

A novel layered bimetallic phosphite intercalating with organic amines: Synthesis and characterization of $\text{Co}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}$

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Abstract

A new layered cobalt–zinc phosphite, $\text{Co}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}$ has been synthesized in the presence of ethylenediamine as the structure-directing agent. The compound crystallizes in the monoclinic system, space group *Cc* (No. 9), $a = 18.2090(8)$, $b = 9.9264(7)$, $c = 15.4080(7)$ Å, $\beta = 114.098(4)^\circ$, $V = 2542.3(2)$ Å³, $Z = 4$, $R = 0.0323$, $wR = 0.0846$. The structure consists of ZnO_4 tetrahedra, CoO_6 octahedra and HPO_3 pseudopyramids through their vertices forming bimetallic phosphite layers parallel to the *ab* plane. Organic cations, which reside between the inorganic layers, are mobile and can be exchanged by NH_4^+ cations without the collapse of the framework. © 2005 Elsevier Inc. All rights reserved.

Keywords: Hydrothermal synthesis; Layer; Cobalt; Zinc phosphite; Ion exchange

1. Introduction

The synthesis of new crystalline microporous materials remains a highly active field due to their commercial applications in catalysis, ion exchange, and separation [1,2]. The discovery of aluminophosphate molecular sieves in 1982 has spurred widespread enthusiasm in making non-alumino-silicate-based zeolitic materials [3]. Recently, many research activities have focused on the synthesis of open-framework metal phosphites. Compared to the tetrahedral phosphate group, phosphite possesses a characteristic pseudopyramidal geometry, which might lead to a new family of frameworks quite different from those found in 4-connected zeolitic networks. Notable examples include $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Cr}(\text{HPO}_3)\text{F}_3]$ with a ladder-like structure [4], $(\text{C}_6\text{H}_5\text{N}_2)\text{Zn}(\text{HPO}_3)$ containing helical chains [5], and $[\text{NH}_2(\text{CH}_2)_2\text{NH}_2]_{0.5} \cdot \text{ZnHPO}_3$ with an unprecedented architecture of two interpenetrated, independent mixed inorganic–organic network [6].

Microporous materials containing heterometals are of particular interest for their potential catalytic applications. Many works to date have concentrated on the doping of cobalt ions into a number of open-framework inorganic solids such as aluminum, gallium and zinc phosphates

[7–10]. For example, CoAPO-18 and DAF-4 have been shown to be effective catalysts on the conversion of methanol into light hydrocarbons [11,12]. We have been exploring the possibility of incorporating cobalt into zinc phosphite framework in the presence of organic amines as the structure-directing agents, with the aim of preparing open-framework cobalt–zinc phosphites. Although many two- and three-dimensional zinc phosphites have been prepared and characterized by now [13–25], there are only three examples of heterometal-containing open-framework zinc phosphites reported in the literature, namely, $\text{Ni}(\text{DETA})(\text{H}_2\text{O})\text{Zn}_2(\text{HPO}_3)_3$, $[\text{M}(\text{C}_6\text{N}_4\text{H}_{18})][\text{Zn}_3(\text{HPO}_3)_4]$ ($M = \text{Ni}, \text{Co}$) and $(\text{C}_4\text{N}_2\text{H}_{12})[\text{Zn}_{(3-x)}\text{Co}_x(\text{HPO}_3)_4(\text{H}_2\text{O})_2]$ [26–28]. All of them possess three-dimensional frameworks.

In the present work, we describe the synthesis, structure and characterization of a new cobalt–zinc phosphite, $\text{Co}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}$. This compound possesses a unique layered structure with the ethylenediamine molecule acting as the structure-directing agent.

2. Experimental

2.1. Synthesis and characterization

The cobalt–zinc phosphite $\text{Co}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}$ was synthesized in the presence of ethylenediamine as the

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structure-directing agent. In a typical synthesis, a mixture of 1.0 g of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, 1.85 ml of H_3PO_3 (50 wt%), 0.271 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.23 ml of ethylenediamine and 40 ml of H_2O in a molar ratio of 1: 3: 0.25: 0.75: 500 was stirred under ambient conditions. The resulting clear solution, with a pH of ~ 3 , was placed in a polypropylene bottle and heated at 100°C for 24 h, followed by a slow cooling to room temperature. The solid product, consisting of single crystals in the form of light-purple prisms (Fig. 1), was recovered by filtration, washed with distilled water and dried in air (15% yield based on zinc). The powder X-ray diffraction (XRD) pattern of the crystals was in good agreement with the one simulated on the basis of the single-crystal structure, indicating the phase purity of as-synthesized compound. The inductively coupled plasma (ICP) analysis of the product gave the contents of Co 6.22 wt% (calcd 6.31 wt%) and Zn 27.15 wt% (calcd 27.98 wt%), indicating a Co:Zn ratio of 1:4. Elemental analysis confirmed the stoichiometry. Anal. Found: C, 2.51%; H, 2.48%; N, 2.93%. Calcd: C, 2.57%; H, 2.59%; N, 3.00%.

Scanning electronic microscopy (SEM) was carried out on a Hitachi S-900 electron microscope operating at 8 kV. IR spectra (KBr pellets) were recorded on a Nicolet Magna 560 spectrometer. Powder XRD data were obtained using an M03X-HF22 (MAC Science Co.) with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The step size was 0.02° and the count time was 4 s. The thermogravimetric analysis was performed on a Thermoplus TG 8120 (Rigaku) analyzer under flowing air atmosphere from 30 to 600°C . Diffusive reflection spectrum (DRS) was taken on a MCPD-2000 UV–Vis diffuse reflection spectrometer (Ohtsuka Electronics) at room temperature. The spectrum was recorded against BaSO_4 white reflectance standard in the range 350–800 nm.

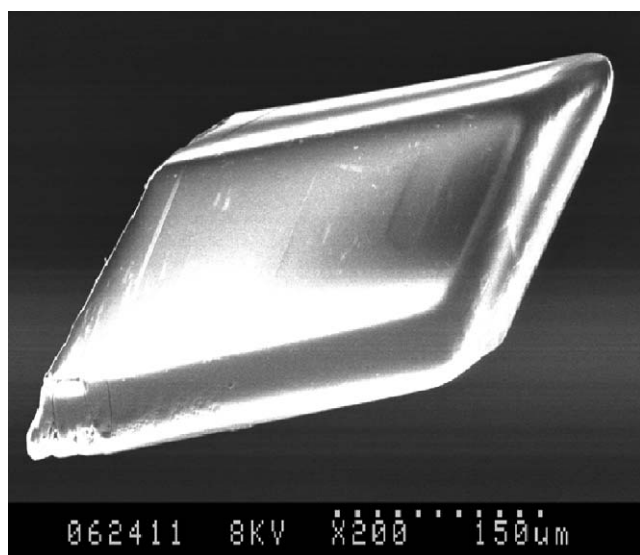


Fig. 1. SEM image showing the morphology of a single crystal of as-synthesized compound.

Magnetic susceptibility data were collected at 10 kG over the temperature range 2–300 K with a SQUID MPMS-7 magnetometer manufactured by Quantum Design.

2.2. Crystal structure determination

A suitable single crystal of as-synthesized compound with the dimensions of $0.35 \times 0.30 \times 0.22 \text{ mm}$ was carefully selected under an optical microscope and glued to a thin glass fiber with epoxy resin. Crystal structure determination by X-ray diffraction was performed on a Siemens SMART CCD diffractometer with graphite-monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation in the ω and ϕ scanning mode at room temperature. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELX97 program package [29,30]. The zinc, cobalt and phosphorus atoms were first located, and the carbon, nitrogen, oxygen atoms and hydrogen atoms in the P–H groups were found in the final difference Fourier map. The hydrogen atoms residing in the ethylenediamine molecules were placed geometrically. All none hydrogen atoms were refined anisotropically. Experimental details for the structural determinations of the compound are presented in Table 1. Selected bond distances are listed in Table 2. CCDC reference number 281621.

2.3. Ion-exchange experiment

An ion-exchange experiment was performed by stirring 110 mg samples of the as-synthesized compounds in 10 ml of 1 M aqueous solution of ammonia chloride at 60°C for 24 h. Following this treatment, the exchanged solids were recovered, washed with water and dried in air.

Table 1
Crystal data and structure refinement for $\text{Co}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}$

Empirical formula	$\text{C}_2\text{H}_{24}\text{N}_2\text{CoO}_{22}\text{P}_6\text{Zn}_4$
Formula weight	934.46
Temperature (K)	293(2)
Wavelength (\AA)	0.71073
Crystal system	Monoclinic
Space group	Cc
a (\AA)	18.2090(8)
b (\AA)	9.9264(7)
c (\AA)	15.4080(7)
β (deg)	114.096(4)
Volume (\AA^3)	2542.3(2)
Z	4
ρ_{calc} (g cm^{-3})	2.441
μ (mm^{-1})	4.831
Reflections collected	9571
Independent reflections	4047 [$R(\text{int}) = 0.0245$]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0323$, $wR_2 = 0.0846$
R indices (all data)	$R_1 = 0.0338$, $wR_2 = 0.0858$

Table 2
Select bond lengths (Å) for $\text{Co}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}^{\text{a}}$

Zn(1)–O(12)	1.898(5)	P(1)–O(7)	1.515(5)
Zn(1)–O(9)	1.935(4)	P(1)–O(6)	1.515(5)
Zn(1)–O(8)	1.943(4)	P(1)–O(8)	1.529(4)
Zn(1)–O(3)	1.980(5)	P(2)–O(12)	1.501(5)
Zn(2)–O(6)	1.928(5)	P(2)–O(18)	1.508(4)
Zn(2)–O(14)#1	1.944(5)	P(2)–O(2)	1.525(5)
Zn(2)–O(18)#2	1.945(4)	P(3)–O(11)	1.499(5)
Zn(2)–O(1)	1.963(6)	P(3)–O(13)	1.513(5)
Zn(3)–O(16)	1.899(5)	P(3)–O(5)	1.532(4)
Zn(3)–O(10)#1	1.921(5)	P(4)–O(10)	1.507(5)
Zn(3)–O(5)	1.937(4)	P(4)–O(15)	1.517(5)
Zn(3)–O(4)#1	1.960(5)	P(4)–O(3)	1.529(5)
Zn(4)–O(15)	1.923(5)	P(5)–O(14)	1.506(6)
Zn(4)–O(17)#3	1.930(4)	P(5)–O(9)	1.513(5)
Zn(4)–O(13)	1.932(5)	P(5)–O(4)	1.525(5)
Zn(4)–O(2)	1.959(6)	P(6)–O(17)	1.513(5)
Co(1)–O(7)#4	2.038(5)	P(6)–O(16)	1.524(5)
Co(1)–O(11)	2.038(5)	P(6)–O(1)	1.533(5)
Co(1)–OW4	2.109(6)	N(1)–C(1)	1.476(1)
Co(1)–OW1	2.115(6)	N(2)–C(2)	1.476(1)
Co(1)–OW2	2.178(7)	C(1)–C(2)	1.405(1)
Co(1)–OW3	2.197(6)		

^aSymmetry transformations used to generate equivalent atoms: #1 $x, y-1, z$; #2 $x-1/2, y-1/2, z$; #3 $x+1/2, y+1/2, z$; #4 $x+1/2, y-1/2, z$; #5 $x, y+1, z$; #6 $x-1/2, y+1/2, z$.

3. Results and discussion

3.1. Description of crystal structure

As seen in Fig. 2, the asymmetric unit contains 37 independent non-hydrogen atoms, of which 33 atoms belong to the framework and the remaining atoms to the guest molecules. There are four crystallographically independent Zn atoms, one Co atom and six P atoms in the asymmetric unit. The Zn atoms are all tetrahedrally coordinated by oxygen atoms with Zn–O bond lengths in the range of 1.898(5)–1.980(5) Å. The Co atom is octahedrally coordinated with two framework oxygen atoms and four oxygen atoms from the water ligands. The Co atom makes two Co–O–P linkages with adjacent P atoms and the bond distances Co–O vary from 2.038(5) to 2.197(6) Å. Of the six crystallographically distinct P atoms, P(2), P(4), P(5) and P(6) each share three oxygen atoms with adjacent Zn atoms [P–O: 1.501(5)–1.533(5) Å], with the fourth ligand being a terminal P–H bond. P(1) and P(3) each share two oxygen atoms with adjacent Zn atoms and one oxygen atom with adjacent Co atoms [P–O: 1.499(5)–1.532(4) Å], with the fourth ligand being a terminal P–H bond.

The framework consists of ZnO_4 tetrahedra, CoO_6 octahedra and HPO_3 pseudopyramids linked through their vertices forming an infinite layer parallel to the ab plane, as shown in Fig. 3. The two-dimensional framework can be conceptually built by the following procedures. Firstly, the connectivity of the strictly alternating ZnO_4 tetrahedra and HPO_3 pseudopyramids results in infinite layers with 4-, 8-

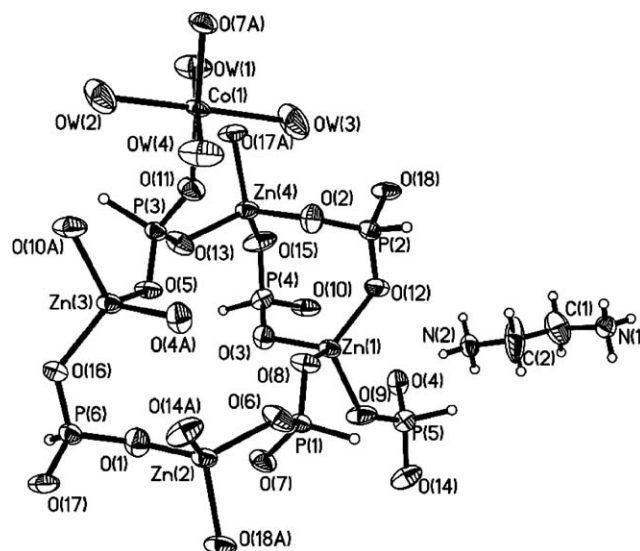


Fig. 2. Asymmetric unit of $\text{Co}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}$ (50% thermal ellipsoids) showing the atomic labeling scheme.

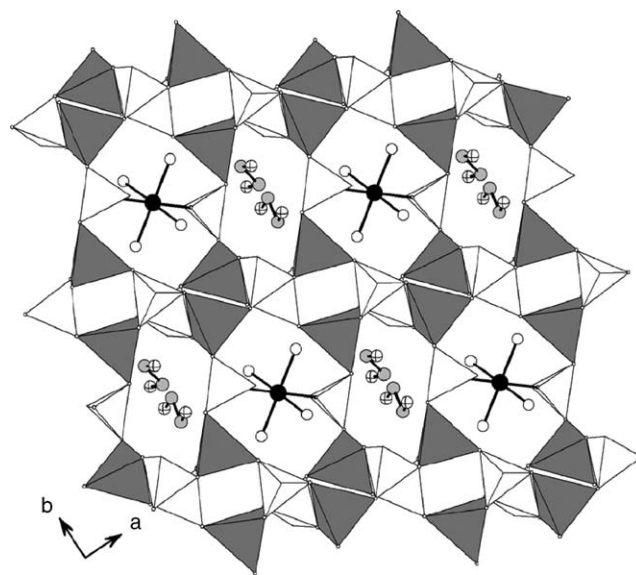


Fig. 3. View of the 12-ring windows encapsulating $[\text{Co}(\text{H}_2\text{O})_4]^{2+}$ complexes in the layered structure. ZnO_4 tetrahedra, medium gray; HPO_3 pseudopyramids, white.

and 12-membered ring. Then, the $\text{Co}(\text{H}_2\text{O})_4$ complexes are encapsulated in the center of the 12-ring windows, forming the macroanionic inorganic layer. The inorganic phosphite layers are stacked along the [001] direction in an ABAB sequence, as shown in Fig. 4.

To balance the negative electrostatic charge of the inorganic framework, the ethylenediamine molecules should be diprotonated. They are inserted between the inorganic layers and interact with the framework through extensive hydrogen bonds. The six hydrogen atoms on N atoms (H7, H8, H9 on N1, and H10, H11, H12 on N2) act with the framework oxygen atoms, with the $\text{H}\cdots\text{O}$

distances between 1.93 and 2.28 Å. Table 3 lists a summary of the H-bonding information.

Compared with other layered metal phosphites, the structure is novel in the sense that it represents the first example of two-dimensional open-framework phosphite containing heterometals in the framework. One intriguing feature of the compound is its closely structural relation to the known zinc phosphite $\text{Zn}(\text{DETA})\text{Zn}_2(\text{HPO}_3)_3$, where a similar zinc phosphite layer with 4.8.12-net encapsulating metal complexes was also observed [31]. The main difference between the two structures is that, in the case of $\text{Zn}(\text{DETA})\text{Zn}_2(\text{HPO}_3)_3$, the organic amines attached directly to the zinc phosphite layer and forms a neutral inorganic–organic hybrid framework. While in the instance of $\text{Co}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}$, the diprotonated organic amines are intercalating between the macroanionic zinc phosphite layers and interact with the inorganic framework through hydrogen bonds.

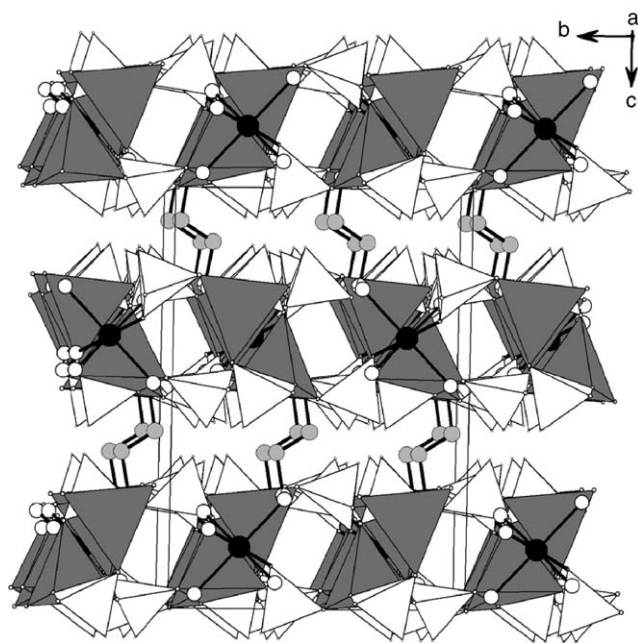


Fig. 4. View of the structure along the [100] direction showing the inorganic layers intercalated with organic cations.

Table 3
Hydrogen bonds (Å and degree) between ethylenediamine and framework oxygen atoms in $\text{Co}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}$ ^a

D–H...A	d(D–H)	d(H...A)	d(D...A)	<D–H...A
N1–H7...O5#1	0.89	2.03	2.847(8)	151.4
N1–H8...O7#1	0.89	2.23	2.954(8)	138.7
N1–H9...O7#1	0.89	1.96	2.845(7)	171.7
N2–H10...O4	0.89	1.93	2.803(8)	165.8
N2–H11...O8#2	0.89	2.02	2.908(8)	174.7
N2–H12...O11#2	0.89	2.28	2.993(8)	136.5

^aSymmetry transformations used to generate equivalent atoms: #1 $x, -y+2, z-1/2$; #2 $x, y+1, z$.

The role of $\text{Co}(\text{H}_2\text{O})_4$ complex is subtle and deserves further discussion. It is well known that metal ions, metal clusters and metal complexes can be trapped at the free voids of open-framework solids such as phosphates and germanates [32–34]. Similar to the role of organic amines in directing the formation of particular open frameworks, these inorganic species, which are chemically bonded to the framework oxygen atoms, also aid the formation of host frameworks and play a structural role in stabilizing these frameworks. Since Ni atom is the congener of Co atom, it may also possibly be used in the formation of such bimetallic phosphite layer. By using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ instead of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, but otherwise similar synthesis conditions, a light-green nickel-zinc phosphite compound was successfully isolated. The powder XRD pattern (Fig. 5a) of this compound is in agreement with the simulated XRD pattern (Fig. 5b) derived from structure analysis data of $\text{Co}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}$, indicating that they may possess a similar layered structure. IR spectrum of the compound is also similar to that of $\text{Co}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}$. Chemical composition analysis gives the content of Ni—6.17 wt%, Zn—26.63 wt%, C—2.52 wt%, N—2.96 wt% and H—2.49 wt%, which indicates the empirical formula $\text{Ni}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}$.

3.2. IR and DRS spectra

The IR spectrum shows the typical sharp peak for P–H groups at 2410 cm^{-1} . The bands in the region $1480\text{--}1650\text{ cm}^{-1}$ are characteristic of ethylenediamine molecules. The bands at 1120 and 1010 cm^{-1} are associated

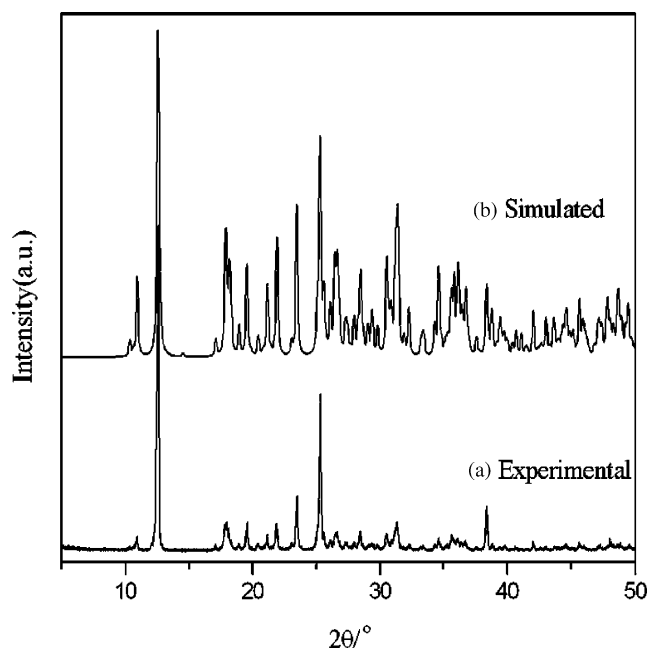


Fig. 5. Experimental XRD pattern of (a) as-synthesized nickel-containing compound and simulated XRD pattern derived from (b) crystal structure data of $\text{Co}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}$.

with the asymmetric stretching vibration of P–O bonds, and the band at 584 cm^{-1} is related to the bending vibration of P–O bonds.

The DRS spectrum exhibits three bands at 471, 493 and 535 nm in the visible region. These absorptions have also been observed in $\text{CoAlP}_2\text{O}_8 \cdot \text{C}_2\text{N}_2\text{H}_9$ for Co^{2+} cations and are believed to arise from the $d-d$ transition of octahedrally coordinated Co^{2+} with a d^7 configuration [35]. The presence of Co ions in the framework is also reflected by the light purple color of the compound.

3.3. Thermogravimetric analysis

Initial thermogravimetric analysis shows a three-step weight loss for a crystalline sample (Fig. 6). The initial weight loss between 110 and 230 °C corresponds to the loss of four water ligands per formula unit (observed, 7.77%; expected, 7.71%). The next two steps occurring between 270 and 530 °C are due to the decomposition of ethylenediamine molecules (observed, 6.40%; expected, 6.43%). To examine the thermal stability of this compound in the absence of water ligands, another sample was heated at 200 °C for 2 h. Powder XRD measurement for the dehydrated product shows that the structure collapses and an unidentified phase is formed.

3.4. Magnetic susceptibility

The molar magnetic susceptibility χ_m increases with decreasing temperature in the range studied, as shown in Fig. 7. The thermal evolution of χ_m follows the Curie–Weiss law at temperature above 40 K, with $C_m = 1.63\text{ cm}^3\text{ K mol}^{-1}$ and $\theta = -20.71\text{ K}$. The value for $\chi_m T$ decreases from $1.52\text{ cm}^3\text{ K mol}^{-1}$ at 300 K to $0.60\text{ K cm}^3\text{ K mol}^{-1}$ at 2 K, indicating the existence of antiferromagnetic interactions. The magnetic moment at

300 K (μ_{eff}) per mole of cobalt atom, determined from the equation $\mu_{\text{eff}} = 2.828(\chi_m T)^{1/2}$, is $3.49\ \mu_B$, in agreement with the expected spin-only value of Co(II) in the high spin state ($3.87\ \mu_B$).

3.5. Ion-exchange experiment

Ion-exchange behavior of the compound was examined by immersing crystalline samples in a solution of ammonia chloride (1.0 M) for 1 d. The powder XRD patterns of the original starting compound (Fig. 8a) and the NH_4^+ exchanged product (Fig. 8b) show similar peak intensity

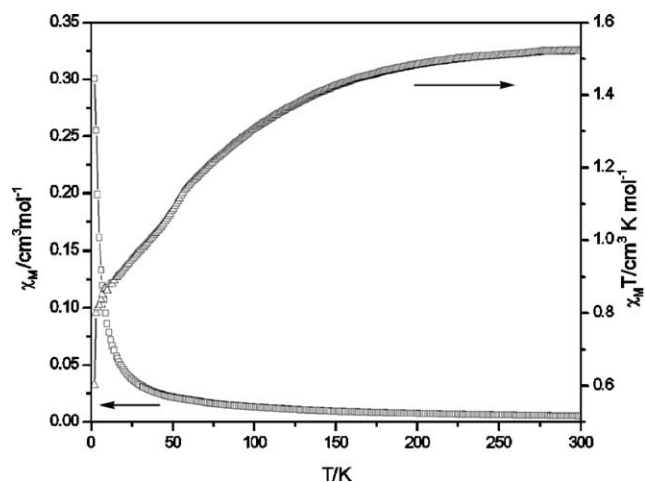


Fig. 7. Thermal evolution of the molar magnetic susceptibility χ_m and the product $\chi_m T$ for $\text{Co}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}$.

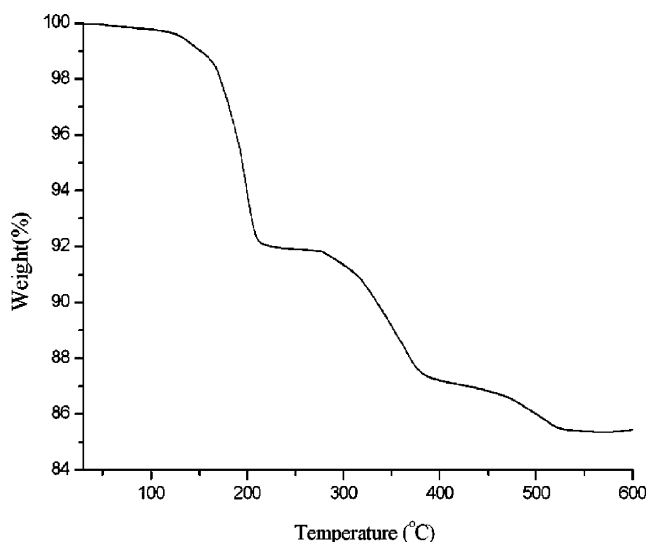


Fig. 6. TGA curve of $\text{Co}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}$.

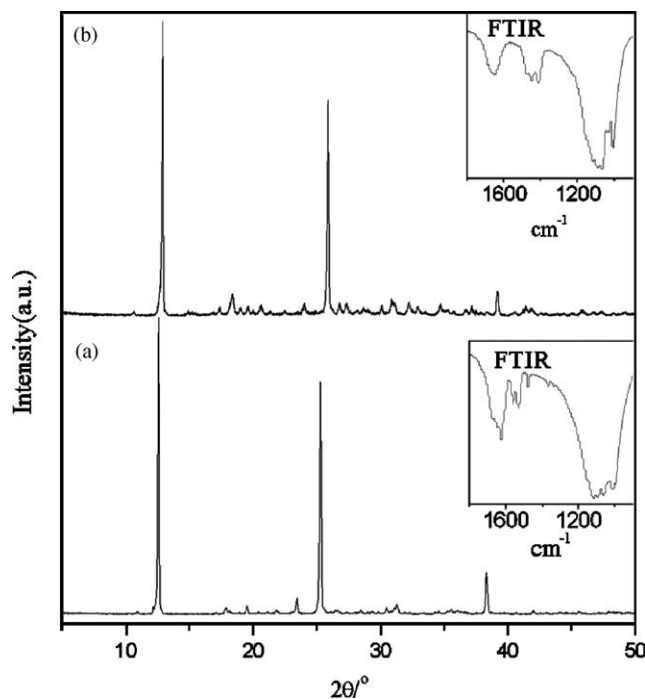


Fig. 8. The XRD patterns and IR spectra (insets) of (a) the as-synthesized $\text{Co}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}$ and (b) ion-exchanged solid.

and relative position, indicating the retention of the layered framework. The shift of the diffraction peaks to a little higher angle is due to the lattice contraction. The exchange of ethylenediamine cations by NH_4^+ cations was confirmed by the disappearance of the strong absorption peaks associated with ethylenediamine molecules at 1560, 1580, and 1480 cm^{-1} and the appearance of NH_4^+ peaks at 1450 and 1410 cm^{-1} in the IR spectra (insets of Fig. 8a, b). CHN analysis of the exchanged compound gives the content of C 0 wt%, N 3.02 wt% and H 2.41 wt%, which confirms the absence of C in the sample and the complete exchange of NH_4^+ for ethylenediamine cations.

4. Conclusions

A new organically templated layered cobalt–zinc phosphite with the formula $\text{Co}(\text{H}_2\text{O})_4\text{Zn}_4(\text{HPO}_3)_6 \cdot \text{C}_2\text{N}_2\text{H}_{10}$ has been synthesized and structurally characterized. The connectivity of ZnO_4 tetrahedra, CoO_6 octahedra and HPO_3 pseudopyramids creates cobalt–zinc phosphite layers parallel to the *ab* plane. The framework can be understood as a zinc phosphate layer encapsulating cobalt complexes. The ethylenediamine cations intercalate between the inorganic layers and interact with the framework through extensive hydrogen bonds. These organic molecules are mobile and can be ion exchanged by NH_4^+ cations.

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