Synthesis and Structure of a Novel Layered Zinc–Cobalt Phosphate, $Zn_{(2-x)}Co_x(HPO_4)_3 \cdot C_3N_2H_{12}$, $x \cong 0.05$, with 12 Rings

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A novel layered zinc–cobalt phosphate $Zn_{(2-x)}Co_x(HPO_4)_3 \cdot C_3N_2H_{12}$ ($x \cong 0.05$), has been solvothermally synthesized, and its structure determined at 293 K with a Siemens Smart 1000 CCD diffractometer [monoclinic, $P2_1/c$, $a = 8.632(2)$ Å, $b = 9.648(4)$ Å, $c = 17.077(6)$ Å, $\beta = 93.63(2)°$, $V = 1419.2(8)$ Å³, $Z = 4$, $R = 0.0274$, $wR = 0.0724$, 2928 collected reflections, 1628 observed reflections with $I > 2\sigma(I)$]. The structure consists of vertex-sharing MO_4 ($M = $ Zn, Co) tetrahedra, $PO_3(OH)$ tetrahedra, and double-protonated organic cations, which results in formation of undulating 4-ring chains and 12-ring sheets. A network of hydrogen bonds involving both layer-to-layer and layer-to-amine interactions holds the phosphate layer together. © 2000 Academic Press

Key Words: solvothermal synthesis; structure; layered zinc–cobalt phosphate.

INTRODUCTION

Since Flanigen and co-workers reported the preparation of AlPOs molecular sieves in 1982 (1), the search for open-framework materials has led to wide interest in a large range of several classes of metal phosphates. Up to now, many other metal phosphates such as ZnPOs (2), CoPOs (3), GaPOs (4), InPOs (5), FePOs (6), ZrPOs (7), SnPOs (8), and TiPOs (9) have been reported in the literature. Many of these materials exhibit unique structures and may have potential applications as molecular sieves in separation, ion exchange, and catalysis.

In the last several years, more than 20 different zinc phosphates with one-dimensional (1D), 2D, or 3D framework structures have been synthesized and characterized (2, 10, 11). Some of these zinc phosphates are organically templated (2, 10) and some are alkali–metal zinc phosphates (11). The structures of these compounds are built mainly from ZnO_4, PO_4, and HPO_4 tetrahedral units, but $Zn_2(OH)PO_4$ contains a condensed network of ZnO_5, ZnO_6, and PO_4 subunits (11f). Harrison *et al.* reported

a new family of thermally stable phases that have novel OZn_4 centers (11c). Interestingly, the structural motifs of a few zinc phosphates have Zn–O–Zn linkages (10a–c). A novel open-framework zinc phosphate with intersecting helical channels has been reported by Rao and co-workers recently (10f). Reports about organically templated cobalt phosphates are few; only two layered (3b) and one three-dimensional (3a) framework cobalt phosphates have so far been prepared. Notably, although numerous ZnPOs have been studied, only a few zinc–cobalt phosphates have been reported. For example, $Zn_2Co_4(PO_4)_4(H_2O)_5 \cdot 2H_2O$ (12) and $Na_6(Co_xZn_{1-x}PO_4)_x \cdot yH_2O$ (13) have a 3D framework structure, and $NH_4[Zn_{2-x}Co_x(PO_4)(HPO_4)_2]$ ($x \cong 0.12$) (14) has a layered structure.

The goal of this work is to synthesize mixed-metal phosphate continuously. Here, we report the synthesis, structure, and characterization of a novel zinc–cobalt phosphate $Zn_{2-x}Co_x(HPO_4)_3 \cdot C_3N_2H_{12}$ ($x \cong 0.05$) (designated ZnCoPO–PDA).

EXPERIMENTAL

Synthesis and Characterization

ZnCoPO–PDA was solvothermally synthesized from a mixture of zinc acetate dihydrate (99%), cobalt chloride hexahydrate (99%), phosphoric acid (85%), ethylene glycol (EG), and 1,3-diaminopropane (1,3-PDA). In a typical synthesis, a mixture of $Zn(Ac)_2 \cdot 2H_2O$ (1.54 g) and $CoCl_2 \cdot 6H_2O$ (0.72 g) was added into EG (12 ml) by stirring for 20 min to form a homogeneous solution; then 1,3-PDA (0.5 ml) was added, followed by dropwise addition of H_3PO_4 (1.7 ml) with stirring. The blue-colored gel thus formed had the molar composition 7ZnO:3CoO:12.5P_2O_5:213EG:6 (1,3-PDA):35.75H_2O. The gel was stirred until homogenous. Crystallization of the final reaction mixture was carried out in a Teflon-lined stainless-steel autoclave (70% filling rate) at 453 K for ca. 8 days. The crystallization product was cleaned by ultrasonication and filtration, washed with distilled water several times, and dried at room temperature. During this procedure, the second powder

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TABLE 1
Crystal Data and Structure Refinement for $Zn_{2-x}(HPO_4)_3 \cdot C_3N_2H_{12}$ ($x \cong 0.05$)

Empirical formula	$Zn_{1.954}Co_{0.046}(HPO_4)_3 \cdot C_3N_2H_{12}$
Formula weight	494.46
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 8.632(2)$ Å
	$b = 9.648(4)$ Å
	$c = 17.077(6)$ Å
	$\beta = 93.63(2)°$
Volume	1419.2 (8) Å^3
Z	4
Density(calculated)	2.292 mg/m^3
Absorption coefficient	3.782 mm^{-1}
$F(000)$	972
Crystal size	$0.30 \times 0.15 \times 0.10$ mm
θ range for data collection	2.36–23.23°
Limiting indices	$-9 \leq h \leq 9, -2 \leq k \leq 10,$
	$-16 \leq l \leq 16$
Reflections collected	2928
Independent reflections	1628 ($R_{int} = 0.0538$)
Maximum and minimum transmission	0.7342, 0.5665
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1628/15/259
Goodness-of-fit on F^2	1.100
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0274, wR2 = 0.0724$
R indices (all data)	$R1 = 0.0293, wR2 = 0.0735$
Largest diffraction peak and hole	0.476 and -0.586 e Å^{-3}

phase was removed. The final product was single crystals in the form of a blue prism. The yield for the typical batch was approximately 0.25 g.

Elemental analyses were performed on a Perkin–Elmer 240C element analyzer. Inductively coupled plasma (ICP) analysis was carried out on a Plasma-Spec(1)ICP-AES in-strument. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. A Perkin–Elmer DTA 1700 differential thermal analyzer was used to perform differential thermal analysis (DTA), and a Perkin–Elmer TGA 7 thermogravimetric analyzer was used to perform thermogravimetric analysis (TGA) in an atmospheric environment at a heating rate of 20 °C min^{-1}.

Determination of Crystal Structure

A blue prismatic crystal of approximate dimensions $0.30 \times 0.15 \times 0.10$ mm was mounted on a glass fiber. The X-ray and intensity data were collected on a Siemens Smart 1000 CCD diffractometer equipped with a normal focus, 2.4-kW sealed-tube X-ray source (MoKα radiation, $\lambda = 0.71073$ Å). Intensity data were collected in 1271 frames with increasing ω (width of 0.3° per frame). The numbers of collected reflections and independent reflections were 2928 and 1628, respectively. An absorption correction [$\mu = 3.782$ mm^{-1}, $F(000) = 972$] was made empirically using a ω scan. The calculated transmission coefficients ranged from 0.5665 to 0.7342. The structure was solved by direct methods: the metal and phosphorus atoms were first located, and the carbon, nitrogen, oxygen, and hydrogen atoms were found in the final difference Fourier map. The metal sites were modeled as 0.023Co occupancy and 0.977Zn occupancy in accordance with the chemical analysis. Refinement was performed by full-matrix least-squares analysis, with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located easily in Fourier maps and relocated in optimized positions $d(O-H) = 0.82$, $d(N-H) = 0.89$, and $d(C-H) = 0.97$ Å, and they were then allowed to ride on the atoms to which they were attached, with free isotropic thermal parameters. Structure solution and refinement were performed using SHELXTL Version 5.1 (15). Crystal data and details of data collection and refinement are given in Table 1.

TABLE 2
Conditions for Synthesis of ZnCoPO–PDA

No.	Gel composition (molar ratio)						$P_2O_5/ZnO + CoO$	Temperature (°C)	Time (days)	Product
	ZnO	CoO	P_2O_5	EG^a	PDA	H_2O				
1	0.5	0.5	1.18	23.0	0.96	4.35	1.18	180	6	Unknown phase
2	0.5	0.5	1.75	23.0	0.96	4.53	1.75	180	6	Unknown phase
3	0.7	0.3	1.25	21.3	0.6	3.58	1.25	180	8	ZCP
4	0.7	0.3	1.5	21.3	0.6	3.65	1.5	180	9	ZCP
5	0.7	0.3	1.7	21.3	0.6	3.70	1.7	180	8	ZCP
6	0.6	0.4	1.25	21.3	0.6	5.18	1.25	180	8	ZCP + am
7	0.4	0.6	1.25	21.3	0.6	5.18	1.25	180	8	am
8	0.3	0.7	1.25	21.3	0.6	5.18	1.25	180	8	am

^{a} EG, ethylene glycol; PDA, 1,3-diaminopropane; ZCP, ZnCoPO–PDA; am, amorphous.

RESULTS AND DISCUSSION

Synthesis of ZnCoPO–PDA

The synthesis conditions and the crystallization products are summarized in Table 2. From Table 2, we can see that ZnCoPO–PDA is formed only when the $P_2O_5/ZnO + CoO$ ratio is 1.25–1.7. Additionally, the Co content in the gel also plays an important role in the crystallization. A low CoO content (ZnO/CoO = 0.7/0.3, 0.6/0.4) results in the

formation of ZnCoPO–PDA, and a high CoO content in the gel (ZnO/CoO = 0.5/0.5, 0.4/0.6, 0.3/0.7) results in an unknown phase and an amorphous phase.

Characterization of ZnCoPO–PDA

ICP analysis indicates that the crystal products contain 23.5 wt% Zn, 0.6 wt% Co, and 17.8 wt% P, respectively, suggesting the molar ratio of $(Zn + Co):P = 1.10:1.63$. Elemental analysis shows that the C, H, and N contents are 7.11, 2.90, and 5.15 wt%, respectively, corresponding to an empirical molar ratio of C:H:N = 1.00:4.89:0.62. These results are in accordance with the formula $Zn_{1.95}Co_{0.05}(HPO_4)_3 \cdot C_3N_2H_{12}$. The TGA curve shows that the weight loss of ZnCoPO–PDA is ca. 20.4% from 290 to 537°C, in

TABLE 3
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for Nonhydrogen Atoms and Isotropic Displacement Parameters for Hydrogen Atoms for $Zn_{1.95}Co_{0.05}(HPO_4)_3 \cdot C_3N_2H_{12}$

atom	x	y	z	$U(\text{eq/iso})^a$
M(1)	6765(1)	1325(1)	212(1)	17(1)
M(2)	7592(1)	5186(1)	−218(1)	18(1)
P(1)	5559(1)	4091(1)	1096(1)	16(1)
P(2)	9903(1)	2537(1)	−107(1)	17(1)
P(3)	5454(1)	−1030(1)	1280(1)	16(1)
O(1)^b	10481(4)	1696(3)	−829(2)	32(1)
O(2)	5512(3)	2761(3)	634(2)	30(1)
O(3)	8976(3)	1605(3)	391(2)	29(1)
O(4)	6591(3)	−500(3)	710(2)	21(1)
O(5)	5394(4)	−127(3)	2002(2)	25(1)
O(6)^b	6091(4)	−2469(3)	1623(2)	26(1)
O(7)^b	6104(3)	3753(3)	1967(2)	25(1)
O(8)	8688(3)	6923(3)	−376(2)	24(1)
O(9)	6167(3)	1237(3)	−905(2)	28(1)
O(10)	6066(3)	5273(3)	−1119(2)	19(1)
O(11)	8925(3)	3684(3)	−506(2)	25(1)
O(12)	6695(3)	5152(3)	788(2)	22(1)
N(1)	2714(5)	1784(4)	1734(3)	30(1)
N(2)	−2403(5)	1644(4)	2919(3)	24(1)
C(1)	−1124(5)	856(5)	2579(3)	31(1)
C(2)	133(5)	1794(4)	2309(3)	23(1)
C(3)	1417(5)	916(5)	1997(3)	29(1)
H(1)	11270(50)	1170(50)	−750(40)	68(19)
H(6)	6400(50)	−2970(50)	1270(20)	36(16)
H(7)	5580(40)	4150(50)	2300(20)	24(14)
H(1A)	3550(40)	1370(50)	1580(30)	37(15)
H(1B)	2420(70)	2280(60)	1300(20)	80(20)
H(1C)	3120(60)	2370(40)	2120(20)	59(18)
H(1AA)	−1600(60)	310(50)	2140(20)	49(15)
H(1AB)	−900(70)	290(50)	3050(20)	70(20)
H(2A)	−2030(50)	2040(50)	3354(19)	40(15)
H(2B)	−2850(50)	2230(40)	2570(20)	45(14)
H(2C)	−3150(40)	1090(50)	3070(30)	49(16)
H(2AA)	560(50)	2390(40)	2730(20)	41(13)
H(2AB)	−240(60)	2370(40)	1870(20)	51(15)
H(3A)	1870(50)	280(40)	2380(20)	33(13)
H(3B)	1020(60)	360(50)	1550(20)	50(15)

^{a} U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor. M(1) and M(2) sites both have occupancies of 0.977Zn and 0.023 Co.

^{b} Oxygen atom of OH group.

TABLE 4
Selected Bond Lengths (Å) and Angles (Degrees) for $Zn_{1.95}Co_{0.05}(HPO_4)_3 \cdot C_3N_2H_{12}$

M(1)–O(2)	1.926(3)	M(1)–O(3)	1.932(3)
M(1)–O(9)	1.946(3)	M(1)–O(4)	1.965(3)
M(2)–O(12)	1.929(4)	M(2)–O(11)	1.934(3)
M(2)–O(8)	1.952(3)	M(2)–O(10)	1.963(2)
P(1)–O(2)	1.505(3)	P(1)–O(10)^a	1.534(3)
P(1)–O(12)	1.534(3)	P(1)–O(7)	1.566(3)
P(2)–O(3)	1.504(3)	P(2)–O(8)^b	1.518(3)
P(2)–O(11)	1.525(3)	P(2)–O(1)	1.581(3)
P(3)–O(9)^c	1.515(3)	P(3)–O(4)	1.514(3)
P(3)–O(5)	1.514(3)	P(3)–O(6)	1.592(3)
O(8)–P(2)^b	1.518(3)	O(9)–P(3)^c	1.515(3)
O(10)–P(1)^a	1.534(3)	N(1)–C(3)	1.490(6)
N(2)–C(1)	1.488(6)	C(1)–C(2)	1.507(6)
C(2)–C(3)	1.518(7)		
O(2)–M(1)–O(3)	114.37(13)	O(2)–M(1)–O(9)	106.13(13)
O(3)–M(1)–O(9)	111.05(13)	O(2)–M(1)–O(4)	114.99(14)
O(3)–M(1)–O(4)	99.13(12)	O(9)–M(1)–O(4)	111.25(13)
O(12)–M(2)–O(11)	119.53(12)	O(12)–M(2)–O(8)	111.30(12)
O(11)–M(2)–O(8)	107.89(12)	O(12)–M(2)–O(10)	114.35(12)
O(11)–M(2)–O(10)	102.29(11)	O(8)–M(2)–O(10)	99.28(11)
O(2)–P(1)–O(10)^a	111.10(15)	O(2)–P(1)–O(12)	112.73(19)
O(10)^a–P(1)–O(12)	110.34(16)	O(2)–P(1)–O(7)	108.49(18)
O(10)^a–P(1)–O(7)	106.20(18)	O(12)–P(1)–O(7)	107.70(17)
O(3)–P(2)–O(8)^b	109.52(16)	O(3)–P(2)–O(11)	112.74(16)
O(8)^b–P(2)–O(11)	113.34(15)	O(3)–P(2)–O(1)	109.83(18)
O(8)^b–P(2)–O(1)	108.54(17)	O(11)–P(2)–O(1)	102.57(17)
O(9)^c–P(3)–O(4)	113.08(17)	O(9)^c–P(3)–O(5)	109.98(18)
O(4)–P(3)–O(5)	112.71(17)	O(9)^c–P(3)–O(6)	109.24(17)
O(4)–P(3)–O(6)	108.02(18)	O(5)–P(3)–O(6)	103.28(18)
P(1)–O(2)–M(1)	144.31(18)	P(2)–O(3)–M(1)	123.37(16)
P(3)–O(4)–M(1)	130.66(18)	P(2)^b–O(8)–M(2)	126.68(16)
P(3)^c–O(9)–M(1)	126.9(2)	P(1)^a–O(10)–M(2)	124.46(18)
P(2)–O(11)–M(2)	138.7(2)	P(1)–O(12)–M(2)	128.14(18)
N(2)–C(1)–C(2)	112.3(4)	C(3)–C(2)–C(1)	109.2(4)
N(1)–C(3)–C(2)	111.8(4)		

$^{a-c}$ Symmetry transformations used to generate equivalent atoms: ^{a} $-x+1, -y+1, -z$; ^{b} $-x+2, -y+1, -z$; ^{c} $-x+1, -y, -z$.

good agreement with the calculated amount of 20.9% (15.4% for decomposition of the template, 5.5% for dehydration of 1.5 M H_2O based on the empirical formula). The DTA curve shows one endothermic peak at ca. 350°C. It is attributed to the decomposition of the template and water. After calcination at 500°C for 4 h, the structure of ZnCoPO–PDA collapses and converts into an amorphous phase. Above 700°C the compound recrystallizes into $Zn_2P_2O_7$ (JCPDS: 34-1275). The IR spectra of ZnCoPO–PDA are assigned as follows: The bands at 3300–3000 cm^{-1} are typically assigned to contributions from hydrogen bonding and N–H bonding. The bands at 3361 and 3743 cm^{-1} may be due to P–OH groups. The bands at 1167, 1086, 1026, and 935 cm^{-1} are associated with asymmetric stretching vibrations of PO_4 units, whereas the band at 775 cm^{-1} corresponds to symmetric stretching vibrations of PO_4 groups. The bands at 584, 526, and 462 cm^{-1} are related to bending vibrations of PO_4 groups or the vibration modes of the four-membered rings of the zinc–cobalt phosphate chain. The bands at 1614, 1527, 1498, and 1371 cm^{-1} are assigned to frequencies of $\delta_{N–H}$, $v_{C–H}$, $v_{C–C}$, and $v_{C–N}$, which are related to the organic template cation $^+H_3NCH_2CH_2CH_2NH_3^+$.

Description of the Structure

The final atomic coordinates and isotropic displacement parameters for ZnCoPO–PDA are listed in Table 3. The selected bond lengths and bond angles are listed in Table 4. It is suggested that ZnCoPO–PDA is a novel organozinc–cobalt phosphate consisting of layers of zinc, cobalt, and phosphorus and discrete cationic molecules of doubly protonated $C_3N_2H_{12}^{2+}$. The asymmetric unit contains 22 independent nonhydrogen atoms, 2 metal atoms, 3 phosphoros atoms, 12 oxygen atoms, 3 carbon atoms, and 2 nitrogen atoms, as shown in Fig. 1.

Both the metal and phosphorus atoms are tetrahedrally coordinated by oxygen. Each $M(1)$ atom via oxygen–atom bridges makes four bonds to phosphorus atom neighbors [P(1), P(2), 2 × P(3)], whereas each $M(2)$ is bound to two P(1) and two P(2) atoms via oxygen atoms, and the bond lengths and angles [$d_{av}(M–O) = 1.943(9)$ Å] are close to those Zn–O bond lengths observed previously in structure determination (2, 10i), as expected given the low concentration of cobalt present in ZnCoPO–PDA. Of the three crystallographically distinct P sites, both P(1) and P(2) atoms make three bonds to neighboring metal atoms via O atoms and one bond to a terminal –OH group, respectively. The terminal oxygen of the OH groups is O(7)H for P(1) and O(1)H for P(2), respectively. The P(3) atom shares two oxygens with adjacent metal units, leaving an oxygen terminal and an unsaturated =O atom. A bond-valence calculation clearly shows that O(5) corresponds to P=O and O(6) to P–OH.
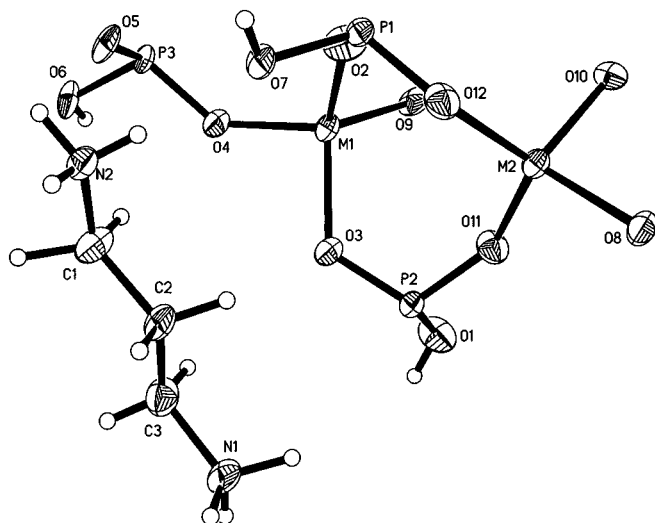

FIG. 1. Asymmetric unit of ZnCoPO–PDA, with thermal ellipsoids shown at 50% probability.

The polyhedral connectivity of the MO_4 and HPO_4 centers in ZnCoPO–PDA leads to a layered structure with parallel 12-rings layers. The two-dimensional sheets are built up from connecting infinite chains, as indicated in Fig. 2, through 4 rings, to form 12 rings. This type of chain contains triple edge-sharing 4-ring units that are linked with P(3) groups which is a hitherto unknown linkage in known zinc phosphates. The triple 4-ring building units have also been reported by Harrison et al. (11d), and include edge-sharing helixes of 4 rings in open-framework $NaZnPO_4 \cdot H_2O$. The 12-ring layers presented in this paper are different from those reported by Harrison et al. (10i, 11i). First, the linkage of 4-ring units that constitute the 12-ring sheets is different. Second, the orientation of the 12-ring sheets is distinct. The 12 rings we describe here are linear and parallel within a layer; those reported by Harrison et al. are split or "bifurcated."

The inorganic sheets are anionic, and are charge-balanced by doubly protonated organic cations. The 1,3-diaminopropane cations occupy interlayer sites toward the holes of the layer, and serve as H-bond donors to the nearest framework oxygen (Fig. 3, Table 5). It can be seen that the inorganic structure is weakly controlled by the organic templates. In addition to the six N–H···O hydrogen bonds the inorganic sheets are held together by strong interlayer H bond. The H bonds are found between O(7) and O(5), and the distance from O(7)–H to O(5) is estimated to be 2.495(5) Å at an angle of 176(5)°. In addition, there may be intralayer hydrogen bonds of P–OH···O (O1···O4, O6···O12) in inorganic sheets.

In summary, a novel layered zinc–cobalt phosphate, $Zn_{1.95}Co_{0.05}(HPO_4)_3 \cdot C_3N_2H_{12}$, has been synthesized under hydrothermal conditions and its structure has been
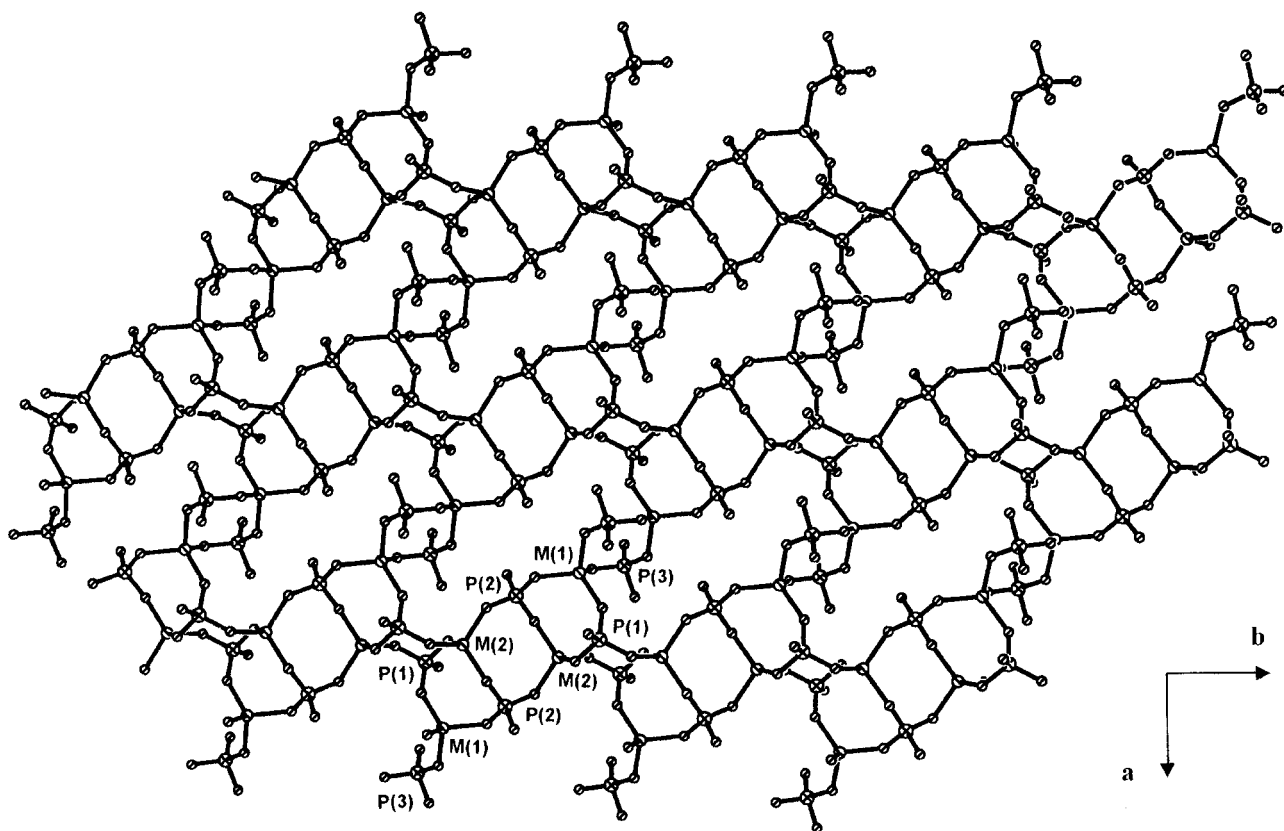
FIG. 2. View down [001] of the ZnCoPO–PDA crystal structure showing the infinite 12-ring layer structure.
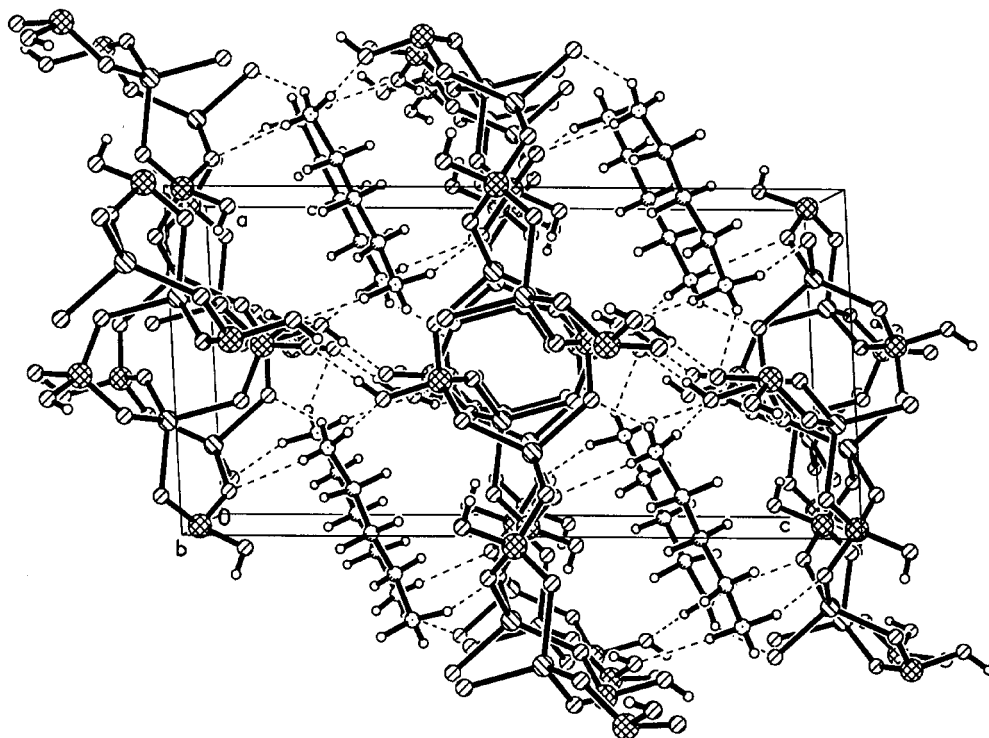

FIG. 3. View down [010] of the structure of the ZnCoPO–PDA. Interlayer hydrogen bonds both layer to layer and layer to 1,3-diaminopropane cation are indicated by dotted lines.

TABLE 5
Possible Hydrogen Bonds

D–H $\cdots$ A	d (D–H) (Å)	d (H$\cdots$A) (Å)	d (D$\cdots$A) (Å)	Angle (D–H$\cdots$A) (°)
O(1)–H(1)$\cdots$O(4)^d	0.86(2)	1.95(3)	2.774(4)	161(6)
O(6)–H(6)$\cdots$O(12)^e	0.83(2)	2.01(3)	2.769(4)	152(5)
O(7)–H(7)$\cdots$O(5)^f	0.84(2)	1.66(2)	2.495(5)	176(5)
N(1)–H(1B)$\cdots$O(8)^a	0.90(2)	1.95(3)	2.835(5)	166(6)
N(1)–H(1A)$\cdots$O(5)	0.88(2)	2.23(4)	2.971(5)	141(4)
N(1)–H(1C)$\cdots$O(6)^f	0.92(2)	2.22(4)	3.014(5)	145(5)
N(2)–H(2A)$\cdots$O(11)^g	0.88(2)	2.18(4)	2.874(5)	135(4)
N(2)–H(2C)$\cdots$O(10)^g	0.89(2)	2.05(3)	2.853(5)	149(4)
N(2)–H(2B)$\cdots$O(7)^h	0.89(2)	1.98(2)	2.859(5)	169(5)

$^{a-h}$ Symmetry transformations used to generate equivalent atoms: $^a -x + 1, -y + 1, -z$; $^b -x + 2, -y + 1, -z$; $^c -x + 1, -y, -z$; $^d -x + 2, -y, -z$; $^e x, y - 1, z$; $^f -x + 1, y + 0.5, -z + 0.5$; $^g x - 1, -y + 0.5, z + 0.5$; $^h x - 1, y, z$.

successfully characterized by single X-ray diffraction methods. It consists of sharing MO_4 ($M = Zn, Co$) and HPO_4 tetrahedral units without M–O–M and P–O–P links. Interestingly, in the structure of compound ZnCoPO–PDA, the sheets of 12 rings are built up from undulating edge-sharing 4-ring chains.

Although many 1D, 2D, and 3D framework phosphates have been prepared, the successful synthesis of the layered zinc–cobalt phosphate ZnCoPO–PDA is still important, and suggests the possibility of synthesizing the other novel structural metal phosphates with different transition elements by varying the templating agent and crystallization conditions.

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