

Layered cobalt phosphate grafted with hydrazinium ligands: $\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{N}_2\text{H}_5$

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The title compound has been hydrothermally synthesized from elemental cobalt, phosphoric acid, and hydrazine, and characterized by single crystal X-ray diffraction [crystal data: triclinic, $P\bar{1}$, $a=5.1393(6)$, $b=6.363(1)$, $c=11.293(1)$ Å, $\alpha=95.65(1)$, $\beta=96.874(9)$, $\gamma=92.79(1)^\circ$], IR, TGA, and magnetic measurement. The structure is made of neutral layers of corner-sharing PO_4 tetrahedra and dimers of edge-sharing 5- and 6-coordinate cobalt polyhedra. The hydrazinium cations, N_2H_5^+ , are coordinated as ligands on both sides of the layers and complete the octahedral coordination of the six-coordinate cobalt. The so-grafted layers are held together by strong and extensive hydrogen bonding. Thermally the compound is stable up to 360 °C, above which it decomposes in a single step to yield cobalt pyrophosphate. Magnetic measurements show paramagnetic Curie–Weiss behavior over the temperature range 5–300 K.

1 Introduction

Organically-templated transition metal phosphates show diverse structural chemistry and have kept the interest of synthetic chemists for years.¹ The exploration of these systems for new compounds with novel structures has been driven by their potential for application as redox catalysts, ion-exchangers, molecular sieves, *etc.*^{2,3} The hydrothermal approach is usually the method of choice in these syntheses and organic mono- and polyamines are generally used as templates. The role of the template is to direct structure formation and fill the “open” space in the framework. In a very few cases, such templates have also acted as ligands to the transition metal atoms. To the best of our knowledge, there are only five such examples, four are zinc phosphates with ligated 1,3-diaminopropane monocation,⁴ diethylenetriamine dication,⁵ diamino-guanidine monocation,⁵ or neutral 4,4'-bipy,⁶ and the fifth example is vanadium phosphate with coordinated ethylenediamine monocation.⁷ Here, we report the synthesis and structure of the first cobalt phosphate with similarly coordinated ligand derived from a carbon-free template, *i.e.* hydrazinium cations. The compound is the result of our continued exploratory synthesis of transition metal and mixed transition metal–aluminium phosphates and borophosphates with carbon-free templates, such as ammonia and/or ammonium cations, or hydrazine and its cations.⁸

2 Experimental

The title compound was initially obtained from a hydrothermal reaction designed to produce a hydrazine-templated cobalt borophosphate analogous to the first and, as yet, only known structure of an organically-templated transition metal borophosphate, that of the parent compound $\text{CoB}_2\text{P}_3\text{O}_{12}(\text{O}-\text{H})\cdot n\text{H}_2\text{O}$,⁹ a structure that we have also found for a number of divalent metals, such as Zn, Fe, Mn, Mg, Ni, *etc.* We have successfully developed a synthetic strategy using elemental transition metals as starting materials, instead of salts, for the hydrothermal reactions.¹⁰ Often, this turns out to be the only method for the synthesis of compounds with reduced or mixed-valent transition metals. This same approach was used in the synthesis of $\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{N}_2\text{H}_5$ for which elemental cobalt, boric acid, phosphoric acid, hydrofluoric acid, hydra-

zine, and water were mixed in molar ratio 1 : 5 : 4 : 3.5 : 2.5 : 200. The mixture was loaded in a Teflon-lined stainless steel autoclave and was heated at 120 °C for 3 d. After the stoichiometry of the compound was determined by single crystal X-ray diffraction it was synthesized more rationally without the boric and hydrofluoric acids. Thus, reaction of cobalt powder, phosphoric acid, hydrazine, and water in the ratio 1 : 4 : 2.5 : 200 (pH 3) at 120 °C readily provides single phase $\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{N}_2\text{H}_5$. The violet, plate-like crystals were filtered off, washed with water, ethanol, and acetone, and then dried under vacuum at room temperature. The formation of a single phase was confirmed by powder X-ray diffraction analysis of the product and comparison with a simulated pattern based on the structure determined from the single crystal studies.

Single crystal X-ray diffraction data (a hemisphere) were collected from a plate-like crystal of $\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{N}_2\text{H}_5$ (0.20 × 0.12 × 0.02 mm) on a CAD4 single crystal diffractometer with monochromated Mo-K α radiation at 21 °C up to $2\theta_{\text{max}}=50^\circ$. The data were corrected for absorption with the aid of three ψ -scans at different θ angles. The structure was solved by direct methods and refined on F^2 with the aid of the SHELXTL-V5.1 software package.¹¹ The positions of all hydrogen atoms were calculated and were refined riding on the atoms to which they are bonded. The final refinement with anisotropic thermal parameters for all non-hydrogen atoms converged to $R1=4.57$, $wR2=13.85\%$ for the observed 1168 reflections ($I \geq 2\sigma_I$) and 127 variables. The maximum positive and negative peaks in the final difference Fourier map were +1.10 and -1.03 e \AA^{-3} , respectively. Details of the data collection and structure refinement are given in Table 1, while the atomic positional and thermal parameters and important distances and angles are listed in Tables 2 and 3, respectively.

CCDC reference number 1145/239. See <http://www.rsc.org/suppdata/jm/b0/b004753h/> for crystallographic files in .cif format.

The magnetization of 71 mg of the compound was measured on a Quantum Design MPMS SQUID magnetometer at a field of 3 T in the temperature range 5–300 K. Thermogravimetry was performed in a flow of air with a heating rate of 5 °C min⁻¹ from room temperature to 800 °C on a CAHN TG-131 unit. IR spectra were taken in the region 400–4000 cm⁻¹ on pellets pressed with KBr.

Table 1 Crystallographic data for $\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{N}_2\text{H}_5$

$M/g\text{ mol}^{-1}$	341.87
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
$a/\text{\AA}$	5.1393(6)
$b/\text{\AA}$	6.363(1)
$c/\text{\AA}$	11.293(1)
$\alpha/^\circ$	95.65(1)
$\beta/^\circ$	96.874(9)
$\gamma/^\circ$	92.79(1)
$V/\text{\AA}^3$	364.18(8)
Z	2
Temperature/K	293
$\lambda(\text{Mo-K}\alpha)/\text{\AA}$	0.71073
μ/mm^{-1}	5.021
$\theta_{\text{max}}/^\circ$	25
Index ranges	$\pm h, k, \pm l$
Total no. of reflections	1395
No. of unique reflections/parameters	1270/127
$R1, wR2 (I \geq 2\sigma_I)$ (%)	4.57, 13.85
$R1, wR2$ (all data) (%)	4.87, 14.29

3 Results and discussion

Synthesis

One of the objectives in the search for new materials with open framework structures is that the initially templated compounds can be de-templated, *i.e.* can have their templates removed after synthesis, without destruction of the framework. The inside surface and volume of such template-free materials can be then effectively utilized for a variety of catalytic applications. However, the presence of carbon in the templates often leads to higher template-removal temperatures, at which the framework can collapse. In order to lower that temperature we have explored the possibilities of using carbon-free templates. Ammonia, the simplest of them, seems to work quite well for templating cobalt-substituted aluminophosphates.⁸ Hydrazine, of course, is the next homologue and was used for the synthesis of the present compound.

As might be expected, the pH of the reaction mixture is quite important in the synthesis of $\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{N}_2\text{H}_4$, since one of the starting materials is elemental cobalt. The compound only forms in the pH range 2–4. More acidic conditions yield clear solutions, while at more basic pH, the starting cobalt powder remains unreacted. The presence of hydrazine in the product was confirmed by elemental analysis for nitrogen. The content obtained by the combustion technique, at 7.91 wt%, compares very well with the calculated value of 8.19 wt%.

Structure description

The structure of $\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{N}_2\text{H}_4$ is two-dimensional, composed of neutral layers of the same formula (Fig. 1). The

layers contain cobalt in two different coordination environments, trigonal bipyramidal, and octahedral. Cobalt is well known to coordinate in a variety of polyhedra in its phosphates, such as octahedra, trigonal bipyramids, square pyramids, tetrahedra, *etc.*,¹² and, furthermore, compounds often contain cobalt in two or more different coordination environments at the same time. The trigonal bipyramid around Co1 is made up of oxygen atoms only, the waist from O1, O4, and O5, with O3 and O6 at the apices (Fig. 2). The octahedron around Co2, on the other hand, is composed of five oxygen atoms (O1, O2, O4, O5, and O6) and a nitrogen, N1, from the hydrazinium cation (Fig. 2). The two types of polyhedra share the edge O4–O6 and are also connected to each other *via* the shared corners O1 and O5 (Fig. 2 and 3). The structure can also be viewed as dimers of edge-sharing octahedra–trigonal bipyramids that are connected to each other *via* shared corners. Due to this extensive sharing of edges and corners, most of the oxygen atoms in the structure are three-bonded to one phosphorus and two cobalt atoms. Thus, only O2 and O3 are two-bonded within the framework of the layers, while O1, O4, O5, and O6 are all three-bonded. The Co–O distances range from 1.978(4) to 2.204(4) Å (Table 3). As might be expected, the distances in the octahedron are somewhat longer than those in the trigonal bipyramid. The Co–N distance, 2.150(5) Å, is comparable with M–N distances observed in metal–hydrazine complexes.¹³

There are two different phosphate groups in the structure, PO_4^{3-} and H_2PO_4^- . All four oxygen atoms around P2 and only two oxygen atoms around P1 are coordinated also to cobalt atoms. The remaining two oxygens, O7 and O8, around P1 are hydroxyl groups (Fig. 2). They point between the layers towards the same groups (related by an inversion center) from the adjacent layer. The interlayer pairs O7–O7 and O8–O8 provide extensive and very strong hydrogen bonding between the layers with very short distances of 2.479(8) and 2.526(8) Å, respectively (Fig. 1 and Table 3). These short distances are most likely due to the fact that each pair is bonded *via* two hydrogen atoms. This extensive and strong hydrogen bonding between the layers gives the structure relatively good overall stability. The P–O distances are well within the expected limits with the two distances to the hydroxyl groups and the distances to the three-bonded oxygens being the longest (Table 3).

The hydrazinium cation $[\text{NH}_2\text{--NH}_3]^+$ is coordinated to Co2 *via* the pair of electrons at the nonprotonated end with an angle of 126.0(4)° at that nitrogen atom, N1 (Fig. 2 and Table 3). This angle compares well with those of molecular transition metal complexes with hydrazinium ligands.¹⁴ There are no hydrogen bonds from N1, while the protonated nitrogen, on the other hand, is extensively hydrogen bonded to four oxygen atoms, all from the same layer (Fig. 1 and Table 3). The N–N distance, 1.382(8) Å, is somewhat shorter than those of hydrazinium ligands in some other transition

Table 2 Atomic coordinates and equivalent displacement parameters for $\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{N}_2\text{H}_5$

Atom	x	y	z	U_{eq}
Co1	0.3183(1)	0.2709(1)	0.60149(6)	0.0108(3)
Co2	0.7773(1)	0.0368(1)	0.68911(6)	0.0107(3)
P1	0.3349(3)	0.2145(2)	0.8564(1)	0.0123(4)
P2	–0.2239(2)	0.2378(2)	0.4405(1)	0.0077(4)
O1	0.0680(7)	0.1868(5)	0.4417(3)	0.0105(8)
O2	0.5963(7)	0.2503(6)	0.8080(4)	0.0171(8)
O3	0.2821(7)	0.5784(5)	0.6350(3)	0.0129(8)
O4	0.7131(7)	0.2883(5)	0.5698(3)	0.0101(8)
O5	0.1140(7)	0.2076(6)	0.7512(3)	0.0117(8)
O6	0.4002(7)	–0.0444(5)	0.6176(3)	0.0111(8)
O7	0.2969(8)	0.4008(7)	0.9495(4)	0.025(1)
O8	0.3176(8)	0.0068(7)	0.9152(4)	0.025(1)
N1	0.763(1)	–0.2090(9)	0.8063(5)	0.033(1)
N2	0.917(1)	–0.381(1)	0.8075(7)	0.053(2)

Table 3 Important distances (Å) and angles (°) in $\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{N}_2\text{H}_5$

Co1–	O1	2.094(4)	P1–	O2	1.525(4)
	O3	1.978(4)		O5	1.537(4)
	O4	2.102(3)		O7	1.541(4)
	O5	2.155(4)		O8	1.540(4)
	O6	2.091(3)	P2–	O1	1.549(4)
	Co2	2.9723(10)		O3	1.534(4)
Co2–	O1	2.194(4)		O4	1.539(4)
	O2	2.139(4)		O6	1.535(3)
	O4	2.204(4)	N1–	N2	1.382(8)
	O5	2.011(4)			
	O6	2.030(3)			
	N1	2.150(5)			
H-bonds					
O7–	O7	2.479(8)	N2–	O2	2.804(8)
O8–	O8	2.526(8)		O3	2.863(7)
				O5	2.893(7)
				O7	2.874(8)
<hr/>					
O3–Co1–O6		163.64(15)	O5–Co2–O1		98.25(14)
O3–Co1–O1		103.81(14)	O6–Co2–O1		92.33(14)
O6–Co1–O1		91.81(14)	O2–Co2–O1		175.39(13)
O3–Co1–O4		97.23(14)	O5–Co2–O4		84.22(13)
O6–Co1–O4		81.31(13)	O6–Co2–O4		80.25(13)
O3–Co1–O5		91.08(15)	O2–Co2–O4		82.23(14)
O6–Co1–O5		79.03(14)	O1–Co2–O4		96.17(13)
O1–Co1–O4		111.03(14)	N1–Co2–O1		88.95(18)
O1–Co1–O5		109.24(14)	N1–Co2–O4		169.41(19)
O4–Co1–O5		135.39(14)	N1–Co2–O5		104.3(2)
O5–Co2–O6		162.06(15)	N1–Co2–O6		90.3(2)
O5–Co2–O2		85.91(14)	N1–Co2–O2		91.94(17)
O6–Co2–O2		83.15(14)	Co2–N1–N2		126.0(4)

metal complexes, such as *trans*-(N_2H_5) $_2\text{FeCl}_4$, which has distances of 1.480(4) and 1.424(3) Å, and (N_2H_5) CuCl_3 with $d_{\text{N-N}} = 1.452$ Å.¹⁴ The two hydrazinium cations in the iron complex show very different distances, an indication that the cations are quite flexible and the N–N distance can vary over a wide range. Thus, the shorter distance in the cobalt phosphate

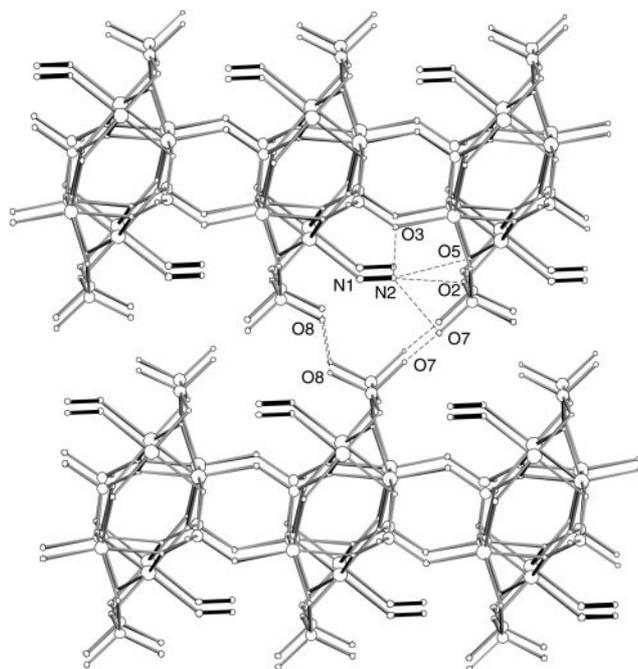


Fig. 1 The structure of $\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{N}_2\text{H}_5$ viewed along the a axis parallel to the layers (Co, P, and O/N are shown as large, medium, and small circles, respectively). The layers are stacked along c (nearly vertical on the drawing). The nitrogen atoms of the hydrazine and the oxygen atoms with hydrogen bonds (broken lines) are labeled. The hydrogen bonds between the terminal hydroxyl group and oxygen atoms O7 and O8 provide the bonding between the layers.

should not be a surprise, bearing in mind that the non-coordinated nitrogen, N2, is well “locked” in position by four relatively short hydrogen bonds. Its position does not depend only on the position of the other nitrogen, N1, as in all molecular complexes, but also on the position of the surrounding oxygen atoms, and the N–N distance is defined by optimization of all five of these interactions.

The IR spectrum of $\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{N}_2\text{H}_5$ shows broad vibrations for both the hydrogen bonded –OH groups of H_2PO_4^- between 2920 and 3300 cm^{-1} and the $-\text{NH}_3^+$ groups of the hydrazinium species at 2636 cm^{-1} . The phosphate bands are in the region 800–1200 cm^{-1} , as expected. The peak at

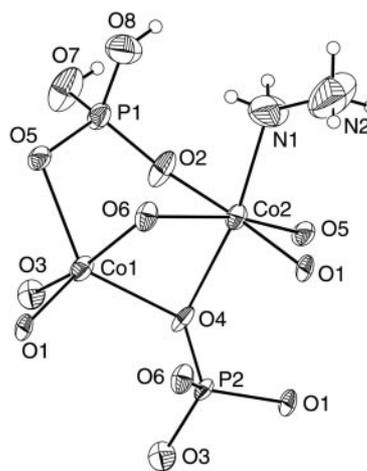


Fig. 2 The basic building unit of the structure of $\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{N}_2\text{H}_5$ (almost the asymmetric unit) showing the two different coordination polyhedra around the cobalt atoms, nearly trigonal bipyramidal for Co1 (O3 and O6 are the apices) and octahedral around Co2. The two polyhedra share the edge O4–O6, while O1 and O5 are shared corners. Atoms O1, O4, O5, and O6 are three-bonded oxygens shared between two cobalts and a phosphorus atom. All non-hydrogen atoms are drawn with thermal ellipsoids at the 70% probability level.

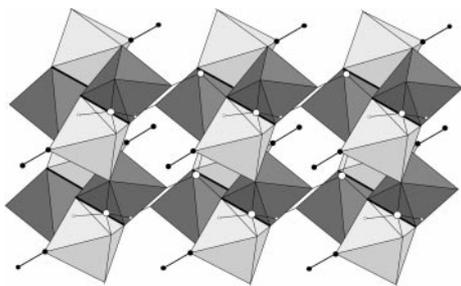


Fig. 3 A polyhedral view of a layer of $\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{N}_2\text{H}_5$ with only the cobalt polyhedra shown. The viewing direction is normal to the layer. The thicker line shows the shared edges between the two types of polyhedra. Large and small open circles represent phosphorus and hydroxyl oxygen atoms, respectively, while the filled circles are the nitrogen atoms of the hydrazine.

999 cm^{-1} can be assigned to the N–N stretching mode of the hydrazinium cation, since the frequency of that stretch for free N_2H_5^+ is 965 cm^{-1} and, for the coordinated species, it is known to shift towards 1000 cm^{-1} .^{14,15}

The thermogravimetric analysis carried out in a flow of air showed a single step in the temperature range $360\text{--}480^\circ\text{C}$ with a weight loss of about 13%. The final product was cobalt pyrophosphate, $\text{Co}_2\text{P}_2\text{O}_7$.¹⁶ The calculated weight loss associated with the loss of N_2H_4 and H_2O in the process $\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{N}_2\text{H}_5 \rightarrow \text{Co}_2\text{P}_2\text{O}_7 + 3\text{H}_2\text{O} + \text{N}_2\text{H}_4$ (as NO_x and H_2O) is 14.6 wt.%.

The magnetic susceptibility of the compound showed standard Curie–Weiss behavior. A plot of $1/\chi$ versus temperature provided $\mu_{\text{eff}} = 7.62\ \mu_{\text{B}}$ and $\theta = -33\text{ K}$, an indication of antiferromagnetic interactions. The effective moment compares well with the spin-only moment calculated for two cobalt(II) atoms in weak field, $6.928\ \mu_{\text{B}}$.

The existence of this layered compound, $\text{Co}_2(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{N}_2\text{H}_5$, grafted with ligated hydrazinium cations is further proof that some amines, both with and without carbon, under appropriate conditions can ligate the transition metal in phosphates with extended structures, rather than just “fill holes” as is usually observed. Although the examples of such behavior are only very few,^{4–7} they clearly point towards the potential to extend the structural chemistry of transition metal phosphates into phases where the amines act as linking groups. This possibility can be and has been further utilized by using organic linkers with both phosphonic and amino groups, such as aminoethylphosphonate in $\text{Zn}(\text{O}_3\text{PC}_2\text{H}_4\text{NH}_2)$, which has a zeolite-like structure, and phosphonated amino acids in $\text{Zn}\{\text{O}_3\text{PCH}_2\text{CH}(\text{NH}_3)\text{COO}\}$ and $\text{Zn}\{\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}(\text{NH}_3)\text{COO}\}$.¹⁷

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