

Synthesis and Structure of a One-Dimensional Cobalt Phosphate: (*R, S*)-(C₅H₁₄N₂)Co(HPO₄)₂

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A one-dimensional cobalt phosphate, (*R, S*)-(C₅H₁₄N₂)Co(HPO₄)₂ **1** has been synthesized in a predominantly nonaqueous environment by using (*R, S*)-2-methylpiperazine as templates and characterized by single-crystal X-ray diffraction. **1** has a so-called square-twisted (ts) chain containing corner-sharing four-ring of alternating CoO₄ and PO₄ tetrahedra. It crystallizes in the monoclinic space group *P2₁/n* with *a* = 8.6115(2) Å, *b* = 14.4387(1) Å, *c* = 10.8109(2) Å, *β* = 95.535(1)°, *V* = 1245.28 Å³, *Z* = 4. Refinement gave *R*₁ = 0.0333, *wR*₂ = 0.0812 for 2263 unique observed reflections (*I* > 2σ(*I*)). © 2000

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Key Words: structure; cobalt phosphate.

INTRODUCTION

Organically templated transition metal phosphate structures are of great current interest because of their potential catalytic applications and novel structures. For example, organically templated Mo (1), V (2), Fe (3,4), Zn (5–8), Co (9), and Ti (10) phosphates have been reported. The structures varied from 1-D to 3-D. Many of them are tetrahedron-based networks, while some of them are complex structures based on various metal–oxygen polyhedra and PO₄ tetrahedra. Among them cobalt is of particular interest owing to its feasibility to tetrahedral coordination and potential catalytic properties. For example, CoAPO-36 and CoAPO-18 are found to be extremely versatile catalysts (11,12). Much work has been done on the incorporation of divalent cobalt cations into aluminum (or gallium) phosphates (13,14). Also, several novel microporous cobalt phosphates with the formula of *M*CoPO₄ (*M* = Na, K, Rb, and NH₄⁺) which are related to zeolite ABW structures have been reported (15). Organically templated cobalt phosphate is rich with structural chemistry, which may form a three-dimensional structure, [H₃NC₂H₄NH₃]_{0.5}CoPO₄ (9), two-dimensional layers including [H₃N(CH₂)₃NH₃]_{0.5}CoPO₄·0.5H₂O, [H₃N(CH₂)₄NH₃]_{0.5}CoPO₄ (16), and (N₂C₄H₁₂)_{1.5}Co₂(HPO₄)(PO₄)·H₂O (17), and one-dimen-

sional structures such as H₃N(CH₂)₃NH₃Co(HPO₄)₂ (18) and (N₂C₄H₁₂)_{1.5}Co₂(HPO₄)(PO₄)·H₂O (17). The chain compounds was synthesized in a nonaqueous solvothermal condition. Nonaqueous systems could provide different solvating and viscosity properties. Furthermore, it could diminish the rate of hydrolysis, and the crystallization of reaction intermediates becomes possible (19). To exploit more possibilities in organically templated cobalt phosphates, solvo-(or hydro-)thermal reactions have been carried out in the system of CoO–P₂O₅–amine(ammonium)–H₂O–organic solvent. Herein, the synthesis and single-crystal structure of a new organically templated 1-D cobalt phosphate, (*R, S*)-(C₅H₁₄N₂)Co(HPO₄)₂, are reported, and its structural relationship to the known layered compound, [H₃N(CH₂)₃NH₃]_{0.5}CoPO₄·0.5H₂O, is described.

EXPERIMENTAL PROCEDURES

Synthesis

The syntheses were carried out in Teflon-lined acid digestion bombs with an internal volume of 23 cm³ under autogeneous pressure by heating the reaction mixture at 190°C for 2 days followed by slow cooling to room temperature at 4.8°C h⁻¹. Compound **1** was prepared from the reaction mixture of Co₃(PO₄)₂·*x*H₂O (1 mmol), 85% H₃PO₄ (4 mmol), (*R, S*)-2-methylpiperazine (6 mmol), H₂C₂O₄·2H₂O (2 mmol), distilled water (1.0 mL), and ethylene glycol (7.0 mL). The product was recovered by filtration and washed with distilled water. The product was a mixture of dark blue needle-like crystals, a pink phase, and white powder. The XRD pattern of manually separated blue-needle crystals compared well with the pattern simulated from the coordinates of the single-crystal study of **1** (see below).

Single-Crystal X-Ray Structure Analysis

The structure of **1** was determined by single-crystal X-ray methods, and crystallographic data are summarized in Table 1. A suitable crystal (0.025 × 0.025 × 0.100 mm) was

TABLE 1
Crystallographic Data for (R,S)-(C₅H₁₄N₂)Co(HPO₄)₂

FW	353.07
Crystal system	monoclinic
Size (mm)	0.025 × 0.025 × 0.100
Habit	blue needle
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	8.6115(2)
<i>b</i> , Å	13.4387(1)
<i>c</i> , Å	10.8109(2)
β , deg	95.535(1)
<i>V</i> , Å ³	1245.28(4)
<i>Z</i>	4
Temp, °C	22
λ , Å	0.71073
<i>T</i> _{max} / <i>T</i> _{min}	0.734, 0.956
ρ_{calcd} , g cm ⁻³	1.883
μ , cm ⁻¹	16.69
<i>F</i> (000)	724
2 θ _{max}	55.96
No. of observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	2263
No. of parameters refined	163
<i>R</i> ₁ ^a	0.0333
<i>wR</i> ₂ ^b	0.0812

RESULTS

Crystal Structure of (R, S)-(C₅H₁₄N₂)Co(HPO₄)₂

The atomic coordinates and the thermal parameters of 1 are given in Table 2, and selected bond lengths, bond angles, and bond valence sums are given in Table 3. The structure contains a so-called square-twisted (ts) chain (22) constructed by corner-sharing four-membered rings of alternating CoO₄ and HPO₄ tetrahedra. Each four-membered ring in the chain is templated by two 2-methylpiperazinium cations. One is in *R* form, the other is in *S* form, Fig. 1. The cobalt ions in 1 are tetrahedrally coordinated by four oxygens with average Co–O bond length of 1.963 Å. Each CoO₄ tetrahedra is cornered-shared with four HPO₄ tetrahedra with an average Co–O–P bond angle of 124.9(1)°. There are two crystallographically distinct P atoms. Each P atom connects to two terminal oxygens

TABLE 2
Atomic Coordinates and Thermal Parameters for 1

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Co(1)	0.2376(1)	0.52811(3)	0.46978(4)	0.0205(1)
P(1)	0.0392(1)	0.5816(1)	0.6887(1)	0.0207(2)
P(2)	0.5486(1)	0.5884(1)	0.3587(1)	0.0202(2)
O(1)	0.1144(2)	0.6118(1)	0.5724(2)	0.028(1)
O(2)	0.0713(2)	0.5068(2)	0.3331(2)	0.030(1)
O(3)	0.1740(2)	0.5479(2)	0.7889(2)	0.034(1)
O(4)	–0.0451(2)	0.6684(2)	0.7411(2)	0.034(1)
O(5)	0.5606(2)	0.4848(2)	0.3038(2)	0.032(1)
O(6)	0.5855(3)	0.6651(2)	0.2563(2)	0.034(1)
O(7)	0.3900(2)	0.6128(2)	0.4002(2)	0.029(1)
O(8)	0.3196(3)	0.3997(2)	0.5357(2)	0.028(1)
N(1)	0.3537(3)	0.3323(2)	0.2445(3)	0.028(1)
N(2)	0.5757(3)	0.2044(2)	0.1493(4)	0.054(1)
C(1)	0.4042(4)	0.2399(3)	0.3126(4)	0.041(1)
C(2)	0.5689(4)	0.2134(3)	0.2835(5)	0.051(1)
C(3)	0.5262(4)	0.2964(3)	0.0816(4)	0.044(1)
C(4)	0.3625(4)	0.3248(3)	0.1080(3)	0.036(1)
C(5)	0.3129(5)	0.4216(4)	0.0472(4)	0.062(1)
H(1A)	0.4084	0.3831	0.2782	0.05
H(1B)	0.2477	0.3400	0.2566	0.05
H(1C)	0.3293	0.1823	0.2776	0.05
H(1D)	0.4024	0.2410	0.4182	0.05
H(2A)	0.6761	0.1851	0.1421	0.05
H(2B)	0.5157	0.1499	0.1209	0.05
H(2C)	0.6465	0.2656	0.3223	0.05
H(2D)	0.6086	0.1582	0.3219	0.05
H(3A)	0.6022	0.3515	0.1218	0.05
H(3B)	0.5273	0.2865	–0.0200	0.05
H(4A)	0.2808	0.2685	0.0773	0.05
H(5A)	0.3755	0.4821	0.0580	0.05
H(5B)	0.1977	0.4483	0.0825	0.05
H(5C)	0.3439	0.4340	–0.0423	0.05
H(3)	0.2726	0.5375	0.7572	0.05
H(6)	0.5321	0.7318	0.2621	0.05

^a *U*_{eq} is defined as one-third of the trace of the orthogonalized *U*_{*ij*} tensor.

glued on a glass fiber and mounted on a Smart CCD diffractometer using MoK α radiation. Intensity data were collected for indexing in 1271 frames with increasing ω (width of 0.3° per frame). Unit cell dimensions for 1 were determined by a least-squares fit of 4480 reflections. Of the 7090 reflections collected, 2263 unique reflections were considered observed (*I*_{obs} > 2 σ (*I*)) after Lp and absorption corrections. The absorption correction was based on symmetry-equivalent reflections using the SADABS programs (20). On the basis of systematic absences and statistic intensity distribution, the space group was determined to be *P*2₁/*n*. Direct methods were used to locate the Co atoms and the P atoms first, and the remaining oxygen, carbon, and nitrogen atoms were found from successive difference maps. All H atoms were located on difference Fourier maps calculated at the final stage of structure refinement. The final cycles of refinement, including the atom coordinates and anisotropic thermal parameters for all nonhydrogen atoms and fixed atomic coordinates and isotropic thermal parameters for the hydrogen atoms, converged at *R*₁ = 0.0333 and *wR*₂ = 0.0812. In the final difference map, the deepest hole was 0.31 eÅ⁻³ and the highest peak was 0.52 eÅ⁻³. Anomalous and secondary extinction correction were applied. All calculations were performed by using the SHELXTL programs (21). Supplementary data (X-ray crystallographic file in CIF format, and observed and calculated structure factors) are available from the author.

TABLE 3
Selected Bond Lengths (Å), Bond Angles (Deg), and Bond Valence Sums (Σ s) for 1

Co(1)–O(1)	1.961 (2)	Co(1)–O(2)	1.980 (2)
Co(1)–O(7)	1.944 (2)	Co(1)–O(8)	1.971 (2)
Σ s(Co(1)–O) = 1.92			
P(1)–O(1)	1.524 (2)	P(1)–O(2)	1.525 (2)
P(1)–O(3)	1.579 (2)	P(1)–O(4)	1.514 (2)
Σ s(P(1)–O) = 5.00			
P(2)–O(5)	1.520 (2)	P(2)–O(6)	1.569 (2)
P(2)–O(7)	1.514 (2)	P(2)–O(8)	1.539 (2)
Σ s(P(2)–O) = 4.99			
N(1)–C(1)	1.482 (5)	N(1)–C(4)	1.492 (5)
N(2)–C(2)	1.464 (7)	N(2)–C(3)	1.476 (6)
C(4)–C(5)	1.503 (6)	C(1)–C(2)	1.528 (6)
C(3)–C(4)	1.518 (5)		
P(1)–O(1)–Co(1)	127.6 (1)	P(1)–O(2)–Co(1)	128.6 (1)
P(2)–O(7)–Co(1)	130.6 (1)	P(2)–O(8)–Co(1)	112.9 (1)

and two bridging oxygens. In order to balance the charge, O(3) and O(6) are suggested as being hydroxyl groups with bond valence sums (BVS) (23) of 1.11 and 1.14, respectively;

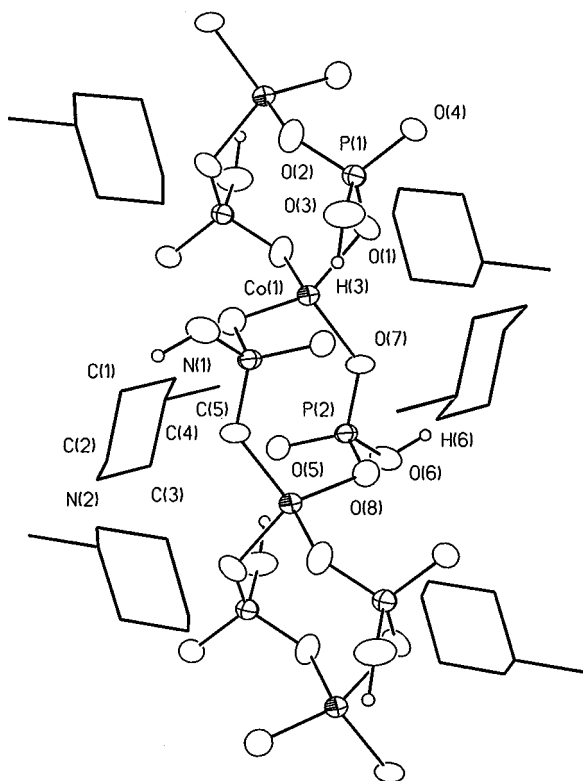


FIG. 1. Structure unit of 1 showing the connection of Co and P atoms: thermal ellipsoids are shown at 60% probability.

and O(4) and O(5) are suggested to be pendant oxygen atoms with BVS 1.32 and 1.30, respectively. The presence of hydroxyl group was confirmed by the observation of peaks in difference Fourier maps close to O(3) and O(6). The short distance between the adjacent oxygen atoms and between the amine nitrogen and oxygen atoms indicates that strong hydrogen bonds exist, Table 4. The intrachain hydrogen bonds of PO(3)–H \cdots O(5)P lead the chain to twist, Fig. 2a. The interchain hydrogen bonds of PO(4)–H \cdots O(6)P as well as the amine-chain hydrogen bonds work together to form the three-dimensional structure of 1, Fig. 2b.

DISCUSSION

The tetrahedron-based one-dimensional metal phosphate structures are of interest because they could provide clues to understand the formation of open-framework metal phosphates. In the case of aluminum phosphate system, a model of the formation of 1-D, 2-D, and 3-D structure based on the corner-sharing four-ring chain, $[\text{AlP}_2\text{O}_8\text{H}_x]^{3-x}$ ($x = 1, 2$), has been proposed by Ozin's group. There are three types of tetrahedron-based 1-D structure in the known aluminum phosphate structures: the corner-sharing four-ring chain (type A) (24–27), the edge-sharing four-ring chain with pendant phosphate groups (type B) (28, 29), and a more complex chain of $[\text{Al}_3\text{P}_5\text{O}_{20}\text{H}]^{5-}$ (type C) (18, 30). Ozin designated the type-A chain as “parent chain.” The chain of type B or C can be derived from the type-A chain. The first reported organically templated cobalt phosphate chain, $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]\text{Co}(\text{HPO}_4)_2$, is with the similar type-B structure as found in aluminum phosphate. The compound 1 is with the type-A structure (single ts chain). Another chain found in the cobalt phosphate system, $(\text{N}_2\text{C}_4\text{H}_{12})_{1.5}\text{Co}_2(\text{HPO}_4)(\text{PO}_4) \cdot \text{H}_2\text{O}$, is with a fused double ts chain structure. The similarity of the low-dimensional structures between the cobalt phosphate system and the aluminum phosphate system might account for the large number of cobalt aluminum phosphate structures reported (13,14). Using the parent chain model, one could envisage that the progressively repetition of the single to double ts chain

TABLE 4
Hydrogen-Bonding Geometry for 1 (Å, Deg)

D–H \cdots A	D–H	H \cdots A	O \cdots A	D–H \cdots A
N1–H1A \cdots O5	0.89	1.90	2.751 (3)	161.3
N1–H1B \cdots O4	0.94	1.75	2.677 (3)	167.8
N2–H2A \cdots O6	0.91	2.25	3.042 (4)	145.1
N2–H2A \cdots O8	0.91	2.10	2.894 (4)	144.2
N2–H2B \cdots O2	0.93	2.14	2.956 (4)	145.7
N2–H2B \cdots O1	0.93	2.33	3.036 (4)	132.2
O3–H3 \cdots O5	0.96	1.66	2.620 (3)	176.8
O6–H6 \cdots O4	1.01	1.50	2.503 (3)	167.7

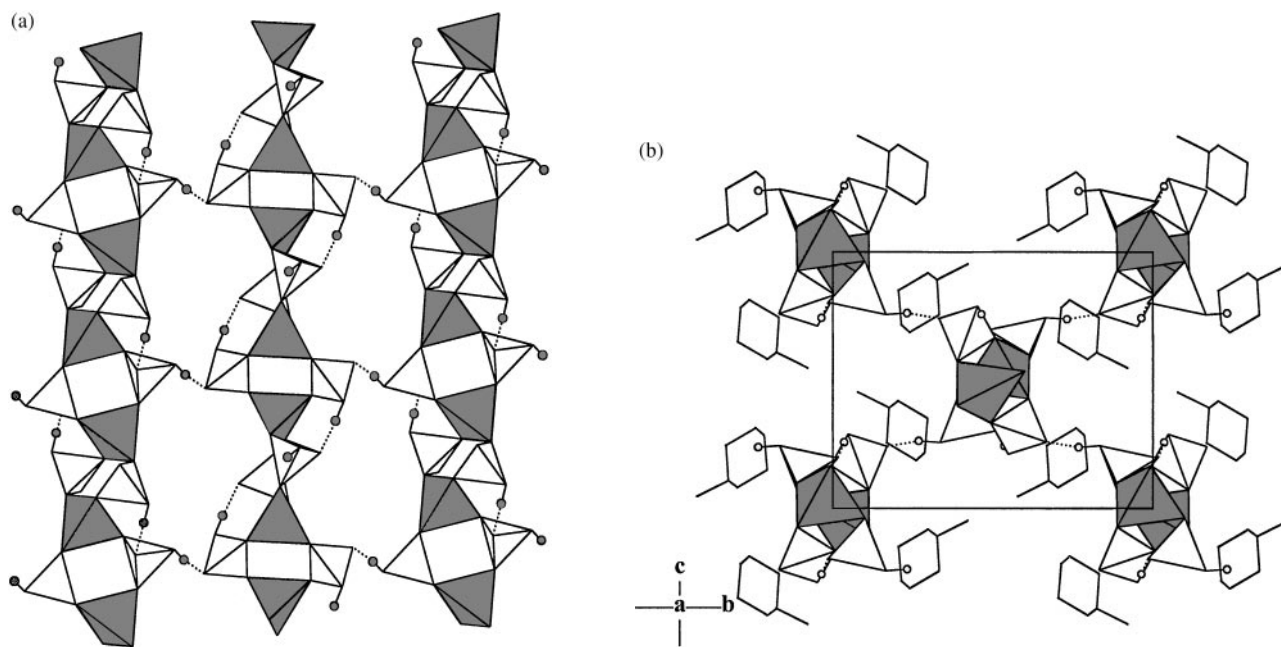


FIG. 2. Polyhedral view of 1 (a) showing the interchain and intrachain hydrogen bonds and (b) projected along the [100] direction. Light tetrahedra, PO_4 ; darker tetrahedra, CoO_4 ; small circles, H; branched hexagons, 2-methylpiperazinium cations.

connection would form a layer. Interestingly, this cobalt phosphate layer is exactly the one found in $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]_{0.5}\text{CoPO}_4$. Alternatively, the fused double ts chain can be viewed as a segment of the $[\text{CoPO}_4]$ layer in the known layered compound. It might be an intermediate in the formation of the layered compound. This assumption is probably true because of the presence of layered compound $(\text{N}_2\text{C}_4\text{H}_{12})_{0.5}\text{CoPO}_4$ in the synthesis of the fused double ts chain compound. The similar metal phosphate layer with three-ring and four-ring patterns found in $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]_{0.5}\text{CoPO}_4$ is also found in other divalent metal framework phosphates, for example, $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)\text{Zn}_6(\text{PO}_4)_4(\text{HPO}_4) \cdot \text{H}_2\text{O}$ (7) and $\text{Be}_3(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ (31). The isolation of 1 might be helpful in understanding the formation of porous divalent cobalt phosphates.

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