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Use of Hydrofluoric Acid as Mineralizer in Hydrothermal and Organothermal Synthesis of Me^{2+}-Substituted Aluminophosphates. I

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Hydrofluoric acid has been used as mineralizer in hydrothermal and organothermal syntheses of Me^{2+}-substituted aluminophosphates at temperatures up to 180 °C. As structure-directing templates triethylamine, di-*n*-propylamine, tripropylamine, 1,4-diazabicyclo[2.2.2]octane and ethylenediamine were used. Single crystals large enough for traditional X-ray single crystal diffraction analyses were obtained of ZnAPO-5, AFI, $(Zn,Al)PO_4 \cdot 0.5C_2H_{10}N_2$, CoAPO-5, AFI, $CoAl(PO_4)_2 \cdot C_2H_9N_2$, $(Co,Al)PO_4 \cdot 0.5C_2H_{10}N_2$ and CoAPO-43, GIS. The microporous compound ZnAPO-35, LEV, was obtained as a powder. The compounds were identified from X-ray powder diffraction patterns and from single crystal X-ray diffraction analysis. The crystal structure of $(Co_{0.84}Al_{0.16})PO_4 \cdot 0.5C_2H_{10}N_2 \cdot 0.5H_2O$ is reported. The unit cell dimensions are $a = 10.1724(6)$ and $c = 9.6060(6)$ Å, and model calculations were made using the space group $I\bar{4}2m$.

Heterogeneous mixtures of solids and water are heated under pressure at temperatures over 100 °C in hydrothermal reactions. This can result in compound formation by chemical reactions or in recrystallization of solids to produce crystalline powders or single crystals. Such reactions performed in pressure vessels can also be made with an organic solvent as the reaction medium and will be called organothermal reactions in the following text. It should be stressed that the liquid used in reactions under pressure at temperatures over the normal boiling point of the liquid may act as a solvent or may take part in chemical reactions with the solids present in the heterogeneous mixture.

Compounds with open framework structures such as zeolites and aluminophosphates are traditionally obtained in hydrothermal synthesis from aqueous media and are in many cases only obtained as powders.[1,2] However, it has been reported that the use of minor quantities of hydrofluoric acid as mineralizer in the hydrothermal synthesis has a drastic effect on the crystal sizes obtained in the hydrothermal synthesis, so that microporous compounds which previously could only be made as powders could now be obtained as crystals large enough for traditional single crystal X-ray analysis.[3] It was also reported that crystals up to 1 mm in size of compounds with open framework structures can be obtained in organothermal synthesis in the temperature range 100–200 °C using the organic solvents pyridine, triethylamine, polyethylene glycol[4] and ethylene glycol.[5] The use of organic solvents most likely results in a slower nucleation and crystal growth rate than in water, which then results in larger crystals in the organothermal synthesis.

A substantial amount of structural information can be gained from powder diffraction data, but more detailed structural information is obtained in single crystal diffraction analysis. It is thus tempting to improve the preparation techniques for the synthesis of microporous materials, and one obvious possibility is to use hydrofluoric acid as mineralizer in organothermal synthesis. The results of an investigation using hydrothermal and organothermal synthesis in the preparation of aluminophosphates and of Zn^{2+}- and Co^{2+}-substituted aluminophosphates are reported below. Similar studies with Mn^{2+}-substituted aluminophosphates are in progress and the results will be published elsewhere.

Experimental

Sample preparation. The amorphous gels used in the hydrothermal and organothermal synthesis were made from the following chemicals: 85% H_3PO_4, HF, $Zn(CH_3COO)_2 \cdot 2H_2O$ and ethylene glycol (ETG) from Merck, and 98% aluminium isopropoxide, triethylamine

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(TEA), ethylenediamine (EDA), di-*n*-propylamine (DPA), tripropylamine (TPA), 1,4-diazabicyclo[2.2.2]octane (DABCO) and $Co(CH_3COO)_2 \cdot 4H_2O$ from Aldrich. A 50–100 ml charge was made of each gel. In the preparation of the ethylene glycol based gels, the procedure was as follows: The transition metal acetate and the aluminium isopropoxided were stirred with the ethylene glycol for approximately 1 h. The 85% H_3PO_4 was added and the mixture was stirred for at least 15 min, and the organic amine was added with continuous stirring for at least 30 min to obtain homogeneity. The HF was finally added from a polyethylene pipette and the pH of the gels was measured using a pH meter. The charges were stored at room temperature in flasks of polyethylene. The gels with water as solvent were made in a similar way. Tables 1 and 2 list the composition of the gels and the experimental conditions for the synthesis. The ethylene glycol based gels are strictly speaking not purely non-aqueous, as they contain water from the 85% H_3PO_4 and from the transition metal acetates. The products of the synthesis were washed with water and dried at room temperature. The structure types AFI, LEV and GIS mentioned in the two tables are described in Ref. 6.

x-ray powder diffraction. X-Ray powder patterns of the products were recorded at 25 °C on a Stoe-Stadi powder diffractometer with a position-sensitive detector. The diffractometer was calibrated with a silicon standard (a = 5.43050 Å) and Cu $K\alpha_1$ radiation was used (λ = 1.5406 Å). Phases identified from the powder patterns and from X-ray single diffraction analysis are listed in Tables 1 and 2.

X-Ray single crystal diffraction. Single crystals were selected using a polarizing microscope and were mounted on glass fibres with a two component glue. A Siemens SMART diffractometer with an area detector was applied using Mo $K\alpha$ radiation (λ = 0.7107 Å). Crystallographic data are in Table 3. The structures were solved using the program SIR,[7] and were refined using the least-squares program LINUS[8] with scattering contributions from neutral atoms.[9]

Results

Zn^{2+}-Substituted aluminophosphates, Table 1. The hydrothermal reactions of the Zn^{2+}-substituted aluminophosphate gels gave with the templates TPA and DPA and hydrofluoric acid as mineralizer single crystals of ZnAPO-5, AFI, large enough for single crystal X-ray analysis. The typical crystal size was 0.30 × 0.08 × 0.08 mm^3. With the template DABCO crystalline ZnAPO-35, LEV, was obtained. The reaction products had crystals smaller than those obtained for ZnAPO-5 and an increase of the mineralizer concentration (experiment no. 260 698) did not improve the crystal size significantly. When aluminium isopropylate was omitted in the reaction mixture (experiment no. 220 798), single crystals of Zn_2PO_4F were obtained with typical sizes of 0.20 × 0.05 × 0.01 mm^3. The X-ray powder pat-

Table 1. Experimental conditions for hydrothermal (H_2O) and organothermal (ETG) syntheses of Zn^{2+}-substituted aluminophosphates.[a]

Sample no.	Template	MeO	Al_2O_3	P_2O_5	HF	Solvent	pH of gel	T/ °C	Time/ h	Product
	TPA	ZnO				H_2O				
031 097	1.60	0.16	0.92	1.00	0.8	300	5.0	170	18	ZnAPO-5, AFI
	DPA									
101 097	1.60	0.40	0.80	1.00	0.8	300	5.0	170	18	ZnAPO-5, AFI
	DABCO									
261 097	1.60	0.40	0.80	1.00	0.8	300	5.2	175	44	ZnAPO-35, LEV
041 197	1.60	0.40	0.80	1.00	0.8	300	5.5	170	48	ZnAPO-35, LEV
020 598	1.60	0.40	0.80	1.00	0.8	300	5.5	170	33	ZnAPO-35, LEV
260 698	1.60	0.40	0.80	1.00	1.9	300	5.3	180	69	ZnAPO-35, LEV
220 798	1.60	1.00		1.00	1.90	300	4.7	180	103	Zn_2PO_4F
	EDA									
251 097	1.60	0.40	0.80	1.00	1.33	300	5.2	175	25	Not identified
041 197	1.60	0.40	0.80	1.00	1.33	300	5.2	170	48	Not identified
081 197 (A)	1.40	0.40	0.80	1.00	1.10	300	6.0	170	48	Not identified
081 197 (B)	1.40	0.40	0.80	1.00	1.10	300	6.0	170	48	Not identified
030 898	1.00	0.40	0.80	1.00	1.00	50	6.6	180	82	Not identified
050 598	2.00	0.42	0.13	1.00	1.65	138	5.8	180	96	$(Zn,Al)PO_4 \cdot 0.5C_2H_{10}N_2$, ACP-2
300 698	2.00	0.70		1.00	1.65	138	4.7	180	71	$ZnPO_4 \cdot 0.5C_2H_{10}N_2$, ACP-2
						ETG				
050 398	1.75	0.25	0.50	1.00		28	7.8	170	72	Not identified
310 798	1.75	0.25	0.50	1.00	1.3	56	5.9	180	72	Not identified
030 398	2.16	0.42	0.13	1.00		33	6.7	180	74	$(Zn,Al)PO_4 \cdot 0.5C_2H_{10}N_2$, ACP-2
070 498	2.16	0.42	0.13	1.00	2.50	33	4.8	180	96	$(Zn,Al)PO_4 \cdot 0.5C_2H_{10}N_2$, ACP-2
120 598	2.00	0.70		1.00	1.65	40	4.5	180	68	$ZnPO_4 \cdot 0.5C_2H_{10}N_2$, ACP-2

[a]Compositions of the reaction mixtures are listed as molar ratios.

Table 2. Experimental conditions for organothermal (ETG) and hydrothermal (H_2O) syntheses of Co^{2+}-substituted aluminophosphates.[a]

Sample no.	Template	MeO	Al_2O_3	P_2O_5	HF	Solvent	pH of gel	*T*/ °C	Time/ h	Product
	TPA	CoO				H_2O				
250 997	1.60	0.16	0.92	1.00	0.8	300		175	17	CoAPO-5, AFI
	TEA									
160 997	1.40	0.16	0.92	1.00		40	6.5	195	70	CoAPO-5, AFI
030 798	1.40	0.16	0.92	1.00	1.55	110	5.4	180	119	Berlinite
						ETG				
280 298	1.00	0.11	0.65	1.00		14	4.6	170	68	CoAPO-5, AFI
070 498	1.00	0.11	0.65	1.00	1.78	14	3.8	180	96	CoAPO-5, AFI
190 298	1.41	0.16	0.92	1.00		11	6.5	175	65	CoAPO-5, AFI
110 498	1.41	0.16	0.92	1.00	0.84	11	6.3	180	96	CoAPO-5, AFI
	DABCO					H_2O				
270 798	1.90	1.00		1.00	1.90	300	5.2	180	82	Co_2PO_4F
	EDA					ETG				
060 398	1.75	0.25	0.50	1.00		28	7.4	170	72	$CoAl(PO_4)_2 \cdot C_2H_9N_2$
110 498-A	1.25	0.25	0.75	1.00		30	6.9	180	96	$CoAl(PO_4)_2 \cdot C_2H_9N_2$
210 298	2.16	0.84	0.13	1.00		33	5.7	180	140	$(Co,Al)PO_4 \cdot 0.5C_2H_{10}N_2$, ACP-3 and $CoAl(PO_4)_2 \cdot C_2H_9N_2$
280 298	2.16	0.42	0.13	1.00		33	6.2	180	69	$(Co,Al)PO_4 \cdot 0.5C_2H_{10}N_2$,ACP-3 and $CoAl(PO_4)_2 \cdot C_2H_9N_2$
170 498	2.00	0.42	0.13	1.00		40	6.3	180	96	$(Co,Al)PO_4 \cdot 0.5C_2H_{10}N_2$, ACP-3
150 698	2.00	0.70		1.00		40	5.4	180	72	$CoPO_4 \cdot 0.5C_2H_{10}N_2$, ACP-3
						H_2O				
020 598	2.00	0.42	0.13	1.00		138	6.8	180	70	$CoAl(PO_4)_2 \cdot C_2H_9N_2$ and CoAPO-43, GIS
						ETG				
070 498-4	1.75	0.25	0.50	1.00	2.24	28	6.2	180	96	Not identified
110 498	1.00	0.20	0.60	1.00	0.32	24	4.5	180	96	X-Ray amorphous
070 498-2	2.16	0.84	0.13	1.00	2.34	33	5.1	180	96	CoAPO-43, GIS and $(Co,Al)PO_4 \cdot 0.5C_2H_{10}N_2$, ACP-3
110 498	1.96	0.55	0.32	1.00	2.29	31	5.3	180	96	Not identified
070 498-S	2.16	0.42	0.13	1.00	1.56	33	5.6	180	96	CoAPO-43, GIS
220 498	2.00	0.42	0.13	1.00	1.65	40	5.4	180	103	CoAPO-43, GIS
100 698	2.00	0.70		1.00	1.65	40	5.1	180	103	$CoPO_4 \cdot 0.5C_2H_{10}N_2$, ACP-3
						H_2O				
280 498	2.00	0.42	0.13	1.00	1.65	138	6.0	180	84	CoAPO-43, GIS

[a]Compositions of the reaction mixtures are listed as molar ratios.

Table 3. Crystallographic data for $CoAlPO_4 \cdot C_2H_9N_2$, $CoPO_4 \cdot 0.5C_2H_{10}N_2$ and $CoPO_4 \cdot 0.5C_2H_{10}N_2 \cdot 0.5H_2O$.[a]

	$CoAlPO_4 \cdot C_2H_9N_2$	$CoPO_4 \cdot 0.5C_2H_{10}N_2$ (ACP-3)	$(Co,Al)PO_4 \cdot 0.5C_2H_{10}N_2 \cdot 0.5H_2O$ (CoAPO-43, GIS)
a/Å	8.6026(6)	10.4123(6)	10.1724(6)
b/Å	15.5520(11)		
c/Å	7.7436(6)	8.9477(8)	9.6060(6)
β/°	110.634(1)		
V/Å^3	969.5(1)	970.1(1)	994.0(1)
Z	4	8	8
Space group	$P2_1/c$	$P4_2/n$	$I\bar{4}2m$
Unique data	1324	563	268
Crystal size/mm	0.10 × 0.10 × 0.01	0.08 × 0.08 × 0.05	0.05 × 0.05 × 0.05
Parameters	146	73	54
R(*F*) (%)	4.2	3.5	5.7
$R_w(F)$ (%)	5.6	5.2	7.9

[a]The number of reflections with $I > 3\sigma(I)$ are listed as unique data. Data collection at 25 °C.

tern of ZnAPO-35, LEV, the reaction product of no. 260 698 is listed in Table 4. It was indexed with the program DICVOL91[10] on a hexagonal cell with a = 13.234(9) and c = 22.31(2) Å, which is similar to the unit cell for Levyne.[11] The powder pattern is very similar to the unindexed pattern of aluminium silicon phosphate quinuclidine, ICDD card no. 47-0062. This pattern was also indexed with the program DICVOL91[10] on a hexagonal cell with a = 13.255(7) and c = 22.36(2) Å, and observed and calculated values are listed in Table 5.

The hydrothermal and organothermal synthesis with EDA as the template and a low ZnO/Al_2O_3 ratio gave products which had powder patterns with many lines difficult to index. With a high ZnO/Al_2O_3 ratio crystalline products were obtained which gave few lines. The X-ray powder pattern of the reaction product from experiment no. 070 498 is listed in Table 6. The pattern was indexed with the program DICVOL91[10] on an orthorhombic unit cell with a = 14.80(1), b = 14.75(1), c = 8.99(1) Å, which is similar to the unit cell of ACP-2,[12] and the product could possibly have a structure similar to that of ACP-2. When aluminium isopropylate was omitted from the reaction mixture, the product in the hydrothermal experiment (no. 300 698) and the organothermal synthesis (experiment no. 120 598) was an ACP-2 type phase with the composition $ZnPO_4 \cdot 0.5C_2H_{10}N_2$.

Table 4. Powder pattern of ZnAPO-35, LEV, sample no. 260 698, Table 1.[a]

$2\theta_{obs}$	$2\theta_{calc}$	d_{obs}	d_{calc}	I_{obs}	h	k	l
8.60	8.67	10.27	10.19	20	1	0	1
11.05	11.06	8.00	7.99	53	1	0	2
11.87	11.89	7.44	7.44	15	0	0	3
13.37	13.37	6.617	6.616	41	1	1	0
15.96	15.96	5.548	5.555	18	2	0	1
17.38	17.38	5.098	5.097	79	2	0	2
17.65	17.67	5.020	5.015	21	1	0	4
21.32	21.35	4.164	4.158	37	1	0	5
21.98	21.99	4.040	4.038	100	2	1	2
23.24	23.27	3.824	3.820	37	3	0	0
23.80	23.75	3.735	3.743	10	2	1	3
25.20	25.16	3.531	3.537	27	1	0	6
26.95	26.93	3.305	3.308	33	2	2	0
28.70	28.70	3.108	3.108	26	2	1	5
32.23	32.23	2.775	2.775	54	4	0	2

[a]Indexed with the hexagonal unit cell a = 13.294(9), c = 22.31(2) Å. Figure of merit $M(15)$ = 11.0.

Table 5. Powder pattern of aluminium silicon phosphate quinuclidine, ICDD card no. 47-0622.[a]

$2\theta_{obs}$	$2\theta_{calc}$	d_{obs}	d_{calc}	I_{obs}	h	k	l
8.66	8.65	10.20[b]	10.212	18	1	0	1
11.04	11.04	8.01	8.009	47	1	0	2
11.89	11.86	7.44	7.454	2	0	0	3
13.38	13.35	6.61	6.627	13	1	1	0
15.99	15.93	5.54	5.559	12	2	0	1
17.37	17.35	5.10	5.106	83 u	2	0	2
17.69	17.63	5.01	5.026	u	1	0	4
17.87	17.89	4.96	4.953	14	1	1	3
21.24	21.30	4.18	4.167	55	1	0	5
21.98	21.96	4.04	4.044	100	2	1	2
23.27	23.23	3.82	3.826	18	3	0	0
23.71	23.71	3.75	3.749	6	2	1	3
25.21	25.22	3.53	3.527	5	2	0	5
25.98	25.97	3.427	3.427	1	2	1	4
26.88	26.88	3.314	3.313	18	2	2	0
26.53	26.52	3.126	3.127	26	2	0	6
28.68	28.64	3.110	3.114	13	2	1	5
29.07	29.14	3.069	3.062	6	3	1	2
32.13	32.18	2.784	2.779	40	4	0	2

[a]Hexagonal unit cell a = 13.255(7), c = 22.36(2) Å. Figure of merit $M(19)$ = 7.8. [b]The d-value listed on the card was 10.10 Å. $2\theta_{obs}$ corresponds to the d-values on the card for Cu $K\alpha_1$ radiation (λ = 1.5406 Å).

Co^{2+}-Substituted aluminophosphates, Table 2. The Co^{2+}-substituted aluminophosphate gels gave with the templates TPA and TEA crystalline samples of CoAPO-5, AFI. The use of hydrofluoric acid as mineralizer gave single crystals of the product with sizes up to 0.30 × 0.05 × 0.05 mm³. In the organothermal synthesis with the template solvent combination TEA–ETG crystalline CoAPO-5 was obtained, but the use of hydrofluoric acid did not improve the crystal size of the product. With EDA as the structure-directing amine the organothermal and hydrothermal synthesis gave

Table 6. Powder pattern of $(Zn,Al)PO_4 \cdot 0.5C_2H_{10}N_2$, ACP-2, sample no. 070 498, Table 1.[a]

$2\theta_{obs}$	$2\theta_{calc}$	d_{obs}	d_{calc}	I_{obs}	h	k	l
11.90	11.95	7.433	7.401	87	2	0	0
15.46	15.50	5.727	5.714	37	2	0	1
16.91	16.96	5.238	5.225	18	2	2	0
19.69	19.64	4.505	4.517	27	2	2	1
	19.73		4.495		0	0	2
21.46	21.44	4.137	4.142	24	1	3	1
23.11	23.13	3.846	3.842	44	2	0	2
24.80	24.78	3.587	3.590	10	4	1	0
26.04	26.02	3.419	3.422	100	4	0	1
26.95	26.99	3.306	3.301	97	2	4	0
	26.93		3.308		4	2	0
28.74	28.74	3.104	3.104	11	4	2	1
30.15	30.20	2.962	2.957	7	4	3	0
32.21	32.20	2.777	2.778	26	2	0	3
	32.22		2.776		0	2	3
32.57	32.56	2.747	2.748	18	5	2	0
33.63	33.61	2.663	2.664	19	4	2	2
34.30	34.30	2.612	2.612	28	4	4	0
35.58	35.57	2.521	2.522	9	1	3	3
	35.55		2.524		3	1	3
36.51	36.52	2.459	2.459	6	0	6	0
37.12	37.15	2.420	2.419	7	2	3	3
	37.13		2.420		3	2	3
38.68	38.63	2.326	2.329	22	4	0	3
	38.68		2.326		0	4	3
40.64	40.59	2.218	2.220	15	4	2	3
	40.63		2.219		2	4	3
40.88	40.87	2.206	2.206	15	3	5	2
	40.82		2.209		5	3	2
43.67	43.67	2.071	2.071	8	2	6	2

[a]Indexed with the orthorhombic unit cell a = 14.80(1), b = 14.75(1), c = 8.99(1) Å. Figure of merit $M(22)$ = 7.1.

two main products, $CoAl(PO_4)_2 \cdot C_2H_9N_2$ and $(Co,Al)PO_4 \cdot 0.5C_2H_{10}N_2$, ACP-3.[13] The crystal sizes were $0.15 \times 0.15 \times 0.03$ and $0.10 \times 0.10 \times 0.05$, respectively. The X-ray diffraction powder pattern of this ACP-3 type compound, the reaction product of no. 170 498, is listed in Table 7. Indexing with DICVOL91[10] gave a tetragonal unit cell with $a = 10.443(5)$ and $c = 9.008(6)$ Å. This unit cell has only half the volume of that of the cell for the Zn^{2+}-substituted aluminophosphate described in Table 6. A powder pattern similar to that of Table 7 was measured for the reaction product of no. 150 698. This synthesis did not contain aluminium in the reaction mixture, so the composition of the product is $CoPO_4 \cdot 0.5C_2H_{10}N_2$, ACP-3.

The X-ray diffraction powder pattern of $CoAl(PO_4)_2 \cdot C_2H_9N_2$ the product of no. 020 598 was indexed with DICVOL91[10] and gave a monoclinic unit cell with $a = 8.62(2)$, $b = 15.55(5)$, $c = 7.79(3)$ Å and $\beta = 111.0(2)°$ (Table 8). This is in good agreement with the unit cell reported in the single crystal structure investigation of $CoAl(PO_4)_2 \cdot C_2H_9N_2$.[14]

The X-ray diffraction powder pattern of the product of the hydrothermal synthesis of experiment no. 280 498 is listed in Table 9. Indexing with DICVOL91[10] gave a tetragonal unit cell with $a = 10.21(2)$ and $c = 9.64(1)$ Å, which is close to the size of the unit cell for the magnesium substituted aluminophosphate MgAPO-43[15] with a structure of the gismondine type. The organothermal and hydrothermal synthesis thus gave with EDA as structure-directing amine and hydrofluoric acid as mineralizer a gismondine-like phase and ACP-2 as the main products.

Crystal structures from single crystal diffractometry. The data analysis of the single crystal diffraction data for $CoAl(PO_4)_2 \cdot C_2H_9N_2$ and $(Co,Al)PO_4 \cdot 0.5C_2H_{10}N_2$ confirmed the previously reported structures.[13,14] The number of reflections was not sufficiently large to improve the structures, and the results were only used to calculate the powder patterns listed in Table 8 using the program LAZY PULVERIX.[16] The size of the unit cell of $(Co,Al)PO_4 \cdot 0.5C_2H_{10}N_2$ is thus half of that found for $(Zn,Al)PO_4 \cdot 0.5C_2H_{10}N_2$ and that reported previously

Table 7. Powder pattern of $(Co,Al)PO_4 \cdot 0.5C_2H_{10}N_2$, ACP-3, sample no. 170 498, Table 2.[a]

$2\theta_{obs}$	$2\theta_{calc}$	d_{obs}	d_{calc}	I_{obs}	h	k	l			
11.90	11.98	7.431	7.384	36	1	1	0			
15.47	15.50	5.723	5.711	26	1	1	1			
16.98	16.97	5.218	5.232	5	2	0	0			
19.68	19.69	4.507	4.504	29	0	0	2			
21.43	21.46	4.143	4.146	13	1	0	2			
23.09	23.12	3.849	3.845	43	1	1	2			
26.06	26.06	3.417	3.416	100	2	2	1			
26.97	26.98	3.303	3.302	45	1	3	0	3	1	0
28.72	28.77	3.106	3.101	17	1	3	1	3	1	1
32.16	32.15	2.781	2.782	21	1	1	3			
32.46	32.44	2.756	2.757	10	2	3	1	3	2	1
33.64	33.62	2.662	2.663	17	1	3	2	3	1	2
34.37	34.32	2.607	2.611	14	4	0	0			
35.51	35.51	2.526	2.526	6	2	1	3	1	2	3
38.63	38.62	2.329	2.330	21	2	2	3			
40.58	40.57	2.221	2.222	13	3	1	3	1	3	3

[a]Indexed with the tetragonal unit cell $a = 10.443(5)$, $c = 9.008(6)$ Å. Figure of merit $M(16) = 18.1$.

Table 8. Powder pattern of $CoAl(PO_4)_2 \cdot C_2H_9N_2$, sample no. 020 598, Table 2.[a]

$2\theta_{obs}$	$2\theta_{calc}$	d_{obs}	d_{calc}	I_{obs}	h	k	l
10.90	10.89	8.110	8.116	6	1	0	0
11.30	11.35	7.824	7.790	10	0	2	0
12.27	12.29	7.208	7.198	100	1	1	0
13.40	13.42	6.602	6.595	76	0	1	1
17.40	17.43	5.093	5.084	9	1	2	−1
20.31	20.28	4.369	4.374	8	1	3	0
20.96	21.00	4.235	4.228	9	0	3	1
21.76	21.76	4.081	4.082	5	2	1	−1
22.22	22.19	3.998	4.004	27	1	2	1
22.73	22.81	3.909	3.895	8	0	4	0
22.97	23.00	3.869	3.864	4	1	0	−2
23.70	23.70	3.751	3.751	4	1	1	−2
24.47	24.44	3.635	3.640	14	0	0	2
25.39	25.34	3.505	3.512	2	1	4	0
27.04	27.02	3.295	3.298	6	0	2	2
27.16	27.17	3.281	3.280	21	2	3	−1
28.77	28.77	3.101	3.100	39	1	3	−2
29.17	29.25	3.059	3.051	4	2	1	1
30.76	30.75	2.904	2.905	7	1	1	2
21.89	31.82	2.804	2.810	22	2	4	0
33.06	33.06	2.707	2.707	11	3	2	−1
33.71	33.68	2.657	2.659	3	0	4	2
35.28	35.28	2.542	2.542	4	2	4	−2

[a]Indexed with the monoclinic unit cell $a = 8.66(1)$, $b = 15.58(2)$, $c = 7.77(1)$ Å, $\beta = 110.5(1)°$. Values for the structure of $CoAl(PO_4)_2 \cdot C_2H_9N_2$ are: $a = 8.603(1)$, $b = 15.552(1)$, $c = 7.744(1)$ Å, $\beta = 110.60(1)°$. Figure of merit $M(23) = 6.6$.

Table 9. Powder pattern of $(Co,Al)PO_4 \cdot 0.5C_2H_{10}N_2 \cdot 0.5H_2O$, CoAPO-43, GIS, sample no. 280 498, Table 2.[a]

$2\theta_{obs}$	$2\theta_{calc}$	d_{obs}	d_{calc}	I_{obs}	h	k	l
12.22	12.30	7.240	7.191	46	1	1	0
12.61	12.66	7.017	6.983	100	1	0	1
17.34	17.42	5.109	5.085	12	2	0	0
18.45	18.46	4.804	4.803	7	0	0	2
21.49	21.60	4.132	4.111	8	2	1	1
22.17	22.44	4.007	3.994	20	1	1	2
25.41	25.48	3.502	3.492	47	2	0	2
27.73	27.72	3.215	3.216	71	3	1	0
	27.88		3.197		3	0	1
29.16	29.22	3.060	3.054	33	1	0	3
30.95	31.04	2.887	2.878	14	2	2	2
32.94	33.08	2.717	2.706	9	3	2	1
33.37	33.50	2.683	2.672	19	3	1	2
34.12	34.22	2.625	2.688	18	2	1	3
37.37	37.48	2.404	2.397	11	3	3	0
	37.62		2.389		4	1	1
38.52	38.64	2.335	2.328	7	3	0	3

[a]Indexed with a tetragonal unit cell $a = 10.21(2)$, $c = 9.64(1)$ Å. Values from the single crystal structure analysis of $(Co_{0.85}Al_{0.15})PO_4 \cdot 0.5C_2H_{10}N_2 \cdot 0.5H_2O$ were $a = 10.1724(6)$, $c = 9.6060(6)$ Å, space group $I\bar{4}2m$ and were used to calculate d_{calc} and $2\theta_{calc}$. Figure of merit $M(10) = 17.5$.

Table 10. Atomic coordinates and displacement parameters (× 10^4) for $(Co_{0.84}Al_{0.16})PO_4 \cdot 0.5C_2H_{10}N_2 \cdot 0.5H_2O$, $R = 5.7\%$.

Atom	*x/a*	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co,Al	0.8668(1)	0.1332(1)	0.3684(2)	71(2)	71(2)	130(3)	8(2)	−18(2)	18(2)
P	0.6646(3)	0.3354(3)	0.1918(4)	84(3)	84(3)	124(3)	23(3)	−18(3)	18(3)
O1	0.7001(9)	0.2999(1)	0.038(2)	138(10)	138(10)	201(24)	43(16)	30(10)	−30(10)
O2	1.020(1)	0.1969(9)	0.2816(9)	118(11)	126(10)	183(10)	−5(10)	−14(11)	88(10)
O3	0.742(2)	0.259(1)	0.286(3)	231(16)	231(16)	401(50)	34(21)	−154(2)	154(23)
O4	0	0	1/2	126(20)	126(20)	150(29)	0	0	0
O5	0	0	0	167(25)	167(25)	206(40)	0	0	0
C	0.504(2)	0.050(2)	0.435(2)	48(14)	92(19)	66(15)	8(24)	0(17)	−2(16)
N	1/2	0.185(2)	1/2	74(13)	86(14)	165(26)	0	−6(15)	0

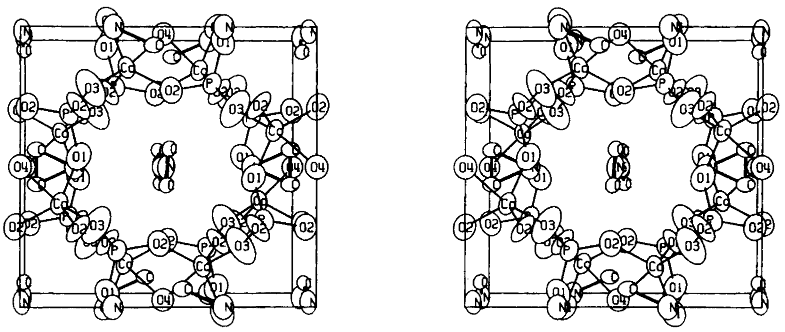

Fig. 1. Stereoscopic drawing of the structure of $(Co_{0.84}Al_{0.16})PO_4 \cdot 0.5C_2H_{10}N_2 \cdot 0.5H_2O$ along [001].

for DAF-2.[17] A single crystal analysis of the product from experiment no. 280 498 showed that the crystal had a gismondine-type structure and the composition $(Co_{0.84}Al_{0.16})$ $PO_4 \cdot 0.5C_2H_{10}N_2 \cdot 0.5H_2O$ (Table 10). It is thus a hydrate obtained in an organothermal synthesis. It was pointed out previously that the syntheses are not non-aqueous, strictly speaking. A list of interatomic distances is given in Table 11.

The cobalt and aluminium content of the sample was deduced from a consideration of the metal–oxygen atoms in the structure, in a linear interpolation between the Co–O and Al–O distances 1.93 and 1.74 Å, respectively.[12] Refinement of the site occupancy of the cobalt atom indicated that this site contained 10–15% aluminium. Figure 1 shows a stereoscopic drawing of the structure along [001]. The oxygen atom O3 has larger thermal displacement parameters than the other atoms of the framework. This possibly indicates a disordered arrangement of O3. The ethylenediamine molecule is placed in the channels of the structure with the carbon atoms arranged statistically in the site 16*j*.

Table 11. Interatomic distances (in Å) of $(Co_{0.84}Al_{0.16})PO_4 \cdot 0.5C_2H_{10}N_2 \cdot 0.5H_2O$.[a]

Co,Al–O2	1.88(1)	
Co,Al–O2^i	1.88(1)	$i = 1-y, 1-x, z$
Co,Al–O1^i	1.89(2)	$i = 1+1/2-x, 1/2-y, 1/2+z$
Co,Al–O3	1.97(1)	
Co,Al–O4^i	2.29(1)	$i = 1+x, y, z$
P–O3	1.43(1)	
P–O2^i	1.53(1)	$i = 1/2+y, 1+1/2+x, 1/2-z$
P–O2^i	1.53(1)	$i = -1/2+x, 1/2-y, 1/2-z$
P–O1	1.56(2)	
N–C	1.52(2)	
C–C^i	1.61(3)	$i = x, -y, 1-z$

[a]Standard deviations in parentheses. The positions of the atoms, with reference to the positions listed in Table 10, are indicated by the *i*-values.

Conclusion

The use of hydrofluoric acid as a mineralizer in the hydrothermal and organothermal synthesis of ZnAPO-5 and CoAPO-5 resulted in single crystals large enough for traditional single crystal X-ray analysis. The templates di-*n*-propylamine, tripropylamine and triethylamine were used. With the template 1,4-diazabicyclo[2.2.2]octane the hydrothermal synthesis gave ZnAPO-35, LEV. The template ethylenediamine gave the zinc-substituted aluminophosphate of the ACP-2 type, and this type of structure was also obtained for a zinc phosphate. The use of hydrofluoric acid as a mineralizer did not result in single crystal of these compounds.

The organothermal synthesis of the Co^{2+}-substituted aluminophosphates gave with the template ethylenediamine the compounds $CoAl(PO_4)_2 \cdot C_2H_9N_2$ and the cobalt aluminophosphate of the ACP-3 type. A cobalt phosphate could also be made at the same experimental conditions with the ACP-3 type structure. Using hydrofluoric acid as a mineralizer in the organothermal and the hydrothermal reactions resulted in several cases in the formation of CoAPO-43, GIS. Single crystals were obtained also in the organothermal and hydrothermal syntheses with ethylenediamine as the template in syntheses where the mineralizer hydrofluoric acid was omitted.

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