Solvothermal synthesis and structure of a novel 3D zincophosphite |Co(en)$_3$|[Zn$_4$(HPO$_3$)$_5$(H$_2$PO$_3$)] containing helical chains

Jian Qiao [a], Lirong Zhang [a,*], Li Liu [b], Yang Yu [a], Minghui Bi [a], Qisheng Huo [a], Yunling Liu [a,*]

[a] *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China*
[b] *Department of Chemistry, Northeast Normal University, Changchun 130024, PR China*

ARTICLE INFO

ABSTRACT

A new three-dimensional (3D) zincophosphite |Co(en)$_3$| [Zn$_4$(HPO$_3$)$_5$(H$_2$PO$_3$)] (**1**) has been solvothermally synthesized by using a racemic mixture of a chiral cobaltammine complex Co(en)$_3$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 $a = 18.6180\,(4)$ Å, $b = 8.7601(18)$ Å, $c = 17.4840(4)$ Å, $\beta = 93.42(3)°$, $V = 2846.4(10)$ Å^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 $\varDelta$ and $\varLambda$ 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 Co(en)$_3$Cl$_3$ template molecules. Further characterization of compound **1** has been performed, including X-ray powder diffraction, ICP, CHN, IR and TG analyses.

© 2008 Elsevier Inc. All rights reserved.

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 Co(en)$_3^{3+}$ and Co(dien)$_2^{3+}$, as templates to prepare chiral materials. To date, much progress has been made in the design of gallium phosphates |$\varDelta$-Co(en)$_3$ |[H$_3$Ga$_2$P$_4$O$_{16}$] [25], |Co(en)$_3$|[Ga$_3$(H$_2$PO$_4$)$_6$(HPO$_4$)$_3$] [26] and zincophosphates |Co^{II}(en)$_3$|[Zn$_4$(H$_2$PO$_4$)$_3$(HPO$_4$)(PO$_4$)(2H$_2$O)$_2$] [27], |Co(en)$_3$|[Zn$_6$P$_8$O$_{32}$H$_8$][28], |Co(en)$_3$|[Zn$_8$P$_6$O$_{24}$Cl] · 2H$_2$O [28] and |Co(dien)$_2$|[Zn$_2$(HPO$_4$)$_4$] · H$_3$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 |Co(en)$_3$|[Zn$_4$(HPO$_3$)$_5$(H$_2$PO$_3$)] (**1**) by using chiral metal complex Co(en)$_3$Cl$_3$ as a structure-directing agent. To the best of our knowledge, compound **1** is the first zincophosphite templated by Co(en)$_3$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 Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). 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-

* Corresponding author. Fax: +86 431 5168624.
E-mail addresses: zlr@jlu.edu.cn (L. Zhang), yunling@jlu.edu.cn (Y. Liu).

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 °C min^{-1}.

2.2. Synthesis

Compound **1** was synthesized using mild solvothermal conditions under autogenous pressure. Typically, 0.22 g (1.0 mmol) Zn(OAc)$_2$ · 2H$_2$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) Co(en)$_3$Cl$_3$, 0.54 g (6.5 mmol) H$_3$PO$_3$, 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 × 0.27 × 0.26 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 ($\lambda = 0.71073$ Å). 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	C$_6$H$_{31}$CoN$_6$O$_{18}$P$_6$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), $\alpha = 90°$
	b (Å) = 8.7601 (18), $\beta = 93.43(3)°$
	c (Å) = 17.484 (4), $\gamma = 90°$
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	$-22 \leqslant h \leqslant 24$, $-11 \leqslant k \leqslant 11$, $-22 \leqslant l \leqslant 22$
Reflections collected/unique	27016/6475[R(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 eÅ^{-3}

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (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(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 °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 °C, is a mixture of cobalt oxide and a dense zinc phosphate (β-Zn$_2$P$_2$O$_7$; JCPDS: 34-1275), indicating the loss of framework structure with the loss of the amine.