



Solvothermal synthesis and structure of a novel 3D zincophosphate $[\text{Co}(\text{en})_3][\text{Zn}_4(\text{HPO}_3)_5(\text{H}_2\text{PO}_3)]$ containing helical chains

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ARTICLE INFO

Article history:

Received 22 April 2008

Received in revised form

28 June 2008

Accepted 18 July 2008

Available online 26 July 2008

Keywords:

Solvothermal synthesis

Crystal structure

Zincophosphate

Helical chain

Metal complex

ABSTRACT

A new three-dimensional (3D) zincophosphate $[\text{Co}(\text{en})_3][\text{Zn}_4(\text{HPO}_3)_5(\text{H}_2\text{PO}_3)]$ (**1**) has been solvothermally synthesized by using a racemic mixture of a chiral cobaltamine complex $\text{Co}(\text{en})_3\text{Cl}_3$ as the structure-directing agent. Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with $a = 18.6180(4) \text{ \AA}$, $b = 8.7601(18) \text{ \AA}$, $c = 17.4840(4) \text{ \AA}$, $\beta = 93.42(3)^\circ$, $V = 2846.4(10) \text{ \AA}^3$, $Z = 4$ with $R_1 = 0.0530$. Its structure is built up from strict alternation of ZnO_4 tetrahedra and HPO_3 pseudo-tetrahedra, giving rise to a 3D inorganic framework with 4-, 6-, 8-, 10- and 12 MRs, and the metal complex molecules, both the Δ and Λ enantiomers, sit in 10-MRs channels. In addition, it is worth noting that left- and right-handed helical chains exist in the framework, which is induced by chiral metal complex $\text{Co}(\text{en})_3\text{Cl}_3$ template molecules. Further characterization of compound **1** has been performed, including X-ray powder diffraction, ICP, CHN, IR and TG analyses.

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1. Introduction

Open-framework metal phosphates have been researched extensively due to their structural architectures and potential applications in catalysis, separation and adsorption [1–3]. Using pyramidal phosphite groups to substitute tetrahedral phosphate units have resulted in a new class of metal phosphites. Among the metal phosphites, the zincophosphites constitute an important family that exhibits a rich structural and compositional diversity. In 2001, the first organic templated zincophosphite was reported by Harrison et al. [4], and considerable interest has been aroused in the study of zincophosphites templated by organic species and metal complexes resulting in the hydrothermal/solvothermal synthesis of more than 30 zincophosphites with novel structures [5–24]. So far, among zincophosphites only a few examples are reported to possess helical features [4,21]. Thus, the design and synthesis of zincophosphite with helical or chiral structures are of current interest and of great challenge. Incorporating organic groups containing helical information is one useful approach to prepare inorganic helical materials, as the nature of the organic group is one of the most important factors when building structures. Furthermore, the synthetic mechanism of such materials is currently a subject consuming research, as it is not

well understood. More and more researchers are interested in using metal complexes, such as $\text{Co}(\text{en})_3^{3+}$ and $\text{Co}(\text{dien})_2^{3+}$, as templates to prepare chiral materials. To date, much progress has been made in the design of gallium phosphates $[\Delta\text{-Co}(\text{en})_3][\text{H}_3\text{Ga}_2\text{P}_4\text{O}_{16}]$ [25], $[\text{Co}(\text{en})_3][\text{Ga}_3(\text{H}_2\text{PO}_4)_6(\text{HPO}_4)_3]$ [26] and zincophosphates $[\text{Co}^{\text{II}}(\text{en})_3][\text{Zn}_4(\text{H}_2\text{PO}_4)_3(\text{HPO}_4)(\text{PO}_4)(2\text{H}_2\text{O})_2]$ [27], $[\text{Co}(\text{en})_3][\text{Zn}_6\text{P}_8\text{O}_{32}\text{H}_8]$ [28], $[\text{Co}(\text{en})_3][\text{Zn}_8\text{P}_6\text{O}_{24}\text{Cl}] \cdot 2\text{H}_2\text{O}$ [28] and $[\text{Co}(\text{dien})_2][\text{Zn}_2(\text{HPO}_4)_4] \cdot \text{H}_3\text{O}$ [29]. These studies indicate that chiral inorganic structural motifs can be induced by chiral complex templates.

In this work, we report the synthesis and crystal structure of a 3D open framework zincophosphite $[\text{Co}(\text{en})_3][\text{Zn}_4(\text{HPO}_3)_5(\text{H}_2\text{PO}_3)]$ (**1**) by using chiral metal complex $\text{Co}(\text{en})_3\text{Cl}_3$ as a structure-directing agent. To the best of our knowledge, compound **1** is the first zincophosphite templated by $\text{Co}(\text{en})_3\text{Cl}_3$ that contains left- and right-handed helical chains.

2. Experimental

2.1. Physical methods

The X-ray powder diffraction (XRD) data were collected on a Rigaku/max-2550 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. The inductively coupled plasma (ICP) analyses were carried out on a Perkin-Elmer Optima 3300DV ICP instru-

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ment. The infrared (IR) spectra were recorded within the 400–4000 cm^{-1} region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. The thermal gravimetric analyses (TGA) were performed on NETZSCH STA449C thermogravimetric analyzer in N_2 flow with a heating rate of $10^\circ\text{C min}^{-1}$.

2.2. Synthesis

Compound **1** was synthesized using mild solvothermal conditions under autogenous pressure. Typically, 0.22 g (1.0 mmol) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ was dissolved in a mixture of 4 mL *N,N*-dimethylformamide and 1 mL 1,4-dioxane with stirring, followed by the addition of 0.06 g (0.17 mmol) $\text{Co}(\text{en})_3\text{Cl}_3$, 0.54 g (6.5 mmol) H_3PO_3 , added dropwise, to the above reaction mixture. After stirring for 30 min, the final reaction mixture was transferred into a sealed Teflon-lined steel autoclave and heated at 140°C for 3 days, then slowly cooled to the room temperature. The resulting product, brown block-like single crystals were separated by filtering, washed with water and acetone, and dried in air. The yield of the reaction was approximately 65% based on zinc content.

2.3. Structural determination

A suitable single crystal with dimensions of $0.30 \times 0.27 \times 0.26 \text{ mm}^3$ was selected for single-crystal X-ray diffraction analysis. The intensity data were collected on a Rigaku RAXIS-RAPID IP diffractometer, using graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The numbers of collected reflections and independent reflections were 6475 and 4759 for compound **1**. Data processing was accomplished with the SAINT processing program. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL Version 5.1 [30]. All the zinc, cobalt and phosphorus atoms were located first, then non-hydrogen atoms (C, N and O) were subsequently found in difference Fourier maps. The hydrogen atoms of the amine molecule were placed geometrically. All non-hydrogen atoms were refined anisotropically. Crystal data and refinement parameters for the structure determination are presented in Table 1. The final atomic coordinates and the selected bond distances and angles are given in Tables 2 and 3, respectively.

Table 1
Crystal data and structure refinement for **1**

Empirical formula	$\text{C}_6\text{H}_{31}\text{CoN}_6\text{O}_{18}\text{P}_6\text{Zn}_4$
Formula weight	981.60
Temperature	293(2) (K)
Wavelength	0.71073(Å)
Crystal system, space group	Monoclinic, $P2(1)/c$
Unit cell dimensions	a (Å) = 18.618 (4), $\alpha = 90^\circ$ b (Å) = 8.7601 (18), $\beta = 93.43(3)^\circ$ c (Å) = 17.484 (4), $\gamma = 90^\circ$
Volume	2846.4(10) Å ³
Z, calculated density	4, 2.291 Mg/m ³
Absorption coefficient	4.314 mm ⁻¹
$F(000)$	1960
Crystal size	0.30 × 0.27 × 0.26 mm
Theta range for data collection	3.11–27.44°
Limiting indices	$-22 \leq h \leq 24$, $-11 \leq k \leq 11$, $-22 \leq l \leq 22$
Reflections collected/unique	27016/6475 [$R(\text{int}) = 0.0847$]
Completeness to theta = 27.44	99.6%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6475/0/388
Goodness-of-fit on F^2	1.058
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0530$, $wR2 = 0.1122$
R indices (all data)	$R1 = 0.0796$, $wR2 = 0.1229$
Largest diff. peak and hole	1.023 and $-1.142 \text{ e \AA}^{-3}$

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1**

Atom	x	y	z	U^a (eq)
Zn(1)	3206(1)	9745(1)	968(1)	17(1)
Zn(2)	156(1)	9912(1)	1155(1)	18(1)
Zn(3)	4072(1)	14816(1)	2624(1)	19(1)
Zn(4)	-1599(1)	5123(1)	-892(1)	17(1)
Co(1)	2656(1)	15281(1)	-1433(1)	15(1)
P(1)	1652(1)	8455(2)	822(1)	16(1)
P(2)	3107(1)	13340(2)	1331(1)	16(1)
P(3)	-464(1)	7402(2)	-23(1)	17(1)
P(4)	-367(1)	10197(2)	2926(1)	18(1)
P(5)	3864(1)	14824(2)	4381(1)	17(1)
P(6)	5490(1)	13000(2)	3240(1)	18(1)
O(1)	2391(2)	8480(4)	1239(2)	23(1)
O(2)	2834(2)	11723(5)	1236(3)	36(1)
O(3)	3392(2)	9306(5)	-77(2)	29(1)
O(4)	3949(2)	9264(5)	1758(2)	29(1)
O(5)	1082(2)	8961(5)	1358(2)	27(1)
O(6)	-522(2)	8709(5)	536(2)	28(1)
O(7)	-314(3)	10247(6)	2081(2)	43(1)
O(8)	227(2)	12038(4)	802(2)	25(1)
O(9)	3230(2)	13733(5)	2171(2)	29(1)
O(10)	3800(2)	15626(5)	3606(2)	29(1)
O(11)	4842(2)	13355(5)	2708(3)	33(1)
O(12)	4187(3)	16477(5)	1925(3)	39(1)
O(13)	-1142(2)	6454(5)	-98(2)	26(1)
O(14)	-1483(2)	3074(4)	-451(2)	23(1)
O(15)	-2611(2)	5533(5)	-889(2)	24(1)
O(16)	-1103(2)	5215(5)	-1824(2)	23(1)
O(17)	223(2)	9123(6)	3296(3)	40(1)
O(18)	3738(2)	13151(5)	4353(3)	35(1)
N(1)	1775(2)	16341(6)	-1150(3)	22(1)
N(2)	2830(2)	17129(5)	-2035(3)	20(1)
N(3)	2414(3)	13385(5)	-893(3)	23(1)
N(4)	2140(3)	14347(6)	-2329(3)	26(1)
N(5)	3602(3)	14453(5)	-1689(3)	23(1)
N(6)	3181(2)	16063(5)	-497(2)	17(1)
C(1)	1836(3)	18000(7)	-1337(4)	28(1)
C(2)	2168(3)	18084(7)	-2098(4)	29(1)
C(3)	2097(3)	12254(7)	-1446(4)	29(2)
C(4)	1669(3)	13096(7)	-2064(4)	31(2)
C(5)	4174(3)	15348(7)	-1261(4)	30(2)
C(6)	3941(3)	15517(7)	-450(3)	26(1)

^a $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

3. Results and discussion

3.1. Characterization of **1**

As seen in Fig. 1, the powder X-ray diffraction pattern of compound **1** is in good agreement with the one simulated based on the data of the single crystal structure, indicating the purity of the as-synthesized product. The differences in reflection intensity are probably due to preferred orientations in the powder sample.

The results of elemental analysis are consistent with the theoretical values calculated by the single-crystal structural analysis. Analysis found (%): Zn, 26.92; Co, 5.66; P, 18.22; C, 7.40; H, 2.73; N, 8.21. Calcd. (%): Zn, 26.65; Co, 6.00; P, 18.93; C, 7.34; H, 3.18; N, 8.56.

The TG analysis of compound (Fig. 2) shows a major weight loss of 14.8% (calc. 15.9%) in the temperature range of 290–600 $^\circ\text{C}$, corresponding to loss of the ethylenediamine of the metal complex in the product. The framework collapses after the loss of the ethylenediamine. XRD studies indicated that the final product, upon calcination above 800 $^\circ\text{C}$, is a mixture of cobalt oxide and a dense zinc phosphate ($\beta\text{-Zn}_2\text{P}_2\text{O}_7$; JCPDS: 34-1275), indicating the loss of framework structure with the loss of the amine.

Table 3
Selected bond lengths (Å) and bond angles (°) for **1**

Zn(1)–O(3)	1.919(4)	Zn(2)–O(7)	1.908(4)
Zn(1)–O(2)	1.934(4)	Zn(2)–O(6)	1.926(4)
Zn(1)–O(4)	1.942(4)	Zn(2)–O(5)	1.929(4)
Zn(1)–O(1)	1.960(4)	Zn(2)–O(8)	1.969(4)
Zn(3)–O(11)	1.920(4)	Zn(4)–O(15)	1.919(4)
Zn(3)–O(12)	1.921(4)	Zn(4)–O(16)	1.922(4)
Zn(3)–O(10)	1.953(4)	Zn(4)–O(14)	1.960(4)
Zn(3)–O(9)	1.959(4)	Zn(4)–O(13)	1.967(4)
Co(1)–N(4)	1.966(5)	Co(1)–N(3)	1.976(5)
Co(1)–N(2)	1.969(4)	Co(1)–N(6)	1.978(5)
Co(1)–N(1)	1.974(5)	Co(1)–N(5)	1.982(5)
P(1)–O(14)#1	1.514(4)	P(2)–O(2)	1.510(4)
P(1)–O(1)	1.517(4)	P(2)–O(9)	1.513(4)
P(1)–O(5)	1.524(4)	P(2)–O(15)#2	1.529(4)
P(1)–H(1)	1.30(8)	P(2)–H(2)	1.32(8)
P(3)–O(13)	1.511(4)	P(4)–O(7)	1.487(4)
P(3)–O(6)	1.514(4)	P(4)–O(16)#3	1.508(4)
P(3)–O(8)#2	1.536(4)	P(4)–O(17)	1.557(5)
P(3)–H(3)	1.27(8)	P(4)–H(4)	1.35(8)
P(5)–O(18)	1.485(4)	P(6)–O(12)#5	1.499(4)
P(5)–O(10)	1.525(4)	P(6)–O(11)	1.510(4)
P(5)–O(3)#4	1.533(4)	P(6)–O(4)#6	1.522(4)
P(5)–H(5)	1.32(8)	P(6)–H(6)	1.37(8)
O(3)–Zn(1)–O(2)	119.83(19)	O(7)–Zn(2)–O(6)	104.04(19)
O(3)–Zn(1)–O(4)	118.15(19)	O(7)–Zn(2)–O(5)	111.09(19)
O(2)–Zn(1)–O(4)	105.84(19)	O(6)–Zn(2)–O(5)	114.55(18)
O(3)–Zn(1)–O(1)	107.63(17)	O(7)–Zn(2)–O(8)	99.43(19)
O(2)–Zn(1)–O(1)	98.91(17)	O(6)–Zn(2)–O(8)	113.28(19)
O(4)–Zn(1)–O(1)	103.60(18)	O(5)–Zn(2)–O(8)	112.97(18)
O(11)–Zn(3)–O(12)	116.3(2)	O(15)–Zn(4)–O(16)	121.05(17)
O(11)–Zn(3)–O(10)	113.98(18)	O(15)–Zn(4)–O(14)	104.83(17)
O(12)–Zn(3)–O(10)	109.18(19)	O(16)–Zn(4)–O(14)	108.96(16)
O(11)–Zn(3)–O(9)	106.48(19)	O(15)–Zn(4)–O(13)	105.67(17)
O(12)–Zn(3)–O(9)	103.05(19)	O(16)–Zn(4)–O(13)	111.36(16)
O(10)–Zn(3)–O(9)	106.75(18)	O(14)–Zn(4)–O(13)	103.43(17)
O(14)#1–P(1)–O(5)	112.3(2)	O(2)–P(2)–O(9)	110.5(3)
O(14)#1–P(1)–O(1)	112.7(2)	O(2)–P(2)–O(15)#2	111.2(3)
O(1)–P(1)–O(5)	110.2(2)	O(9)–P(2)–O(15)#2	113.3(2)
O(14)#1–P(1)–H(1)	104(4)	O(2)–P(2)–H(2)	106(4)
O(1)–P(1)–H(1)	109(4)	O(9)–P(2)–H(2)	110(4)
O(5)–P(1)–H(1)	108(4)	O(15)#2–P(2)–H(2)	106(4)
O(13)–P(3)–O(6)	112.3(2)	O(7)–P(4)–O(16)#3	114.2(3)
O(13)–P(3)–O(8)#2	112.4(2)	O(7)–P(4)–O(17)	110.1(3)
O(6)–P(3)–O(8)#2	111.5(2)	O(16)#3–P(4)–O(17)	111.5(2)
O(13)–P(3)–H(3)	107(4)	O(7)–P(4)–H(4)	106(3)
O(6)–P(3)–H(3)	108(4)	O(16)#3–P(4)–H(4)	111(3)
O(8)#2–P(3)–H(3)	105(3)	O(17)–P(4)–H(4)	103(4)
O(18)–P(5)–O(10)	114.9(3)	O(12)#5–P(6)–O(11)	112.4(3)
O(18)–P(5)–O(3)#4	114.6(2)	O(12)#5–P(6)–O(4)#6	111.4(3)
O(10)–P(5)–O(3)#4	107.6(2)	O(11)–P(6)–O(4)#6	112.0(3)
O(18)–P(5)–H(5)	110(3)	O(12)#5–P(6)–H(6)	102(4)
O(10)–P(5)–H(5)	107(4)	O(11)–P(6)–H(6)	110(3)
O(3)#4–P(5)–H(5)	102(4)	O(4)#6–P(6)–H(6)	109(4)
P(1)–O(1)–Zn(1)	125.8(2)	P(1)–O(5)–Zn(2)	131.4(3)
P(2)–O(2)–Zn(1)	138.0(3)	P(3)–O(6)–Zn(2)	135.0(3)
P(5)#7–O(3)–Zn(1)	129.2(3)	P(4)–O(7)–Zn(2)	154.1(3)
P(6)#5–O(4)–Zn(1)	128.3(2)	P(3)#2–O(8)–Zn(2)	127.5(2)
P(2)–O(9)–Zn(3)	125.1(2)	P(3)–O(13)–Zn(4)	135.3(2)
P(5)–O(10)–Zn(3)	127.1(3)	P(1)#1–O(14)–Zn(4)	128.8(2)
P(6)–O(11)–Zn(3)	138.5(3)	P(2)#2–O(15)–Zn(4)	133.1(2)
P(6)#6–O(12)–Zn(3)	149.1(3)	P(4)#8–O(16)–Zn(4)	136.6(3)

Symmetry transformations used to generate equivalent atoms: #1 $x, -y+1, -z$ #2 $-x, -y+2, -z$ #3 $x, -y+3/2, z+1/2$ #4 $x, -y+5/2, z+1/2$ #5 $-x+1, y-1/2, -z+1/2$ #6 $-x+1, y+1/2, -z+1/2$ #7 $x, -y+5/2, z-1/2$ #8 $x, -y+3/2, z-1/2$.

3.2. Crystal structure of **1**

Single-crystal X-ray diffraction analysis indicates that compound **1** crystallizes in the monoclinic space group $P2_1/c$ with the formula of $[\text{Co}(\text{en})_3][\text{Zn}_4(\text{HPO}_3)_5(\text{H}_2\text{PO}_3)]$. As seen in Fig. 3, each asymmetric unit contains 41 non-hydrogen atoms, of which 28 atoms belong to the host framework and the remaining to guest

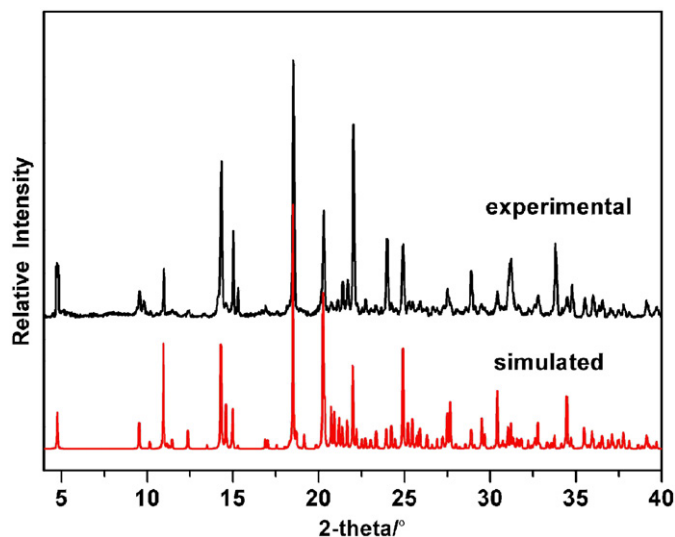


Fig. 1. Simulated and experimental X-ray powder diffraction patterns of **1**.

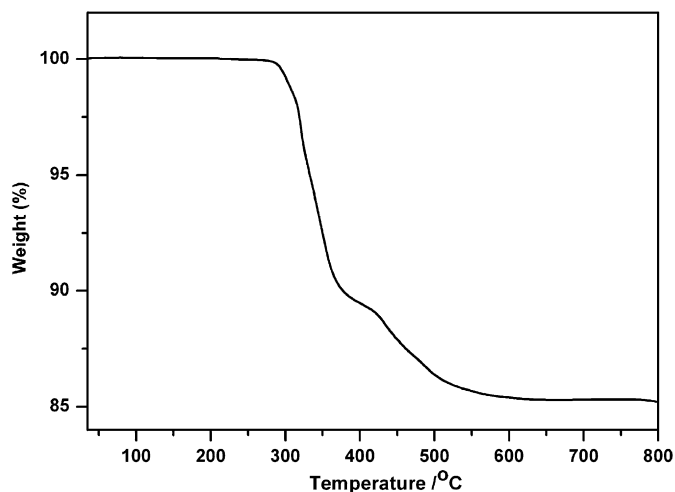


Fig. 2. Thermal-gravimetric analysis curve for **1**.

molecules. In the host framework, there are four crystallographically distinct Zn atoms and six distinct P atoms. The Zn(1), Zn(2), Zn(3) and Zn(4) each share four oxygen atoms to form ZnO_4 tetrahedron with an average Zn–O bond length of 1.945(4) Å. The O–Zn–O bond angles are in the range of 98.91(17)–121.05(17)°. Of the six crystallographically independent P atoms, P(1), P(2), P(3) and P(6) atoms are linked to three Zn atoms via bridging oxygen atoms and to one H atom. The P(4) atom bridges two Zn atoms and possesses one terminal –OH group and one P–H bond. The P(5) atom bridges two Zn atoms and possesses one P–H bond and one terminal O(18) atom. The average value of P–O bond lengths is 1.493(4) Å, the O–P–O bond angles are in the range of 110.5(3)–114.9(3)°. The average P–H bond length is 1.322(8) Å. One distinct Co atom lies in the general position of the metal complex molecule (average Co–N bond distance: 1.974(5) Å). Assuming the usual valence of Zn, P in H_3PO_3 , O and H to be +2, +3, –2 and +1, respectively, the network stoichiometry of $[\text{Zn}_4(\text{HPO}_3)_5(\text{H}_2\text{PO}_3)]$ creates a net charge of –3. The presence of $\text{Co}(\text{en})_3$ molecule accounts for +3, arising from the Co(III).

Compound **1** is built up from strictly alternating ZnO_4 tetrahedra and HPO_3 pseudo-tetrahedra, which are linked through their vertices, giving rise to a complex three-dimensional (3D)

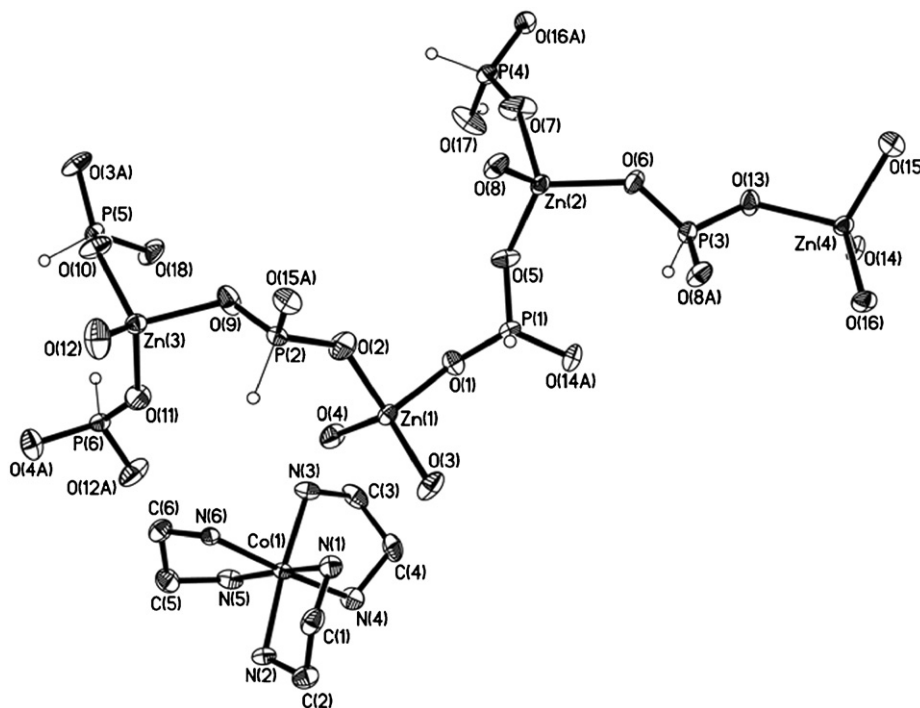


Fig. 3. ORTEP view of the asymmetric unit of **1** (50% thermal ellipsoids).

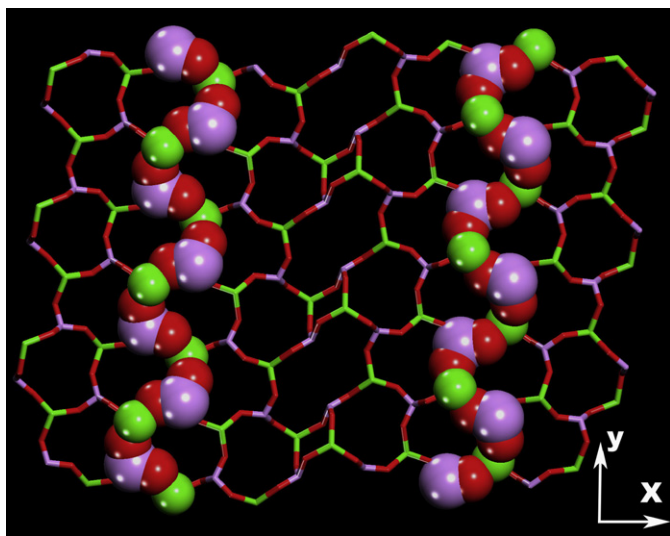


Fig. 4. The 4.6.8-net sheet of **1** parallel to the *ab* plane, which contains left- and right-handed helical chains with space-filling view. H atoms and organic species are omitted for clarity. Color code: Zn: green; P: purple and O: red.

open framework. It can be described on the basis of 2D sheets parallel to the *ab* plane, which consist of 4.6.8-net along *a*-axis. In the layer, the 6-MRs constitute a honeycomb-like fraction containing left- and right-handed helical chains that are formed by the racemic chiral metal complex template, as shown in Fig. 4. Each fraction connects via 4MR (Zn2–P3–Zn2–P3) and 8MR (Zn2–P3–Zn4–P1–Zn2–P3–Zn4–P1), by sharing edge Zn2–P3 atoms. These layers were further connected with each other by {P4} and {P5} atoms to generate the 10-MR (Zn1–P1–Zn2–P3–Zn2–P4–Zn4–P2–Zn3–P5) channels of **1**. It also contains 12-MR windows perpendicular to this 10 MR channel. The metal complex molecules, of both the Δ and Λ enantiomers, sit in 10-MR channels (as shown in Fig. 5). The central axis of each helical chain

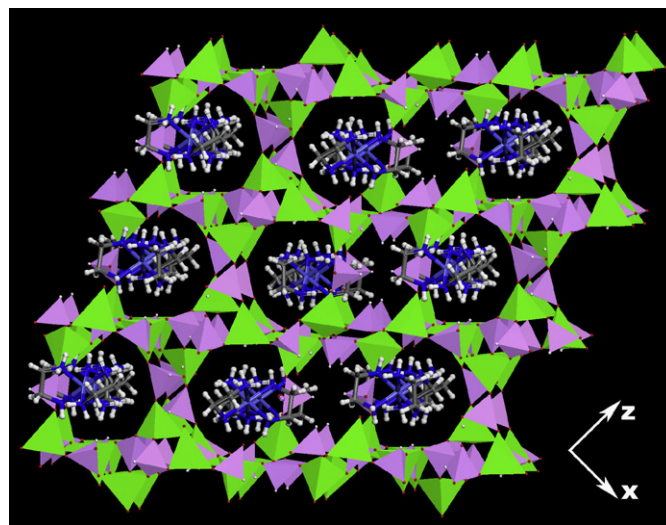


Fig. 5. A polyhedral view of the framework of **1** along the [010] direction. The $\text{Co}(\text{en})_3^{3+}$ cations reside in the 10-membered ring channels.

is a twofold screw axis along the crystallographic *b*-axis. Fig. 6 shows a space-filling view of the left- and right-handed helical chains with the Δ and Λ $\text{Co}(\text{en})_3^{3+}$ complexes. The H-bonding arrangement between the complex cations and the host framework is illustrated in Fig. 7. Each $\text{Co}(\text{en})_3^{3+}$ ion forms a total of 14 H-bonds to the bridging and terminal oxygen atoms in the structural framework. The N...O distances are in the range of 2.818(7)–3.287(7) Å (Table 4).

3.3. Discussion

By inspection of structure **1**, it is believed that the airscrew-like metal complexes play a leading role in the formation of the

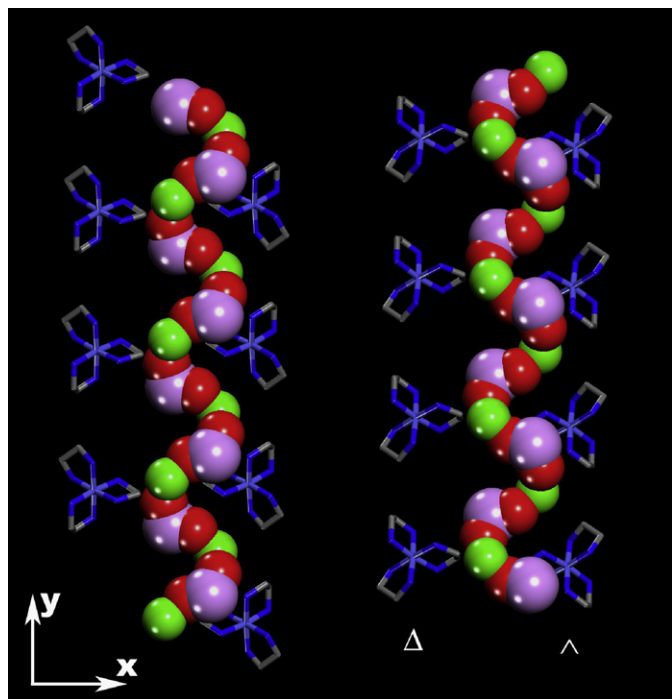


Fig. 6. A space-filling view of the left- and right-handed helical chains with the Δ and Λ $\text{Co}(\text{en})_3^{2+}$ cations along the b -axis exhibited by **1**. Δ and Λ stand for the absolute configurations of chiral $\text{Co}(\text{en})_3^{2+}$ cations.

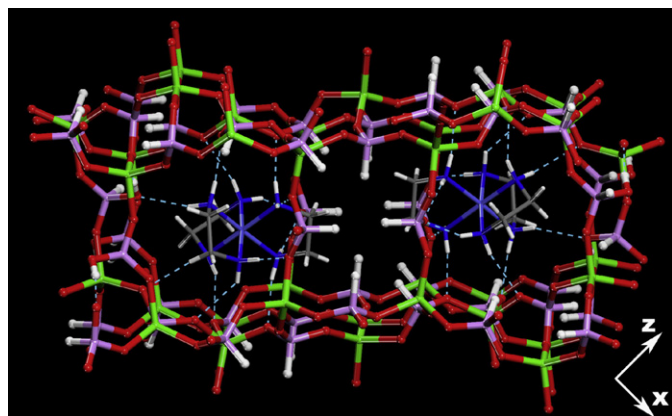


Fig. 7. H-bonding arrangement between the $\text{Co}(\text{en})_3^{2+}$ complex cations and the host framework.

helices. The $\text{Co}(\text{en})_3\text{Cl}_3$ molecules, acting as structure-directing agents, might impose the helix-transferring effect on $-\text{Zn}-\text{O}-\text{P}-$ chains, thus inducing the helical array of the 4.6.8-net of the open framework. In 2003, a 2D layered zincophosphate has been reported by J Yu and colleagues [21], which consists of left- and right-handed helical chains that are connected through oxygen atoms to form an undulated sheet structure with 4.8-net. Meanwhile, comparing to zincophosphates with helical channels, such as $[\text{Co}^{\text{II}}(\text{en})_3][\text{Zn}_4(\text{H}_2\text{PO}_4)_3(\text{HPO}_4)(\text{PO}_4)(2\text{H}_2\text{O})_2]$ [27], $[\text{Co}(\text{en})_3][\text{Zn}_6\text{P}_8\text{O}_{32}\text{H}_8]$ [28], $[\text{Co}(\text{en})_3][\text{Zn}_8\text{P}_6\text{O}_{24}\text{Cl}] \cdot 2\text{H}_2\text{O}$ [28], the notable stereospecific correspondence between the metal complex and inorganic framework is attributed to the hydrogen bonding between the host framework and the guest molecules. In compound **1**, the HPO_3^{2-} could offer special hydrogen bonds to the metal complex as a result of helix transfer from the metal complex.

Table 4
Hydrogen bonds [\AA and deg.] for **1**

D–H...A	$d(\text{D–H})$ (\AA)	$d(\text{H}\cdots\text{A})$ (\AA)	$d(\text{D}\cdots\text{A})$ (\AA)	Ang(DHA) (deg.)
O(17)–H(17)...O(8)#3	0.82	1.77	2.586(6)	170.8
N(1)–H(1A)...O(17)#2	0.90	2.20	3.019(6)	151.0
N(1)–H(1B)...O(14)#1	0.90	2.09	2.929(6)	155.6
N(2)–H(2A)...O(10)#4	0.90	1.98	2.854(6)	162.6
N(2)–H(2B)...O(1)#2	0.90	2.39	3.125(6)	138.3
N(2)–H(2B)...O(4)#2	0.90	2.52	3.288(6)	143.9
N(3)–H(3A)...O(18)#2	0.90	1.99	2.818(7)	152.3
N(3)–H(3B)...O(13)#1	0.90	2.15	3.020(6)	161.1
N(4)–H(4A)...O(5)#2	0.90	2.45	3.287(7)	155.4
N(4)–H(4A)...O(1)#2	0.90	2.66	3.201(6)	120.0
N(4)–H(4B)...O(2)#2	0.90	2.20	3.038(6)	155.2
N(5)–H(5A)...O(18)#2	0.90	2.13	2.921(6)	146.7
N(5)–H(5B)...O(4)#2	0.90	2.21	3.043(6)	153.7
N(6)–H(6A)...O(3)#5	0.90	2.11	2.954(6)	156.2
N(6)–H(6B)...O(15)#1	0.90	2.16	3.042(6)	165.0

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y+2, -z$ #2 $x, -y+5/2, z-1/2$ #3 $-x, y-1/2, -z+1/2$ #4 $x, -y+7/2, z-1/2$ #5 $x, y+1, z$.

In addition, by comparing with those known zinc phosphites, the title compound exhibits a novel 3D open framework structure with a 4.6.8-net containing left- and right-handed helical chains and 10-MR channels. In 2003, a 3D zinc phosphite open-framework with 4-, 6-, 8- and 12-MRs was reported by S Feng and colleagues [7], which contains 12MR channels with walls composed of alternated 4-, 6- and 8-rings. Although 3D open-framework structures with 4.6.8-nets are common patterns in zinc phosphites [7,13], 3D open framework structures with 4.6.8-net containing left- and right-handed helical chains and 10-MR channels are rare.

4. Conclusion

A novel 3D zincophosphate, $[\text{Co}(\text{en})_3][\text{Zn}_4(\text{HPO}_3)_5(\text{H}_2\text{PO}_3)]$, has been synthesized by using $\text{Co}(\text{en})_3\text{Cl}_3$ as structure-directing agents under mild solvothermal conditions. Compound **1** consists of ZnO_4 tetrahedra and HPO_3 pseudo-tetrahedra, giving rise to a three-dimensional structure with a 4.6.8-net and 10-MR channels. The metal complex molecules sit in the 10MR channels. Also there are left- and right-handed helical chains in the structure which have been formed by template molecules. It is believed that more zincophosphites with novel structures will be synthesized by varying the metal complex with helical information and crystallization conditions.

Supporting information and structure details

Crystallographic data for the structure reported in this paper in the form of CIF file have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-668764 for **1**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

The authors acknowledge the financial support of the Natural Science Foundation of China (Grant no. 20671041, no. 20701015) and the State Key Laboratory of Inorganic Synthesis and Preparative Chemistry of Jilin University.

Appendix A. Supporting information and structure details

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2008.07.026.

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