Inorg. Chem. **2007**, *46*, 6683–6687

Inorganic Chemistry
Article

Syntheses and Characterizations of Three Low-Dimensional Chloride-Rich Zincophosphates Assembled about [*d*-Co(en)$_3$]$^{3+}$ and [*dl*-Co(en)$_3$]$^{3+}$ Complex Cations

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Received November 4, 2006

Three new chloride-rich zincophosphates including two zero-dimensional (0D) clusters [*dl*-Co(en)$_3$]$_2$[Zn$_4$(H$_2$PO$_4$)$_2$(HPO$_4$)$_2$Cl$_8$] (denoted ZnPO-CJ33) and [*d*-Co(en)$_3$]$_2$[Zn$_4$(H$_2$PO$_4$)$_2$(HPO$_4$)$_2$Cl$_8$] (denoted ZnPO-CJ34), and one-dimensional (1D) zincophosphate chain [*dl*-Co(en)$_3$][Zn$_2$(H$_2$PO$_4$)(HPO$_4$)$_2$Cl$_2$] (denoted ZnPO-CJ35) have been solvothermally prepared. ZnPO-CJ33 and ZnPO-CJ34 possess the same cluster structure as the macroanionic [Zn$_4$H$_6$P$_4$O$_{16}$Cl$_8$]$^{6-}$ unit formed by alternation of ZnOCl$_3$/ZnO$_3$Cl and HPO$_4$/H$_2$PO$_4$ tetrahedra but differ in the countercations. The racemic [*dl*-Co(en)$_3$]$^{3+}$ cations are located among the clusters of ZnPO-CJ33, whereas chiral [*d*-Co(en)$_3$]$^{3+}$ cations are located among the clusters of ZnPO-CJ34. ZnPO-CJ34 templated by the optically pure chiral [*d*-Co(en)$_3$]$^{3+}$ cations is the first chiral monomeric zincophosphate. ZnPO-CJ35 templated by the racemic [*dl*-Co(en)$_3$]$^{3+}$ cations possesses a 1D infinite chain structure formed by the alternation of ZnO$_3$Cl and HPO$_4$/H$_2$PO$_4$ tetrahedra. The 1D chain structure of ZnPO-CJ35 can also be viewed as generated from the condensation of 0D clusters of ZnPO-CJ33, with the terminal Cl ions replaced by HPO$_4$ groups. Experimentally, the structural transformation from ZnPO-CJ33 to ZnPO-CJ35 has been investigated.

Introduction

Open-framework metal phosphates have received much attention recently because of their potential applications in catalysis, separation, optics, and magnetics, and so forth, and because of their rich structure chemistry.[1−5] Among them, a large number of organically templated zincophosphates have been hydrothermally/solvothermally prepared with zero-dimensional (0D) clusters, one-dimensional (1D) chains or ladders, two-dimensional (2D) layers, and three-dimensional (3D) structures by various structure-directing agents.[6−8] In particular, the use of racemic mixtures or optically pure chiral−metal complexes as the templates instead of organic amines has led to the preparation of templated network metal phosphates with novel structures, such as [*trans*-Co(dien)$_2$][Zn$_2$(HPO$_4$)$_4$]·H$_2$O, [*dl*-Co(en)$_3$][Zn$_8$P$_6$O$_{24}$Cl]·H$_2$O, [*dl*-Co(en)$_3$]$_2$[Zn$_6$P$_8$O$_{32}$H$_8$], [*dl*-Co(tn)$_3$][Al$_3$P$_4$O$_{16}$]·2H$_2$O, [*d*-Co(en)$_3$][H$_3$Ga$_2$P$_4$O$_{16}$], [*d*-Co(en)$_3$][AlP$_2$O$_8$]·6.5H$_2$O, and [*d*-Co(en)$_3$][Zn$_3$(H$_{0.5}$PO$_4$)$_2$(HPO$_4$)$_2$], and so forth.[9−22] Significantly,

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10.1021/ic062103+ CCC: $37.00

the introduction of the chiral−metal complex into the preparation of metal phosphates has proven to be an effective route for generating open-framework metal phosphates with chiral features.[13−17] H-bonding between the host and guest is believed to play an important role in the chirality transfer from the guest chiral−metal complex to the host inorganic framework.

Notably, several zincophosphates have been prepared with low-dimensional frameworks such as 0D clusters and 1D chains. So far, there are four examples of 0D cluster structures, among which $C_6N_2H_{18}Zn(HPO_4)(H_2PO_4)_2$[23] and $N(CH_3)_4Zn(H_2PO_4)_3$[24] possess the simple $Zn_2P_2O_4$ 4-rings with additional terminal (di)hydrogen phosphate moieties attached to the Zn atoms, and the other two are hybrid zincophosphates.[25,26] The 1D chain zincophosphates are either corner-shared or edge-shared 4-ring chains formed by the alternation of P-centered and Zn-centered tetrahedra.[6,27−37] Zincophosphates comprised of 0D clusters and 1D chains are of particular interests because they might be used as precursors to build up more-complex structures.[38−40] Recently, Rao et al. have shown that the precursor, constituted of fundamental building unit 4-rings, can readily be transformed to 2D layers and 3D templated network structures.

Herein, we present the syntheses, characterizations, and structures of three new low-dimensional chloride-rich zincophosphates including two 0D clusters and one 1D chain templated by racemic or chiral cobalt complexes. Transformations from 0D cluster to 1D chain and from low-dimensional precursors to 2D layer structures have been investigated.

Experimental Section

Syntheses and Characterizations. ZnPO-CJ33 and ZnPO-CJ34 were prepared from a reaction mixture of $ZnCl_2$ (0.14 g, 1 mmol), H_3PO_4 (0.14 mL, 2 mmol), *dl*-$Co(en)_3Cl_3$[41a] (0.086 g, 0.25 mmol)/ *d*-$Co(en)_3I_3$[41b] (0.15 g, 0.25 mmol), and *n*-BuOH (8 mL) in 18 mL Teflon-lined autoclaves at 110 °C for 6 d by using *dl*-$Co(en)_3Cl_3$ and *d*-$Co(en)_3I_3$ as the templates, respectively. ZnPO-CJ35 was prepared from a reaction mixture of $ZnCl_2$ (0.14 g, 1 mmol), H_3PO_4 (0.35 mL, 5 mmol), *dl*-$Co(en)_3Cl_3$ (0.08 g, 0.25 mmol), and *n*-BuOH (8 mL) in 18 mL Teflon-lined autoclaves at 130 °C for 6 d. For all three compounds, the obtained orange crystals were filtered, washed with *n*-BuOH, and then air-dried. These three compounds could also be prepared by using other alcohols such as EtOH, *n*-PrOH, *2*-BuOH, *n*-HexOH, and *n*-OctOH instead of *n*-BuOH as a solvent under similar synthetic conditions.

A Perkin-Elmer TGA 7 unit was used to carry out the thermogravimetric analyses in air with a heating rate of 20 °C/min. The elemental analyses were conducted on a Perkin-Elmer 2400 element analyzer. Inductive coupled plasma (ICP) analyses were performed on a Perkin-Elmer Optima 3300DV spectrometer. Compositional analyses of ZnPO-CJ33, ZnPO-CJ34, and ZnPO-CJ35 showed that they contained 4.80, 10.37, 10.23, 12.51, 8.21, 14.56 wt %, 4.83, 10.01, 10.34, 12.42, 7.96, 14.47 wt %, and 18.02, 12.65, 7.92, 9.76, 10.12, 11.40 wt % for Zn, P, Co, C, H, and N (calcd, 4.71, 10.08, 10.28, 12.57, 7.51, 14.66 wt % for ZnPO-CJ33 and ZnPO-CJ34, and 17.91, 12.73, 8.07, 9.87, 9.33, 11.52 wt % for ZnPO-CJ35), respectively. The analysis results were in agreement with the calculated values based on the empirical formula suggested by single-crystal X-ray structural analyses. The thermogravimetric (TG) analyses of ZnPO-CJ33, ZnPO-CJ34, and ZnPO-CJ35 were carried out under an air atmosphere from 50 to 800 °C. Major weight losses of 25.94 wt % at 264 °C for ZnPO-CJ33, 25.32 wt % at 268 °C for ZnPO-CJ34 (calcd, 25.58 wt %), and 25.96 wt % at 288 °C for ZnPO-CJ35 (calcd, 24.70 wt %) were observed, which corresponded to the decomposition of the metal complex. Further weight losses of 19.46 wt % for ZnPO-CJ33 and 21.55 wt % for ZnPO-CJ34 (calcd, 20.55 wt %) corresponded to the release of HCl and Cl_2, and 12.66 wt % for ZnPO-CJ35 (12.46 wt %) corresponded to the release of HCl, H_2O.

Determination of Crystal Structures. Suitable single crystals of ZnPO-CJ33 ($0.2 \times 0.15 \times 0.15$ mm^3), ZnPO-CJ34 ($0.12 \times 0.12 \times 0.1$ mm^3), and ZnPO-CJ35 ($0.2 \times 0.08 \times 0.08$ mm^3) were selected for single-crystal X-ray diffraction analysis. Structural analysis of ZnPO-CJ33 was performed on a Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data processing was accomplished with the *SAINT* processing program.[42] The data collection and structural analyses of ZnPO-CJ34 and ZnPO-CJ35 were performed on a Rigaku RAXIS-RAPID diffractometer equipped with a narrow-focus, 5.4 kW, sealed-tube X-ray source (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å). The data processing was accomplished with the *PROCESS-AUTO* processing program. All of the data were collected at a temperature of 20 ± 2 °C. Structures were solved by

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Table 1. Crystal Data and Structural Refinements for ZnPO-CJ33, ZnPO-CJ34 and ZnPO-CJ35

identification code	ZnPO-CJ33	ZnPO-CJ34	ZnPO-CJ35
empirical formula	$C_{12}H_{54}Cl_8Co_2N_{12}O_{16}P_4Zn_4$	$C_{24}H_{108}Cl_{16}Co_4N_{24}O_{32}P_8Zn_8$	$C_6H_{28}Cl_2CoN_6O_{12}P_3Zn_2$
fw	1409.49	2818.98	729.82
cryst syst, space group	monoclinic, *C2/c*	monoclinic, *C*2	monoclinic, $P2_1/c$
unit cell dimensions	$a = 30.989(6)$ (Å) $b = 8.9600(18)$ (Å) $c = 16.326(3)$ (Å) $\beta = 100.10(3)°$	$a = 31.103(6)$ (Å) $b = 9.0456(18)$ (Å) $c = 16.499(3)$ (Å) $\beta = 100.43(3)°$	$a = 12.778(3)$ (Å) $b = 12.136(2)$ (Å) $c = 15.527(3)$ (Å) $\beta = 112.12(3)°$
V (Å^3)	4462.9(16)	4565.2(16)	2230.6(8)
Z, D_{calcd} (mg/m^3)	4, 2.098	2, 2.051	4, 2.173
F(000)	2832	2832	1472
limiting indices	$-41 \leq h \leq 39$, $-10 \leq k \leq 11$, $-21 \leq l \leq 21$	$-40 \leq h \leq 40$, $-11 \leq k \leq 11$, $-21 \leq l \leq 21$	$-16 \leq h \leq 16$, $-15 \leq k \leq 15$, $-20 \leq l \leq 20$
data/restraints/params	5003/54/262	10113/49/524	5080/0/290
GOF	1.072	0.810	1.085
Final R indices [$I > 2\delta(I)$]	R1 = 0.0726, wR2 = 0.1450	R1 = 0.0860, wR2 = 0.1732	R1 = 0.0557, wR2 = 0.1188
R indices (all data)	R1 = 0.1045, wR2 = 0.1560	R1 = 0.1685, wR2 = 0.2434	R1 = 0.0945, wR2 = 0.1367
flack parameter		0.01(4)	
largest diff. peak, hole (e Å^{-3})	0.770, −0.587	1.243, −1.237	0.979, −1.229

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) for ZnPO-CJ33[a]

Zn(1)−O(5)	1.976(6)	Zn(1)−Cl(4)	2.221(3)
Zn(1)−Cl(3)	2.266(3)	Zn(1)−Cl(1)	2.272(3)
Zn(2)−O(1′)#1	1.906(18)	Zn(2)−O(3)	1.912(7)
Zn(2)−O(7)	1.953(7)	Zn(2)−O(1)#1	1.97(2)
Zn(2)−Cl(2)	2.223(3)	P(1)−O(1′)	1.606(18)
P(1)−O(8)	1.486(17)	P(1)−O(7)	1.499(7)
P(1)−O(6)	1.522(8)	P(2)−O(3)	1.481(8)
P(2)−O(2)	1.593(10)	P(2)−O(4)	1.504(7)
P(2)−O(5)	1.516(7)	P(1)−O(7)−Zn(2)	131.0(4)
P(2)−O(3)−Zn(2)	146.1(5)	P(2)−O(5)−Zn(1)	125.9(4)

[a] Symmetry transformations used to generate equivalent atoms, #1: $-x, -y + 2, -z + 1$.

Table 3. Selected Bond Lengths (Angstroms) and Angles (Degrees) for ZnPO-CJ34

Zn(1)−O(2)	1.924(8)	Zn(1)−O(1)	1.943(10)
Zn(1)−O(7)	1.981(11)	Zn(1)−Cl(8)	2.249(5)
Zn(2)−O(3′)	1.890(16)	Zn(2)−O(5)	1.910(12)
Zn(2)−O(3)	1.94(3)	Zn(2)−O(8)	1.998(11)
Zn(2)−Cl(5)	2.253(5)	Zn(3)−O(12)	1.980(8)
Zn(3)−Cl(4)	2.280(5)	Zn(3)−Cl(6)	2.282(4)
Zn(3)−Cl(2)	2.289(4)	Zn(4)−O(14)	1.977(9)
Zn(4)−Cl(1)	2.284(4)	Zn(4)−Cl(7)	2.298(5)
Zn(4)−Cl(3)	2.302(5)	P(1)−O(1)	1.520(9)
P(1)−O(15)	1.532(10)	P(1)−O(8)	1.537(13)
P(1)−O(11)	1.538(11)	P(2)−O(14)	1.505(10)
P(2)−O(4)	1.52(3)	P(2)−O(3′)	1.523(17)
P(2)−O(10)	1.546(11)	P(2)−O(3)	1.580(18)
P(3)−O(2)	1.498(10)	P(3)−O(12)	1.524(10)
P(3)−O(9)	1.525(13)	P(3)−O(6)	1.594(9)
P(4)−O(7)	1.496(13)	P(4)−O(16)	1.529(14)
P(4)−O(13)	1.554(12)		
P(1)−O(1)−Zn(1)	135.0(6)	P(2)−O(14)−Zn(4)	127.2(6)
P(3)−O(2)−Zn(1)	146.4(9)	P(2)−O(3′)−Zn(2)	143.6(13)
P(2)−O(3)−Zn(2)	134(2)	P(4)−O(7)−Zn(1)	130.5(7)
P(1)−O(8)−Zn(2)	128.4(7)	P(3)−O(12)−Zn(3)	123.7(6)

Table 4. Selected Bond Lengths (Angstroms) and Angles (Degrees) for ZnPO-CJ35[a]

Zn(1)−O(9)	1.906(4)	Zn(1)−O(7)	1.947(4)
Zn(1)−O(5)	1.961(4)	Zn(1)−Cl(2)	2.2592(17)
Zn(2)−O(12)	1.929(4)	Zn(2)−O(11)	1.932(4)
Zn(2)−O(3)	1.945(4)	Zn(2)−Cl(1)	2.2873(17)
P(1)−O(9)	1.493(5)	P(1)−O(12)	1.517(4)
P(1)−O(2)	1.536(5)	P(1)−O(6)	1.572(4)
P(2)−O(1)	1.515(5)	P(2)−O(7)	1.517(4)
P(2)−O(3)#1	1.518(5)	P(2)−O(8)	1.584(5)
P(3)−O(11)	1.517(4)	P(3)−O(5)#2	1.518(4)
P(3)−O(4)	1.536(4)	P(3)−O(10)	1.573(4)
P(2)#2−O(3)−Zn(2)	130.5(3)	P(3)#1−O(5)−Zn(1)	128.7(3)
P(2)−O(7)−Zn(1)	135.9(3)	P(1)−O(9)−Zn(1)	151.6(3)
P(3)−O(11)−Zn(2)	138.5(3)	P(1)−O(12)−Zn(2)	131.6(2)

[a] Symmetry transformations used to generate equivalent atoms, #1: $x, -y + {}^1/_2, z - {}^1/_2$; #2: $x, -y + {}^1/_2, z + {}^1/_2$.

direct methods and refined on F^2 by full-matrix least-squares using the *SHELXTL Program*.[43] The heaviest atoms Zn, Co, Cl, and P were easily located, and then non-hydrogen atoms (O, N, and C) were placed from subsequent Fourier-difference maps. All of the non-hydrogen atoms were refined anisotropically. The flack parameter 0.01(4) further confirmed the determined absolute structure of ZnPO-CJ34, which crystallized in a chiral space group *C*2. Experimental details for the structural determination are presented in Table 1. Selected bond distances and angles are given in Tables 2, 3, and 4 for ZnPO-CJ33, ZnPO-CJ34, and ZnPO-CJ35, respectively.

Results and Discussion

Description of the Structures. ZnPO-CJ33 possesses a 0D anionic cluster of macroanionic $[Zn_4(H_2PO_4)_2(HPO_4)_2Cl_8]^{6-}$, and racemic $[dl\text{-}Co(en)_3]^{3+}$ cations are located among the clusters to balance the negative charge of the clusters. All of the Zn and P atoms are tetrahedrally coordinated (Figure 1). The Zn(1) atom is connected to three terminal chlorine ions and one bridging oxygen atom, and the Zn(2) atom is connected to three bridging oxygen atoms and one terminal chlorine ion (average Zn−Cl, 2.246 Å; average Zn−O, 1.943 Å; and average O(Cl)−Zn−O(Cl), 110.7°). Each P atom shares two O bridges with the adjacent Zn atoms, leaving two =O/−OH groups to form $HP(1)O_4$ and $H_2P(2)O_4$ tetrahedra (average P−O, 1.527 Å and average O−P−O, 108.6°). The O(1) and O(8) atoms are disordered over two sites with equivalent occupancy (0.5/0.5). The structure of ZnPO-CJ33 consists of 4-rings formed by ZnO_3Cl and $PO_3(OH)$ tetrahedra. The pendant $-H_2P(2)O_4-Zn(1)Cl_3$ moieties hang from the Zn(2) center, as shown in Figure 2,

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(43) Sheldrick, G. M. *SHELXTL Program*, version 5.1; Siemens Industrial Automation: Madison, WI, 1997.

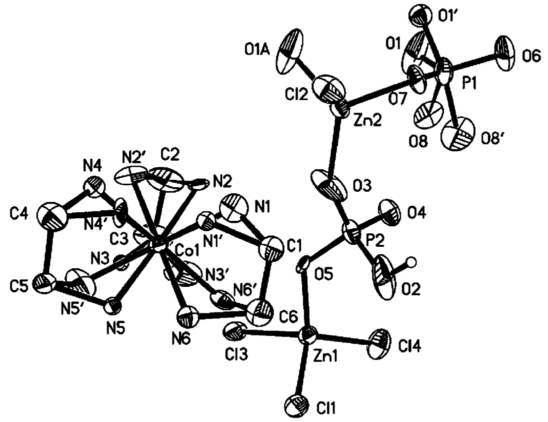

Figure 1. ORTEP diagram of ZnPO-CJ33. Thermal ellipsoids are given at 50% probability. Symmetry transformations used to generate equivalent atoms, O1A: $-x$, $1 - y$, $^1/_2 - z$.

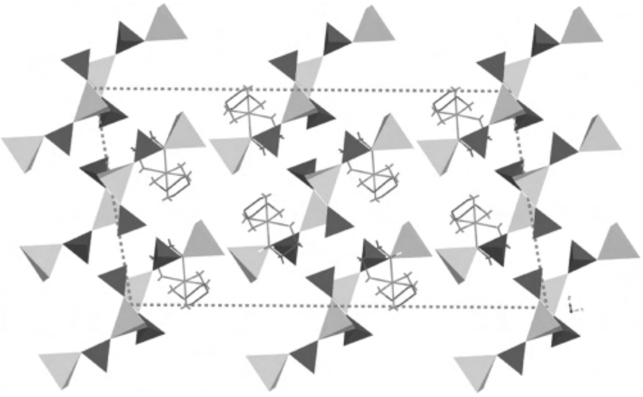

Figure 2. Packing of the clusters of ZnPO-CJ33, viewed along the [010] direction.

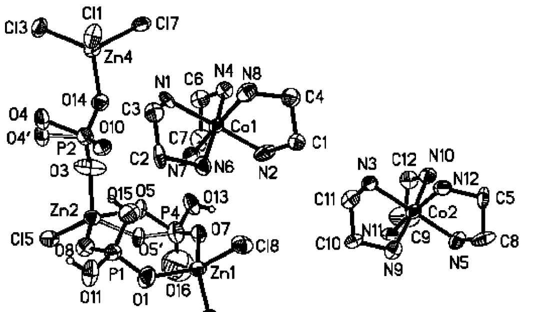

Figure 3. ORTEP diagram of ZnPO-CJ34. Thermal ellipsoids are given at 50% probability.

and are stabilized by extensive H-bonds with the cobalt complex cations.

ZnPO-CJ34 is analogous to ZnPO-CJ33 (Figure 3), but it crystallizes in chiral space group $C2$ instead of $C2/c$ of ZnPO-CJ33 as a result of the existence of optically pure [d-Co(en)$_3$]$^{3+}$ cations. The O(4) and O(5) atoms are disordered over two sites: O(4) and O(4′) (0.5/0.5), and O(5) and O(5′) (0.5/0.5), respectively. The coordination environments of the P and Zn atoms are similar to those of ZnPO-CJ33, and the observed bond lengths and angles are typical values for zincophosphates.[11,13,16] It is worthy noting that ZnPO-CJ34 is the first chiral 0D zincophosphate cluster. Optical rotation measurement reveals that [d-Co(en)$_3$]$^{3+}$ cations are predominantly involved in the as-synthesized product of ZnPO-CJ34. Furthermore, the use of l-Co(en)$_3$I$_3$ as the template under similar conditions leads to the formation of [l-Co(en)$_3$]$_2$[Zn$_4$(H$_2$PO$_4$)$_2$(HPO$_4$)$_2$Cl$_8$].

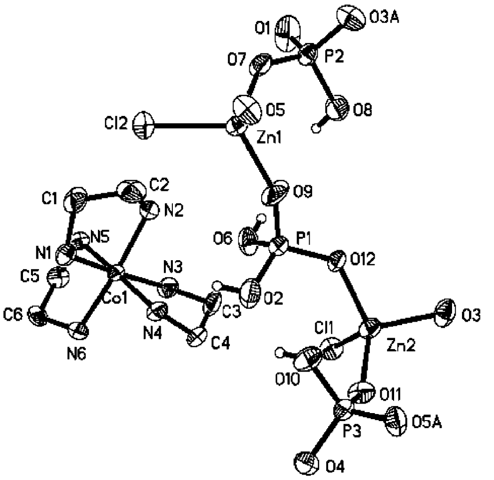

Figure 4. ORTEP diagram of ZnPO-CJ35. Thermal ellipsoids are given at 50% probability. Symmetry transformations used to generate equivalent atoms, O3A: $+x$, $-y$, $-^1/_2 + z$; O5A: $+x$, $-y$, $+z$.

ZnPO-CJ35 possesses a 1D anionic chain structure of [Zn$_2$(H$_2$PO$_4$)(HPO$_4$)$_2$Cl$_2$]$^{3-}$, and racemic [dl-Co(en)$_3$]$^{3+}$ cations are located among the adjacent chains (Figure 4). Zn(1) and Zn(2) atoms each are tetrahedrally coordinated to one terminal chlorine ion and three oxygen bridges that are shared by P atoms (average Zn−Cl, 2.273 Å; average Zn−O, 1.937 Å; and average O−Zn−O(Cl), 109.39°). Each P atom shares two oxygen atoms with the adjacent Zn atoms, leaving two terminal −OH groups for the P(1) atom and one terminal =O and one terminal −OH groups for the P(2) and P(3) atoms (average P−O, 1.533 Å; average O−P−O, 109.43°). The alternating linkage of H$_2$PO$_4$/HPO$_4$ and ZnO$_3$-Cl tetrahedra constitutes a 1D infinite chain structure (Figure 5). It contains 4-rings formed by the HPO$_4$ and ZnOCl$_3$ tetrahedra, which are connected by the PO$_2$(OH)$_2$ tetrahedra through a Zn−O−P linkage. To the best of our knowledge, only corner-shared or edge-shared 4-ring chain structures have been known in zincophosphates.[6,27−37]

Discussions

ZnPO-CJ33 and ZnPO-CJ35 are both prepared in the reaction mixture of ZnCl$_2$, H$_3$PO$_4$, dl-Co(en)$_3$Cl$_3$, and n-BuOH. ZnPO-CJ33 is crystallized at 110 °C, whereas ZnPO-CJ35 is crystallized at 130 °C. Strikingly, a close structural relationship has been found between the structures of ZnPO-CJ33 and ZnPO-CJ35. ZnPO-CJ35 can be viewed as generated from condensation of ZnPO-CJ33 with its terminal Cl ions replaced by HPO$_4$ groups (Figure 6). To investigate the structural relationship of ZnPO-CJ33 and ZnPO-CJ35 further, 0.14 g of finely grounded ZnPO-CJ33 powder was added into 0.084 mL H$_3$PO$_4$ and 8 mL n-BuOH, followed

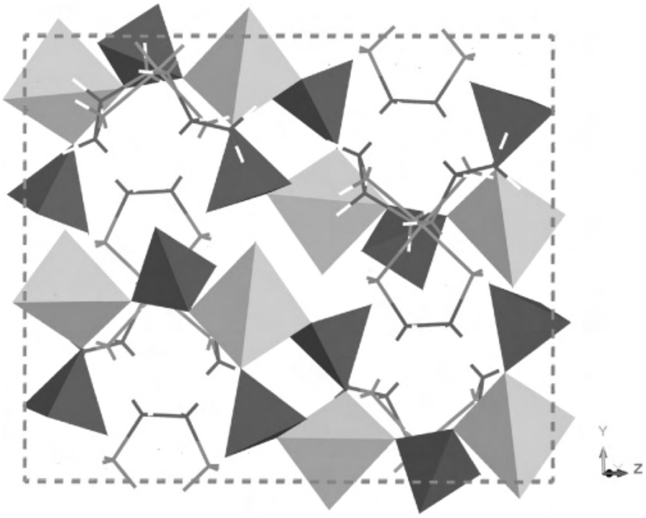

Figure 5. Packing of the chains in ZnPO-CJ35, viewed along the [100] direction.

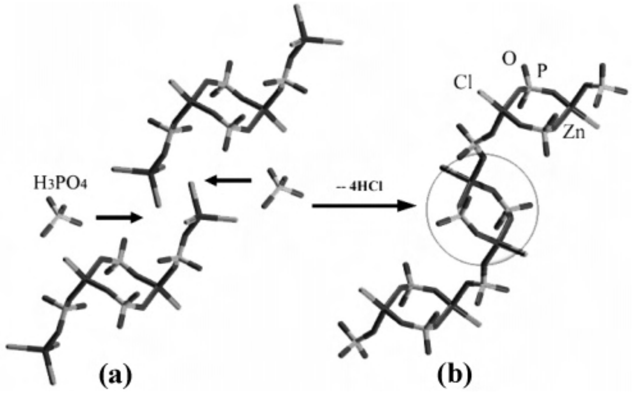

Figure 6. A schematic illustration of the structural relationship between ZnPO-CJ33 and ZnPO-CJ35. (a) The cluster structure of ZnPO-CJ33, (b) the chain structure of ZnPO-CJ35.

by being held at 130 °C for 4 d, and the dominant product obtained is ZnPO-CJ35. It is proposed that the terminal Cl ions attached to the Zn(1) atom of ZnPO-CJ33 might be replaced by H_3PO_4 groups when a large amount of H_3PO_4 existed in the reaction mixture and the condensation of the 0D clusters of ZnPO-CJ33 occurs to form the 1D infinite chain of ZnPO-CJ35 at high-temperature (Figure 6). Further investigation is under way.

As far as we know, ZnPO-CJ33, ZnPO-CJ34, and ZnPO-CJ35 are unusual because they are all chloride-rich zincophosphates with Cl:Zn ratios of 2:1, 2:1, and 1:1, respectively.[11,44,45] As compared to the reported low-dimensional zincophosphates, these compounds not only possess unique framework structures but also have more terminal groups such as =O, −OH, and −Cl groups, which have the potential to undergo further condensation giving rise to more-complex structures under suitable conditions. Moreover, zincophosphates with novel structures could be prepared by using them as a precursor. For instance, 2D layered zincophosphate $[Co(en)_3]_2[Zn_6H_8P_8O_{32}]$[11] is obtained when ZnPO-CJ33 (0.14 g)/ ZnPO-CJ35 (0.07 g) is added to 0.06 mL H_3PO_4 and 4 mL deionized water followed by being heated to 110−130 °C, and 2D layered zincophosphate $[d\text{-}Co(en)_3][Zn_3(H_{0.5}PO_4)_2(HPO_4)_2]$[16] is obtained if ZnPO-CJ34 (0.14 g) is added to 0.03 mL H_3PO_4 and 4 mL deionized water followed by being heated to 110−130 °C. The phase purity of the products is confirmed by the XRD patterns.

Conclusion

Three new low-dimensional chloride-rich zincophosphates have been solvothermally synthesized in the system $ZnCl_2$−H_3PO_4-*dl*-$Co(en)_3Cl_3$/*d*-$Co(en)_3I_3$-*n*-BuOH. The structure of ZnPO-CJ33 possesses a monomeric cluster containing a 4-ring with terminal Cl ions. The ZnPO-CJ34 analogue of ZnPO-CJ33 is a chiral 0D zincophosphate templated by chiral $[d\text{-}Co(en)_3]^{3+}$ cations. ZnPO-CJ35 possesses a new type of chain structure constructed from an alternating connection of Zn_2P_2 4-rings and H_2PO_4 groups. Under the condition at high temperature or with high H_3PO_4 concentration, ZnPO-CJ33 could transform to ZnPO-CJ35, revealing a structural build-up process from 0D cluster to 1D chain structures. Further experimental results indicate that more-complex structures of zincophosphates could be prepared by using these low-dimensional chloride-rich zincophosphates as the precursors.

Acknowledgment. This work is supported by the National Natural Science Foundation of China and the State Basic Research Project of China (Grant 2006CB806103).

Supporting Information Available: Crystallographic data in CIF format and tables of bond distances and angles. This material is available via the Internet free of charge at http://pubs.acs.org.

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