DALTON
FULL PAPER

Synthesis and structure of an open-framework cobalt zincophosphate

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Introducing cobalt into a Zn–P–O–amine system and using oxalates as starting materials, an amine containing open-framework cobalt zincophosphate, $[C_4N_2H_{12}][Co_{0.14}Zn_{1.86}(PO_4)(H_{1.5}PO_4)_2]$ (**1**), has been hydrothermally synthesized and structurally determined. It crystallizes in the monoclinic space group *C*2/*c* (No. 15) with cell parameters a = 13.374(3) Å, b = 12.827(3) Å, c = 8.1940(16) Å, β = 94.77(3)°, V = 1400.9(5) Å^3, Z = 4, D_{cal} = 2.399 g cm^{-3}. The linkages of ZnO_4 and PO_4 give rise to four-membered rings, which serve as the secondary building unit for compound **1**. The four-membered rings (four-MR) share their corners leading to chains. Connection of these chains results in a complex three-dimensional channel system. Eight-MR, twelve-MR and highly distorted twelve-MR channels can be observed along the [010], [110] and [101] directions, respectively. The prominent feature of compound **1** is the clover-like 16-MR channel along the [001] direction. The channel spaces are occupied by the diprotonated piperazine molecules with H-bonds to the framework.

Introduction

The synthesis and application of porous materials are an active area of solid-state chemistry due to their specific properties such as catalytic, ion exchange and intercalation. After the successful synthesis of aluminophosphates, templated metal phosphates with open-framework structures have been much studied with a view to preparing new architectures, compositions and pore topologies.[1] Since the first microporous zincophosphate with zeolite topology reported by Gier and Stucky,[2] a great deal of effort has been devoted to the pursuit of novel structures of this type.[3] Their structures consist of vertex-sharing networks of ZnO_4 and PO_4 tetrahedrals, corresponding to the anionic framework $[ZnPO_4^-]$, that are equivalent to those encountered in aluminosilicates of composition $[AlSiO_4^-]$. Some eye-catching results have been the synthesis of a series of zincophosphates possessing 12- and 18-membered ring channels with very low framework densities in $N(CH_3)_4[ZnH_3(PO_4)_2]$.[4] The most exciting compound is $Zn_3(PO_4)_2(PO_3OH)(H_2DACH)_2 \cdot H_2O$ with hexagonal 24-ring channels.[5] Another goal is to incorporate transition metals into the known phases. Transition atom incorporation has bestowed powerful catalytic properties upon porous materials.[6] Several new topologies have also been reported by incorporating transition metal species into the Al–P–O system.[7] However, of the known open-framework phosphates, those incorporating transition metals are few. Although a number of iron phosphates have been isolated,[8] cobalt phosphates have seldom been reported. Cobalt(II) easily exhibits tetrahedral in addition to five- and six-coordination and cobalt doping would give rise to interesting magnetic properties and enhanced catalytic performance. This has stimulated substantial efforts to synthesize cobalt-doped and pure cobalt phosphates with open-framework structures. Cobalt doping framework structures such as alumino-, gallo-, and indium phosphates have been isolated.[9] Several open-framework cobalt phosphates have also been synthesized recently.[10] While a number of transition metal doped aluminophosphates have been characterized, very few transition metal containing zincophosphates have been identified.[11] Our recent research has been engaged in the synthesis of new open-framework phosphates by introducing transition metals into a Zn–P–O–amine system. With a view to preparing a bimetallic phosphate, a cobalt zincophosphate, $[C_4N_2H_{12}][Co_{0.14}Zn_{1.86}(PO_4)(H_{1.5}PO_4)_2]$ **1**, was hydrothermally synthesized. Compound **1** is a structural analogue of $[C_4N_2H_{12}]_{0.5}[Zn(HPO_4)(H_2PO_4)]$, which was recently reported by Rao's group.[3] Here we report the synthesis and structure of compound **1**.

Experimental

Synthesis and initial characterizations

Compound **1** was hydrothermally synthesized from a solution consisting of $ZnC_2O_4 \cdot 2H_2O$ (0.5 g, 2.64 mmol), $CoC_2O_4 \cdot 2H_2O$ (0.5 g, 2.73 mmol), H_3PO_4 (85%, 1 mL, 16.84 mmol), piperazine (0.5 g, 6.01 mmol) and H_2O (15 g, 833 mmol). The mixture at a pH of *ca.* 3 was heated at 170 °C for 3 days in a Teflon-lined autoclave. The reaction produced blue prism crystals. Simulated X-ray patterns based on the single-crystal structure, which were in agreement with the experimental powder X-ray data, indicates the purity of the phase. The zinc and cobalt content was measured by energy-dispersive X-ray analysis. The results of three samples give an average Co to Zn value of 7 : 93, which is in good agreement with the chemical analysis result (Co 6.18 μg mL^{-1}, Zn 95.6 μg mL^{-1}, 6.7Co : 93.3Zn). Thermogravimetric analysis (TGA) was carried out at a heating rate of 10 °C min^{-1} in air. TGA in the range of room temperature to 800 °C shows two-step weight loss. Between 270 °C and 400 °C, all the water and piperazine molecules are lost with the total loss being 10.1%, in agreement with the calculated value of 9.7%. This compound is thermally unstable. The sample becomes amorphous after being calcined at 400 °C for two hours, as indicated by X-ray powder diffraction.

Structure determination

A blue prism crystal with approximate dimensions of 0.3 × 0.25 × 0.2 mm^3 was selected and mounted on a glass fiber for

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Table 1 Details of data collection, processing and structure refinement

Empirical formula	$[C_4N_2H_{12}][Co_{0.14}Zn_{1.86}(PO_4)(H_{1.5}PO_4)_2]$
Formula weight	505.93
Temperature/K	293 (2)
Wavelength/Å	0.71073
Crystal system, space group	Monoclinic, *C*2/*c* (No. 15)
Unit cell dimensions	
a/Å, α/°	13.374 (3), 90
b/Å, β/°	12.827 (3), 94.77 (3)
c/Å, γ/°	8.1940 (16), 90
Volume/Å^3	1400.9 (5)
Z, Calculated density/g cm^{-3}	4, 2.399
Absorption coefficient/mm^{-1}	3.762
F(000)	1014
Crystal size/mm^3	0.3 × 0.25 × 0.2
Theta range for data collection/°	2.20–33.45
Limiting indices	$-20 < h < 16$, $-11 < k < 19$, $-12 < l < 11$
Reflections collected/unique	6496/2607
Absorption correction	Empirical
Max. and min. transmission	0.112 and 0.016
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.075
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0249$, $wR2 = 0.0673$
R indices (all data)	$R1 = 0.0276$, $wR2 = 0.0681$
Large diff. peak and hole/e A^{-3}	−0.594 and −0.104

structure determination. The room temperature (293 ± 2 K) single-crystal X-ray experiments were performed on a Bruker P4 diffractometer equipped with a CCD area detector device. Data were collected in the range of $2.20° < \theta < 33.5°$. A total of 6496 data were collected and merged to give 2607 unique reflections with 2343 observed. The structure was solved by direct methods using the SHELXS-97 program package. Raw intensities were corrected for Lorentz and polarization effects and absorption by empirical methods based on ψ-scan data. Direct phase determination yielded the positions of metal atoms, P and some of the oxygen atoms. The other oxygen atoms, piperazine and hydrogen atoms of the phosphate were located in successive difference Fourier syntheses. The hydrogen atoms of piperazine were generated theoretically and rided on their parent atoms in refinement. The metal positions are randomly occupied by cobalt and zinc atoms. The occupancies of these positions in the final refinement were assigned as 0.07Co + 0.93Zn in accord with the results for refinement of occupancy and elemental analysis. The final full-matrix least-squares refinement on F^2 converged with $R = 0.0249$ and $R_w = 0.0673$ for the observed reflections [$I \geq 2\sigma(I)$]. The final difference electron density map shows no features. Details of crystal parameters, data collection and structure refinement are given in Table 1. Selected bond lengths and angles are listed in Table 2.

CCDC reference number 178612.

See http://www.rsc.org/suppdata/dt/b2/b201089p/ for crystallographic data in CIF or other electronic format.

Results and discussion

Compound **1** crystallizes in the monoclinic space group *C*2/*c*. Its structure is comprised of an anionic coordination network with the stoichiometry $[Co_{0.14}Zn_{1.86}(PO_4)(H_{1.5}PO_4)_2]^{2-}$ that contains channels occupied by diprotonated piperazine. The asymmetric unit of **1** contains twelve non-hydrogen atoms, of which nine belong to the framework and three to the guest. The metal site M(1) is randomly occupied by Co and Zn atoms in the ratio of 0.07Co : 0.93Zn. The metal atoms are tetrahedrally coordinated by oxygen atoms (Fig. 1). The bond lengths of M(1)–O are in the range of 1.9128(11) Å and 1.9689(14) Å with bond angles of 103.86(5)–113.58(6)°, which are typical of Zn or Co in a tetrahedral coordination. The metal atoms are connected to the P atoms *via* oxygen atoms without any M–O–M and P–O–P linkages. The M–O–P bond angles range from 125.33° to 150.34°. Each of the two P atoms are tetrahedrally coordinated with bond lengths in the range from 1.4888(13) Å to 1.5689(15) Å and bond angles of 104.85(7)–114.14(8)°. Assuming the valences of Co, Zn, P and O are +2, +2, +5 and −2, respectively, the framework of $[Co_{0.14}Zn_{1.86}(PO_4)_3]$ creates a negative charge of −5. Besides the diprotonated piperazine molecule, three protons are needed for charge balance, in agreement with the hydrogen positions associated with the terminal P–O groups observed in the difference Fourier maps. According to the structure refinement, P(2)–O(3) and P(2)–O(5) are P–OH groups.

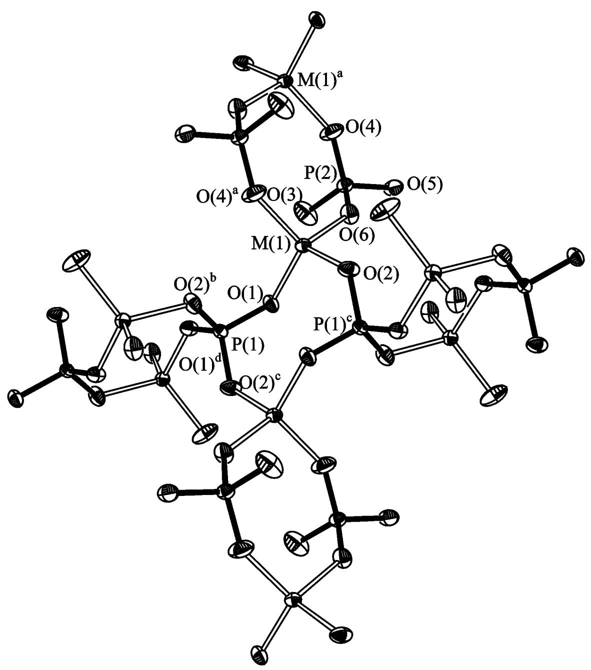

Fig. 1 An ORTEP view of **1** with 50% probability ellipsoids, showing the labeling scheme.

The framework structure of **1** is constructed by alternative MO_4 and PO_4 tetrahedrals, which are linked through their vertices giving rise to a three-dimensional architecture with apertures. The linkage of MO_4 and PO_4 results in four-membered rings as the secondary building units. The corner-shared connectivity of the four-membered rings gives rise to infinite chains running in two different directions (Fig. 2). The linkages of these chains form a complex channel system. Along the [010] direction, 8-membered ring channels can be observed

Table 2 Bond lengths (Å) and bond angles (°)

	M(1)^a–O(4)^b	1.9128(14)	P(2)–O(6)	1.5104(11)
	M(1)–O(1)	1.9229(13)	P(2)–O(5)	1.5339(12)
	M(1)–O(2)	1.9285(11)	P(2)–O(3)	1.5689(15)
	M(1)–O(6)	1.9689(11)	N(1)–C(1)	1.477(2)
	P(1)–O(2)^c	1.5247(11)	N(1)–C(2)^f	1.490(2)
	P(1)–O(2)^d	1.5247(11)	C(1)–C(2)	1.505(2)
	P(1)–O(1)	1.5398(11)	C(2)–N(1)^f	1.490(2)
	P(1)–O(1)^e	1.5398(11)	O(2)–P(1)^d	1.5247(11)
	P(2)–O(4)	1.4888(13)	O(4)–M(1)^b	1.9128(14)
	O(4)^b–M(1)–O(1)	112.53(6)	O(4)–P(2)–O(5)	108.18(7)
	O(4)^b–M(1)–O(2)	113.58(6)	O(6)–P(2)–O(5)	109.69(7)
	O(1)–M(1)–O(2)	108.60(5)	O(4)–P(2)–O(3)	111.58(10)
	O(4)^b–M(1)–O(6)	107.59(5)	O(6)–P(2)–O(3)	104.85(7)
	O(1)–M(1)–O(6)	110.32(5)	O(5)–P(2)–O(3)	108.24(8)
	O(2)–M(1)–O(6)	103.86(5)	C(1)–N(1)–C(2)^f	111.22(13)
	O(2)^c–P(1)–O(2)^d	112.66(10)	N(1)–C(1)–C(2)	111.39(13)
	O(2)^c–P(1)–O(1)	108.31(6)	N(1)^f–C(2)–C(1)	110.71(14)
	O(2)^d–P(1)–O(1)	109.99(7)	P(1)–O(1)–M(1)	130.80(7)
	O(2)^c–P(1)–O(1)^e	109.99(7)	P(1)^d–O(2)–M(1)	125.33(7)
	O(2)^d–P(1)–O(1)^e	108.31(6)	P(2)–O(4)–M(1)^b	150.34(10)
	O(1)–P(1)–O(1)^e	107.46(9)	P(2)–O(6)–M(1)	137.62(8)
	O(4)–P(2)–O(6)	114.14(8)		
Hydrogen bonding				
	H(5) ··· O(5)^g	1.24(1)	H(3) ··· O(5)^h	1.89(1)
	H(1A) ··· O(1)^g	1.80(1)	H(1B) ··· O(6)	1.92(1)
	O(5)–H(5) ··· O(5)^g	166.6(2)	N(1)–H(1A) ··· O(1)^g	169.5(2)
	O(3)–H(3) ··· O(5)^h	169.5(2)	N(1)–H(1B) ··· O(6)	169.7(2)

^{a} M = 0.93Zn + 0.07Co. Symmetry transformation code:^{b} $(0.5 - x, 0.5 - y, -z)$; ^{c} $(x, -y, -0.5 + z)$; ^{d} $(1 - x, -y, -z)$; ^{e} $(1 - x, y - 0.5, -z)$; ^{f} $(0.5 - x, 0.5 - y, 1 - z)$, ^{g} $(1 - x, y, 0.5 - z)$, ^{h} $(x, 1 - y, -0.5 + z)$.

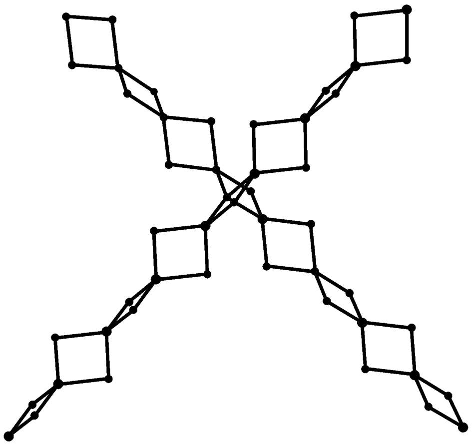

Fig. 2 The structure of the four-membered ring chains.

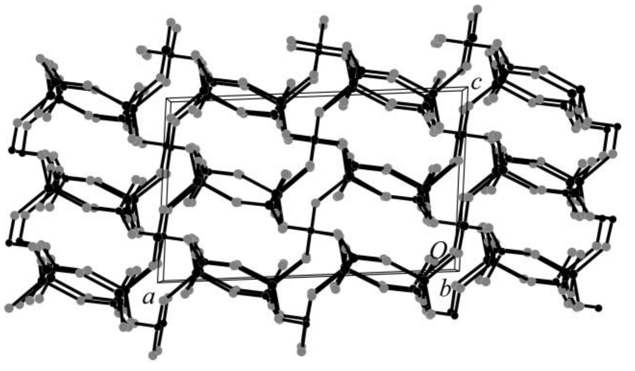

Fig. 3 The structure of **1** viewed along the [010] direction, showing the eight-membered ring channels.

(Fig. 3). The connection of MO_4 and PO_4 groups gives rise to 12-membered ring channels along the [110] direction (Fig. 4). Another highly distorted 12-membered ring channel, which looks like a six-membered ring, can be observed along the [101] direction (Fig. 5). The linkages of the four-membered ring chains lead to fascinating 16-membered ring clover-like channels along the [100] direction (Fig. 6), which are similar to the 20-membered ring channels of the well-known gallophosphate cloverite .[12]

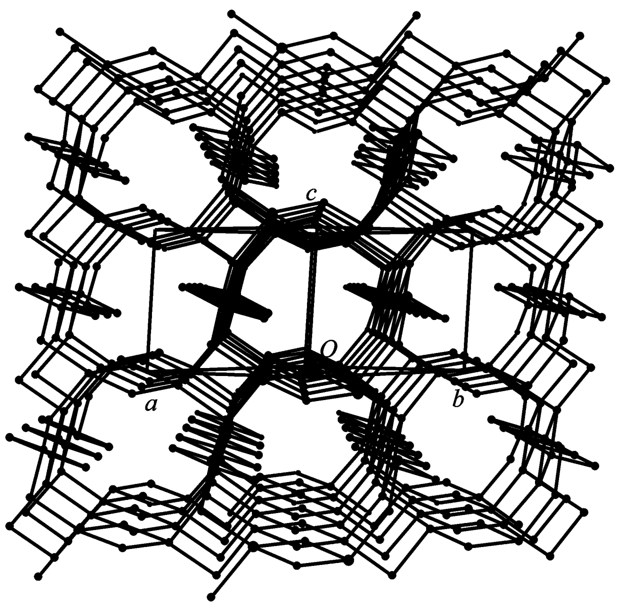

Fig. 4 The 12-membered ring channels viewed along the [110] direction. The oxygen atoms and piperazine molecules are omitted.

The diprotonated piperazine molecules are located in the channel spaces to compensate for the negative framework charge. Each of the NH_2 groups form well-directed hydrogen bonds to oxygen atoms in the framework [$d_{\mathrm{H(1A)}\cdots\mathrm{O(1)}}$ = 1.80(1) Å, $d_{\mathrm{H(1B)}\cdots\mathrm{O(6)}}$ = 1.92 Å]. Two P(2)O(5)H hydrogenphosphates share hydrogen atoms in 2.456 Å [O(5)–H(5)–O(5), $d_{\mathrm{H(5)–O(5)}}$ = 1.24(1) Å]. The hydrogen atom of the P(2)O(3)H bonds to the neighboring $P(2)O_4$ group [$d_{\mathrm{H(3)}\cdots\mathrm{O(5)}}$ = 1.89(1) Å].

Conclusions

Interest in the incorporation of transition metal ions into open-framework phosphates was initiated by the discovery of

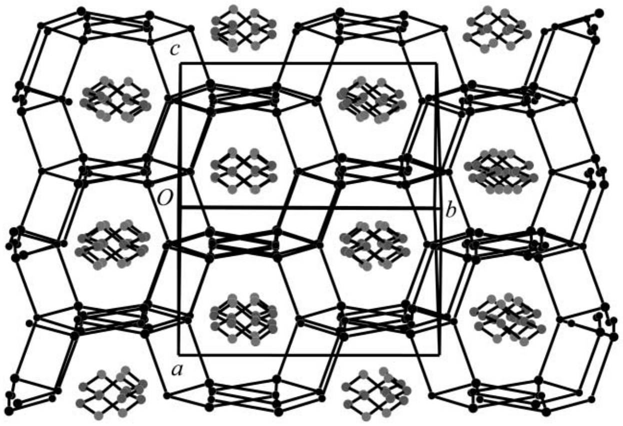

Fig. 5 The topology of **1** viewed along the [101] direction showing the highly distorted 12-membered ring channels with the encapsulated piperazine molecules. The oxygen atoms are omitted.

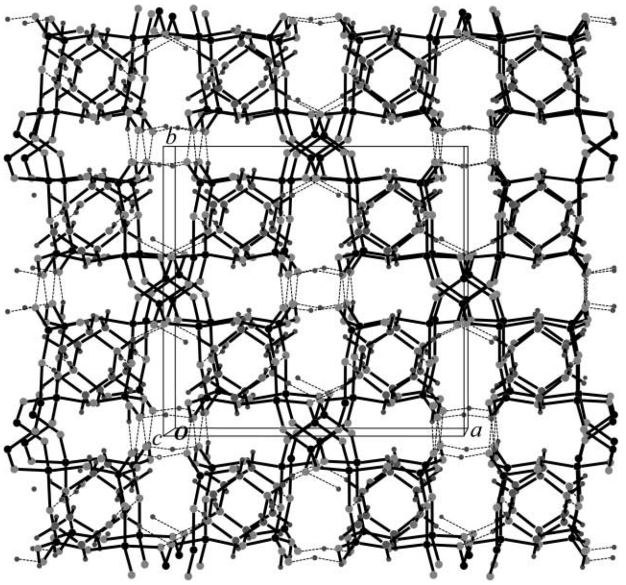

Fig. 6 A view of packing along the [001] direction showing the sixteen-membered ring channels with dashed lines showing the hydrogen bonds.

the MAPO-*n* series,[13] which is of paramount importance in the development of clean technology for chemical conversions under mild conditions.[6] A number of new structures have been found in transition metal doped alumino- and gallophosphates.[1,6,7] While the numbers of known open-framework zincophosphates has grown rapidly, studies on transition metal incorporation have seldom been reported. Introducing cobalt species into a Zn–P–O–amine system, a cobalt zincophosphate has been hydrothermally synthesized using piperazine as the template. Structure determination shows that its structure contains corner-shared four-membered ring chains. The connection of MO_4 and PO_4 groups results in a complex channel system. Eight-MR, 12-MR and 16-MR channels can be observed along the [010], [110], [101] and [001] directions, respectively. The diprotonated piperazine is located in the channels. The unique structure of compound **1** gives us further understanding of metal phosphates. The successful synthesis of compound **1** also implies that more structures may be isolated in this system by varying the synthetic conditions.

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