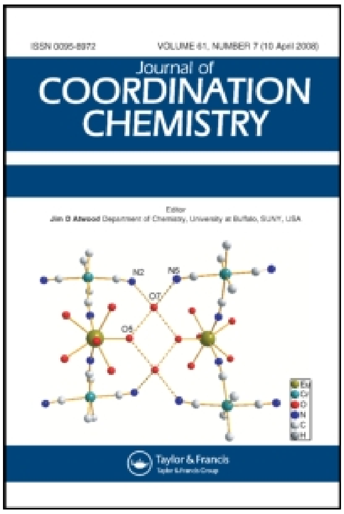

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Tae-Sun Chang[a]; Chong-Hyeak Kim[a]; Dong-Koo Lee[a]; Tianyou Song[b]
[a] Division of Advanced Chemical Technology, Korea Research Institute of Chemical Technology, Yuseong, Daejeon 305-600, Korea [b] Department of Chemistry, Jilin University, Changchun 130023, P.R. China

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SYNTHESIS AND CRYSTAL STRUCTURE OF THE LAYERED COBALT PHOSPHATE WITH RACEMIC 1,2-DIAMINOPROPANE TEMPLATE

TAE-SUN CHANG[a], CHONG-HYEAK KIM[a,*],
DONG-KOO LEE[a] and TIANYOU SONG[b]

[a]*Division of Advanced Chemical Technology, Korea Research Institute of Chemical Technology, P.O. Box 107, Yuseong, Daejeon 305-600, Korea;* [b]*Department of Chemistry, Jilin University, Changchun 130023, P.R. China*

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A novel layered cobalt phosphate with a racemic 1,2-diaminopropane templating agent, $[CH_2(NH_3)CH(NH_3)CH_3][CoPO_4]_2$, has been synthesized and structurally characterized by single crystal X-ray diffraction. The compound crystallizes in the monoclinic system, space group $P2_1/c$ with $a = 10.457(2)$, $b = 7.849(1)$, $c = 6.692(1)$ Å, $\beta = 103.30(1)^\circ$, $V = 534.5(2)$ Å^3, $Z = 2$. The combination of cobalt phosphate anion layers and doubly protonated cationic 1,2-diaminopropane templates is mainly through ionic bonding. The crystal structure is stabilized by a network of hydrogen bonds between layers and templating agents.

Keywords: Cobalt phosphate; 1,2-Diaminopropane; Templating agent; Crystal structure

INTRODUCTION

The synthesis and characterization of transition metal phosphates [1–4] with zeolite-like and/or clay-like structure is rapidly becoming an important area of inorganic chemistry because of their applications as catalysts, sorbents and ion exchangers [5–9]. To understand their properties it is necessary to investigate their structure, so that the preparation of single-crystal phosphates is currently considered a challenge in this research field. The synthesis of cobalt phosphates has received much attention owing to cobalt's tendency to adopt tetrahedral coordination and it's potential properties [10,11]. Numerous cobalt phosphates, such as the one-dimensional chain structure, (R,S)-$(C_5H_{14}N_2)Co(HPO_4)_2$ [10], two-dimensional layer structures, $[H_3N(CH_2)_4NH_3]_{0.5}[Co(PO_4)]$ [12] and $[NH_3CH_2CH(OH)CH_2NH_3][Co_2(PO_4)_2]$ [13], and the three-dimensional zeolite-like structures, $(H_3NC_2H_4NH_3)_2Co_7(PO_4)_6$ [11] and $[H_3NCH_2CH_2NH_3]_{0.5}[CoPO_4]$ [14] have been determined by X-ray powder

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*Author for correspondence. E-mail: chkim@krict.re.kr

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diffraction and/or X-ray single-crystal diffraction methods. Among the organically templated cobalt phosphates, many possess three-dimensional architectures and Stucky's group has characterized several cobalt phosphates possessing zeolite-like structures [15–17]. However, very few cobalt phosphate structures with layered architecture have been synthesized in the presence of organic amines [12]. Here we report the synthesis and structural characterization of a new layered cobalt phosphate compound, $[CH_2(NH_3)CH(NH_3)CH_3][CoPO_4]_2$, with racemic 1,2-diaminopropane as a templating agent.

EXPERIMENTAL

Synthesis and Analysis of $[CH_2(NH_3)CH(NH_3)CH_3][CoPO_4]_2$

In the synthesis of the title compound, distilled water and ethylene glycol (EG) were the mixture solvent, racemic 1,2-diaminopropane (DAP) was the templating agent and $Co(CH_3COO)_2 \cdot 4H_2O$ and H_3PO_4 were the respective sources of cobalt and phosphorus. The reaction mixture with the composition of $CoO{:}2.75P_2O_5{:}5.0DAP{:}36EG{:}56H_2O$ was stirred for about 2 h, and then heated at 150°C for 5 days in a Teflon-lined stainless-steel autoclave under autogeneous pressure. The resulting product was a single blue crystal of the title compound, mixed with some amorphous materials. The single crystal was picked out and submitted to composition analysis and structure determination.

The IR spectrum of the crystal was recorded on a BioRad Digilab FTS-165 infrared spectrophotometer using a KBr wafer. 1,2-Diaminopropane was assigned by the relevant IR absorption bands [18]. The EDS spectrum obtained on a Philips XL-30S FEG scanning electron microscope/EDAX Phoenix energy-dispersive X-ray spectrometer showed the presence of C, N, O, P and Co. Carbon, hydrogen, nitrogen and oxygen were determined by a CE EA-1110 elemental analyzer. Co content was determined by Jobin-Yvon Ultima-C inductively coupled plasma emission spectrometer. The composition of the crystal was deduced from the elemental analyses; the formula $[CH_2(NH_3)CH(NH_3)CH_3][CoPO_4]_2$ is consistent with the results of single-crystal X-ray diffraction analysis. Yield: *ca.* 50%. Anal. Calcd. for $C_3H_{12}Co_2N_2O_8P_2$ (%): C, 9.38; H, 3.15; N, 7.30; O, 33.34; P, 16.13; Co, 30.70. Found: C, 9.30; H, 3.30; N, 7.20; O, 32.13; Co, 30.65.

X-ray Crystallography

A blue plate crystal of the title compound was coated with epoxy glue in order to prevent spontaneous liberation of templating agent from the specimen under ambient conditions. The epoxy-coated crystal was mounted on a Siemens P4 four-circle X-ray diffractometer and the intensity data were collected in the θ–2θ scan mode using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell parameters and an orientation matrix for the compound was determined from the least-squares fit of 42 accurately centered reflections with θ range of 4.76~19.75°. Three standard reflections were monitored every 97 reflections; no remarkable decays were observed through data collection. Lorentz and polarization corrections were applied to the intensity data, and a semi-empirical absorption correction based on the psi-scans were applied [19].

All calculations in the structural solution and refinement were performed using the Siemens SHELXTL crystallographic software package [20]. Space groups were assigned based on the systematic absences and intensity statistics, and were confirmed by successful refinements. The structure was solved by the direct method [21] and successively refined by the full-matrix least-squares method followed by difference Fourier maps. All the non-hydrogen atoms were refined anisotropically; all the hydrogen atoms were put into calculated positions with the isotropic thermal parameters. Final difference electron density maps contained no significant features. Further details of the crystallographic and experimental data are given in Table I.

RESULTS AND DISCUSSION

The refined atomic parameters and selected bond lengths and angles for $[CH_2(NH_3)CH(NH_3)CH_3][CoPO_4]_2$ are listed in Tables II and III, respectively. The asymmetric unit and crystal packing diagram of $[CH_2(NH_3)CH(NH_3)CH_3][CoPO_4]_2$ are shown in Figs. 1 and 2, respectively.

As shown in Fig. 2, the crystal structure of the title compound is a novel layered structure with empty channels. The fundamental units of the crystal structure are "CoO_4" and "PO_4" groups, that is oxygen tetrahedrally coordinated with cobalt or phosphorus. The combination of CoO_4 and PO_4 forms cobalt phosphate anion layers with empty channels parallel to the *bc* crystallographic plane. The layers are combined

TABLE I Crystal data and structure refinement details for $[CH_2(NH_3)CH(NH_3)CH_3][CoPO_4]_2$

Chemical formula	$C_3H_{12}Co_2N_2O_8P_2$
Formula weight	383.95
Temperature (K)	294(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	10.457(2)
b (Å)	7.849(1)
c (Å)	6.692(1)
α (°)	90
β (°)	103.30(1)
γ (°)	90
V (Å^3)	534.5(2)
Z	2
Density (calcd.), (g cm^{-3})	2.386
μ(Mo Kα) mm^{-1}	3.436
F(000)	384
θ range for data collection (°)	2.0–25.0
Index range	$-12 \le h \le 12$, $-1 \le k \le 9$, $-1 \le l \le 7$
Reflections measured	1380
Independent reflections	941 ($R_{\text{int}} = 0.0418$)
Data/restraints/parameters	941/0/82
Goodness of fit on F^2	1.185
Final R indices [$I > 2\sigma(I)$]	0.0470, 0.1341
R indices (all data)	0.0491, 0.1361

TABLE II Atomic coordinates and equivalent thermal parameters for $[CH_2(NH_3)CH(NH_3)CH_3][CoPO_4]_2$

Atom	x	y	z	U_{eq} (Å^2)
Co	0.9728(1)	0.7483(1)	−0.0106(1)	0.014(1)
P	0.8281(1)	0.4547(1)	0.1886(2)	0.012(1)
O(1)	0.8560(3)	0.5563(4)	0.0076(5)	0.021(1)
O(2)	0.8563(3)	0.5606(4)	0.3869(5)	0.021(1)
O(3)	0.9298(3)	0.3025(4)	0.2256(5)	0.017(1)
O(4)	0.6912(3)	0.3860(4)	0.1412(6)	0.025(1)
C(5)	0.5441(4)	−0.0359(6)	0.0982(7)	0.022(1)
C(6)	0.5737(11)	−0.2191(15)	0.0920(30)	0.048(4)
N(7)	0.6762(4)	0.0446(5)	0.1338(6)	0.020(1)

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

TABLE III Selected bond lengths (Å) and angles (°) for $[CH_2(NH_3)CH(NH_3)CH_3][CoPO_4]_2$

Co–O(1)	1.962(3)	Co–O(2)^a	1.955(3)
Co–O(3)^b	1.985(3)	Co–O(3)^c	1.990(3)
P–O(1)	1.533(3)	P–O(2)	1.536(3)
P–O(3)	1.581(3)	P–O(4)	1.494(3)
C(5)–C(6)	1.473(13)	C(5)–N(7)	1.488(6)
C(5)–C(5)^d	2.310(5)		
O(1)–Co–O(2)^a	105.3(1)	O(1)–Co–O(3)^b	108.8(1)
O(1)–Co–O(3)^c	107.1(1)	O(2)^a–Co–O(3)^b	106.4(1)
O(2)^a–Co–O(3)^c	108.2(1)	O(3)^b–Co–O(3)^c	120.2(2)
O(1)–P–O(2)	111.6(2)	O(1)–P–O(3)	105.9(2)
O(1)–P–O(4)	111.6(2)	O(2)–P–O(3)	106.7(2)
O(2)–P–O(4)	111.3(2)	O(3)–P–O(4)	109.7(2)
P–O(1)–Co	133.1(2)	P–O(2)–Co^e	134.3(2)
P–O(3)–Co^b	118.5(2)	P–O(3)–Co^f	119.3(2)
Co^b–O(1)–Co^e	114.6(1)	C(6)–C(5)–N(7)	103.0(5)
C(6)–C(5)–C(5)^d	103.0(5)	N(7)–C(5)–C(5)^d	109.6(4)

Symmetry transformations used to generate equivalent atoms:
[a] $x, -y+3/2, z-1/2$.
[b] $-x+2, -y+1, -z$.
[c] $-x+2, y+1/2, -z+1/2$.
[d] $x, -y+3/2, y+1/2$.
[e] $-x+2, y-1/2, -z+1/2$.
[f] $-x+1, -y, -z$.

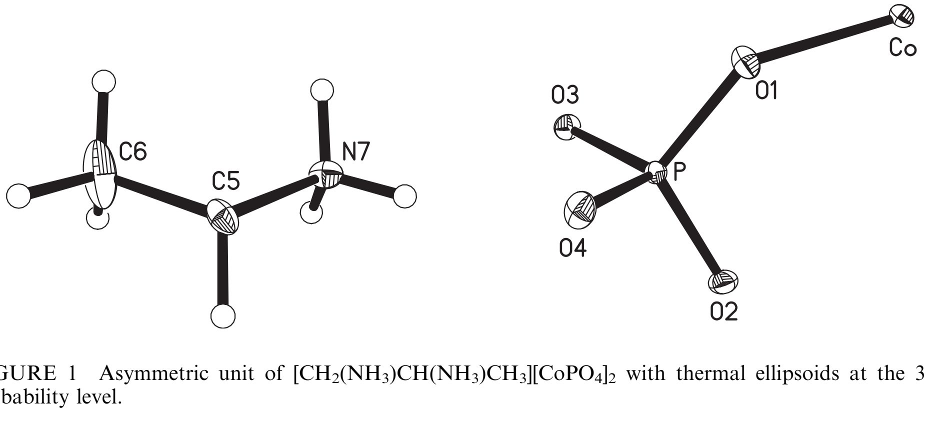


FIGURE 1 Asymmetric unit of $[CH_2(NH_3)CH(NH_3)CH_3][CoPO_4]_2$ with thermal ellipsoids at the 30% probability level.

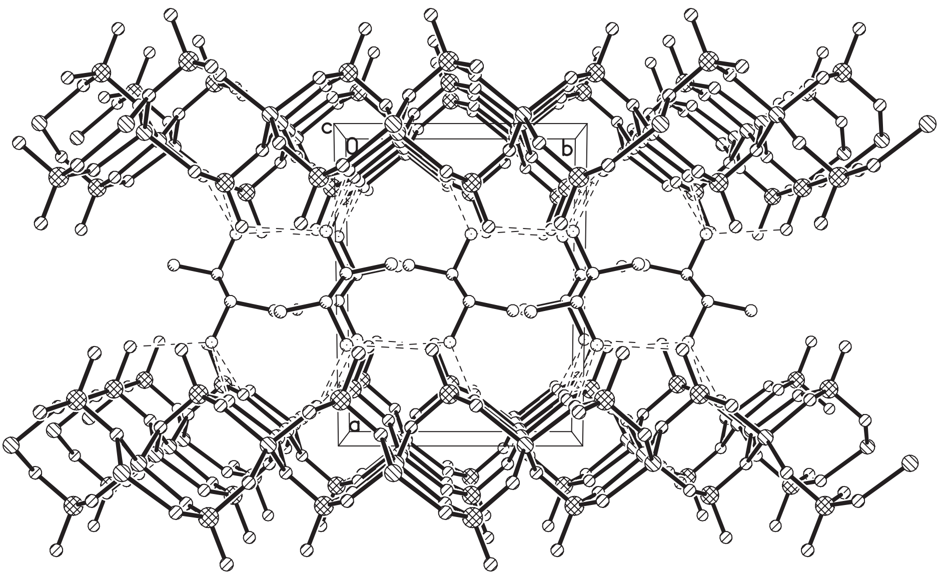


FIGURE 2 Crystal packing diagram of $[CH_2(NH_3)CH(NH_3)CH_3][CoPO_4]_2$ projected along the *c* axis.

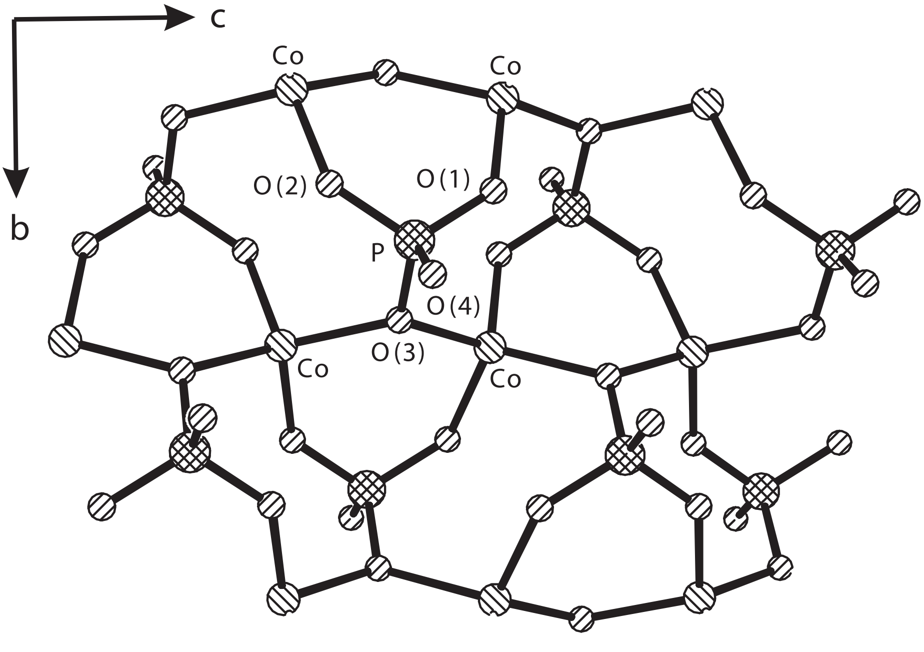


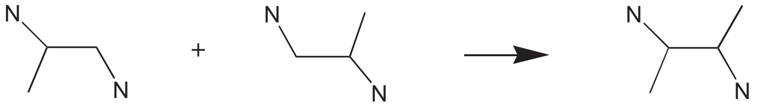
FIGURE 3 Framework of $[CoPO_4]$ layer parallel to the *bc* plane.

along the *a* axis through propanediammonium cations lying between every two layers. The framework structure of the cobalt phosphate anion layer is shown in Fig. 3. Every two adjacent CoO_4 tetrahedra share a common vertex, oxygen atom O(3), to form a linear chain of CoO_4 that is parallel to the *c* axis. This chain and the neighboring

CoO_4 chain are linked through PO_4. Two oxygen atoms, O(1) and O(2), of each PO_4 bridge to two adjacent Co atoms on the neighboring CoO_4 chain. The third oxygen atom of the PO_4 is the common atom O(3) between two CoO_4 in a second chain. The last oxygen atom O(4) of the PO_4 is a terminal oxygen, which points towards the interlayer space. All the Co and P atoms are four-coordinated by O atoms. O(3) is three-coordinated and each is shared by one P and two Co atoms.

The chemical formula of one layer is $CoPO_4$, and it is electrically negative. There are cationic molecules of doubly protonated 1,2-diaminopropane, i.e., templating agent, in the intralayer space. It is very important because it is the first successful use of 1,2-diaminopropane as a templating agent in the single crystal synthesis. The function of the template is very important in the formation of the crystal structure. The templating cation causes the crystal to be electrically neutral and the size of the cation, especially the N···N vector determines the interlayer distance. The cobalt phosphate layers and propane-1,2-diammonium templates are mainly held together through ionic bonding. There are also many hydrogen bonds between layers and templating agents, which increase the strength of the combination [N(7)–H(7a)···O(4) 2.684(5) Å, 165.8°; N(7)–H(7c)···O(1) 2.873(5) Å, 172.2°; N(7)–H(7b)···O(2) 2.896(5) Å, 158.1°].

The templating agent, 1,2-diaminopropane, used in the synthesis is a racemic compound. The final result of the structure measurement can be shown as



so that templating agent appears to possess four carbon atoms, i.e., $[CH_2(NH_3)CH(NH_3)CH_3]$ $[C_0PO_4]_2$. It is noteworthy that the result of single-crystal X-ray diffraction indicates that the spatial occupancy of both the end carbon atoms is 0.5 while all others are 1.0.

Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

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