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FULL PAPER

Study of formation of cobalt and zinc phosphates in solvothermal synthesis using piperazine and 2-methylpiperazine as templating molecules. Structure investigations of $[C_4H_8N_2H_4][(Co_{0.44(1)}Zn_{0.56(1)})_2(PO_4)(H_{1.5}PO_4)_2]$ and of $[C_5N_2H_{14}][(Co_{0.25(3)}Zn_{0.75(3)})(HPO_4)_2]$

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The compounds $[C_4H_8N_2H_4][Zn_2(PO_4)(H_{1.5}PO_4)_2]$, $[C_4H_8N_2H_4][(Co_{0.44(1)}Zn_{0.56(1)})_2(PO_4)(H_{1.5}PO_4)_2]$, $[C_5N_2H_{14}][Zn(HPO_4)_2]$ and $[C_5N_2H_{14}][(Co_{0.25(3)}Zn_{0.75(3)})(HPO_4)_2]$ were obtained in solvothermal synthesis using piperazine or 2-methylpiperazine as templating molecules. Syntheses were made in Teflon-lined pressure vessels at temperatures up to 190 °C and the crystallization processes were investigated by real time *in situ* measurements of synchrotron X-ray powder diffraction patterns at temperatures up to 200 °C.

Introduction

Microporous compounds such as zeolites and aluminophosphates are traditionally obtained by hydrothermal synthesis. In the synthesis of aluminophosphates from reaction mixtures organic template molecules act as structure directing compounds.[1] Amines are often used as template molecules, and transition metal amine complexes have also been used as structure directing compounds.[2–5] The framework aluminium atom can partly be substituted by divalent atoms like Mg, Zn, Co and possibly Mn. It has also been reported that framework structures of phosphates with the transition metals iron and zinc can be obtained with a number of structure directing organic amines like guanidine,[6] *trans*-1,2-diaminocyclohexane,[7] piperazine[8,9] and 1,4-diazabicyclo[2.2.2]octane.[10]

The present investigation was made to study the formation of phosphates of Co and Zn in solvothermal synthesis using the amines piperazine and 2-methylpiperazine as template molecules with *in situ* investigation of the crystallization,[11] crystal synthesis in pressure vessels and characterization by X-ray powder and single crystal diffraction analysis.

Experimental

Sample preparation

The solvents used in the solvothermal reactions were mixtures of water and ethylene glycol (ETG) from Merck. The chemicals used were: 85% H_3PO_4, $Co(CH_3CO_2)_2\cdot4H_2O$, $Zn(CH_3CO_2)_2\cdot2H_2O$ from Merck, piperazine (PIP) and 2-methylpiperazine (2MPIP) from Aldrich. Table 1 lists examples of compositions of reaction mixtures and experimental conditions for the syntheses in pressure vessels. The compositions are listed as quantities in grams used in the preparation of the batches for the synthesis, typically 40 to 80 g, enough for a few solvothermal syntheses and for *in situ* investigations. Using experiment No. 14, Table 1, as an example the procedure was as follows. The solvent was a 1 : 1 by volume mixture of ethylene glycol and water. 1.756 g $Zn(CH_3CO_2)_2\cdot2H_2O$ were dissolved in 18 ml of the solvent and 2.404 g 2-methylpiperazine were added under stirring. 5.980 g 85% H_3PO_4 were dissolved in 18 ml of the solvent and added with stirring to the zinc 2-methylpiperazine solution. The pH of the mixture was measured on pH-indicator strips (Alcilit pH 0–6, Merck), and the mixture stored in polyethylene flasks at room temperature. In the solvothermal synthesis the mixtures were kept in Teflon-lined pressure vessels heated in an oven at the experimental conditions listed in Table 1. The reaction products were washed with water, filtered and dried in air at room temperature.

X-Ray powder diffraction

X-Ray powder patterns of reaction products from the solvothermal synthesis were recorded at 25 °C on a Stoe-Stadi powder diffractometer with a position sensitive detector. A linear detector covering 5° in 2θ was used in a step scan mode to obtain patterns of high resolution in 2θ. The diffractometer was calibrated with a silicon standard ($a = 5.43050$ Å) and Cu-Kα_1 radiation was used ($\lambda = 1.540598$ Å). Powder patterns of cobalt containing samples were measured at 25 °C on a Philips diffractometer using Cu-Kα_1 radiation. The diffractometer has an analyser crystal which eliminates the background from the fluorescence of the sample, and a step scan mode was used in the 2θ range 8–60° with $\Delta2\theta = 0.02°$. The Co–Zn composition of samples containing these two elements was determined from X-ray fluorescense analysis using a MaXim 2040 EnVac Scanning Electron Microscope.

***In-situ* investigations.** The *in situ* synchrotron X-ray powder diffraction investigation of the reaction mixtures was made on a MAR diffractometer at the beam line X7B at NSLS, Brookhaven National Laboratory. The reaction mixtures were kept in 0.7 mm diameter quartz glass capillaries at an internal pressure of up to 25 atm, and the capillaries were heated with hot air using a temperature ramp from 25 to 200 °C. The temperature of the hot air flow was monitored with a chromel–alumel thermocouple and the temperature of the capillary was calibrated from measurements of the thermal expansion of a sample of a powder of silver and of the melting point of sulfur housed in a capillary. The wavelength used was 0.9378 Å

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Table 1 Experimental conditions for synthesis of metal phosphates. Quantities of components in g

Sample No.	Template PIP	2MPIP	Acetate[a] CoAc	ZnAc	85% H_3PO_4	Solvent ETG	water	pH of mixture	Age of gel/h	T/°C	Time/h	Main product	Impurity
1	0.52		0.50	3.51	1.50	4.5	4.5	4.5	1	184	47	$Co_7(HPO_4)_4(PO_4)_2$	
2	4.50		4.33	0.88	11.96	36	36	4.0	1	135	46	$Co_3(OH)_2(HPO_4)_2$	
3	4.50		4.33	3.51	11.96	36	36	4.0	1	185	49	$Co_3(OH)_2(HPO_4)_2$	
4	6.24		6.70	1.76	8.31	25	25	5.5	1	135	48	Not identified	**F**
5	6.24		6.70	1.76	8.31	25	25	5.5	1	185	48	$Co_3(OH)_2(HPO_4)_2$	**G**
6		2.40	1.98	1.76	2.99	18	18	5.5	1	135	91	$Co_3(OH)_2(HPO_4)_2$	
7		2.40	1.98	1.76	2.99	18	18	5.5	720	150	43	$Co_3(OH)_2(HPO_4)_2$	
8		2.40	1.98	1.76	2.99	18	18	5.5	720	170	43	$Co_3(OH)_2(HPO_4)_2$	
9		2.40	1.98	1.76	2.99	18	18	5.5	1	185	91	$Co_3(OH)_2(HPO_4)_2$	
10	4.14				11.96	36	36	3.5	1	135	47	**D**	**A**
11	1.03				2.99	9	9	3.5	1	185	49	**D**	
12	4.14				11.96	36	36	3.5	1	185	48	**D**	
13		2.40			5.98	18	18	4.0	1	135	48	**J**	
14		2.40			5.98	18	18	4.0	1	185	48	**J**	
15		2.40			5.98	18	18	3.5	1	135	94	**J**	
16		2.40			5.98	18	18	3.5	1	185	94	**J**	
17		2.40			2.99	18	18	5.5	1	150	43	**J**	
18		2.40			2.99	18	18	5.5	1	170	43	**J**	
19	2.59		2.49	2.20	7.48	22	22	4.3	1	190	24	**H**	
20	4.68		3.35	4.37	12.46	38	38	4.0	1	135	44	**I**	
21	4.68		3.35	4.37	12.46	38	38	4.0	1	185	45	**H**	
22		2.72	1.76	2.18	6.23	19	19	3.5	1	135	48	**K**	
23		2.72	1.76	2.18	6.23	19	19	3.5	1	185	48	**K**	
24		2.72	0.84	1.09	6.23	18	18	3.5	1	135	93	**K**	
25		2.72	0.84	1.09	6.23	18	18	3.5	1	185	93	**K**	
26		2.41	0.84	1.02	2.99	18	18	3.5	1	150	43	**K**	
27		2.41	0.84	1.02	2.99	18	18	3.5	1	170	43	**K**	

For composition of the products **A** to **K** see Table 2. [a] CoAc = $Co(CH_3CO_2)_2\cdot 4H_2O$, ZnAc = $Zn(CH_3CO_2)_2\cdot 2H_2O$.

and Bragg reflections out to (sin θ)/λ = 0.22 Å^{-1} could be recorded. The MAR diffractometer recorded a diffraction frame in 82 s, and the temperature ramp was set from 25 to 200 °C in 120 min, yielding 88 frames for this range corresponding to ΔT = 2 °C per frame. The frames were integrated using the software FIT2D[12,13] and the powder patterns displayed as a stack showing Bragg reflections to turn up or disappear during the experiment. The crystalline reaction products were identified from their X-ray diffraction powder patterns.

X-Ray single crystal diffraction

A Siemens SMART diffractometer with an area detector was applied using Mo-Kα radiation (λ = 0.71073 Å). In structure solution the direct method program SIR[14] was used, and the least-squares program LINUS[15] with scattering contributions from neutral atoms[16] was used in the structure refinement.

Results and discussion

Solvothermal synthesis

A number of zinc phosphates containing the protonated piperazine molecule have been investigated and their structures reported, see Table 2. In addition, two cobalt phosphates containing the protonated piperazine molecule and one containing protonated 2-methylpiperazine[17] have been described. The crystallographic data reported[8,9] were used to calculate the powder patterns of these compounds using the program LAZY PULVERIX.[18] In the solvothermal synthesis the zinc phosphate $[C_4H_8N_2H_3][Zn_2(PO_4)(H_2PO_4)_2]$, **D** and the cobalt–zinc phosphate $[C_4H_8N_2H_4][(Co_xZn_{1-x})_2(PO_4)(H_{1.5}PO_4)_2]$ **H** containing the protonated piperazine ion were formed as single crystals. The structure of $[C_4H_8N_2H_3][Zn_2(PO_4)(H_2PO_4)_2]$ was recently reported,[8] including a detailed description of its framework structure. However, in analogy to the results of the present investigation, see below, it is suggested to use the formula $[C_4H_8N_2H_4][Zn_2(PO_4)(H_{1.5}PO_4)_2]$ **D** for the compound.

Table 2 Compositions of zinc and cobalt phosphates containing the piperazine cation $C_4H_8N_2H_4^{2+}$ and the 2-methylpiperazine cation $C_5N_2H_{14}^{2+}$

Chemical composition	Ref.	Short notation, this work
$[C_4H_8N_2H_4][Zn(HPO_4)_2(H_2O)]$	9	**A**
$[C_4H_8N_2H_4][Zn_{3.5}(PO_4)_3(H_2O)]$	9	**B**
$[C_4H_8N_2H_4][Zn_2(H_2O)(HPO_4)(PO_4)]_2$	8,9	**C**
$[C_4H_8N_2H_4][Zn_2(PO_4)(H_{1.5}PO_4)_2]$[a]	8,9	**D**
$[C_4H_8N_2H_4][Zn_2(HPO_4)_2(H_2PO_4)_2]$	9	**E**
$[C_4H_8N_2H_4]_{1.5}[Co(HPO_4)_2(PO_4)(H_2O)]$	9	**F**
$[C_4H_8N_2H_4]_{1.5}[Co(HPO_4)_2(PO_4)(H_2O)]$	9	**G**
$[C_4H_8N_2H_4][(Co,Zn)_2(PO_4)(H_{1.5}PO_4)_2]$[a]		**H**
$[C_4H_8N_2H_4][(Co,Zn)(HPO_4)_2(H_2O)]$		**I**
$[C_5N_2H_{14}][Zn(HPO_4)_2]$[a]		**J**
$[C_5N_2H_{14}][(Co,Zn)(HPO_4)_2]$[a]		**K**
(R,S)-$[C_5H_{14}N_2][Co(HPO_4)_2]$	17	**L**

[a] Composition according to this work.

Using the template molecule 2-methylpiperazine the following crystalline compounds were formed in the solvothermal syntheses, see Tables 1 and 2: $[C_5N_2H_{14}][Zn(HPO_4)_2]$ **J** and $[C_5N_2H_{14}][(Co_xZn_{1-x})(HPO_4)_2]$ **K**.

In situ investigations

Zinc–piperazine–phosphate. The composition of the sample is listed in Table 1, experiment No. 11, age of gel 792 h. The heating ramp is from 25 to 200 °C, and the stack of powder patterns displayed in Fig. 1 shows three crystalline phases in this temperature interval. The starting reaction mixture is partly crystalline and this phase is present in the temperature interval 25 to 120 °C. From 120 to 180 °C an intermediate phase is

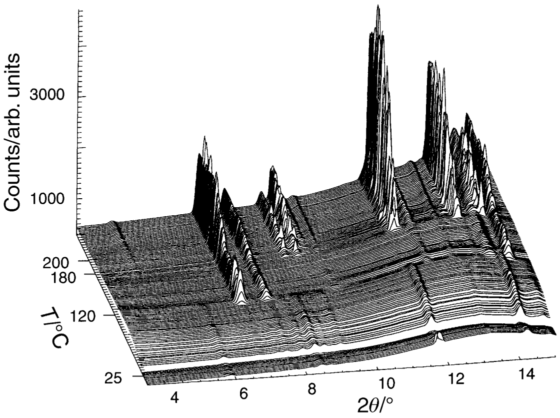

Fig. 1 Stack of powder patterns showing crystallization of zinc–piperazine–phosphates.

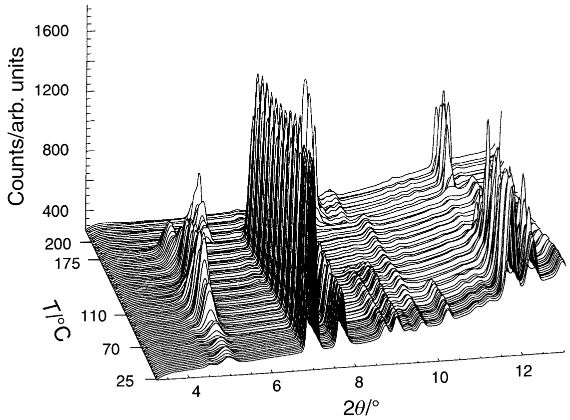

Fig. 2 Stack of powder patterns showing crystallization of cobalt–zinc–piperazine–phosphates.

formed, identified as $[C_4H_8N_2H_4][Zn(HPO_4)_2(H_2O)]$ **A**. The second reaction product starts to be formed from 180 °C, and the observed Bragg reflections all belong to the powder pattern of **A** and of this unidentified phase. The *in situ* experiment with the short heating time thus does not result in the final reaction product found in experiment No. 11, which was $[C_4H_8N_2H_4][Zn_2(PO_4)(H_{1.5}PO_4)_2]$ **D**. This phase would possibly be formed if the capillary was kept for longer time at 200 °C, as the transformation from **A** to **D** is a matter of removing H_2O from compound **A**.

Cobalt–zinc–piperazine–phosphate. The composition of the sample is listed in Table 1, experiment No. 21, age of gel 696 h. The heating ramp is from 25 to 200 °C. The stack of powder patterns, Fig. 2, shows Bragg reflections from at least five crystalline phases. The starting reaction mixture is crystalline. One phase is present in the temperature range 25 to 175 °C and this phase is $[C_4H_8N_2H_4][Zn(HPO_4)_2(H_2O)]$ **A**, or the analogous solid Co–Zn solution compound $[C_4H_8N_2H_4][(Co,Zn)(HPO_4)_2(H_2O)]$ **I**. One unknown phase is present in the temperature interval 25 to 70 °C, with Bragg reflections at $d = 10.7$ and 5.3 Å. A second unknown phase is present in the interval 25 to 110 °C with Bragg reflections at $d = 6.2$, 6.0, 4.6 and 4.5 Å, respectively. A strong Bragg reflection at $d = 11.0$ Å is present in the temperature interval 70 to 175 °C and possibly belongs to $CoHPO_4{\cdot}3H_2O$. The reaction product is formed from 175 °C and is identified as $[C_4H_8N_2H_4][(Co_xZn_{1-x})_2(PO_4)(H_{1.5}PO_4)_2]$ **H**, which is the same as the product found in the batch experiment.

Cobalt–piperazine–phosphate. The composition of the sample is listed in Table 1, experiment No. 5, age of gel 672 h. The heating ramp is from 25 to 200 °C and the stack of powder patterns, Fig. 3, shows Bragg reflections of four crystalline phases. The starting mixture is crystalline and the crystalline phase exists in the temperature range 25 to 125 °C and has Bragg reflections at the *d* values 12.4, 11.6, 8.1, 7.1 and 6.7 Å. In the range 70 to 150 °C a new crystalline phase exists. It has Bragg reflections similar to those of $[C_4H_8N_2H_4][Zn(HPO_4)_2(H_2O)]$ **A**, and is thus most likely $[C_4H_8N_2H_4][Co(HPO_4)_2(H_2O)]$. In the temperature range 125 to 170 °C the two phases mentioned above are consumed, and the background is increased in the low 2θ range indicating that an amorphous phase is formed. In addition, a new crystalline phase is formed with Bragg reflections at the *d* positions 6.2, 5.9, 5.3, 5.1, 4.3, 4.1, and 4.0 Å. The final reaction product is formed at temperatures above 170 °C. It has Bragg reflections at the *d* values 7.7, 5.8, 5.3, 5.1, 4.9, 4.8, 4.6, 4.4, 4.1, 4.0 and 3.8 Å.

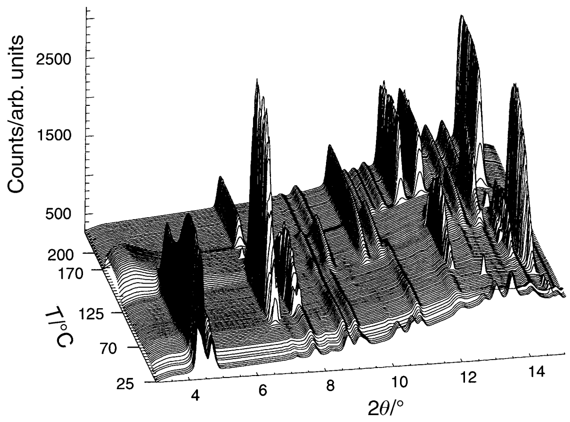

Fig. 3 Stack of powder patterns showing crystallization of cobalt–piperazine–phosphates.

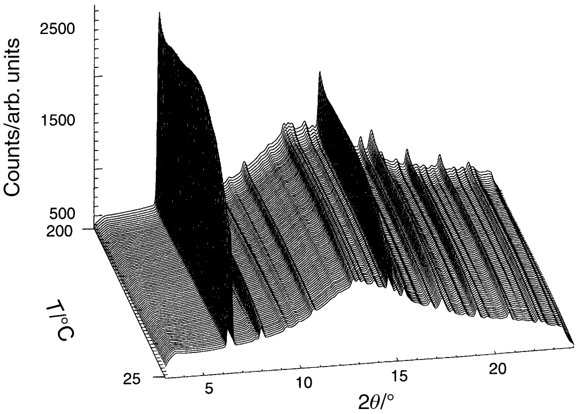

Fig. 4 Stack of powder patterns showing crystallization of zinc–2-methylpiperazine–phosphates.

Zinc–2-methylpiperazine–phosphate. The composition of the sample is listed in Table 1, experiment No. 16, age of gel 552 h. The heating ramp was from 25 to 200 °C and the stack of powder patterns is displayed in Fig. 4. The reaction mixture is crystalline at the start of the experiment and the Bragg reflections increase in intensity during the heating corresponding to additional crystallization of amorphous material. The reaction product is identified from the powder patterns as a pure sample of $[C_5N_2H_{14}][Zn(HPO_4)_2]$ **J**. This is also the reaction product obtained in the batch experiment.

Cobalt–zinc–2-methylpiperazine–phosphate. The composition of the sample is listed in Table 1, experiment No. 25, age of gel 576 h. The heating ramp was from 45 to 200 °C and the stack of powder patterns is displayed in Fig. 5. The reaction mixture is crystalline at the beginning of the experiment and from the similarity with Fig. 4 the product is identified as $[C_5N_2H_{14}][(Co_xZn_{1-x})(HPO_4)_2]$ **K**. An impurity phase is observed in the

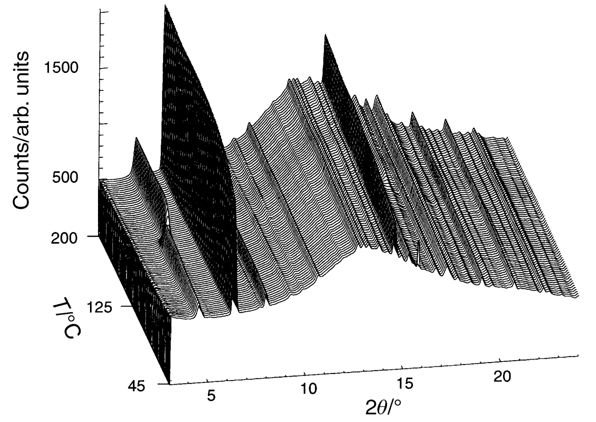

Fig. 5 Stack of powder patterns showing crystallization of cobalt–zinc–2-methylpiperazine–phosphates.

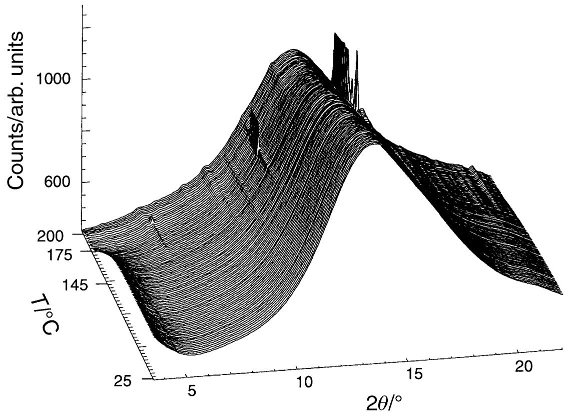

Fig. 6 Stack of patterns of a sample of cobalt–2-methylpiperazine–phosphate.

temperature interval 45 to 125 °C with a Bragg reflection at $d = 11.9$ Å, and another impurity phase is observed from 125 to 200 °C with $d = 10.7$ Å. The composition of these two impurity phases is not known. The main reaction product is the same as found in the batch experiment.

Cobalt–2-methylpiperazine–phosphate. The composition of the sample is listed in Table 1, experiment No. 6, age of gel 600 h. The heating ramp is from 25 to 200 °C and the stack of powder patterns is displayed in Fig. 6. The reaction mixture is amorphous and shows an amorphous background in the powder patterns in the 2θ range 3.2 to 5° at temperatures up to 175 °C. Crystallization takes place in the range 140 to 200 °C. Large crystals are formed which are observed as single crystal spots on the MAR detector and the powder patterns obtained are thus poor, see Fig. 6. The broad peak in the background is due to scattering from the quartz capillary and from the solvent in the sample. Two Bragg reflections from the single crystals have the d values 5.03 and 3.69 Å, respectively, which indicates that the crystals formed are (R,S)-[$C_5H_{14}N_2$][$Co(HPO_4)_2$] **L**.

The *in situ* experiments performed in a temperature ramp show phases occurring on the way to the end product. Experiments in the pressure vessels (Table 1) give only the end products and are performed in much longer time at a high reaction temperature compared to the heating of the capillaries in the 2 h *in situ* experiments using a temperature ramp. This does not necessarily give the most stable phase, which is assumed to be the phase formed in the pressure vessel experiments (Table 1).

The zinc–piperazine–phosphate experiments, Fig. 1, show the formation of [$C_4H_8N_2H_4$][$Zn(HPO_4)_2(H_2O)$] **A**, but the reaction stops before the compound [$C_4H_8N_2H_4$][$Zn_2(PO_4)(H_{1.5}PO_4)_2$] **D**, is formed. In the batch synthesis the reaction product of experiment 10 performed at 235 °C is a mixture of **A** and **D**, and of 11 and 12 performed at 185 °C, is pure **D**.

The cobalt–zinc–piperazine–phosphate experiment, Fig. 2, shows at the beginning a phase analogous to **A** (indicated as **I** in Table 1), and transforms to the compound analogous to **D** (indicated as **H**). This is in agreement with the batch synthesis where the reaction product of experiment 20 performed at 135 °C is **I**, and that of 21 performed at 185 °C is **H**.

The cobalt–piperazine–phosphate experiment, Fig. 3, shows many intermediates. The only identified phase is a hydrate with a pattern similar to that of **A**, and it goes through additional phases but does not reach the products found in the batch synthesis. An important feature is an amorphous phase which coexists with crystalline phases in the temperature range 125–170 °C. The batch experiment 4 made at 135 °C and 5 made at 185 °C showed powder patterns of mixtures where not all phases could be identified, but the products contained most likely the compound [$C_4H_8N_2H_4$][$Co(HPO_4)_2(PO_4)(H_2O)$]$_{1.5}$ in two modifications, **F** and **G** (see Table 1), and $Co_3(OH)_2(HPO_4)_2$.

The zinc–2-methylpiperazine–phosphate experiment, Fig. 4, shows a small quantity of the crystalline reaction product at the start of the heating, which quantity increases during the heating ramp. The reaction product was [$C_5N_2H_{14}$][$Zn(HPO_4)_2$] **J**, which is also the only reaction product found in the batch experiments 13 to 18 (Table 1) made at temperatures from 135 to 185 °C.

The cobalt–zinc–2-methylpiperazine–phosphate experiment, Fig. 5, has a similar crystal growth during the ramp. However, it shows a coexistent $CoHPO_4{\cdot}3H_2O$ phase in the entire temperature range. The Bragg reflection for this phase shows a small change in position at 140 °C which could indicate a partial dehydration of the compound.

The cobalt–2-methylpiperazine–phosphate experiment, Fig. 6, has a completely different reaction pattern, probably due to the fact that the pH of the reaction mixture was 5.5 and that of the zinc-2-methylpiperazine mixture was 3.5, and this could explain the different crystal growth rates of the two mixtures.

The time resolved X-ray diffraction experiments, Figs. 1–6, show a wide range of reaction pathways from those giving small amounts of the final products initially, to no reaction to the final product in the ramp. In some cases many intermediate phases are observed during the ramp of the experiment, and it is assumed that the final products obtained in the batch experiments would also be formed in the *in situ* experiments when the capillaries were kept for longer time at the highest temperature of the heating ramp.

Single crystal diffraction analysis

Crystal data for [$C_4H_8N_2H_4$][$(Co_{0.44(1)}Zn_{0.56(1)})_2(PO_4)(H_{1.5}PO_4)_2$]. $C_4H_{15}Co_{0.88(1)}N_2O_{12}P_{13}Zn_{1.12(1)}$, $M = 501$, monoclinic, space group $C2/c$ (no. 15), $a = 13.4102(9)$, $b = 12.8569(9)$, $c = 8.1890(5)$ Å, $\beta = 94.643(1)°$, $U = 1407.3(5)$ Å^3, $Z = 4$, $\mu = 34$ cm^{-1}, $T = 300$ K, $R1 = 0.024$ for 1584 unique reflections.

Crystal data for [$C_5N_2H_{14}$][$Co_{0.25(3)}Zn_{0.75(3)})(HPO_4)_2$]. $C_5H_{16}Co_{0.25(3)}N_2O_8P_2Zn_{0.75(3)}$, $M = 358$, monoclinic, space group $P2_1/n$ (no. 14), $a = 8.546(5)$, $b = 13.641(5)$, $c = 10.719(5)$ Å, $\beta = 95.360(5)°$, $U = 1244.11$ Å^3, $Z = 4$, $\mu = 22$ cm^{-1}, $T = 300$ K, $R1 = 0.035$ for 2201 unique reflections.

CCDC reference numbers 161751 and 161752.

See http://www.rsc.org/suppdata/dt/b0/b009677f/ for crystallographic data in CIF or other electronic format.

[$C_4H_8N_2H_4$][$(Co_{0.44(1)}Zn_{0.56(1)})_2(PO_4)(H_{1.5}PO_4)_2$]. The crystal was from experiment 21, Table 1. The degree of cobalt-substitution on the zinc site is high. A Co : Zn ratio of 0.79(1) : 1 was found in the X-ray fluorescense analysis, corre-

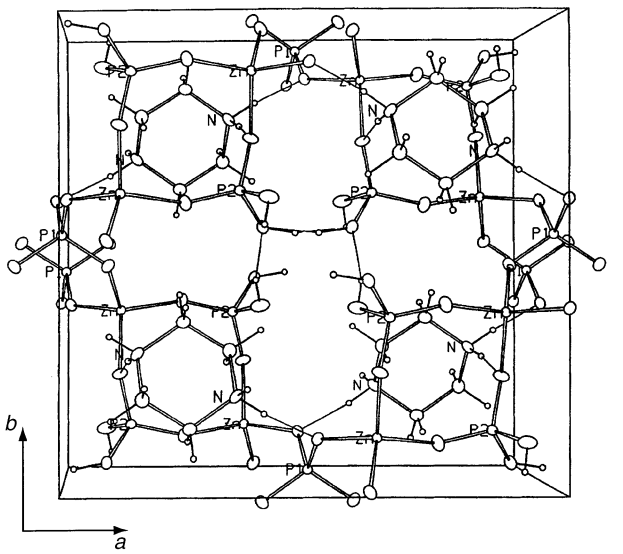

Fig. 7 Projection of the structure of $[C_4H_8N_2H_4][(Co_{0.44(1)}Zn_{0.56(1)})_2(PO_4)(H_{1.5}PO_4)_2]$ along [001].

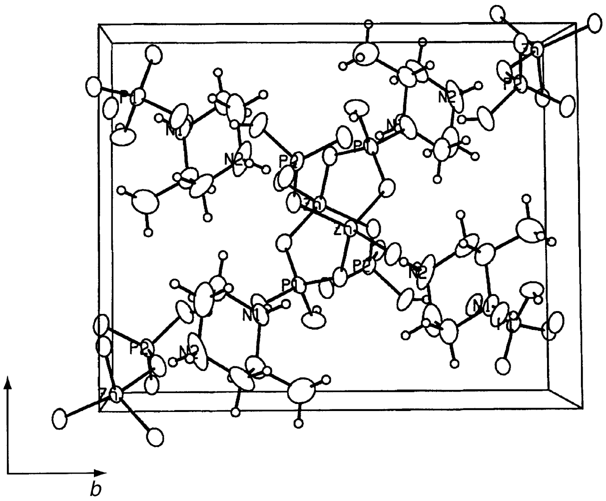

Fig. 8 Projection of the structure of $[C_5N_2H_{14}][(Co_{0.25(3)}Zn_{0.75(3)})(HPO_4)_2]$ along [100].

sponding to the composition $Co_{0.44(1)}Zn_{0.56(1)}$ for that site. The structure is similar to that described in detail for $[C_4H_8N_2H_3][Zn_2(PO_4)(H_2PO_4)_2]$ with respect to the metal phosphate framework,[8] but the present investigation gives unambiguously the positions of all hydrogen atoms. It is clear that the piperazine is indeed found as the dication, see Fig. 7, which is a drawing of the structure along [001]. Two hydrogenphosphate ions share a hydrogen atom in a short, 2.451(3) Å, two-minima hydrogen bond across a 2 axis. The same oxygen atom accepts a hydrogen bond, 2.731(3) Å, from a hydrogenphosphate related by a glide plane. The piperazine hydrogens form hydrogen bonds to oxygen atoms as described previously.[8] The average Co,Zn–O distance is 1.941(2) Å, and the average Zn–O distance in ref. 8 is 1.933(3) Å. It is interesting that synthesis with cobalt phosphate mixtures yielded the compound $Co_7(HPO_4)_4(PO_4)_2$ and $Co_3(OH)_2(HPO_4)_2$ and cobalt–zinc phosphate mixtures gave the blue compound $[C_4H_8N_2H_4][(Co_{0.44(1)}Zn_{0.56(1)})_2(PO_4)(H_{1.5}PO_4)]$ with a high degree of substitution of Zn with Co in the structure.

$[C_5N_2H_{14}][(Co_{0.25(3)}Zn_{0.75(3)})(HPO_4)_2]$. The crystal was from experiment 23, Table 1. A Co : Zn ratio of 0.33(4) : 1 was found in the X-ray fluorescense analysis corresponding to the composition $Co_{0.25(3)}Zn_{0.75(3)}$ at the metal site. The degree of cobalt-substitution on the zinc site is high as in the structure described above. The positions of the hydrogen atoms in the 2-methylpiperazine molecule were calculated but were not refined. The coordinates of the hydrogen atoms in the HPO_4^{2-} ion were refined. The 2-methylpiperazine is present as a dication, see Fig. 8, which is a drawing of the structure along [100]. Hydrogen bonds are formed between the hydrogenphosphate ions with a distance of 2.64(1) Å. The average (Co,Zn)–O distance is 1.972(3) Å consistent with a relatively high degree of substitution of Zn with Co in the structure, and the structure is similar to that of (*R*,*S*)-$[C_5N_2H_{14}][Co(HPO_4)_2]$,[17] where the average Co–O distance is 1.964(2) Å.

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References

1 S. T. Wilson, B. M. Lok and E. M. Flanigen, *U.S. Pat.*, 4310440, 1982.
2 M. J. Gray, J. D. Jasper, A. P. Wilkinson and J. C. Hanson, *Chem. Mater.*, 1997, **9**, 976.
3 K. R. Morgan, G. J. Grainsford and N. B. Milestone, *Chem. Commun.*, 1997, 61.
4 D. A. Bruce, A. P. Wilkinson, M. G. White and J. A. Bertrand, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 2059.
5 K. Morgan, G. Grainsford and N. Milestone, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 425.
6 W. T. A. Harrison and M. L. F. Phillips, *Chem. Mater.*, 1997, **9**, 1837.
7 G.-Y. Yang and S. C. Sevov, *J. Am. Chem. Soc.*, 1999, **121**, 8389.
8 P. Feng, X. Bu and G. D. Stucky, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 1745.
9 C. N. R. Rao, S. Natarajan and S. Neeraj, *J. Solid State Chem.*, 2000, **152**, 302.
10 K. Ahmadi, A. Hardy, J. Patarin and L. Huve, *Eur. J. Solid State Inorg. Chem.*, 1995, **32**, 209.
11 A. N. Christensen, P. Norby and J. C. Hanson, *Microporous Meseporous Mater.*, 1998, **20**, 349.
12 A. P. Hammersley, ESRF (European Synchrotron Radiation Facility) Internal Report, ESRF98HA01T, FIT2D V9. 129, Reference Manual V3.1, Grenoble, France, 1998.
13 A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch and D. Häuserman, *High Pressure Res.*, 1996, **14**, 235.
14 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
15 W. R. Busing, K. O. Martin and H. A. Levy, ORFLS, A Fortran Crystallographic Least Squares Program, Report ORNL-TM 305, Oak Ridge National Laboratory, Oak Ridge, TN, 1962; LINUS is a 1971 version of ORFLS.
16 D. T. Cromer and J. T. Waber, Report LA-3056, Los Alamos Scientific Laboratory of the University of California, Los Alamos, NM, 1964.
17 R.-K. Chiang, *J. Solid State Chem.*, 2000, **153**, 180.
18 K. Yvon, W. Jeitschko and E. Parthé, *J. Appl. Crystallogr.*, 1977, **10**, 73.