

# The Synthesis and Characterization of a Two-Dimensional Cobalt–Zinc Phosphate: $\text{NH}_4[\text{Zn}_{2-x}\text{Co}_x(\text{PO}_4)(\text{HPO}_4)]$ ( $x \approx 0.12$ )<sup>§</sup>

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A new layered ammonium cobalt–zinc phosphate has been synthesized under solvothermal conditions at 160 °C and the structure solved using room-temperature single-crystal X-ray diffraction data.  $(\text{NH}_4[\text{Zn}_{2-x}\text{Co}_x(\text{PO}_4)(\text{HPO}_4)]$  ( $x \approx 0.12$ ),  $M_r = 339.75$ , triclinic, space group  $P-1$ ,  $a = 5.237(1)$  Å,  $b = 8.949(1)$  Å,  $c = 9.728(1)$  Å,  $\alpha = 74.99(1)^\circ$ ,  $\beta = 77.64(1)^\circ$ ,  $\gamma = 72.92(1)^\circ$ ,  $V = 416.19(1)$  Å<sup>3</sup>,  $Z = 2$ , 1511 observed data measured with  $I > 3\sigma(I)$ ,  $R = 4.31\%$  and  $R_w = 4.67\%$ . The structure consists of  $\text{MO}_4$  ( $M = \text{Zn}, \text{Co}$ ),  $\text{PO}_4$ , and  $\text{PO}_3(\text{OH})$  tetrahedra linked to form buckled layers containing three- and four-membered rings between which ammonium cations reside. A network of hydrogen bonds involving both interlayer and layer-to-ammonium interactions holds the phosphate layers together.

## Introduction

The potential catalytic applications achievable by doping heteroatoms, in particular transition-metal cations, into microporous materials have long been recognized. Much work to date has concentrated on the incorporation of cobalt ions into a number of open-framework materials such as aluminum and gallium phosphates. Examples of the latter materials include  $(\text{C}_5\text{H}_6\text{N})[\text{CoGa}_2\text{P}_3\text{O}_{12}]$ ,<sup>1</sup> which has the laumontite structure,  $(\text{C}_4\text{H}_{10}\text{N})[\text{CoGaP}_2\text{O}_8]$ ,<sup>2</sup> which has the gismondine structure, and  $(\text{C}_6\text{N}_2\text{H}_{14})_2[\text{Co}_4\text{Ga}_5\text{P}_9\text{O}_{36}]$ ,<sup>3</sup> which has a unique framework topology (IZA structure type CGF). Examples of the former compounds, taken from the work of Professor Sir John Thomas include  $\text{CoAPO-18}^4$  and  $\text{DAF-4}$ ,<sup>5</sup> both of which selectively catalyze the conversion of methanol to light olefins.

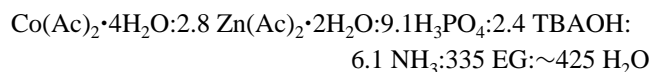
We have been exploring the possibility of incorporating cobalt into zinc–phosphate frameworks, with the aim of preparing microporous  $\text{CoZnPOs}$ . Although numerous  $\text{ZnPOs}$ , both layered and three-dimensional, have now been characterized, there are only two examples of cobalt–zinc phosphates reported in the literature, namely,  $\text{Zn}_2\text{Co}_4(\text{PO}_4)_4(\text{H}_2\text{O})_5 \cdot 2\text{H}_2\text{O}$ <sup>6</sup> and  $\text{Na}_6(\text{Co}_x\text{Zn}_{1-x}\text{PO}_4)_6 \cdot y\text{H}_2\text{O}$  ( $0 \leq x \leq 0.3$ ).<sup>7</sup> Both have three-dimensional tetrahedral framework structures, and analogues containing cobalt only<sup>8</sup> and zinc only<sup>7</sup> are known to exist for the latter material.

In the present work, we report the synthesis and single-crystal characterization of the first layered  $\text{CoZnPO}$ . The material contains ammonium ions as template, and the layers are closely related to those found in  $\text{NaH}(\text{ZnPO}_4)_2$ .<sup>9</sup>

## Experimental Section

The title compound was synthesized under solvothermal conditions from a predominantly nonaqueous system. A mixture of zinc acetate dihydrate (1 g) and cobalt acetate tetrahydrate (0.4 g) was dispersed in ethylene glycol (EG) (30 cm<sup>3</sup>) by vigorous stirring for about 20 min. An aqueous solution of tetrabutylammonium hydroxide (TBAOH) (10 cm<sup>3</sup>, 40 wt %) was then added followed by dropwise addition of orthophos-

phoric acid (1 cm<sup>3</sup>, 85 wt %) with continued stirring. Ammonia–water solution (0.6 cm<sup>3</sup>, 30%  $\text{NH}_3$  by weight) was then added to adjust the pH of the reaction mixture to  $\sim 6$  and to give a gel of overall composition:



The gel was stirred for a further 30 min, sealed in a Teflon-lined stainless steel autoclave, and heated at 160 °C for 22 days under autogenous pressure. The solid product, consisting of single crystals in the form of pale-blue plates, was collected by filtration, washed with distilled water, and dried in air at ambient temperature.

A finely ground sample of the product was studied by energy-dispersive X-ray analysis, performed using a JEOL 2000FX analytical electron microscope.  $\text{Co}_2\text{P}_2\text{O}_7$  and  $\text{Zn}_2\text{P}_2\text{O}_7$  were used as calibration standards.<sup>10</sup> Twelve crystallites were examined, all of which contained Co, Zn, and P. The Co:Zn ratio showed some variation between crystallites but the total metal concentration was approximately equal to that of phosphorus, i.e.,  $(\text{Co} + \text{Zn}):P$  was always  $\sim 1:1$ . The framework formula can therefore be written as  $\text{Co}_{0.12(3)}\text{Zn}_{1.88(5)}\text{P}_2\text{O}_y$  (the oxygen content cannot be determined from electron microscopy measurements). The presence of ammonium ions in the structure is confirmed by a band at 1458 cm<sup>−1</sup> in the infrared spectrum of a finely ground sample pressed into a KBr disk, which corresponds to an N–H deformation mode.<sup>11</sup> Combustion analysis further confirmed the absence of tetrabutylammonium ions in the final product.

Room-temperature X-ray diffraction data were collected from a suitable single crystal using an Enraf-Nonius MACH3 diffractometer (graphite-monochromated  $\text{Cu K}\alpha$  radiation,  $\lambda = 1.5418$  Å) in the  $\omega$ – $2\theta$  scanning mode. X-ray absorption was measured using a 360°  $\psi$  scan using a strong reflection with  $\chi \approx 90^\circ$ . Full experimental information is given in Table 1. The unit cell was determined as triclinic from the measurement of 25 centered reflections and cell parameters optimized by least-squares refinement. Intensity data reduction and corrections for absorption were carried out using the program RC93.<sup>12</sup> The structure was solved in the space group  $P-1$  using the direct methods program SIR92<sup>13</sup> and the non-hydrogen atoms of the

<sup>§</sup> This paper is dedicated to Professor Sir John Meurig Thomas FRS on the occasion of the 65th anniversary of his birthday.

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**TABLE 1: Crystal Data for  $\text{NH}_4[\text{Zn}_{2-x}\text{Co}_x(\text{PO}_4)(\text{HPO}_4)]$  ( $x \approx 0.12$ )**

molecular formula	$\text{Co}_{0.12}\text{Zn}_{1.88}\text{P}_2\text{O}_8\text{NH}_5$
formula weight	339.75
crystal system	triclinic
<i>a</i> (Å)	5.237(1)
<i>b</i> (Å)	8.949(1)
<i>c</i> (Å)	9.728(1)
$\alpha$ (deg)	74.99(1)
$\beta$ (deg)	77.64(1)
$\gamma$ (deg)	72.92(1)
unit-cell volume (Å <sup>3</sup> )	416.19(1)
space group, <i>Z</i>	<i>P</i> -1, 2
temperature (K)	293
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	2.678
linear absorption coefficient (cm <sup>-1</sup> )	126.20
crystal size (mm)	0.15 × 0.06 × 0.03
radiation	Cu K $\alpha$ ( $\lambda = 1.5418$ Å)
$\theta$ max (deg)	74
scan type	$\omega$ -2 $\theta$
total data collected	1715
unique data	1574
observed data ( $I > 3\sigma(I)$ )	1511
merging <i>R</i>	0.0181
weighting scheme	Chebyshev 3 term
residual electron density (min, max) (e Å <sup>-3</sup> )	-1.27, 0.85
no. of parameters refined	134
<i>R</i>	0.0431 <sup>a</sup>
<i>R<sub>w</sub></i>	0.0467 <sup>b</sup>

$$^a R = \sum[|F_o| - |F_c|]/\sum|F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}.$$

framework located. The nitrogen atom of the ammonium counterion was located in an observed Fourier map and all the hydrogen atoms were located in difference Fourier maps. All Fourier calculations and subsequent full-matrix least-squares refinements were carried out using the program CRYSTALS.<sup>14</sup> The coordinates of the framework hydroxyl hydrogen were refined with the O–H bond length restrained to be 1.00(5) Å. The positions of the ammonium hydrogen atoms were, however, poorly defined and the ion was modeled as a rigid regular tetrahedron with bond length of 1 Å. The isotropic thermal parameters of all hydrogen atoms were fixed at 0.05 Å<sup>2</sup>. All other atoms were refined anisotropically. The metal sites were modeled as 0.06 Co occupancy and 0.94 Zn occupancy in accordance with the electron microscopy results. In the final cycle, a three-term Chebyshev polynomial weighting scheme was applied and 134 parameters refined to give residuals of *R* = 4.31 and *R<sub>w</sub>* = 4.67%. Atomic coordinates and thermal parameters are given in Table 2 and selected interatomic distances and bond angles in Table 3.

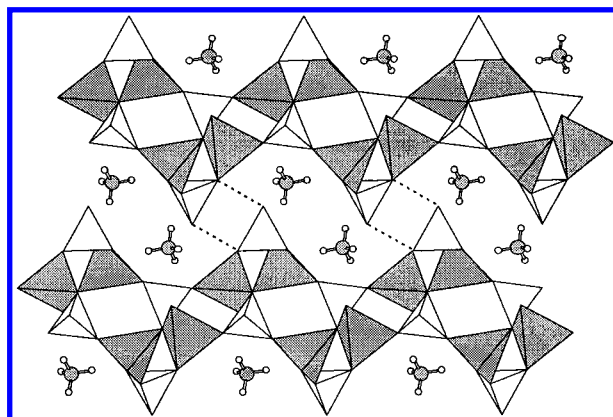
## Discussion

The structure consists of infinite layers of formula  $[\text{M}(\text{PO}_4)(\text{PO}_3(\text{OH}))^-]_n$  charge balanced by ammonium cations

**TABLE 2: Atomic Coordinates and Isotropic Thermal Parameters for  $\text{NH}_4[\text{Zn}_{2-x}\text{Co}_x(\text{PO}_4)(\text{HPO}_4)]$  ( $x \approx 0.12$ ) (with Estimated Standard Deviations in Parentheses)<sup>a</sup>**

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (iso)/Å <sup>2</sup>
M(1)	0.70213(7)	0.10820(4)	0.10870(3)	0.0161
M(2)	0.88459(7)	0.38401(4)	0.22549(3)	0.0153
P(1)	1.1680(1)	0.24443(7)	-0.05120(7)	0.0134
P(2)	0.3940(1)	0.24377(7)	0.38539(7)	0.0152
O(1)	0.9689(4)	0.2360(2)	0.0950(2)	0.0193
O(2)	0.5172(4)	0.3849(2)	0.3200(2)	0.0224
O(3)	1.0911(4)	0.2936(2)	0.3854(2)	0.0229
O(4)	0.9234(4)	0.5952(2)	0.1493(2)	0.0242
O(5)	0.5357(4)	0.1021(2)	0.3129(2)	0.0228
O(6)	0.4543(4)	0.2152(3)	-0.0254(2)	0.0280
O(7)	0.8700(4)	-0.1159(2)	0.1181(2)	0.0219
O(8)	0.4373(5)	0.1905(2)	0.5485(2)	0.0232
N(1)	0.2117(5)	0.7000(3)	0.3307(3)	0.0238
H(1)	0.302(6)	0.590(2)	0.313(3)	0.05
H(2)	0.105(6)	0.692(4)	0.430(1)	0.05
H(3)	0.352(5)	0.759(3)	0.322(3)	0.05
H(4)	0.088(5)	0.759(3)	0.258(3)	0.05
H(5)	0.40(1)	0.096(5)	0.592(5)	0.05

<sup>a</sup> NB: M(1) and M(2) sites both have occupancies of 0.94 Zn and 0.06 Co.



**Figure 1.** Polyhedral representation of  $\text{NH}_4[\text{M}(\text{PO}_4)(\text{PO}_3(\text{OH}))]$  (*M* = Zn, Co) showing interlayer hydrogen bonding interactions represented as dotted lines. Key:  $\text{MO}_4$  units, grey tetrahedra;  $\text{PO}_4$  and  $\text{PO}_3(\text{OH})$  units, white tetrahedra; N atoms, grey spheres, extraframework H atoms, white spheres (drawing package: ATOMS<sup>15</sup>).

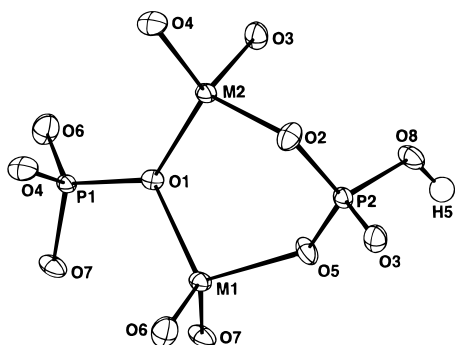
located in the interlayer voids (Figure 1). The layers are closely related to those observed in  $\text{NaH}(\text{ZnPO}_4)_2$ <sup>9</sup> and contain three- and four-membered rings generated from the vertex linking of  $\text{MO}_4$  and  $\text{PO}_4$  tetrahedra. The presence of a small amount of  $\text{Co}^{2+}$  in a tetrahedral environment is confirmed by the pale-blue color of the crystals.

The structure contains two distinct  $\text{MO}_4$  tetrahedra, one  $\text{PO}_4$ , and one  $\text{PO}_3(\text{OH})$  tetrahedron. The M–O and P–O bond lengths and angles are similar to those observed previously in

**TABLE 3: Selected Interatomic Distances and Angles for  $\text{NH}_4[\text{Zn}_{2-x}\text{Co}_x(\text{PO}_4)(\text{HPO}_4)]$  ( $x \approx 0.12$ )<sup>a</sup>**

M(1)–O(1)	2.014(2)	O(1)–M(1)–O(5)	99.38(8)	P(2)–O(3)	1.516(2)	O(4)–P(1)–O(6)	111.6(1)
M(1)–O(5)	1.985(2)	O(1)–M(1)–O(6)	110.68(8)	P(2)–O(5)	1.530(2)	O(6)–P(1)–O(7)	104.4(1)
M(1)–O(6)	1.911(2)	O(5)–M(1)–O(6)	113.86(9)	P(2)–O(8)	1.579(2)	O(4)–P(1)–O(7)	107.7(1)
M(1)–O(7)	1.925(2)	O(1)–M(1)–O(7)	112.84(8)	O(8)–H(5)	0.90(4)	O(6)–P(1)–O(7)	112.7(1)
		O(5)–M(1)–O(7)	99.84(8)				
M(2)–O(1)	1.962(2)	O(6)–M(1)–O(7)	118.23(9)			O(2)–P(2)–O(3)	110.9(1)
M(2)–O(2)	1.945(2)					O(2)–P(2)–O(5)	111.7(1)
M(2)–O(3)	1.950(2)	O(1)–M(2)–O(2)	104.98(8)			O(3)–P(2)–O(5)	112.7(1)
M(2)–O(4)	1.897(2)	O(1)–M(2)–O(3)	110.94(9)			O(2)–P(2)–O(8)	106.6(1)
		O(2)–M(2)–O(3)	102.40(8)			O(3)–P(2)–O(8)	106.4(1)
P(1)–O(1)	1.572(2)	O(1)–M(2)–O(4)	118.91(8)			O(5)–P(2)–O(8)	108.1(1)
P(1)–O(4)	1.511(2)	O(2)–M(2)–O(4)	111.14(9)	M(1)–O(1)–M(2)	117.85(9)	M(2)–O(4)–P(1)	148.1(1)
P(1)–O(6)	1.508(2)	O(3)–M(2)–O(4)	107.26(9)	M(1)–O(1)–P(1)	113.0(1)	M(1)–O(5)–P(2)	127.8(1)
P(1)–O(7)	1.538(2)			M(2)–O(1)–P(1)	126.0(1)	M(1)–O(6)–P(1)	144.3(1)
		O(1)–P(1)–O(4)	109.2(1)	M(2)–O(2)–P(2)	128.5(1)	M(1)–O(7)–P(1)	134.6(1)
P(2)–O(2)	1.518(2)	O(1)–P(1)–O(6)	110.8(1)	M(2)–O(3)–P(2)	130.2(1)		

<sup>a</sup> Distances in angstroms, angles in degrees.



**Figure 2.** View of the local coordination showing the three-membered ring generated from M(1)O<sub>4</sub>, M(2)O<sub>4</sub>, and P(2)O<sub>4</sub> tetrahedra (drawing package: CAMERON<sup>16</sup>).

structures containing similar polyhedra. In particular, the M–O<sub>av</sub> and P–O<sub>av</sub> values of 1.949 and 1.534 Å respectively are close to the average values observed for the Zn–O and P–O bond lengths in NaH(ZnPO<sub>4</sub>)<sub>2</sub> (1.941(5) and 1.533(6) Å), as expected given the low concentration of cobalt present in the title compound.

Each M(1) atom is bonded through oxygen bridges to three different P(1) atoms and one P(2), whereas each M(2) is bonded to two P(1) and two P(2) atoms. The M atoms are also bonded to each other via oxygen O(1), which is three-coordinate (Figure 2). All the oxygen atoms of the P(1)O<sub>4</sub> unit are involved in bonding to metal atoms whereas the P(2)O<sub>4</sub> contains an –OH group, as shown from the rather longer P(2)–O(8)H length of 1.579(2) Å.

The buckled layers thus generated are rather unusual in that they contain three-membered rings, and the strict alternation of the tetrahedral framework atoms, so common in other microporous metal phosphates, is not maintained. The layers are held together by two types of hydrogen-bonding interaction. The first involves interlayer bonding between the terminal –OH group on one layer and an oxygen on the adjacent layer (O(8)···O(5) 2.595(3) Å) and the second involves four shorter and two longer interactions between the NH<sub>4</sub><sup>+</sup> cation and oxygen atoms from both neighboring layers (N(1)···O(2) 2.820(3) Å, N(1)···O(3) 2.880(3) Å, N(1)···O(7) 2.878(3) Å, N(1)···O(8) 2.880(3) Å, N(1)···O(4) 3.017(3) Å, N(1)···O(6) 3.137(3) Å).

This hydrogen-bonding behavior is similar to that observed in NaH(ZnPO<sub>4</sub>)<sub>2</sub> in which the corresponding interlayer O···O distance is 2.693 Å. Replacement of Na<sup>+</sup> or NH<sub>4</sub><sup>+</sup> by the larger counterion Cs<sup>+</sup> leads to the formation of CsH(ZnPO<sub>4</sub>)<sub>2</sub>,<sup>9</sup> which has a less buckled layer structure in which the layers are more separated and interlayer hydrogen bonding is precluded.

## Conclusion

NH<sub>4</sub>[Zn<sub>2–x</sub>Co<sub>x</sub>(PO<sub>4</sub>)(HPO<sub>4</sub>)] (*x* ≈ 0.12), the first layered CoZnPO to be prepared, extends the known range of open-

framework metal phosphate structures which can accommodate redox-active centers and is of importance because of the accompanying potential catalytic properties of such a material. A number of unsubstituted two-dimensional ZnPOs are now known, including NaH(ZnPO<sub>4</sub>)<sub>2</sub>,<sup>9</sup> which contains metal–phosphate layers isostructural with those of the title compound. However, open-framework CoPOs remain relatively rare. Examples include [H<sub>3</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>]<sub>0.5</sub>(CoPO<sub>4</sub>), a zeolitic phase,<sup>17</sup> and two layered templated cobalt phosphates, [H<sub>3</sub>N(CH<sub>2</sub>)<sub>3</sub>–NH<sub>3</sub>]<sub>0.5</sub>(CoPO<sub>4</sub>)·0.5H<sub>2</sub>O and [H<sub>3</sub>N(CH<sub>2</sub>)<sub>4</sub>NH<sub>3</sub>]<sub>0.5</sub>(CoPO<sub>4</sub>),<sup>18</sup> all of which contain CoO<sub>4</sub> tetrahedra sharing common vertices. It remains to be seen whether it is possible to synthesize a cobalt-only analogue of the present lamellar framework.

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**Supporting Information Available:** Anisotropic thermal parameters, including displacement parameters for non-hydrogen atoms, and observed and calculated structure factors and calculated phase angles (15 pages). Ordering information is given on any current masthead page.

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