

Open-Framework Cobalt (II) Phosphates with Sodalite-Related Architectures

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Three new framework cobalt (II) phosphates have been synthesized hydrothermally in the presence of piperazine as a structure-directing agent. Crystal data: compound I, $[C_4N_2H_{12}][Co(HPO_4)_2]$, monoclinic space group = $P2_1/n$ (no. 14), $a = 8.5521(10)$ Å, $b = 13.5791(15)$ Å, $c = 10.0405(11)$ Å, $\beta = 96.855(2)^\circ$, $V = 1157.7(2)$ Å³, $Z = 4$, $M = 339.04$, $D_c = 1.945$ g cm⁻³, $MoK\alpha$, $\lambda = 0.71073$ Å, $R_1(F_o) = 0.053$; compound II, $[C_4N_2H_{11}][Co_2(PO_4)(H_2PO_4)_2]$, monoclinic space group = $C2/c$ (no. 15), $a = 13.444(5)$ Å, $b = 12.874(5)$ Å, $c = 8.224(2)$ Å, $\beta = 94.64(2)^\circ$, $V = 1418.8(2)$ Å³, $Z = 8$, $M = 494.96$, $D_c = 2.317$ g cm⁻³, $MoK\alpha$, $\lambda = 0.71073$ Å, $R_1(F_o) = 0.047$; compound III, $[C_4N_2H_{12}]_2[Co_4(HPO_4)_6]$, monoclinic space group = $P2_1/c$ (no. 14) $a = 12.8780(13)$ Å, $b = 26.671(3)$ Å, $c = 8.2592(8)$ Å, $\beta = 96.931(2)^\circ$, $V = 2816.0(5)$ Å³, $Z = 4$, $M = 987.90$, $D_c = 2.330$ g cm⁻³, $MoK\alpha$, $\lambda = 0.71073$ Å, $R_1(F_o) = 0.048$. The structure of I consists of one-dimensional chains built up of corner-shared four rings (Co_2P_2) which are key structural units that form the sodalite cage. Compounds II and III 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. The modes of the interruptions in II and III differ in relation to the structure of a regular sodalite cage. © 2002 Elsevier Science (USA)

INTRODUCTION

Amongst the many inorganic open-framework structures known to date, the metal phosphates constitute one of the largest families (1, 2). The synthesis of these solids 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 structure-directing agent. Numerous other strategies and subtle modifications in the synthetic methodologies have been

employed, including the use of non-aqueous solvents instead of water (3). Other strategies include varying the choice of reactants; in some cases, for example, organometallic, metal-organic and inorganic metal complexes have been used as sources of metal ion in the synthesis media (4–7). Amines can be added to the reaction mixture either as part of a metal-organic precursor or separately as a reactant. The source of phosphorus is typically either phosphoric acid or phosphorus pentoxide. However, amine phosphates have been used as a source of both amine and phosphorus (8, 9), and we have recently reported the synthesis of zinc, cobalt and iron phosphates obtained by using tributyl phosphate (TBP) as a phosphorus source (10). The use of an organic source of phosphorus facilitates the use of non-aqueous media for the synthesis and has been especially helpful in the synthesis of open-framework cobalt (II) phosphates, which are difficult to prepare under aqueous conditions.

A number of zincophosphates that are structural analogs of naturally occurring zeolites have been characterized in recent years (11–14), but only isolated cases of pure cobalt phosphates with zeolitic topologies are known (6, 15). However, a large number of cobalt-substituted aluminophosphates with zeolitic architectures are known in the literature (16). In this paper, we describe three new cobalt phosphates that were obtained using the TBP synthetic method in an alcohol solvent; the first one possesses a one-dimensional chain structure, whereas the other two possess interrupted sodalite-type structures.

EXPERIMENTAL

Synthesis of Cobalt Phosphates

In a typical synthesis of the title compounds, a known amount of $CoCl_2 \cdot 6H_2O$ (0.121 g) was dissolved in butan-2-ol (6 g) and tributyl phosphate (0.57 g) added to the solution under stirring. The amine piperazine (0.271 g) was added after a few minutes and the mixture stirred until

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TABLE 1
Crystal Data and Structure Refinement Parameters for I–III

| Structural parameter | I | II | III |
|---|---|---|---|
| Chemical formula | [C ₄ N ₂ H ₁₂][Co(HPO ₄) ₂] | [C ₄ N ₂ H ₁₁][Co ₂ (PO ₄)(H ₂ PO ₄) ₂] | [C ₄ N ₂ H ₁₂] ₂ [Co ₄ (HPO ₄) ₆] |
| Formula mass | 339.04 | 493.96 | 987.90 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>n</i> | <i>C</i> 2/ <i>c</i> | <i>P</i> 2 ₁ / <i>c</i> |
| T (K) | 293 | 293 | 293 |
| <i>a</i> (Å) | 8.5521(10) | 13.444(5) | 12.8780(1) |
| <i>b</i> (Å) | 13.5791(15) | 12.874(5) | 26.671(3) |
| <i>c</i> (Å) | 10.0405(11) | 8.224(2) | 8.2592(8) |
| β (deg) | 96.855(2) | 94.64(2) | 96.931(2) |
| <i>V</i> (Å ³) | 1157.7(2) | 1418.8(8) | 2816.0(5) |
| <i>Z</i> | 4 | 8 | 4 |
| μ (mm ⁻¹) | 1.791 | 2.745 | 2.765 |
| 2 θ range data collected | 5.06, 56.50 | 4.38, 56.54 | 3.06, 56.58 |
| Total data collected | 6717 | 4153 | 16,596 |
| Unique data | 2634 | 1644 | 6463 |
| Observed data ($\sigma > 2\sigma(I)$) | 2190 | 1291 | 4168 |
| <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 $\sigma(I)$] | 0.053, 0.143 | 0.048, 0.133 | 0.048, 0.109 |
| <i>R</i> (all data) | 0.063, 0.150 | 0.060, 0.139 | 0.086, 0.122 |

it became homogeneous. The gels were heated in Parr autoclaves at 180°C for 60 h. The products, consisting of deep-blue crystals, were filtered under vacuum and washed with minimum amount of methanol and dried at 70°C. Compounds **I** and **III** were isolated from the same reaction gel, 0.5 CoCl₂·6H₂O:3.0 C₄N₂H₁₀:2.0 P(O)(*OBu*)₃:125 *i*-BuOH, whereas **II** was isolated when the gel composition was 0.5 CoCl₂·6H₂O:1.5 C₄N₂H₁₀:1.0 P(O)(*OBu*)₃:125 *i*-BuOH (*Bu* = C₄H₉).

Single Crystal Structure Determination

A suitable single crystal of each of the title compounds was 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 (MoK α 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 20 s per frame). An empirical correction based on symmetry equivalent reflections was applied using the SADABS program (17). The structure was solved by direct methods using SHELX-97 and difference Fourier syntheses (18). 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 determinations of the metal phosphates **I–III** are presented in Table 1. Full matrix leastsquares refinement against $|F^2|$ was carried out using the SHELXTL-

PLUS package of programs (19). The last cycles of refinement included atomic positions and anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms.

RESULTS

Structure of [C₄N₂H₁₂][Co(HPO₄)₂], **I**

The atomic coordinates of [C₄N₂H₁₂][Co(HPO₄)₂], **I**, are presented in Table 2. The asymmetric unit of **I**, shown in

TABLE 2
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å² $\times 10^3$) for [C₄N₂H₁₂][Co(HPO₄)₂], **I**

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} |
|-------|-----------|----------|----------|------------------------|
| Co(1) | 2325(1) | 5327(1) | 4713(1) | 20(1) |
| P(1) | −527(1) | 4375(1) | 2792(1) | 21(1) |
| P(2) | 5406(1) | 5984(1) | 3525(1) | 19(1) |
| O(1) | 3865(3) | 6211(2) | 4080(3) | 28(1) |
| O(2) | 3202(3) | 4071(2) | 5366(3) | 26(1) |
| O(3) | 617(4) | 5206(2) | 3225(3) | 31(1) |
| O(4) | 1280(3) | 6057(2) | 6036(3) | 30(1) |
| O(5) | 267(3) | 3578(2) | 2051(3) | 34(1) |
| O(6) | −1871(3) | 4852(3) | 1784(3) | 33(1) |
| O(7) | 5369(3) | 5069(2) | 2656(3) | 31(1) |
| O(8) | 5798(3) | 6882(2) | 2621(3) | 29(1) |
| C(1) | 11,585(4) | 8500(3) | 3011(4) | 23(1) |
| C(2) | 11,220(5) | 8235(4) | 4351(5) | 38(1) |
| C(3) | 9170(5) | 7102(3) | 3332(6) | 37(1) |
| C(4) | 9546(6) | 7371(4) | 2002(6) | 52(2) |
| N(1) | 9514(6) | 7913(4) | 4319(5) | 62(2) |
| N(2) | 11,234(6) | 7654(4) | 2066(5) | 55(1) |

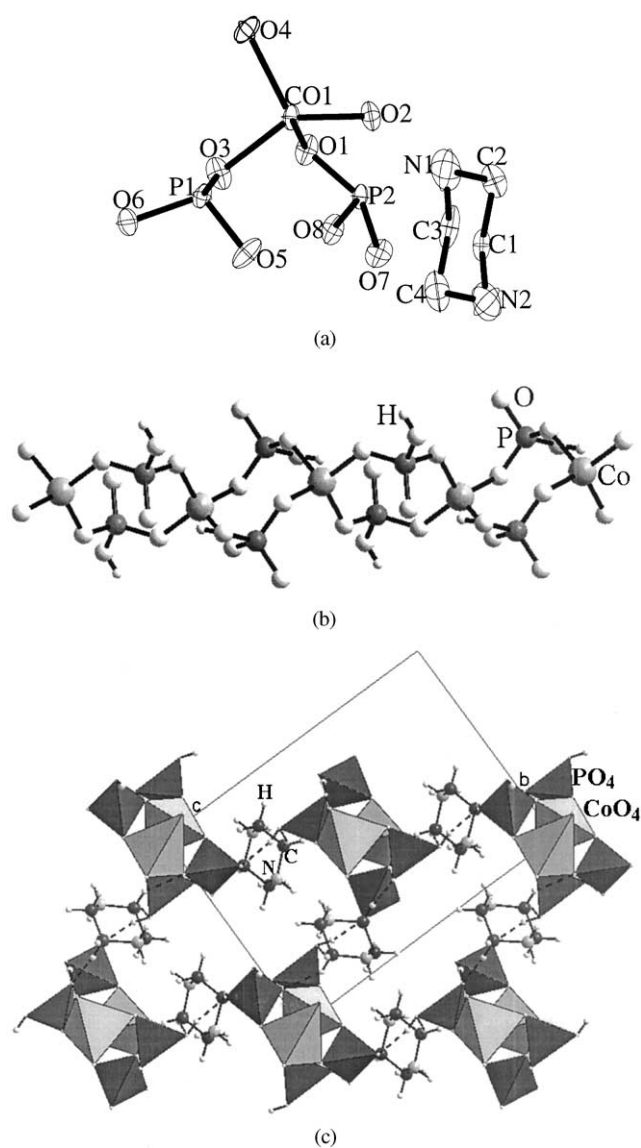


FIG. 1. (a) ORTEP plot of the asymmetric unit of $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Co}(\text{HPO}_4)_2]$, **I**; (b) a corner-shared (CS) four ring chain of **I**; (c) Structure of **I** along the a -axis (chain axis) showing the CS chains and the hydrogen-bonded amine molecules. The chains are shown in polyhedral view and the amines are shown in ball and stick model. The dotted lines represent the hydrogen bonding interactions.

Fig. 1a, consists of 17 non-hydrogen atoms. The structure is formed of CoO_4 and PO_4 tetrahedra linked via oxygen atoms to form the basic unit of the structure, a four-membered ring (Fig. 1b). P–O distances are in the range 1.515(3)–1.580(3) Å (av. 1.537 Å) and the O–P–O bond angles are in the range 104.77(17)–114.68(17)° (av. 109.4°) (Table 3). All the cobalt atoms are four coordinated with respect to oxygen. The Co–O distances are in the range 1.944(3)–1.968(3) Å (av. 1.954 Å) and the O–Co–O bond angles are in the range 101.52(13)–113.84(13)° (av. 109.3°) (Table 3). The framework structure consists of infinite

TABLE 3
Bond Distances and Angles in $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Co}(\text{HPO}_4)_2]$, **I**

| Moiety | Distance (Å) | Moiety | Angle (deg) |
|---------------|--------------|---------------------|-------------|
| | | O(1)–Co(1)–O(2) | 113.76(12) |
| | | O(1)–Co(1)–O(4) | 106.90(13) |
| | | O(2)–Co(1)–O(4) | 113.84(13) |
| | | O(1)–Co(1)–O(3) | 105.91(13) |
| Co(1)–O(1) | 1.944(3) | O(2)–Co(1)–O(3) | 113.84(12) |
| Co(1)–O(2) | 1.945(3) | O(4)–Co(1)–O(3) | 101.52(13) |
| Co(1)–O(4) | 1.957(3) | O(5)–P(1)–O(3) | 110.99(18) |
| Co(1)–O(3) | 1.968(3) | O(5)–P(1)–O(4) # 1 | 111.06(17) |
| P(1)–O(5) | 1.519(3) | O(3)–P(1)–O(4) # 1 | 112.41(18) |
| P(1)–O(3) | 1.523(3) | O(5)–P(1)–O(6) | 108.19(18) |
| P(1)–O(4) # 1 | 1.524(3) | O(3)–P(1)–O(6) | 105.84(18) |
| P(1)–O(6) | 1.577(3) | O(4) # 1–P(1)–O(6) | 108.08(17) |
| P(2)–O(7) | 1.515(3) | O(7)–P(2)–O(1) | 114.68(17) |
| P(2)–O(1) | 1.523(3) | O(7)–P(2)–O(2) # 2 | 109.90(17) |
| P(2)–O(2) # 2 | 1.532(3) | O(1)–P(2)–O(2) # 2 | 112.00(17) |
| P(2)–O(8) | 1.580(3) | O(7)–P(2)–O(8) | 107.06(17) |
| | | O(1)–P(2)–O(8) | 107.80(16) |
| | | O(2) # 2–P(2)–O(8) | 104.77(17) |
| | | P(2)–O(1)–Co(1) | 130.08(18) |
| | | P(2) # 2–O(2)–Co(1) | 121.46(17) |
| | | P(1)–O(3)–Co(1) | 132.22(19) |
| | | P(1) # 1–O(4)–Co(1) | 126.74(18) |
| | | Organic | |
| C(1)–C(2) | 1.462(6) | C(2)–C(1)–N(2) | 110.2(4) |
| C(1)–N(2) | 1.498(7) | C(1)–C(2)–N(1) | 111.2(4) |
| C(2)–N(1) | 1.520(7) | C(4)–C(3)–N(1) | 112.1(4) |
| C(3)–C(4) | 1.457(7) | C(3)–C(4)–N(2) | 110.1(4) |
| C(3)–N(1) | 1.487(8) | C(3)–N(1)–C(2) | 109.9(4) |
| C(4)–N(2) | 1.488(7) | C(4)–N(2)–C(1) | 110.2(4) |

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

$[\text{Co}(\text{HPO}_4)_2]^{2-}$ chains stacked along the a -axis, each chain consisting of corner-shared four-membered rings (Figs. 1b and c). The anionic chains are held together by strong

TABLE 4
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)_2]$, **II**

| Atom | x | y | z | U_{eq} |
|-------|---------|---------|-----------|-----------------|
| Co(1) | 3788(1) | 8784(1) | 403(1) | 14(1) |
| P(1) | 3591(1) | 6289(1) | 1001(1) | 16(1) |
| P(2) | 5000 | 9583(1) | – 2500 | 13(1) |
| O(1) | 2494(2) | 8969(3) | – 784(5) | 36(1) |
| O(2) | 4064(2) | 9754(2) | 2193(4) | 25(1) |
| O(3) | 4868(2) | 8871(2) | – 1025(4) | 17(1) |
| O(4) | 3809(2) | 7402(2) | 1487(4) | 23(1) |
| O(5) | 4074(2) | 5551(2) | 2299(4) | 26(1) |
| O(6) | 4128(3) | 6133(3) | – 619(5) | 39(1) |
| N(1) | 2573(3) | 8598(4) | 4638(6) | 39(1) |
| C(1) | 3465(3) | 7916(3) | 4729(4) | 11(1) |
| C(2) | 1647(3) | 7975(4) | 4143(6) | 30(1) |

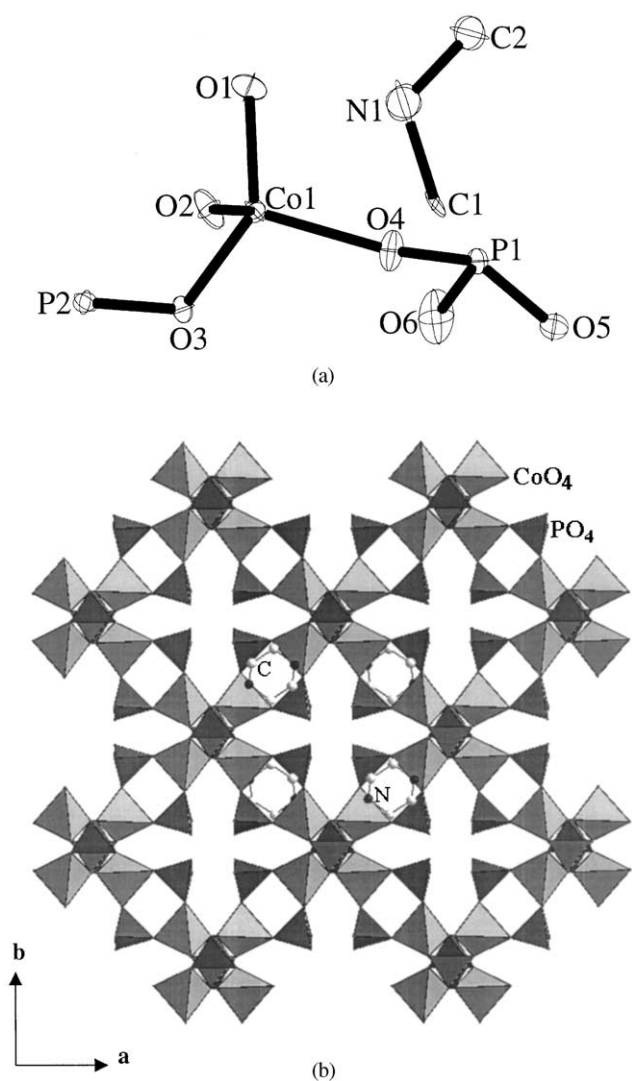


FIG. 2. (a) ORTEP plot of the asymmetric unit of $[\text{C}_4\text{N}_2\text{H}_{11}][\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)_2]$, **II**; (b) polyhedral view of **II** along $[001]$ axis showing the clover-shaped 16-membered channels. The amine molecule is also shown in ball and stick view.

hydrogen bond interactions between the terminal $-\text{OH}$ groups and protonated piperazine molecules located between the chains (Fig. 1c).

Structure of $[\text{C}_4\text{H}_8\text{N}_2\text{H}_3][\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)_2]$, **II**

The atomic coordinates of $[\text{C}_4\text{N}_2\text{H}_{11}][\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)_2]$, **II**, are presented in Table 4. The asymmetric unit shown in Fig. 2a consists of 12 atoms of which nine belong to the framework and three belong to the guest species. There is one crystallographically independent cobalt and two phosphorus atoms. All Co atoms are linked to the P atom via oxygen atoms and there are no Co–O–Co linkages present in the structure.

The Co–O distances are in the range 1.939(3)–1.989(3) Å and the O–Co–O angles are in the range 103.94(13)–114.27(15)° which are typical of Co atoms in a tetrahedral environment (Table 5). All the P atoms have P–O distances in the range 1.492(3)–1.578(4) Å and the O–P–O angles are in the range 104.56(18)–114.15(19)° (Table 5).

Compound **II** has a three-dimensional structure built up of infinite corner-shared chains containing four rings running perpendicular to each other and connected at various junctions. Four such junctions form a 16-membered clover-shaped aperture, with the pendant hydroxyl groups from the phosphorus projecting in the cavities. The protonated piperazine molecules balance the negative charge of the framework (Fig. 2b).

Structure of $[\text{C}_4\text{N}_2\text{H}_{12}]_2[\text{Co}_4(\text{HPO}_4)_6]$, **III**

The atomic coordinates of $[\text{C}_4\text{N}_2\text{H}_{12}]_2[\text{Co}_4(\text{HPO}_4)_6]$, **III**, are presented in Table 6. **III** also possesses a three-dimensional architecture built of CoO_4 and PO_4 tetrahedra. The asymmetric unit shown in Fig. 3a consists of 46 atoms of which 34 belong to the framework and 12 belong to the

TABLE 5
Bond Distances and Angles in $[\text{C}_4\text{N}_2\text{H}_{11}][\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)_2]$, **II**

| Moiety | Distance (Å) | Moiety | Angle (deg) |
|---------------|--------------|------------------------|-------------|
| | | O(1)–Co(1)–O(2) | 114.27(15) |
| | | O(1)–Co(1)–O(3) | 111.87(15) |
| | | O(2)–Co(1)–O(3) | 108.30(12) |
| | | O(1)–Co(1)–O(4) | 108.38(14) |
| | | O(2)–Co(1)–O(4) | 103.94(13) |
| | | O(3)–Co(1)–O(4) | 109.75(12) |
| Co(1)–O(1) | 1.939(3) | O(1) # 1–P(1)–O(4) | 114.15(19) |
| Co(1)–O(2) | 1.943(3) | O(1) # 1–P(1)–O(5) | 107.48(19) |
| Co(1)–O(4) | 1.944(3) | O(4)–P(1)–O(5) | 109.95(18) |
| Co(1)–O(3) | 1.989(3) | O(1) # 1–P(1)–O(6) | 112.4(3) |
| P(1)–O(1) # 1 | 1.492(3) | O(4)–P(1)–O(6) | 104.56(18) |
| P(1)–O(4) | 1.511(3) | O(5)–P(1)–O(6) | 108.2(2) |
| P(1)–O(5) | 1.533(3) | O(2) # 2–P(2)–O(2) # 3 | 111.9(3) |
| P(1)–O(6) | 1.578(4) | O(2) # 2–P(2)–O(3) # 4 | 108.49(16) |
| P(2)–O(2) # 2 | 1.525(3) | O(2) # 3–P(2)–O(3) # 4 | 110.36(16) |
| P(2)–O(2) # 3 | 1.525(3) | O(2) # 2–P(2)–O(3) | 110.36(16) |
| P(2)–O(3) # 4 | 1.542(3) | O(2) # 3–P(2)–O(3) | 108.49(16) |
| P(2)–O(3) | 1.542(3) | O(3) # 4–P(2)–O(3) | 107.1(2) |
| | | P(1) # 1–O(1)–Co(1) | 149.4(3) |
| | | P(2) # 2–O(2)–Co(1) | 126.16(18) |
| | | P(2)–O(3)–Co(1) | 130.46(16) |
| | | P(1)–O(4)–Co(1) | 137.3(2) |
| | | Organic | |
| N(1)–C(1) | 1.483(5) | C(1)–N(1)–C(2) | 110.2(4) |
| N(1)–C(2) | 1.510(6) | N(1)–C(1)–C(2) # 5 | 111.4(3) |
| C(1)–C(2) # 5 | 1.491(6) | C(1) # 5–C(2)–N(1) | 111.3(4) |

Note. Symmetry transformations used to generate equivalent atoms: #1 – $x + \frac{1}{2}, -y + \frac{3}{2}, -z$; #2 – $x + 1, -y + 2, -z$; #3 – $x, -y + 2, z - \frac{1}{2}$; #4 – $x + 1, y, -z - \frac{1}{2}$; #5 – $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.

TABLE 6
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{C}_4\text{N}_2\text{H}_{12}]_2[\text{Co}_4(\text{HPO}_4)_6]$, III

| Atom | x | y | z | U_{eq} |
|--------|----------|----------|-----------|-----------------|
| Co(1) | 200(1) | 127(1) | 7508(1) | 15(1) |
| Co(2) | 5287(1) | -2401(1) | 7617(1) | 22(1) |
| Co(3) | 1514(1) | -1873(1) | 5022(1) | 17(1) |
| Co(4) | -3677(1) | -623(1) | 10,184(1) | 19(1) |
| P(1) | 4005(1) | -1870(1) | 4549(2) | 17(1) |
| P(2) | -1370(1) | -612(1) | 9338(2) | 15(1) |
| P(3) | 1197(1) | -689(1) | 5450(2) | 16(1) |
| P(4) | 6525(1) | -3200(1) | 5733(2) | 20(1) |
| P(5) | 220(1) | -2743(1) | 6731(2) | 17(1) |
| P(6) | -4554(1) | 196(1) | 12,548(2) | 16(1) |
| O(1) | -934(3) | -182(1) | 8461(4) | 27(1) |
| O(2) | 1220(3) | -347(1) | 6907(4) | 25(1) |
| O(3) | 1133(3) | 592(1) | 8834(4) | 26(1) |
| O(4) | -226(3) | 624(1) | 5789(4) | 24(1) |
| O(5) | 4114(3) | -2811(2) | 8072(5) | 39(1) |
| O(6) | 5896(4) | -1904(2) | 9174(5) | 62(2) |
| O(7) | 6420(3) | -2823(1) | 7043(5) | 34(1) |
| O(8) | 4945(3) | -1916(1) | 5855(4) | 27(1) |
| O(9) | 3004(3) | -1962(2) | 5239(5) | 40(1) |
| O(10) | 719(3) | -1865(1) | 2887(5) | 37(1) |
| O(11) | 947(3) | -2314(2) | 6580(5) | 42(1) |
| O(12) | 1298(3) | -1225(1) | 6065(4) | 29(1) |
| O(13) | -3718(3) | -112(1) | 11,854(5) | 29(1) |
| O(14) | -2541(2) | -662(1) | 8819(4) | 22(1) |
| O(15) | -3653(4) | -1272(1) | 11,296(5) | 56(2) |
| O(16) | -4989(3) | -588(1) | 8689(4) | 27(1) |
| O(17) | 4018(3) | -1307(1) | 3884(5) | 30(1) |
| O(18) | -836(3) | -1101(1) | 8709(4) | 26(1) |
| O(19) | 2149(3) | -557(2) | 4498(5) | 33(1) |
| O(20) | 7737(7) | -3278(6) | 5900(30) | 36(5) |
| O(20A) | 7618(11) | -3086(8) | 4940(30) | 52(6) |
| O(21) | -200(3) | -2980(1) | 5111(4) | 28(1) |
| O(22) | -781(3) | -2535(1) | 7428(5) | 30(1) |
| O(23) | -4129(3) | 434(1) | 14,170(4) | 22(1) |
| O(24) | -5489(3) | -169(1) | 12,811(4) | 31(1) |
| N(1) | -2256(4) | -725(2) | 4660(7) | 42(1) |
| N(2) | -2580(4) | -1752(2) | 5627(7) | 42(1) |
| C(1) | -1660(4) | -1150(2) | 4004(5) | 12(1) |
| C(2) | -1538(4) | -1583(2) | 5156(7) | 26(1) |
| C(3) | -3186(3) | -1324(2) | 6233(5) | 10(1) |
| C(4) | -3299(4) | -899(2) | 5044(7) | 26(1) |
| N(3) | 2610(4) | -711(2) | 10,379(6) | 41(1) |
| N(4) | 2467(4) | -1772(2) | 9595(7) | 43(1) |
| C(5) | 3417(4) | -1473(2) | 9339(7) | 34(1) |
| C(6) | 3556(3) | -1033(2) | 10,476(5) | 14(1) |
| C(7) | 1649(4) | -1020(2) | 10,569(7) | 26(1) |
| C(8) | 1525(3) | -1442(2) | 9388(5) | 10(1) |

guest species. There are four crystallographically independent cobalt and six phosphorus atoms. All Co atoms are linked to the P atom via oxygen atoms and there are no Co–O–Co linkages present in the structure.

The Co–O distances are in the range 1.920(4)–1.972(3) Å and the O–Co–O angles are in the range 94.28(15)–122.23(15)° which are typical of Co atoms in a tetrahedral

environment (Tables 7 and 8). All the six P atoms have P–O distances in the range 1.463(4)–1.649(12) Å and the O–P–O angles are in the range 91.5(11)–123.1(9)° (Tables 7 and 8). All the long P–O bonds bear a terminal hydroxyl group.

Assuming the valences of Co, P, O and H to be +2, +5, –2 and +1, respectively, the framework stoichiometry of $\text{Co}_4(\text{HPO}_4)_6$ creates a framework charge of –4. The negative charge of the framework is balanced by two diprotonated piperazine molecules present per formula unit. The connectivity between CoO_4 and HPO_4 moieties results in a three-dimensional architecture with 6-, 10- and 14-membered channels running along the *c*-axis (Fig. 3b).

DISCUSSION

A closer examination of the three cobalt phosphates reported here reveals their relationship to the sodalite structure (Fig. 4a). The corner-sharing (CS) chains of four rings found in **I** are a key structural element of the sodalite

TABLE 7
Bond Distances in $[\text{C}_4\text{N}_2\text{H}_{12}]_2[\text{Co}_4(\text{HPO}_4)_6]$, III

| Moiety | Distance (Å) | Moiety | Distance (Å) |
|---------------|--------------|----------------|--------------|
| Co(1)–O(1) | 1.925(3) | P(2)–O(3) # 2 | 1.504(4) |
| Co(1)–O(2) | 1.930(3) | P(2)–O(14) | 1.523(3) |
| Co(1)–O(3) | 1.966(3) | P(2)–O(18) | 1.590(4) |
| Co(1)–O(4) | 1.972(3) | P(3)–O(2) | 1.508(4) |
| Co(2)–O(5) | 1.937(4) | P(3)–O(12) | 1.519(4) |
| Co(2)–O(6) | 1.944(4) | P(3)–O(4) # 3 | 1.527(3) |
| Co(2)–O(7) | 1.946(4) | P(3)–O(19) | 1.574(4) |
| Co(2)–O(8) | 1.958(3) | P(4)–O(6) # 1 | 1.463(4) |
| Co(3)–O(9) | 1.920(4) | P(4)–O(7) | 1.496(4) |
| Co(3)–O(10) | 1.929(4) | P(4)–O(15) # 4 | 1.508(4) |
| Co(3)–O(11) | 1.949(4) | P(4)–O(20) | 1.564(9) |
| Co(3)–O(12) | 1.964(3) | P(4)–O(20A) | 1.649(12) |
| Co(4)–O(13) | 1.944(4) | P(5)–O(11) | 1.493(4) |
| Co(4)–O(14) | 1.954(3) | P(5)–O(10) # 5 | 1.507(4) |
| Co(4)–O(15) | 1.960(4) | P(5)–O(21) | 1.520(4) |
| Co(4)–O(16) | 1.971(3) | P(5)–O(22) | 1.575(4) |
| P(1)–O(9) | 1.491(4) | P(6)–O(13) | 1.521(4) |
| P(1)–O(5) # 1 | 1.507(4) | P(6)–O(23) | 1.522(3) |
| P(1)–O(8) | 1.526(4) | P(6)–O(16) # 6 | 1.527(4) |
| P(1)–O(17) | 1.599(4) | P(6)–O(24) | 1.584(4) |
| P(2)–O(1) | 1.501(3) | O(20)–O(20A) | 0.941(15) |
| Organic | | | |
| N(1)–C(4) | 1.490(7) | N(3)–C(6) | 1.487(7) |
| N(1)–C(1) | 1.507(7) | N(3)–C(7) | 1.511(7) |
| N(2)–C(3) | 1.502(6) | N(4)–C(8) | 1.491(6) |
| N(2)–C(2) | 1.511(7) | N(4)–C(5) | 1.497(7) |
| C(1)–C(2) | 1.492(6) | C(5)–C(6) | 1.500(7) |
| C(3)–C(4) | 1.496(7) | C(7)–C(8) | 1.487(7) |

Note. Symmetry transformations used to generate equivalent atoms: # 1 – x , – $y - \frac{1}{2}$, $z - \frac{1}{2}$; # 2 – x , – y , – $z + 2$; # 3 – x , – y , – $z + 1$; # 4 – $x + 1$, – $y - \frac{1}{2}$, $z - \frac{1}{2}$; # 5 – x , – $y - \frac{1}{2}$, $z + \frac{1}{2}$; # 6 – $x - 1$, – y , – $z + 2$; # 7 – $x - 1$, – $y - \frac{1}{2}$, $z + \frac{1}{2}$.

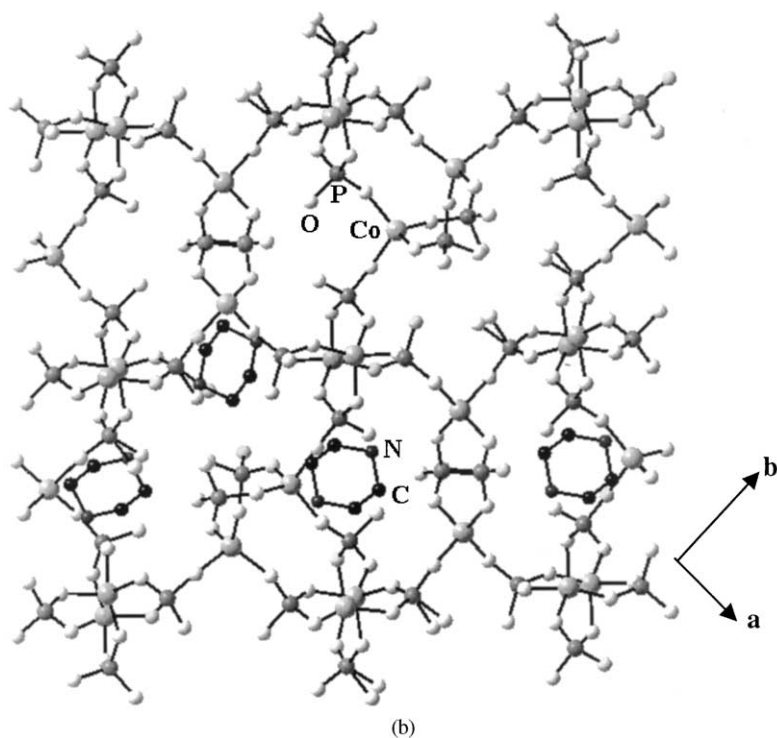
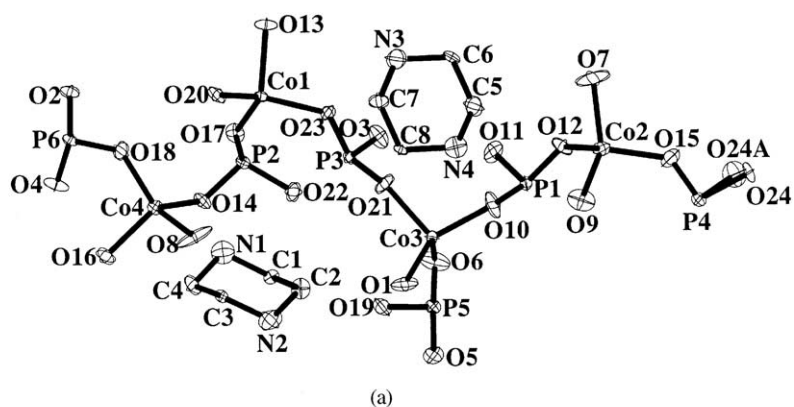


FIG. 3. (a) ORTEP plot of the asymmetric unit of $[\text{C}_4\text{N}_2\text{H}_{12}]_2[\text{Co}_4(\text{HPO}_4)_6]$, **III**; (b) structure of **III** along the c -axis showing the 6-, 10- and 14-membered channels along with the amine molecules.

structure (Figs. 4b and 5a). Apart from other cobalt phosphates (20, 21), similar four ring CS chains have also been isolated in other zinc, aluminum and gallium phosphates (9, 22–25). The T-atom connectivity of **II** and **III** (Figs. 4c and 4d) reveals that both possess interrupted sodalite-type structure. These interrupted sodalite-type cobalt (II) phosphates can be derived from the normal cobalt phosphate sodalite cage $[\text{Co}_{12}\text{P}_{12}\text{O}_{48}]^{12-}$; Fig. 4a), which has not been synthesized to date. However, the zincophosphate analog of sodalite has been reported in literature (12). Removal of Co^{2+} from one of the three two-fold axes passing through opposing four rings of the normal sodalite cage structure

results in the interrupted sodalite-type structure of **II** $[\text{Co}_8\text{P}_{12}\text{O}_{48}]^{20-}$ (Figs. 4c and 5b). The structure of **III** can also be derived by removal of Co^{2+} from sites related by two of the three two-fold axes passing through opposing four rings of the normal sodalite cage structure (Figs. 4d and 5c). However, the Co^{2+} ions in **III** are removed in an unsymmetrical fashion.

The interrupted sodalite cages have point group symmetries that are lower than that of a regular sodalite cage. The interrupted cage in **II** is built around the inversion center on which the template molecule is located (Fig. 6a), whereas the inversion center in **III** no longer lies on the template

TABLE 8
Bond Angles in $[C_4N_2H_{12}]_2[Co_4(HPO_4)_6]$, **III**

| Moiety | Angle (deg) | Moiety | Angle (deg) |
|---------------------|-------------|-------------------------|-------------|
| O(1)–Co(1)–O(2) | 113.50(16) | O(12)–P(3)–O(19) | 109.7(2) |
| O(1)–Co(1)–O(3) | 118.99(16) | O(4) # 3–P(3)–O(19) | 105.4(2) |
| O(2)–Co(1)–O(3) | 99.58(15) | O(6) # 1–P(4)–O(7) | 114.8(3) |
| O(1)–Co(1)–O(4) | 115.08(14) | O(6) # 1–P(4)–O(15) # 4 | 111.2(3) |
| O(2)–Co(1)–O(4) | 113.18(15) | O(7)–P(4)–O(15) # 4 | 112.0(2) |
| O(3)–Co(1)–O(4) | 94.28(15) | O(6) # 1–P(4)–O(20) | 123.1(9) |
| O(5)–Co(2)–O(6) | 121.2(2) | O(7)–P(4)–O(20) | 101.5(5) |
| O(5)–Co(2)–O(7) | 110.26(18) | O(15) # 4–P(4)–O(20) | 92.0(8) |
| O(6)–Co(2)–O(7) | 107.5(2) | O(6) # 1–P(4)–O(20A) | 91.5(11) |
| O(5)–Co(2)–O(8) | 113.95(15) | O(7)–P(4)–O(20A) | 108.5(5) |
| O(6)–Co(2)–O(8) | 94.47(17) | O(15) # 4–P(4)–O(20A) | 117.6(9) |
| O(7)–Co(2)–O(8) | 108.00(16) | O(20)–P(4)–O(20A) | 33.9(5) |
| O(9)–Co(3)–O(10) | 120.09(19) | O(11)–P(5)–O(10) # 5 | 111.2(2) |
| O(9)–Co(3)–O(11) | 108.24(18) | O(11)–P(5)–O(21) | 114.0(2) |
| O(10)–Co(3)–O(11) | 114.18(17) | O(10) # 5–P(5)–O(21) | 110.4(2) |
| O(9)–Co(3)–O(12) | 105.10(17) | O(11)–P(5)–O(22) | 108.1(2) |
| O(10)–Co(3)–O(12) | 107.69(16) | O(10) # 5–P(5)–O(22) | 108.5(2) |
| O(11)–Co(3)–O(12) | 99.03(18) | O(21)–P(5)–O(22) | 104.4(2) |
| O(13)–Co(4)–O(14) | 122.23(15) | O(13)–P(6)–O(23) | 111.2(2) |
| O(13)–Co(4)–O(15) | 106.68(17) | O(13)–P(6)–O(16) # 6 | 110.5(2) |
| O(14)–Co(4)–O(15) | 104.60(19) | O(23)–P(6)–O(16) # 6 | 111.9(2) |
| O(13)–Co(4)–O(16) | 108.46(15) | O(13)–P(6)–O(24) | 107.7(2) |
| O(14)–Co(4)–O(16) | 106.64(15) | O(23)–P(6)–O(24) | 109.5(2) |
| O(15)–Co(4)–O(16) | 107.43(19) | O(16) # 6–P(6)–O(24) | 105.9(2) |
| O(9)–P(1)–O(5) # 1 | 112.7(3) | P(2)–O(1)–Co(1) | 150.5(2) |
| O(9)–P(1)–O(8) | 111.4(2) | P(3)–O(2)–Co(1) | 130.7(2) |
| O(5) # 1–P(1)–O(8) | 112.6(2) | P(2) # 2–O(3)–Co(1) | 128.2(2) |
| O(9)–P(1)–O(17) | 109.3(2) | P(3) # 3–O(4)–Co(1) | 133.8(2) |
| O(5) # 1–P(1)–O(17) | 104.2(2) | P(1) # 5–O(5)–Co(2) | 128.7(2) |
| O(8)–P(1)–O(17) | 106.1(2) | P(4) # 5–O(6)–Co(2) | 148.0(3) |
| O(1)–P(2)–O(3) # 2 | 114.5(2) | P(4)–O(7)–Co(2) | 134.5(3) |
| O(1)–P(2)–O(14) | 110.3(2) | P(1)–O(8)–Co(2) | 131.8(2) |
| O(3) # 2–P(2)–O(14) | 111.1(2) | P(1)–O(9)–Co(3) | 147.6(3) |
| O(1)–P(2)–O(18) | 105.5(2) | P(5) # 1–O(10)–Co(3) | 135.3(2) |
| O(3) # 2–P(2)–O(18) | 108.3(2) | P(5)–O(11)–Co(3) | 143.7(3) |
| O(14)–P(2)–O(18) | 106.7(2) | P(3)–O(12)–Co(3) | 133.8(2) |
| O(2)–P(3)–O(12) | 108.1(2) | P(6)–O(13)–Co(4) | 136.7(2) |
| O(2)–P(3)–O(4) # 3 | 113.7(2) | P(2)–O(14)–Co(4) | 128.1(2) |
| O(12)–P(3)–O(4) # 3 | 111.1(2) | P(4) # 7–O(15)–Co(4) | 132.4(3) |
| O(2)–P(3)–O(19) | 108.8(2) | P(6) # 6–O(16)–Co(4) | 133.1(2) |
| Organic | | | |
| C(4)–N(1)–C(1) | 110.7(4) | C(6)–N(3)–C(7) | 110.8(4) |
| C(3)–N(2)–C(2) | 111.8(4) | C(8)–N(4)–C(5) | 109.6(4) |
| C(2)–C(1)–N(1) | 111.8(4) | N(4)–C(5)–C(6) | 111.5(4) |
| C(1)–C(2)–N(2) | 111.5(4) | N(3)–C(6)–C(5) | 112.6(4) |
| C(4)–C(3)–N(2) | 111.8(4) | C(8)–C(7)–N(3) | 111.7(4) |
| N(1)–C(4)–C(3) | 110.9(4) | C(7)–C(8)–N(4) | 110.6(4) |

Note. Symmetry transformations used to generate equivalent atoms: # 1 $-x, -y - \frac{1}{2}, z - \frac{1}{2}$; # 2 $-x, -y, -z + 2$; # 3 $-x, -y, -z + 1$; # 4 $-x + 1, -y - \frac{1}{2}, z - \frac{1}{2}$; # 5 $-x, -y - \frac{1}{2}, z + \frac{1}{2}$; # 6 $-x - 1, -y, -z + 2$; # 7 $-x - 1, -y - \frac{1}{2}, z + \frac{1}{2}$.

molecule but lies in the middle of one of the four rings shared by two interrupted sodalite-type cages (Figs. 5c and 6b). The piperazine molecule in the chair conformation has

a point group symmetry of $2/m$, and imposes its individual symmetry constraint on to the framework of **II** (Fig. 6a). In the case of structure **III**, there is no such constraint imposed by the symmetry of the template molecule (Fig. 6b). The interruptions result in the lowering of symmetry from *cubic* to *monoclinic C* in **II**, to *monoclinic P* in **III**.

The unit cell volume of **II**, $1418.8(8)\text{\AA}^3$, is close to the analogous zincophosphate, which has a volume of $1402.8(7)\text{\AA}^3$ (26), and is slightly more than twice the cell volume of the normal zincophosphate sodalite, $688.01(3)\text{\AA}^3$ (12). This is consistent with the four interrupted cages per unit cell. Assuming that the hypothetical cobalt phosphate sodalite has the same volume as that of zincophosphate sodalite, the volume increase per cage over the hypothetical cobalt phosphate sodalite is only 3%. The cell volume of **III**, which has eight interrupted cages per unit cell, is $2816.0(5)\text{\AA}^3$, approximately twice that of **II**. The volume increase per cage over the hypothetical cobalt phosphate sodalite is again small (2.3%), suggesting that the dimension of template molecule piperazine is ideally suited for this type of four ring assembly.

The interrupted sodalite-cage structure of **II** has been previously observed in a zinc phosphate templated with piperazine (26). However, the interruptions observed in the

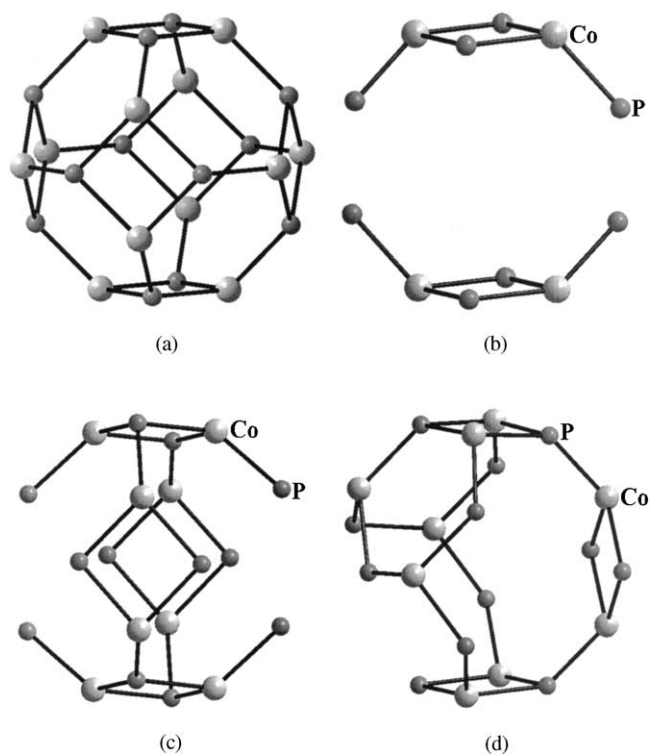


FIG. 4. (a) The normal aluminosilicates sodalite cage; (b) the CS chain in **I** (interruptions in a sodalite cage in two crystallographic directions leading to the reduction in dimensionality); (c) the interrupted sodalite cage in **II**; (d) the interrupted sodalite cage in **III**. Note the difference in interruptions in **II** and **III**.

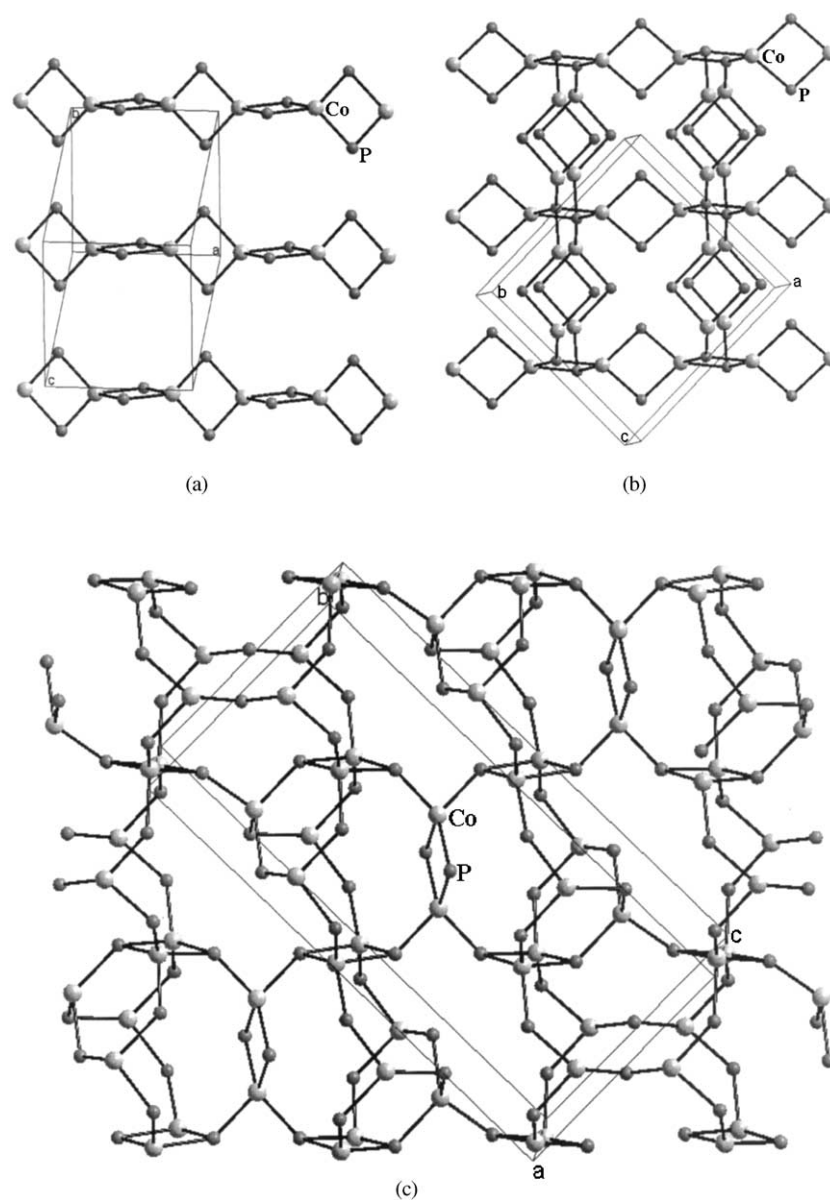
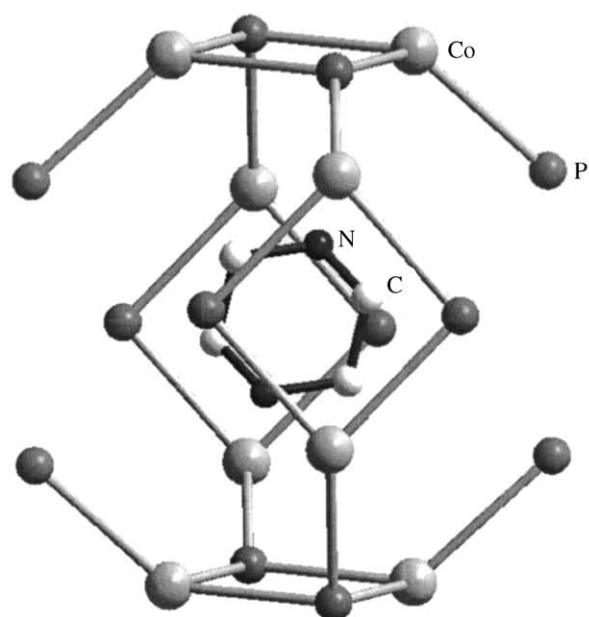


FIG. 5. Illustration of the framework structure resemblance to the sodalite-type cage linkage: (a) the framework of **I** made of CS chains, as in sodalite; (b) four interrupted sodalite cages in **II** sharing a common four ring. Note the presence of four rings and absence of six rings in a single interrupted cage; (c) The framework of **III** formed from interrupted sodalite cages. Note that a single cage consists of three four rings and two six-rings.

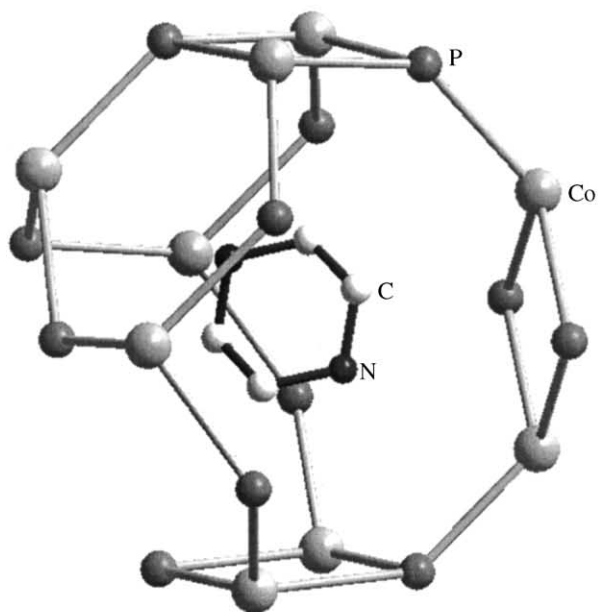
III have not been found previously in metal phosphate frameworks. The interruption of framework structures has been a key feature in several zincophosphates and aluminophosphates (13, 27, 28), and some cobalt phosphate analogs of these interrupted zincophosphates have also been reported (29).

The choice of tributylphosphate as a phosphorylating agent is crucial to these syntheses as it enables the reaction to be carried out in non-aqueous conditions. This is known to be very important for the formation of the open-framework cobalt phosphates, since the use of phosphorus

pentoxide or phosphoric acid often leads to the formation of dense cobalt phosphates. Non-aqueous (alcoholic) conditions favor the formation of tetrahedral cobalt species, whereas when other sources of P are used the cobalt tends to be octahedrally coordinated. The slow hydrolysis of tributyl phosphate ester is also important because it influences the kinetics of the reaction by controlling the release of phosphate ions in solution. The non-aqueous solvent and the organophosphate ester also influence the polarity and viscosity of the medium, thereby affecting the mass transfer and the kinetics.



(a)



(b)

FIG. 6. The interrupted sodalite cage in **II** with the template molecule located on the inversion center; (b) The interrupted sodalite cage in **III** which no longer lies on any of the symmetry elements (i , 2 or m) of the molecule and framework.

The present results underscore the significance of the new synthetic methodology involving an organophosphate and demonstrate the possibility of imposing the symmetry of the template molecule onto the framework topology, as has

been observed in both cobalt and zincophosphates (26). Despite this success, however, the results also point towards a gap in our understanding of how to control the transfer of molecular symmetry from the template to the extended inorganic framework. In cases where the various factors of template symmetry, charge-matching and directed hydrogen bonding between the guest and the host have worked in a cohesive manner, it has been feasible to synthesize architectures with a fair degree of control. However, the interplay between these factors and their control remains an exercise of trial and error, as the discovery of **III** demonstrates.

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