A new mixed divalent metal phosphate with zeolite thomsonite framework topology†

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The synthesis and crystal structure of $[Zn_{(10-x)}Co_x(PO_4)_8(HPO_4)_2](C_3N_2H_{12})_4(H_2O)_3$ ($x \approx 3.45$) (ZCP-THO), which is the first mixed cobalt and zinc phosphate with zeolite THO topology, are described. ZCP-THO is characterized by means of single-crystal and powder X-ray diffraction. The structure has a 3-D 8-ring channel system with protonated 1,3-propanediamine cations and water molecules occupying the channel junctions. The structure collapsed after the removal of the organic template by heating.

Zeolite analogs containing transition metals are highly desirable for industrial processes.[1,2] There have been many efforts to synthesize transition-metal-containing zeolite analogs.[3] Incorporation of transition metals has been successful in a number of systems, particularly in the Al-P-O-based and Ga-P-O-based families.[4–9] Recently, the degree of substitution for Al^{3+} by divalent transition elements has increased to about 90%.[6,7] Compared with the aluminophosphate and gallophosphate structures, the divalent metal phosphate framework is highly negatively charged. Incorporation of cobalt atoms into aluminophosphate can modify the reactivity and distribution of the active sites. For example, CoAPO-5 and CoAPO-11 have been used as catalysts in the autoxidation of cyclohexane[10] and *p*-cresol;[11] CoAPO-18 can selectively catalyze the conversion of methanol to light olefins.[12] Although a large number of divalent metal phosphates, most of which were zinc phosphates, have been synthesized by using organic amine templates, the structures with zeolite analogues are scarce. The difficulties of synthesizing zeolites in the T^{2+}/T^{5+} system can be ascribed to the host–guest charge mismatch, which often results in interrupted structures.[13] Only a few divalent phosphate zeolite analogs, for example, $CoPO_4 \cdot 0.5C_2H_{10}N_2$ (DFT),[14] UiO-20 (DFT),[15] UiO-21 (CHA),[16] NH_4CoPO_4-ABW[17] and NH_4ZnPO_4-ABW,[18] have been synthesized.

We are interested in introducing different metal atoms into one open framework,[19] which can lead to the modification of the physical and chemical properties of the parent compounds.[20] Herein, we report the synthesis and crystal structure of $[Zn_{(10-x)}Co_x(PO_4)_8(HPO_4)_2](C_3N_2H_{12})_4(H_2O)_3$ ($x \approx 3.45$) (ZCP-THO), a novel mixed divalent metal phosphate with a thomsonite (THO) topology. Up to now, a few zeolite analogs with THO topology have been synthesized,[6,21] but none of them were based on a pure divalent metal phosphate. To our knowledge, ZCP-THO is the first organically templated divalent phosphate zeolite having THO topology.

Experimental

ZCP-THO was prepared by employing hydrothermal methods. Typically, ZnO (240 mg), $2CoCO_3 \cdot 3Co(OH)_2 \cdot xH_2O$ (600 mg), H_3PO_4 (85%, 0.6 ml) and 4 ml H_2O were mixed together and stirred for about half an hour. Then 1,3-propanediamine (PDA, 0.8 ml) was added. The mixture was stirred until homogeneous, then transferred to a Teflon-coated autoclave. After heating at 180 °C for two weeks, the autoclave was cooled to room temperature at a rate of 10 °C min^{-1}. The product, a crop of blue crystals, was recovered by suction filtration, washed with deionized water and dried under ambient temperature and conditions. The purity of the resulting solid product was checked by X-ray powder diffraction (Fig. 1). The ratio of Zn : Co was determined by using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The analysis was carried out on an Automscan Advantage instrument (Thermo Jarrel Ash Corporation) and indicates that the crystal products contain 22.1 wt% Zn, 10.6 wt% Co and 15.79 wt% P, suggesting that the molar ratio of (Zn + Co) : P = 0.52 : 0.51. The Zn : Co molar ratio is 0.655 : 0.345.

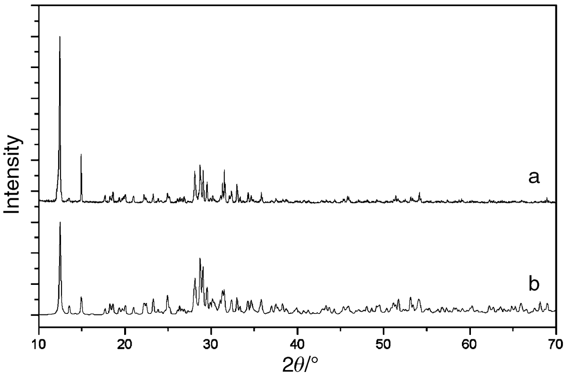

Fig. 1 (a) X-ray powder diffraction (XRD) patterns of ZCP-THO. The data were collected on an MXP 18AHF powder X-ray diffractometer with Cu-Kα radiation ($\lambda_{K_\alpha} = 1.540\,56$ Å) at room temperature. Comparison of the experimental data with that deduced from the structure determination (b) indicates that the product is a pure phase.

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† Electronic supplementary information (ESI) available: TGA and DTA spectra of ZCP-THO. Table of selected bond lengths and angles for ZCP-THO. See http://www.rsc.org/suppdata/nj/b1/b104331p/

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Table 1 Crystal data and structure refinement for ZCP-THO

Empirical formula	$C_{12}H_{56}Co_{3.45}Zn_{6.55}N_8O_{43}P_{10}$
Formula weight	1941.3
T/K	293(2)
λ/Å	0.710 73
Crystal system	Monoclinic
Space group	Pn (no. 7)
a/Å	13.0469(14)
b/Å	14.1260(16)
c/Å	14.2105(16)
β/°	91.110(2)
u/Å^3	2618.5(5)
Z	2
μ(Mo-Kα)/mm^{-1}	2.37
Reflections collected	19 152
Independent reflections	10 461
R_{int}	0.0375
Reflections observed ($>2\sigma$)	9008
Final R indices [$I > 2\sigma(I)$]	$R = 0.0430$, $wR = 0.1017$
R indices (all data)	$R = 0.0496$, $wR = 0.1038$

A suitable single crystal was selected and mounted on a Bruker Smart Apex CCD diffractometer. Data collection was performed at 295 K. The SMART program package was used to determine the unit cell parameters and for data collection. The raw frame data was processed using SAINT[22] and SADABS[23] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[24] program. Structures were solved by direct methods. The metal sites were modeled at 0.345 Co occupancy and 0.655 Zn occupancy in accordance with the ICP-AES results. Refinement was performed by full-matrix least-squares analysis, with anisotropic thermal parameters for all non-hydrogen atoms. The analytical scattering factors for neutral atoms were used throughout the analysis. Propanediamine hydrogen atoms were located by difference syntheses and their coordinates and isotropic parameters were refined. Other hydrogen atoms were placed in calculated positions and not refined. Non-hydrogen atoms were refined anisotropically. The residual electron densities were of no chemical significance. Experimental data and refinement parameters are summarized in Table 1. Selected inter-atomic distances and bond angles are given in the ESI.

CCDC reference number 171459. See http://www.rsc.org/suppdata/nj/b1/b104331p/ for crystallographic data in CIF or other electronic format.

Results and discussion

There are ten unique M (Zn or Co) and ten unique P atoms in the asymmetric unit, all of which are tetrahedrally coordinated by oxygen atoms. MO_4 and PO_4 tetrahedra are strictly alternating in the framework. The structure is built from these tetrahedra connected *via* M–O–P bonds; the channels are occupied by extra-framework 1,3-propanediamine cations and water molecules. All of the metal atoms are four-fold coordinated by PO_4 groups with average metal–oxygen bond distances of 1.941 Å. The O–M–O bond angles are in the range 98.5(2)–121.3(2)° [$(\text{O–M–O})_{\text{av}} = 109.41°$]. All of the P atoms make four P–O–M bonds. The P–O bond distances are in the range 1.510(6)–1.559(5) Å [$(\text{P–O})_{\text{av}} = 1.532$ Å] and the O–P–O angles are in the range 105.7(4)–111.9(3)° [$(\text{O–P–O})_{\text{av}} = 109.46°$]. The ideal bonds are 1.95 Å for Zn–O and 1.93 Å for Co–O. These geometrical parameters are in good agreement with those found in cobalt or zinc phosphate. Assuming the normal valences of M (Zn and Co), P and O to be +2, +5 and −2, respectively, the framework stoichiometry of $M_{10}(PO_4)_{10}$ creates a charge of −10. Taking into account the presence of the four diprotonated 1,3-propanediamine molecules, the excess negative charge of −2 can be balanced by the protonation of two of the PO_4 groups.

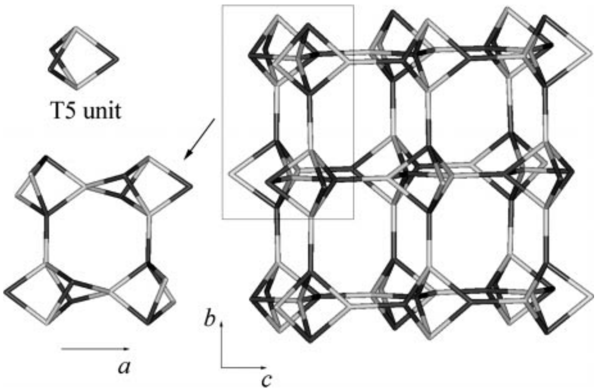

Fig. 2 Configuration of the fi chain in the structure. Organic amines and oxygen atoms are omitted for charity. M (Zn or Co): black stick, P: gray stick.

The structure is built up by using a second building block made up of T5 units which are T_5O_{10} configured linked units. The T5 units are linked by pure translations along the [100] direction (*a*) and form a fibrous chain (fi chain, Fig. 2).[25,26] Each fi chain is joined directly to two others along the [010] direction (*c*) to form a sheet. These two dimensional sheets are stacked along the [001] direction (*b*) to form a three dimensional framework. The chains in neighboring sheets are related by a 180° rotation about an axis parallel to the [010] direction. The topology of this structure is identical to the zeolite type THO denoted by IZA. It belongs to a group of three zeolites known as fibrous zeolites (edingtonite and natronite being the other two) because these structures all comprise fi chains. The differences among THO, EDI[8] and NAT[27] topologies are based on the direction of the fibrous chain. In THO, the direction of the fi chains in adjacent sheets is different. In the EDI topology, all the fi chains are in one direction, while the reversed fi chains are strictly alternating in the NAT topology. In ZCP-THO, there are four 8-ring channel systems propagating in the [100] direction [Fig. 3(a): A, B, C and D], with dimensions of 5.65 × 6.30, 6.47 × 6.81, 7.06 × 6.64 and 6.55 × 6.55 Å, respectively (calculated from the nearest O···O distance). The channels along [010] have dimensions of 6.00 × 5.83 and 5.36 × 5.55 Å [Fig. 3(b): E and F] while the channels along [001] have dimensions of 5.62 × 5.98 and 6.00 × 6.17 Å [Fig. 3(c): G and H].

There are four diprotonated PDA cations and three water molecules in the asymmetric unit. These guest species are accommodated in the channel junctions and hydrogen bonded to oxygen atoms of the framework (Fig. 4). The water molecules are located at the center of an 8-ring circle and hydrogen bond to PO_4 groups. One of the PDA cations is significantly distorted. The distances C10–C11, C11–C12 and C10–N7 are 1.24, 1.66 and 1.86 Å, which are far from those found in the other three PDA cations. The high displacement parameters of C10 and C11 are probably indicative of positional disorder. Nevertheless, the final *R* factors were satisfactory (Table 2), and the most important part of the structure, the framework, is well determined.

A number of unsubstituted three-dimensional zinc phosphates have been reported. However, only several open framework cobalt phosphates are known. Examples include $[H_3N(CH_2)_2NH_3]_{0.5}(CoPO_4)$,[14] NH_4CoPO_4,[17] $[C_2N_2H_{10}]_2$-$[Co_4(PO)_4]H_2O$ and $[C_4N_3H_{16}]_3[Co_6(PO_4)_3]H_2O$.[28] To date, only a few zinc–cobalt mixed phosphates have been reported. For example, $Zn_2Co_4(PO_4)_4(H_2O)_5 \cdot 2H_2O$[29] and $Na_6(CoZn_{1-x}PO_4)_x \cdot yH_2O$[30] have 3D framework structures, $NH_4[Zn_{2-x}Co_x(PO_4)(HPO_4)_2]$[31] and $Zn_{2-x}Co_x(HPO_4)_3$-$C_3N_2H_{12}$[32] have layer structures. ZCP-THO is the first organically templated zinc–cobalt phosphate zeolite with THO topology. It seems that the behavior of mixed zinc and cobalt is not the same as that of the individual components

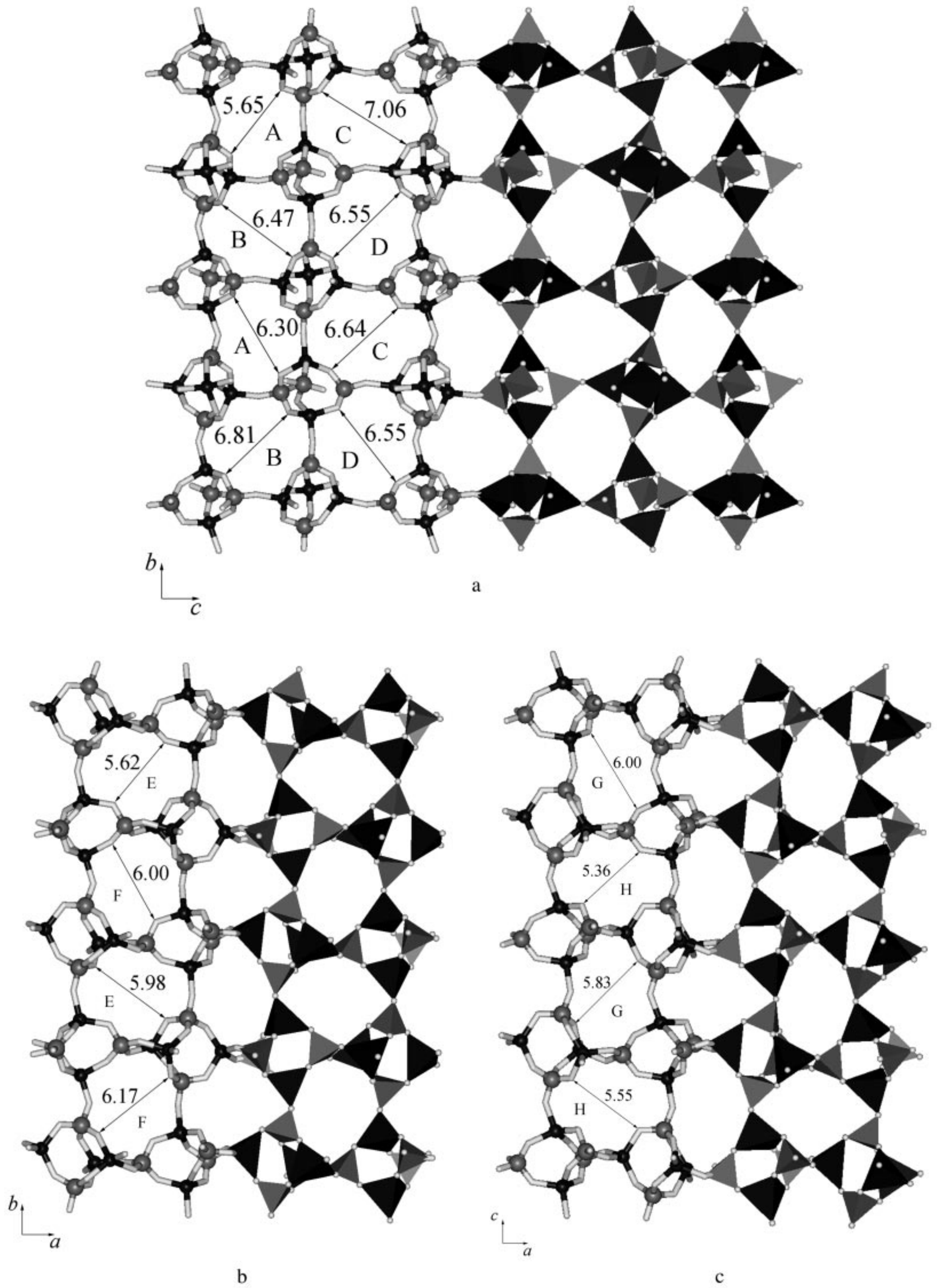

Fig. 3 Polyhedral and ball-stick representations of the structure. (a): Viewed down the [100] direction; (b) viewed down the [010] direction; (c) viewed down the [001] direction. H atoms and 1,3-propanediamine and H_2O molecules are omitted for clarity. M (Zn or Co): small black ball, P: large gray ball, O: light gray stick.

used in the synthesis since no zinc or cobalt phosphates having the thomsonite topology have been found.

The DTA and TGA analyses were performed under an atmosphere of N_2. The DTA-TGA curves of ZCP-THO (given in the ESI) showed that there is one weight loss step of about 2.21% between 200 and 340 °C, which is attributed to the loss of H_2O in the channels (calc. 2.78%). Between 340 and 550 °C, there are three other weight loss steps totaling about 16.23%, which is ascribed to the loss of PDA (calc. 15.25%). Endothermic peaks accompany these steps. Between 590 and 600 °C, there was one weight loss step of about 1.9% accompanied by an endothermic event, which is attributed to the loss of OH from the protonated PO_4 group (calc. 1.85%). After heating at 500 °C for half an hour, the sample became dark. X-Ray powder diffraction and IR spectra show that the structure collapsed when the template molecule was removed.

In summary, a zinc–cobalt phosphate has been synthesized using PDA as a structure directing agent. The compound is the first organically templated zinc–cobalt phosphate zeolite with THO topology. Since the analogous structure has still not been found in zinc or cobalt phosphates, the synthesis of this 3D phosphate is important. The discovery of ZCP-THO indicates that it is possible to use mixed metals to synthesize new open framework phosphate structures.

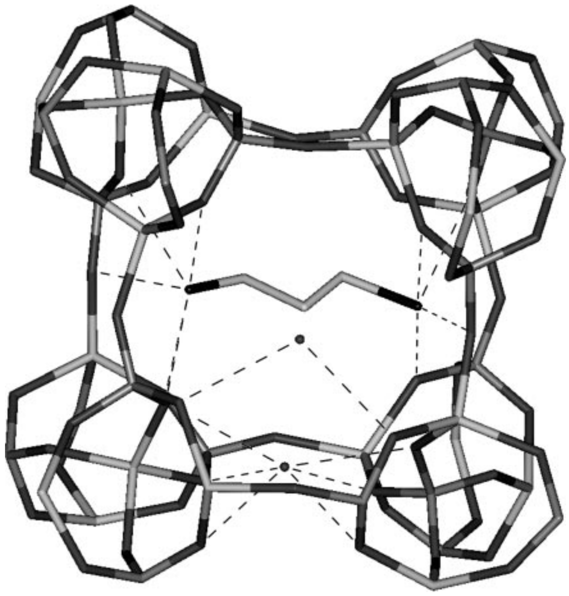

Fig. 4 Possible hydrogen bonds between host and guest species.

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