogen atoms in the asymmetric unit (Figure 5). The structure comprises a network of CoO_4 and PO_4 tetrahedra that strictly alternate and consist entirely of Co−O−P linkages. The structure-directing diethylenetriamine (DETA) sits in the middle of the channels formed by these linkages. The six distinct cobalt atoms are all tetrahedrally coordinated to oxygens with an average bond distance of 1.966 Å [Co(1)−O =1.963; Co(2)−O = 1.972; Co(3)−O = 1.951, Co(4)−O = 1.985, Co(5)−O = 1.963, and Co(6)−O = 1.959 Å]. The cobalt atoms make four Co−O−P bonds to eight distinct P atom neighbors, with angles spread over the range 109.1−162.2°, with an average value of 135.5°. There are eight crystallographically independent phosphate tetrahedra in **II**. The P atoms, on the other hand, makes only three connections with the adjacent Co atoms via P−O−Co bonds and the remaining being terminal. The P−O distances are in the range 1.515−1.575 Å (av 1.538 Å), and the O−P−O bond angles are in the range 105.4−113.5° (av 109.5°). From the bond distances and bond angles it is clear that the PO_4 tetrahedra is more regular than the CoO_4 tetrahedra (Tables 6 and 7). The resulting $Co_6(PO_4)_8$ framework stoichiometry has a total charge of −12. There are three extraframework guest species, in the form of diethylenetriamine (DETA) cations. Assuming all the nitrogen atoms of the DETA are protonated, the framework must have three protons, for charge-balancing purposes. Of the eight terminal P−O bonds, three are likely to have protons, which were located in difference Fourier maps, and also matches with the uncoordinated P−O bond lengths. Bond valence sum calculations[20] on the framework also agrees with the above formalism. Thus, O(27), O(28), and O(29) with P−O distances of 1.571, 1.575, and 1.571 Å are formally −OH groups consistent with the known range of values (~1.56−1.60 Å).[21] The geometrical data are in agreement with the available structures of similar compounds.[9−11]

The polyhedral connectivity in **II** leads to the open-framework network shown in Figure 6. The CoO_4, PO_4, and HPO_4 groups are connected, in a manner to form four-membered rings, which may be the fundamental building in open-framework metal phosphates. Thus, there are no Co−O−Co or P−O−P linkages seen in this material. The four-membered rings are joined together edge- and corner-wise forming 16-membered elliptical one-dimensional channels, of width 17.1 × 4.0 Å, along the *b* axis as shown in Figure 7. This is the first time, to our knowledge, such large channels are formed in an open-framework cobalt phosphate material. The structure-directing amine, triply protonated DETA species occupies the channels along with water molecules and interact with the framework via hydrogen bonding.

Discussion

Two new cobalt phosphates, **I**, $[C_2N_2H_{10}]_2[Co_4(PO_4)_4]H_2O$, and **II**, $[C_4N_3H_{16}]_3[Co_6(PO_4)_5(HPO_4)_3]H_2O$, have been synthesized by the reaction of an amine phosphate with Co^{2+} ions under hydrothermal conditions at 150 °C. Compound **I**, could also be synthesized by reacting the Co-amine complex with phosphoric acid. In the first method, the amine phosphate contains the phosphate and amine needed for the formation of the open-framework structure. Although, the synthesis of **I** was carried out starting with DETAPHOS, the final product had en in the channels. Such a decomposition as well as reaction of the organic amine during the hydrothermal synthesis has been known to occur in phosphate-based framework materials.[22,23] Compound **II**, on the other hand, has triply protonated DETA molecules within the channels. In the second method, the tris-amine complex acts as a source for both the metal as well as the amine. It is possible that the amine released by the decomposition of the complex forms the amine phosphate by interaction with H_3PO_4. The formation of both **I** and **II** under identical conditions indicate that the energies of the two are comparable. Furthermore, it has not been possible to achieve the synthesis of pure **I** or **II**.

Both **I** and **II** are constructed only from the tetrahedra involving Co and P, which strictly alternate. This situation leads to a solid where there are no Co−O−Co or P−O−P linkages and the entire structure is built up from only Co−O−P connections, despite **II** having a Co:P ratio of 1.33:1. While **I** does not have any terminal P−O bonds, **II** possess one terminal P−O linkage for each of the phosphorus atom. The differences in the linkages between the polyhedra leads to distinct variations in both the structures. While **II** forms as one-dimensional channels bound by 16-T (T = Co, P) atoms, **I** forms three-dimensional channels bound by 8-T atoms. Although large

---

(21) Lightfoot, P.; Masson, D. *Acta Crystallogr., Sect. C.* **1996**, *52*. 1077.

(22) Chippindale, A. M.; Natarajan, S.; Thomas, J. M.; Jones, J. M. *J. Solid State Chem.* **1994**, *114*, 18.

(23) Natarajan, S.; Gabriel, J.-C. P.; Cheetham, A. K. *Chem. Commun.* **1996**, 1415 and references therein.

Table 5. Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [Å$^2 \times 10^3$] for **II**, $[C_4N_3H_{16}]_3[Co_6(PO_4)_5(HPO_4)_3]H_2O$

atom	*x*	*Y*	*z*	$U_{(eq)}$[a]
Co(1)	1282(1)	−2809(1)	595(1)	16(1)
Co(2)	3716(1)	−7919(1)	−896(1)	17(1)
Co(3)	2495(1)	−4950(1)	1088(1)	16(1)
Co(4)	2465(1)	137(1)	−1333(1)	17(1)
Co(5)	5077(1)	−7381(1)	−115(1)	15(1)
Co(6)	64(1)	2412(1)	−136(1)	18(1)
P(1)	1693(1)	−5320(2)	2054(1)	14(1)
P(2)	2190(1)	−2071(2)	−97(1)	17(1)
P(3)	638(1)	−173(2)	1098(1)	18(1)
P(4)	2817(1)	−6551(2)	−584(1)	19(1)
P(5)	5648(1)	−10371(2)	−600(1)	16(1)
P(6)	564(1)	−4452(2)	−807(1)	16(1)
P(7)	4428(1)	−5190(2)	−1289(1)	14(1)
P(8)	3255(1)	−10299(2)	−2232(1)	17(1)
O(1)	1714(2)	−2309(7)	−119(3)	34(1)
O(2)	1489(2)	−3757(6)	1686(3)	24(1)
O(3)	854(2)	−4228(6)	25(3)	23(1)
O(4)	1092(1)	−710(6)	1040(3)	21(1)
O(5)	5948(2)	−10473(6)	207(3)	24(1)
O(6)	3245(2)	−7299(7)	−279(3)	26(1)
O(7)	4000(2)	−5886(6)	−1147(3)	24(1)
O(8)	3533(2)	−8824(6)	−2019(3)	25(1)
O(9)	2952(2)	−9914(8)	−3011(4)	47(2)
O(10)	2548(2)	−6373(6)	133(3)	28(1)
O(11)	1990(2)	−6015(6)	1440(3)	24(1)
O(12)	2436(2)	−2743(6)	708(3)	24(1)
O(13)	2580(2)	−7515(6)	−1317(3)	24(1)
O(14)	3020(2)	−10786(6)	−1487(3)	30(1)
O(15)	1945(2)	−4893(7)	2894(3)	27(1)
O(16)	2290(2)	−275(6)	−181(3)	21(1)
O(17)	4781(2)	−6451(6)	−1141(3)	26(1)
O(18)	5296(2)	−11640(7)	−638(3)	28(1)
O(19)	5462(2)	−8686(6)	−723(3)	23(1)
O(20)	5483(2)	−6247(6)	690(3)	26(1)
O(21)	190(2)	−3268(7)	−829(3)	27(1)
O(22)	511(2)	1074(7)	420(3)	37(2)
O(23)	344(2)	−1627(7)	1052(3)	32(1)
O(24)	387(2)	−6184(6)	−830(3)	25(1)
O(25)	1357(2)	−6576(6)	2145(3)	26(1)
O(26)	2325(2)	−2865(6)	−904(3)	27(1)
O(27)	615(2)	692(6)	1967(3)	26(1)
O(28)	2893(2)	−4849(6)	−963(4)	29(1)
O(29)	5905(2)	−10700(6)	−1366(3)	26(1)
O(30)	795(2)	−4226(7)	−1579(3)	27(1)
O(31)	4420(2)	−4591(6)	−2205(3)	25(1)
O(32)	3540(2)	−11748(6)	−2398(4)	32(1)
O(100)	3317(6)	−6722(27)	−3551(13)	106(7)
N(3)	5146(2)	3217(7)	−2743(4)	24(2)
N(2)	5920(2)	3863(7)	−1580(3)	21(1)
N(1)	6387(2)	2796(9)	507(4)	32(2)
C(4)	5426(2)	4651(8)	−2830(4)	24(2)
C(3)	5641(2)	5186(8)	−1963(4)	24(2)
C(2)	6173(2)	4413(9)	−782(4)	31(2)
C(1)	6445(2)	3013(10)	−407(4)	34(2)
N(6)	563(2)	4636(9)	1583(4)	38(2)
N(5)	846(2)	3443(8)	3377(4)	29(2)
N(4)	1651(2)	3380(8)	5315(4)	30(2)
C(8)	520(4)	5589(13)	2364(5)	73(4)
C(7)	472(3)	4513(14)	3091(6)	65(4)
C(6)	1156(2)	4137(9)	4074(4)	28(2)
C(5)	1402(3)	2757(9)	4521(5)	38(2)
N(9)	3338(3)	−5049(14)	−2430(6)	81(3)
N(8)	2412(3)	−6151(11)	−2831(5)	61(2)
N(7)	1576(2)	−3527(7)	−2026(4)	26(2)
C(12)	3067(4)	−4830(16)	−3262(7)	83(4)
C(11)	2748(3)	−6121(14)	−3420(7)	66(3)
C(10)	2142(3)	−4685(10)	−2788(5)	49(3)
C(9)	1786(2)	−5066(8)	−2239(5)	28(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 6. Selected Bond Distances in **II**, $[C_4N_3H_{16}]_3[Co_6(PO_4)_5(HPO_4)_3]H_2O$

moiety	distance, Å	moiety	distance, Å
Co(1)−O(1)	1.931(5)	P(2)−O(12)	1.530(5)
Co(1)−O(2)	1.954(5)	P(2)−O(1)	1.532(5)
Co(1)−O(3)	1.953(5)	P(2)−O(16)	1.544(5)
Co(1)−O(4)	2.013(5)	P(2)−O(26)	1.551(5)
Co(2)−O(5)[a]	1.971(5)	P(3)−O(22)	1.521(6)
Co(2)−O(6)	1.960(5)	P(3)−O(4)	1.531(5)
Co(2)−O(7)	1.988(5)	P(3)−O(23)	1.532(6)
Co(2)−O(8)	1.967(5)	P(3)−O(27)	1.571(5)
Co(3)−O(9)[b]	1.928(5)	P(4)−O(10)	1.515(5)
Co(3)−O(10)	1.953(5)	P(4)−O(6)	1.531(5)
Co(3)−O(11)	1.979(5)	P(4)−O(13)	1.542(5)
Co(3)−O(12)	1.944(5)	P(4)−O(28)	1.575(5)
Co(4)−O(13)[d]	1.996(5)	P(5)−O(5)	1.514(5)
Co(4)−O(14)[d]	1.975(5)	P(5)−O(19)	1.533(5)
Co(4)−O(15)[a,c]	1.960(5)	P(5)−O(18)	1.541(5)
Co(4)−O(16)	2.008(5)	P(5)−O(29)	1.571(5)
Co(5)−O(17)	1.952(5)	P(6)−O(21)	1.547(5)
Co(5)−O(18)[a]	1.965(5)	P(6)−O(3)	1.537(5)
Co(5)−O(19)	1.978(5)	P(6)−O(24)	1.553(5)
Co(5)−O(20)	1.957(5)	P(6)−O(30)	1.518(5)
Co(6)−O(21)[e]	1.954(5)	P(7)−O(7)	1.526(5)
Co(6)−O(22)	1.945(5)	P(7)−O(20)[f]	1.540(5)
Co(6)−O(23)[e]	1.953(5)	P(7)−O(17)	1.543(5)
Co(6)−O(24)[d]	1.982(5)	P(7)−O(31)	1.540(5)
P(1)−O(15)	1.521(5)	P(8)−O(9)	1.518(6)
P(1)−O(25)	1.521(5)	P(8)−O(14)	1.530(5)
P(1)−O(2)	1.545(5)	P(8)−O(8)	1.535(5)
P(1)−O(11)	1.553(5)	P(8)−O(32)	1.556(5)
Organic Moiety			
N(3)−C(4)	1.512(7)	N(5)−C(6)	1.513(7)
C(4)−C(3)	1.535(7)	C(6)−C(5)	1.526(8)
C(3)−N(2)	1.505(7)	C(5)−N(4)	1.506(7)
N(2)−C(2)	1.497(7)	N(9)−C(12)	1.508(9)
C(2)−C(1)	1.536(8)	C(12)−C(11)	1.486(9)
C(1)−N(1)	1.499(7)	C(11)−N(8)	1.505(8)
N(6)−C(8)	1.496(8)	N(8)−C(10)	1.503(8)
C(8)−C(7)	1.488(9)	C(10)−C(9)	1.548(8)
C(7)−N(5)	1.520(8)	C(9)−N(7)	1.507(7)

[a] $-x+1, -y-2, -z$. [b] $x, -y-{}^3/_2, z+{}^1/_2$. [c] $x, -y-{}^1/_2, z-{}^1/_2$. [d] $x, y+1, z$. [e] $-x, -y, -z$. [f] $-x+1, -y-1, -z$.

apertures are known to occur within many framework solids, including layered materials,[24] 16-membered channels are rarely observed. Examples of such apertures and channels are very few,[25] the apertures being generally restricted to a maximum of 12-membered rings.[26,27] In cobalt phosphates, **II** appears to be the first example with such a large channel.

The "openness" of a structure is defined in terms of the tetrahedral atom density[14] (framework density, FD) defined as the number of tetrahedral (T) atoms per 1000 Å^3. In the case of **I**, the number of T atoms per 1000 Å^3 (Co and P) is 16.0. This value is identical to the framework density of merlinoite.[14] The position of the amine in **I** as well the its interaction with the framework are such that well defined 8-membred channels are formed in all the crystallographic directions. In the case of **II**, however, The FD values are found to be lower, 13.3, indicating a more open architecture. This is the lowest FD value observed

---

(24) Thomas, J. M.; Jones, R. H.; Chen, J.; Xu, R.; Chippindale, A. M.; Natarajan, S.; Cheetham, A. K. *J. Chem. Soc., Chem. Commun.* **1992**, 929.

(25) Loiseau, T.; Ferey, G. *J. Solid State Chem.* **1994**, *111*, 403; *J. Mater. Chem.* **1996**, *6*, 1073.

(26) Harrison, W. T. A.; Hannooman, L. *Angew. Chem. Int. Ed.* **1997**, *36*, 640 and references therein.

(27) Chidambaram, D.; Neeraj, S.; Natarajan, S.; Rao, C. N. R. *J. Solid State Chem.* **1999**, *147*, 154.

Table 7. Selected Bond Angles in **II**, $[C_4N_3H_{16}]_3[Co_6(PO_4)_5(HPO_4)_3]H_2O$

moiety	angle (deg)	moiety	angle (deg)
O(1)−Co(1)−O(3)	111.6(2)	O(12)−P(2)−O(1)	112.5(3)
O(1)−Co(1)−O(2)	114.8(2)	O(12)−P(2)−O(16)	109.8(3)
O(3)−Co(1)−O(2)	108.3(2)	O(1)−P(2)−O(16)	109.7(3)
O(1)−Co(1)−O(4)	106.5(2)	O(12)−P(2)−O(26)	111.8(3)
O(3)−Co(1)−O(4)	118.0(2)	O(1)−P(2)−O(26)	109.7(3)
O(2)−Co(1)−O(4)	97.2(2)	O(16)−P(2)−O(26)	105.4(3)
O(6)−Co(2)−O(8)	113.1(2)	O(22)−P(3)−O(4)	109.6(3)
O(6)−Co(2)−O(5)^{a}	107.6(2)	O(22)−P(3)−O(23)	113.5(3)
O(8)−Co(2)−O(5)^{a}	109.2(2)	O(4)−P(3)−O(23)	110.1(3)
O(6)−Co(2)−O(7)	105.6(2)	O(22)−P(3)−O(27)	105.9(3)
O(8)−Co(2)−O(7)	103.9(2)	O(4)−P(3)−O(27)	109.2(3)
O(5)^{a}−Co(2)−O(7)	117.7(2)	O(23)−P(3)−O(27)	108.4(3)
O(9)^{b}−Co(3)−O(12)	109.0(2)	O(10)−P(4)−O(6)	111.4(3)
O(9)^{b}−Co(3)−O(10)	114.6(3)	O(10)−P(4)−O(13)	110.4(3)
O(12)−Co(3)−O(10)	110.5(2)	O(6)−P(4)−O(13)	111.6(3)
O(9)^{b}−Co(3)−O(11)	109.5(3)	O(10)−P(4)−O(28)	109.1(3)
O(12)−Co(3)−O(11)	117.6(2)	O(6)−P(4)−O(28)	108.6(3)
O(10)−Co(3)−O(11)	95.3(2)	O(13)−P(4)−O(28)	105.4(3)
O(15)^{c}−Co(4)−O(14)^{d}	126.1(2)	O(5)−P(5)−O(19)	111.0(3)
O(15)^{c}−Co(4)−O(13)^{d}	104.6(2)	O(5)−P(5)−O(18)	112.5(3)
O(14)^{d}−CO(4)−O(13)^{d}	102.6(2)	O(19)−P(5)−O(18)	110.9(3)
O(15)^{c}−Co(4)−O(16)	104.5(2)	O(5)−P(5)−O(29)	108.2(3)
O(14)^{d}−CO(4)−O(16)	113.3(2)	O(19)−P(5)−O(29)	106.9(3)
O(13)^{d}−Co(4)−O(16)	103.1(2)	O(18)−P(5)−O(29)	107.0(3)
O(17)−Co(5)−O(20)	125.1(2)	O(30)−P(6)−O(3)	112.4(3)
O(17)−Co(5)−O(18)^{a}	113.9(2)	O(30)−P(6)−O(21)	110.4(3)
O(20)−Co(5)−O(18)^{a}	101.8(2)	O(3)−P(6)−O(21)	109.2(3)
O(17)−Co(5)−O(19)	121.6(2)	O(30)−P(6)−O(24)	107.8(3)
O(20)−Co(5)−O(19)	100.7(2)	O(3)−P(6)−O(24)	108.4(3)
O(18)^{a}−Co(5)−O(19)	121.6(2)	O(21)−P(6)−O(24)	108.6(3)
O(22)−Co(6)−O(23)^{e}	122.6(3)	O(7)−P(7)−O(20)^{f}	108.2(3)
O(22)−Co(6)−O(21)^{e}	101.7(2)	O(7)−P(7)−O(31)	110.3(3)
O(23)^{e}−Co(6)−O(21)^{e}	114.1(2)	O(20)^{f}−P(7)−O(31)	108.3(3)
O(22)−Co(6)−O(24)^{d}	101.0(2)	O(7)−P(7)−O(17)	111.7(3)
O(23)^{e}−Co(6)−O(24)^{d}	97.4(2)	O(20)^{f}−P(7)−O(17)	111.0(3)
O(21)^{e}−Co(6)−O(24)^{d}	120.8(2)	O(31)−P(7)−O(17)	107.4(3)
O(15)−P(1)−O(25)	112.7(3)	O(9)−P(8)−O(14)	111.4(3)
O(15)−P(1)−O(2)	107.0(3)	O(9)−P(8)−O(8)	108.0(3)
O(25)−P(1)−O(2)	110.4(3)	O(14)−P(8)−O(8)	111.5(3)
O(15)−P(1)−O(11)	110.0(3)	O(9)−P(8)−O(32)	110.9(4)
O(25)−P(1)−O(11)	107.0(3)	O(14)−P(8)−O(32)	105.9(3)
O(2)−P(1)−O(11)	109.8(3)	O(8)−P(8)−O(32)	109.1(3)
Organic Moiety			
N(3)−C(4)−C(3)	110.9(6)	N(5)−C(6)−C(5)	108.1(6)
C(4)−C(3)−N(2)	109.4(6)	C(6)−C(5)−N(4)	108.9(6)
C(3)−N(2)−C(2)	110.8(5)	N(9)−C(12)−C(11)	111.9(10)
N(2)−C(2)−C(1)	108.7(6)	C(12)−C(11)−N(8)	115.6(10)
C(2)−C(1)−N(1)	109.9(6)	C(11)−N(8)−C(10)	117.9(8)
N(6)−C(8)−C(7)	110.6(8)	N(8)−C(10)−C(9)	108.7(6)
C(8)−C(7)−N(5)	116.1(7)	C(10)−C(9)−N(7)	109.1(6)
C(7)−N(5)−C(6)	114.7(7)		

[a] $-x+1, -y-2, -z$. [b] $x, -y-{}^{3}/_{2}, z+{}^{1}/_{2}$. [c] $x, -y-{}^{1}/_{2}, z-{}^{1}/_{2}$. [d] $x, y+1, z$. [e] $-x, -y, -z$. [f] $-x+1, -y-1, -z$.

for open-framework cobalt phosphates and the value is close to that of MAPSO-46, which has only 8- and 12-membered channels.[14]

Both **I** and **II** show dominant hydrogen bonding involving the amine and the framework (Tables 8 and 9). The strongest hydrogen bond interactions are observed for the hydrogen atoms attached to the nitrogens and the framework oxygens. The donor−acceptor (O···H) distances around 2.0 Å and the majority of the angles above 150° (O···H−N) indicate that the hydrogen bond interactions in **I** and **II** are strong. In **I**, the presence of extraframework water molecules, typical of zeolites, also contribute significantly for the hydrogen bond interactions. The complete list of all the observed hydrogen bond interactions are presented in Table 8.

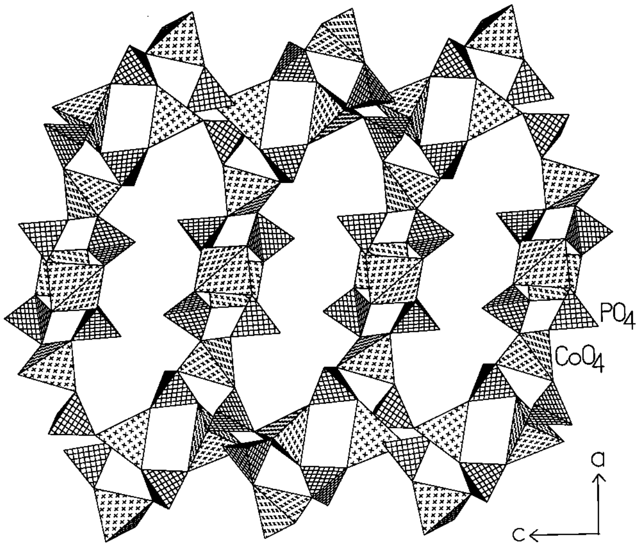

Figure 6. Polyhedral view of **II** along the [010] direction showing the 16-membered channels. Amine and water molecules are not shown for clarity.

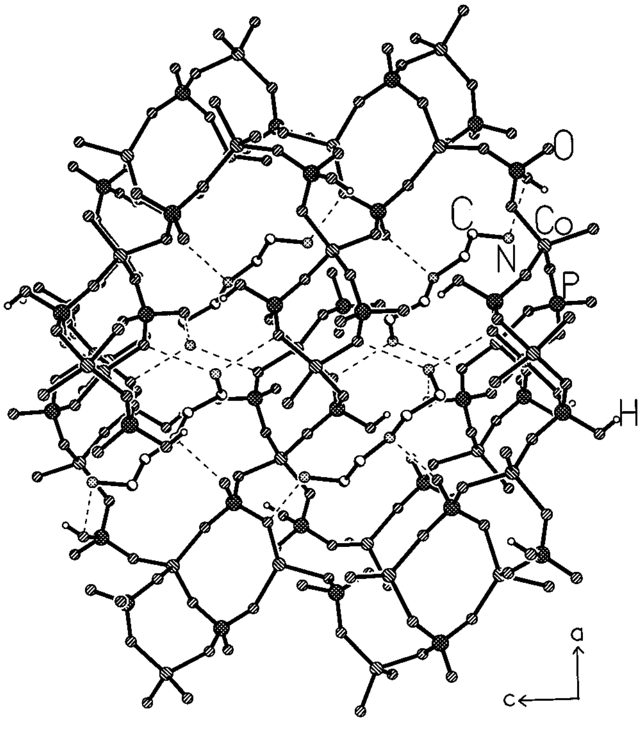

Figure 7. Structure of **II** along the [010] direction showing the position of the amine within the channels. Dotted lines represent the possible hydrogen-bond interactions.

The synthesis of **I** and **II** is significant as these represent only the second report of three-dimensional cobalt phosphate materials, synthesized hydrothermally in the presence of organic amines. We attribute this to the novel synthetic route employed in this study. Our study establishes the possible role of amine phosphates as intermediates in the formation of open-framework phosphate materials. It is noteworthy that **I** could be formed by conventional hydrothermal methods starting from two different starting materials. While the first method involved the use of an amine phosphate as the starting material, the second method uses the metal amine complex, although it is possible that the

Table 8. Important Hydrogen-Bond Interactions Observed in **I**, $[C_2N_2H_{10}]_2[Co_4(PO_4)_4]H_2O$

moiety	distance, Å	moiety	angle (deg)
O(15)−H(1)	2.167(1)	O(15)−H(1)−N(1)	154.4(1)
O(10)−H(3)	2.285(1)	O(10)−H(3)−N(1)	160.2(1)
O(8)−H(8)	1.982(1)	O(8)−H(8)−N(2)	143.7(1)
O(2)−H(9)	2.237(1)	O(2)−H(9)−N(2)	160.1(2)
O(13)−H(10)	2.040(1)	O(13)−H(10)−N(2)	152.4(1)
O(10)−H(11)	2.321(1)	O(10)−H(11)−N(3)	145.8(1)
O(6)−H(12)	2.035(1)	O(6)−H(12)−N(3)	164.5(1)
O(16)−H(13)	1.849(1)	O(16)−H(13)−N(3)	164.7(1)
O(12)−H(18)	2.063(2)	O(12)−H(18)−N(4)	161.0(3)
O(3)−H(19)	2.166(2)	O(3)−H(19)−N(4)	158.6(1)
O(5)−H(20)	2.109(2)	O(5)−H(20)−N(4)	143.9(1)
O(16)−H(101)	2.088(2)	O(16)−H(101)−O(100)	167.1(1)
O(9)−H(102)	2.388(2)	O(9)−H(102)−O(100)	169.8(1)
O(4)−H(14)	2.549(1)	O(4)−H(14)−C(3)	160.3(1)
O(13)−H(15)	2.520(2)	O(13)−H(15)−C(3)	176.4(1)
O(8)−H(17)	2.529(1)	O(8)−H(17)−C(4)	160.6(1)

amine released by the complex form the amine phosphate. On the basis of the structure of **II** and the hydrogen bond interactions present therein, a tentative mechanism for the formation of such large voids can be proposed. The triply protonated DETA molecules are positioned in such a manner that they interact strongly with the framework oxygens forming N−H···O bonds (Figure 7 and Table 9). DETA is known to direct the formation of 8- and 10-membered channels in open-framework zinc phosphates.[28] Thus, the interaction between the protonated amine and water with the framework leads only to eight-membered channels in **I**, just as in many framework phosphates. In **II**, however, two DETA cations along with one molecule of water present in 16-membered channels interact with the framework through hydrogen bonds. These interactions, along with the positions of the amine and water molecules could impose constraints on the framework and give rise to the large channels.

Table 9. Selected Hydrogen-Bond Interaction Observed in **II**, $[C_4N_3H_{16}]_3[Co_6(PO_4)_5(HPO_4)_3]H_2O$

moiety	distance (Å)	moiety	angle (deg)
O(20)−H(2)	2.282(2)	O(20)−H(2)−N(1)	143.6(1)
O(14)−H(3)	2.008(1)	O(14)−H(3)−N(1)	159.2(1)
O(32)−H(8)	1.665(1)	O(32)−H(8)−N(2)	170.3(2)
O(19)−H(9)	2.147(2)	O(19)−H(9)−N(2)	158.2(1)
O(31)−H(14)	1.975(1)	O(31)−H(14)−N(3)	142.2(1)
O(17)−H(15)	2.159(2)	O917)−H(15)−N(3)	145.8(4)
O(31)−H(15)	2.393(1)	O(31)−H(15)−N(3)	143.5(1)
O(18)−H(16)	1.972(1)	O(18)−H(16)−N(3)	153.1(1)
O(16)−H(17)	1.900(1)	O(16)−H(17)−N(4)	165.0(1)
O(4)−H(18)	2.151(1)	O(4)−H(18)−N(4)	151.8(1)
O(11)−H(19)	1.944(2)	O(11)−H(19)−N(4)	160.9(1)
O(27)−H(25)	2.505(1)	O(27)−H(25)−N(5)	143.8(1)
O(25)−H(30)	1.945(1)	O(25)−H(30)−N(6)	155.8(2)
O(21)−H(31)	1.959(1)	O(21)−H(31)−N(6)	158.6(3)
O(3)−H(32)	2.108(2)	O(3)−H(32)−N(6)	148.9(3)
O(26)−H(33)	2.103(3)	O(26)−H(33)−N(7)	143.8(2)
O(2)−H(34)	1.991(2)	O(2)−H(34)−N(7)	149.0(1)
O(30)−H(35)	1.919(3)	O(30)−H(35)−N(7)	152.1(1)
O(13)−H(40)	1.844(2)	O(13)−H(40)−N(8)	150.7(2)
O(11)−H(41)	2.030(2)	O(11)−H(41)−N(8)	162.1(3)
O(28)−H(46)	1.994(2)	O(28)−H(46)−N(9)	170.8(2)
O(8)−H(47)	2.468(3)	O(8)−H(47)−N(9)	149.8(3)
O(32)−H(48)	2.100(1)	O(32)−H(48)−N(9)	139.2(1)
O(31)−H(50)[a]	1.826(1)	O(31)−H(50)−O(29)[a]	148.5(2)
O(9)−H(51)[a]	2.061(2)	O(9)−H(51)−O(28)[a]	172.5(2)
O(30)−H(52)[a]	1.833(1)	O(30)−H(52)−O(27)[a]	161.4(3)
O(7)−H(7)	2.597(1)	O(7)−H(7)−C(2)	141.3(2)
O(15)−H(22)	2.571(2)	O(15)−H(22)−C(6)	145.0(4)
O(25)−H(37)	2.365(1)	O(25)−H(37)−C(9)	147.6(1)
O(10)−H(43)	2.229(1)	O(10)−H(43)−C(11)	161.2(3)

[a] Intra-framework.

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

Supporting Information Available: Two X-ray crystallographic files, in CIF format, are available.

IC991223X

---

(28) Neeraj, S.; Natarajan, S.; Rao, C. N. R. *Chem. Commun.* **1999**, 165; *New. J. Chem.* **1999**, *23*, 303; *Chem. Mater.* **1999**, *11*, 1390.