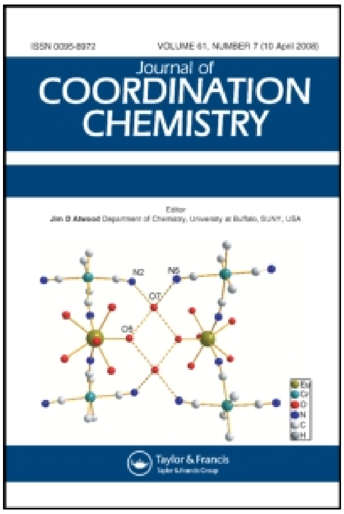

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Synthesis and crystal structure of a layered cobalt phosphate with a racemic 1,2-Diaminopropane template

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

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A novel layered cobalt phosphate with racemic 1,2-diaminopropane as the 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 methods. 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 interaction of cobalt phosphate anionic layers and doubly protonated 1,2-diaminopropane cations is mainly ionic. The crystal structure is stabilized by a hydrogen bonding network between layers and templating cations.

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 structures is rapidly becoming an important area of inorganic chemistry because of applications as catalysts, sorbents and ion exchangers [5–9]. In order to understand their properties it is necessary to investigate their structures, so the preparation of single crystal phosphates is currently considered a challenge in this field. Among such research, the synthesis of cobalt phosphates has received much attention owing to its possible tetrahedral coordination and potential properties [10,11]. Numerous cobalt phosphates such as one-dimensional chain structures, (*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], $[NH_3CH_2CH(OH)CH_2NH_3][Co_2(PO_4)_2]$ [13], and three-dimensional zeolite-like structures, $(H_3NC_2H_4NH_3)_2Co_7(PO_4)_6$ [11], $[H_3NCH_2CH_2NH_3]_{0.5}[CoPO_4]$ [14] have been determined by X-ray powder and/or single-crystal diffraction methods. Among the organically templated cobalt phosphates, many possess three-dimensional

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architectures and several possess zeolite-like structures [15–17]. However, very few cobalt phosphate structures with a layered architecture have been synthesized. 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 templating agent.

EXPERIMENTAL

$[CH_2(NH_3)CH(NH_3)CH_3][CoPO_4]_2$

In the synthesis, distilled water and ethylene glycol (EG) were used as mixed solvent, recemic 1,2-diaminopropane (DAP) was the templating agent, and $Co(CH_3COO)_2 \cdot 4H_2O$ and H_3PO_4 were the source of cobalt and phosphorous, respectively. A reaction mixture of composition of $CoO : 2.75P_2O_5 : 5.0DAP : 36EG : 56H_2O$ was stirred for about 2 h, then heated at 150°C for 5 days in a Teflon-lined stainless steel autoclave under autogeneous pressure. The resulting single crystals of the title compound were blue and mixed with some amorphous material. Single crystals were hand-picked from the mixture.

IR spectra were recorded on a BioRad Digilab FTS-165 infrared spectrophotometer using KBr wafers. 1,2-Diaminopropane was identified by relevant IR absorption bands [18]. EDS spectra 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 using a CE EA-1110 elemental analyzer. Co was determined by Jobin–Yvon Ultima-C inductively coupled plasma emission spectrometer. The composition of the crystal was deduced from 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 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 an Siemens P4 four-circle diffractometer and intensity data were collected in the θ–2θ scan mode using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Unit cell parameters and an orientation matrix were determined from the least-squares fit of 42 accurately centred reflections with a θ range of $4.76 \sim 19.75°$. Three standard reflections were monitored every 97 reflections; no significant decay was observed during data collection. Lorentz and polarization corrections were applied to the intensity data, and a semi-empirical absorption correction based on the psi-scans was applied [19].

All calculations in structural solution and refinement were performed using the Siemens SHELXTL crystallographic software package [20]. Space group was assigned based on systematic absences and intensity statistics, and was confirmed by successful refinement. The structure was solved by direct methods [21] and refined by successive full-matrix least-squares techniques followed by difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located in calculated positions with 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

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 a crystal packing diagram of $[CH_2(NH_3)CH(NH_3)CH_3][CoPO_4]_2$ are shown in Fig. 1 and 2, respectively.

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 (calculated) (g cm^{-3})	2.386
μ(MoKα) (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 ($R_{int} = 0.0418$)
Data/restrains/parameters	941/0/82
Goodness of fit on F^2	1.185
Final R indices [$I > 2\sigma(I)$], $R1$, $wR2$[a]	0.0470, 0.1341
R indices (all data)	0.0491, 0.1361

[a] Weight, $w = \{\sigma^2 F_o^2 + (0.0845\rho)^2 + 1.0762\rho\}^{-1}$, where $\rho = \{F_0^2 + 2F_c^2\}/3$.

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

Atom	x/a	y/b	z/c	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 Selelcted 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)^{i}	1.955(3)
Co–O(3)^{ii}	1.985(3)	Co–O(3)^{iii}	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)^{vi}	2.310(5)		
O(1)–Co–O(2)^{i}	105.3(1)	O(1)–Co–O(3)^{ii}	108.8(1)
O(1)–Co–O(3)^{iii}	107.1(1)	O(2)^{i}–Co–O(3)^{ii}	106.4(1)
O(2)^{i}–Co–O(3)^{iii}	108.2(1)	O(3)^{ii}–Co–O(3)^{iii}	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^{iv}	134.3(2)
P–O(3)–Co^{ii}	118.5(2)	P–O(3)–Co^{v}	119.3(2)
Co^{ii}–O(1)–Co^{v}	114.6(1)	C(6)–C(5)–N(7)	103.0(5)
C(6)–C(5)–C(5)^{vi}	103.0(5)	N(7)–C(5)–C(5)^{vi}	109.6(4)

Symmetry transformations used to generate equivalent atoms: $^{i}x, -y+3/2, z-1/2$; $^{ii}-x+2, -y+1, -z$; $^{iii}-x+2, y+1/2; -z+1/2$; $^{iv}x, -y+3/2, z+1/2$; $^{v}-x+2, y-1/2, -z+1/2$; $^{vi}-x+1, -y, -z$.

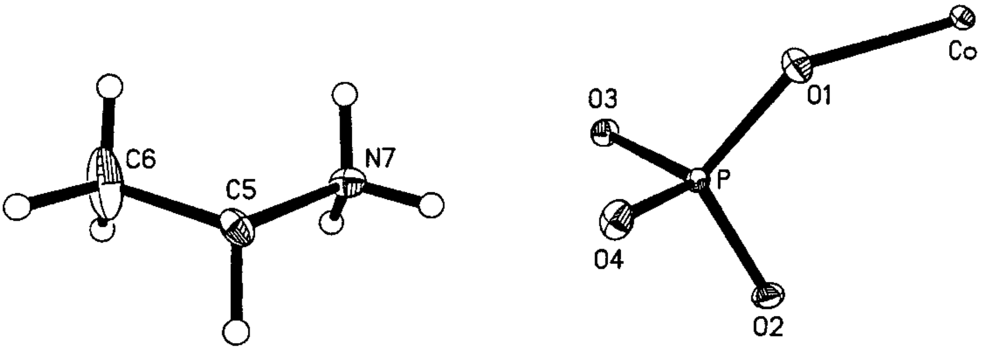

FIGURE 1 The asymmetric unit of [$CH_2(NH_3)CH(NH_3)CH_3$][$CoPO_4$]$_2$ showing the numbering scheme with thermal ellipsoids drawn at the 30% probability level.

As shown in Fig. 2, the crystal structure of the title compound possesses a novel layered structure with empty channels. The fundamental units of the crystal structure are tetrahedral CoO_4 and PO_4 groups. Combination of CoO_4 and PO_4 forms anionic cobalt phosphate layers with empty channels parallel to the *bc* crystallographic plane. Layers are stacked along the *a* axis with propanediammonium cations lying between every second layer. The framework structure of the cobalt phosphate 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 groups parallel to the *c* axis. This chain and a neighboring CoO_4 chain are linked through PO_4. Two oxygen atoms, O(1) and O(2), of each PO_4 bridge two adjacent Co atoms of a neighboring CoO_4 chain. One PO_4 oxygen atom is the common atom O(3) between two CoO_4 groups. The last oxygen atom O(4) of PO_4 is a terminal oxygen, which points towards the interlayer space. All Co and P atoms are 4-coordinated by O atoms. O(3) is 3-coordinated and each O(3) is shared by one P and two Co atoms.

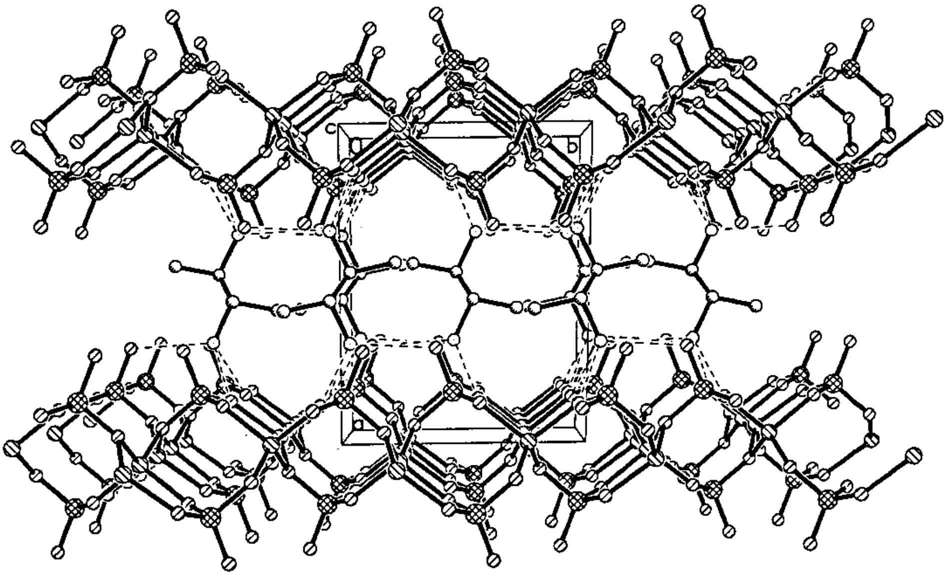

FIGURE 2 Crystal packing diagram of $[CH_2(NH_3)CH(NH_3)CH_3][CoPO_4]_2$ projected along the *c* axis.

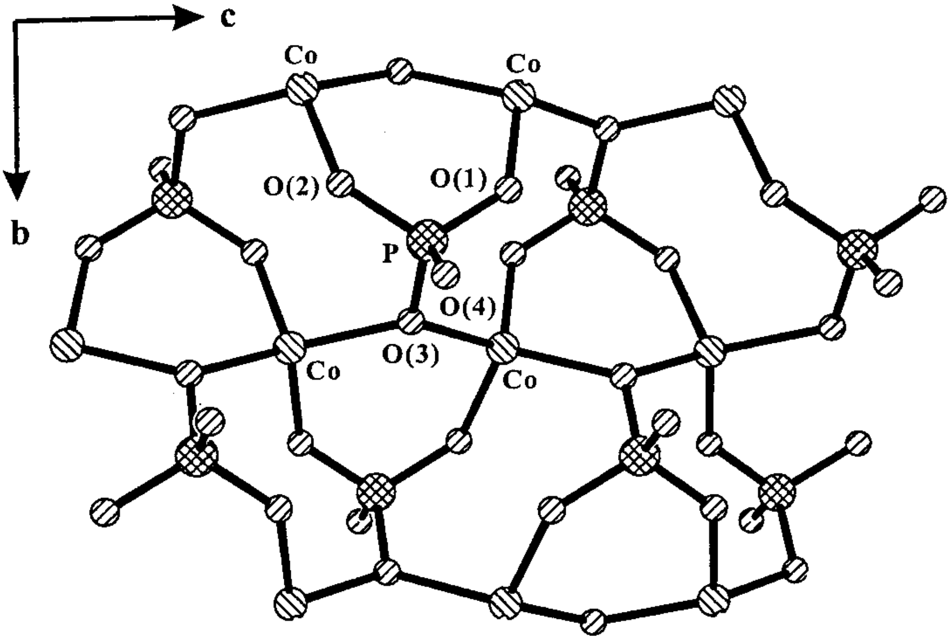

FIGURE 3 Framework of the $[CoPO_4]$ layer parallel to the *bc* plane.

The reduced 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. the templating agent, in the intralayer space. The function of the template is very important in the formation of the structure. The templating cation causes the crystal to be electrically neutral and the size of the cation, especially the N···N vector, decides the distance between layers. The attraction of cobalt phosphate layers and propane-1,2-diammonium templates is mainly ionic. There are many hydrogen bonds between layers and templating agent, which strengthen 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 structure shows the methyl group to be disordered to give a centric aggregate; thus the occupancy of the methyl group is 0.5.

Supplementary Material

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

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