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Unusual dual role of the organic amine in an open-framework structure

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The hydrothermal synthesis and single crystal structure determination of a new open-framework zinc phosphate, $[NH_3(CH_2)_3NH_3]_2[NH_3(CH_2)_3NH_2]_2[Zn_{12}(OH_2)_2(PO_4)_{10}]\cdot H_2O$, is reported. Crystal data: monoclinic, space group *Pn* (no. 7), $a=13.092(2)$, $b=14.272(2)$, $c=14.220(1)$ Å, $\beta=90.3(2)°$, $V=2656.9(1)$ Å^3, $Z=2$, $M=1927.6$, $R=0.04$. The structure is made up of tetrahedral linkages between ZnO_4, ZnO_3N and PO_4 moieties forming distinct channels. The structure-directing amine is present in two distinct forms, in the free state and as a ligand to zinc, the two species occurring in distinct channels.

Introduction

A large variety of open-framework metal phosphates have been synthesized over the years by employing organic amines as templates.[1] The role of the amines in the formation of these fascinating structures, however, remains somewhat mysterious. It has been suggested that factors such as the shape of the amine and its pK_a may be of significance.[2] Davis and Lobo[3] proposed that the amine acts as a space-filling agent if the open-framework structure is flexible, and acts as a structure-directing agent when the shape of the amine and the framework are related. During the course of our investigations of open-framework zinc phosphates, we have found even more curious roles played by organic amines. Thus, we have recently shown that in some zinc phosphates the organic amine acts as a ligand to Zn, while at the same time forming the open-framework structure.[4] More importantly, we have just discovered an open-framework structure where the organic amine plays the dual role of a metal ligand as well as of a structure-directing or space-filling agent. We report the synthesis and structure of this unusual open-framework zinc phosphate, $[NH_3(CH_2)_3NH_3]_2$-$[NH_3(CH_2)_3NH_2]_2[Zn_{12}(OH_2)_2(PO_4)_{10}]\cdot H_2O$ **I**, with eight- and ten-membered rings, containing two types of amine molecules.

Experimental

Synthesis and initial characterization

Compound **I** was synthesized hydrothermally starting from a zinc phosphate gel containing 1,3-diaminopropane (DAP) as the structure-directing agent. In a typical synthesis, 0.7 g of oxalic acid and 0.251 g of zinc oxide was dispersed in 4 ml of deionized water. 1.0 ml of DAP was added to the mixture which was stirred for 15 min, then 0.08 ml of H_3PO_4 was added and the stirring continued to attain homogeneity.† The final composition of the mixture was $ZnO:0.4H_3PO_4:3.0H_2C_2O_4:4.7DAP:72H_2O$. The mixture was sealed in a Teflon lined stainless steel autoclave (Parr, USA) and heated initially at 170 °C for 48 h and then finally at 180 °C for 48 h. The resulting product was predominantly comprised of large cube-like single crystals, suitable for single crystal X-ray diffraction, which were filtered off and washed thoroughly with deionized water. EDAX analysis indicated a Zn : P ratio of 55 : 45 which is in excellent agreement with the formula. The powder X-ray diffraction pattern of the powdered single crystals indicated that the product was a new material and the pattern was entirely consistent with the structure determined by single-crystal X-ray diffraction (Table 1). A least-squares fit of the powder XRD lines gave the following cell: $a=13.075(1)$, $b=14.282(1)$, $c=14.202(2)$ Å, $\beta=93.4°$, which is in close agreement with that determined by single crystal XRD (Table 2). Thermogravimetric analysis (TGA) was carried out under a flow of nitrogen (40 ml min^{-1}) from room temperature to 700 °C using a heating rate of 5 °C min^{-1}.

Structure determination

A suitable colorless cube-shaped single crystal ($0.08\times0.08\times0.1$ mm) of **I** was selected and mounted at the tip of a glass fiber using cyanoacrylate (superglue) adhesive. Crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo-Kα radiation, $\lambda=0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data were collected at room temperature in 1321 frames with ω scans (width of 0.30° and exposure time of 20 s per frame). The final unit cell constants were determined by a least-squares fit of 8192 reflections in the range $1.43\leqslant\theta\leqslant23.3$ and are presented in Table 2.

The structure was solved by direct methods using SHELXS-86[6] and difference Fourier syntheses. The absorption correction was based on symmetry equivalent reflections using the SADABS[7] program. Other effects such as absorption by the glass fiber were simultaneously corrected. All the hydrogen positions of the free amine molecules were found in the difference Fourier maps and for the final refinement the hydrogen atoms on the amine molecule were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions, anisotropic thermal parameters for all the framework atoms and free amine molecules and isotropic thermal parameters for the bonded amine molecules and all the hydrogen atoms. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS[8] package of programs. The final Fourier

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†In the absence of oxalic acid a layered material with a twelve-membered ring window is formed. The current solid was made at a pH of 7.5 (zinc phosphates are usually made at a pH of *ca.* 6). We do not exactly understand the role of oxalic acid.

Table 1 Powder X-ray diffraction data for $[NH_3(CH_2)_3NH_3]_2[NH_3(CH_2)_3NH_2]_2[Zn_{12}(OH_2)_2(PO_4)_{10}]\cdot H_2O$ **I**

d_{obs}/Å	d_{calc}/Å	I_{rel} (%)	*hkl*
9.4750	9.6058	6.8	1 0 1
7.0847	7.1097	100	0 2 2
5.6831	5.7127	4.9	1 1 2
4.7579	4.7572	10.0	0 3 0
4.4251	4.4491	8.3	1 0 3
4.2235	4.2475	4.6	1 1 3
3.9621	3.9538	20.1	0 3 2
3.7616	3.7754	3.8	1 2 3
3.7053	3.7117	4.3	2 3 1
3.5497	3.5549	10.5	0 0 4
3.3605	3.3742	7.3	2 2 3
3.1746	3.1819	15.0	0 2 4
3.1119	3.1163, 3.1169	18.6	4 1 −1, 2 0 4
3.0346	3.0452	38.8	2 1 4
2.9635	2.9671	10.3	4 0 2
2.8523	2.8563, 2.8543, 2.8506	11.3	2 2 4, 0 5 0, 0 4 3
2.7666	2.7622	7.9	3 4 0
2.7141	2.7133, 2.7131	6.3	3 4 −1, 3 1 −4
2.6414	2.6471, 2.6418, 2.6402	6.0	4 3 1, 0 2 5, 4 1 3
2.5602	2.5652, 2.5610	6.4	3 2 4, 2 1 5
2.5187	2.5183, 2.5175, 2.5143	6.4	0 4 4, 3 2, 4 2 3
2.4021	2.4048, 2.4024, 2.4016, 2.4014	10.5	1 5 −3, 1 5 3, 1 3 −5, 4 0 4
2.3903	2.3901	9.7	3 4 −3
2.3156	2.3196	3.5	5 2 2
2.2661	2.2664, 2.2663, 2.2650	7.8	3 5 −2, 5 3 −1, 3 2 −5
2.2277	2.2257, 2.2245, 2.2239, 2.2223	3.7	0 5 4, 2 0 6, 0 4 5, 1 6 2
2.0071	2.0090, 2.0057, 2.0053, 2.0050	3.8	1 0 −7, 1 0 7, 3 6 −2, 6 2 −2
1.9752	1.9769, 1.9741	10.7	0 6 4, 0 4 6
1.9487	1.9477	3.3	2 7 0

map had minimum and maximum peaks of −0.76 and 1.18 e Å^{-3}. Final *R* values, $R=0.04$ and $R_w=0.1$ and $S=1.16$ were obtained for a total of 745 parameters. The final atomic coordinates are presented in Table 3.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/178. See http://www.rsc.org/suppdata/jm/1999/2789 for crystallographic files in .cif format.

Table 2 Summary of crystal data, intensity measurements and structure refinement parameters for $[NH_3(CH_2)_3NH_3]_2$-$[NH_3(CH_2)_3NH_2]_2[Zn_{12}(OH_2)_2(PO_4)_{10}]\cdot H_2O$ **I**

Empirical formula	$Zn_{12}P_{10}O_{43}C_{12}N_8H_{52}$
Crystal system	Monoclinic
Space group	*Pn* (no. 7)
Crystal size/mm	0.08 × 0.08 × 0.1
a/Å	13.092(2)
b/Å	14.272(2)
c/Å	14.220(1)
α/°	90.0
β/°	90.3(2)
γ/°	90.0
V/Å^3	2656.9(1)
Z	2
M_r	1927.6
D_c/g cm^{-3}	2.73
λ(Mo-Kα)/Å	0.71073
μ/mm^{-1}	6.6
θ range/°	1.43–23.27
Total data collected	10808
Index ranges	$-14\leqslant h\leqslant 12$, $-15\leqslant k\leqslant 15$, $-15\leqslant l\leqslant 15$
Unique data	5571
Observed data $[I>2\sigma(I)]$	5332
Refinement method	Full-matrix least-squares on $\lvert F^2\rvert$
R indices $[I>2\sigma(I)]$	$R=0.037$, $R_w=0.10$
R indices (all data)	$R=0.04$, $R_w=0.11$
Goodness of fit (*S*)	1.16
No. of variables	745
Largest difference map peak and hole/e Å^{-3}	1.18 and −0.76

Results and discussion

To arrive at the oxidation states of the various species in **I** as well as to find out the extent of protonation of the amine molecules, extensive bond-valence sum analysis[9] was undertaken. The calculations indicate that the valence states of Zn, P and O to be +2, +5 and −2, respectively. Oxygens O(41) and O(42) are formally water molecules and are found to be terminally bonded. Similar terminal water molecules have been observed previously in open-framework zinc phosphate materials.[10]

The asymmetric unit of **I** consists of 85 non-hydrogen atoms (Fig. 1). The structure involves a network of ZnO_4, ZnO_3N and PO_4 tetrahedra with shared vertices. The network between these polyhedra produce adamantane type units, comprised of three- and four-membered rings, connected in various ways forming the channels. The structure of **I** viewed along two different directions is shown in Fig. 2 and 3. Along the *a* axis, there are four-membered rings comprised of two Zn and two P atoms with the P atoms connected to ZnO_4 units and the Zn atoms to PO_4 units, giving rise to a spherical, basic building block (see inset in Fig. 2). These building blocks are connected to each other by Zn–O–Zn linkages (which form a three-membered ring) and ZnO_3N tetrahedra. The connectivity between the various units gives rise to two distinct channels along the *c* and *a* axes as can be seen from Fig. 2 and 3. The channels are filled by the protonated 1,3-DAP and water molecules. Two distinct types of amine molecules (two of each type) are present in the channels of this material, a diprotonated amine and a monoprotonated amine acting as a ligand to zinc. For convenience, we designate these two amine species as 'free' and 'bonded', respectively.

Along the *c* axis, the bonded and free amine molecules are both located within the channels delineated by ten-membered

Table 3 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters for $[NH_3(CH_2)_3NH_3]_2[NH_3(CH_2)_3NH_2]_2[(Zn_{12}(OH_2)_2(PO_4)_{10}]\cdot H_2O$ **I**

Atom	x	y	z	10^3U_{eq}/Å^2	Atom	x	y	z	10^3U_{eq}/Å^2
Zn(1)	7572(1)	25309(1)	6699(1)	13(1)	O(24)	8904(8)	25236(8)	-914(8)	35(3)
Zn(2)	10423(1)	19757(1)	6680(1)	15(1)	O(25)	6803(7)	22578(6)	5786(7)	26(2)
Zn(3)	10839(1)	20142(1)	4204(1)	14(1)	O(26)	7993(7)	20878(6)	4923(7)	23(2)
Zn(4)	6679(1)	26243(1)	792(1)	15(1)	O(27)	6425(8)	20593(6)	6540(7)	28(2)
Zn(5)	6480(1)	18775(1)	5107(1)	13(1)	O(28)	5664(8)	21177(6)	4404(7)	25(2)
Zn(6)	9782(1)	25158(1)	226(1)	16(1)	O(29)	9314(8)	25403(8)	4783(8)	36(3)
Zn(7)	6674(1)	21316(1)	5393(1)	13(1)	O(30)	7626(7)	23799(6)	4821(7)	26(2)
Zn(8)	8076(1)	24961(1)	4232(1)	16(1)	O(31)	6974(7)	25892(6)	4190(6)	21(2)
Zn(9)	13630(1)	20120(1)	5704(1)	17(1)	O(32)	8527(7)	24793(6)	2945(6)	20(2)
Zn(10)	6954(1)	23725(1)	469(1)	17(1)	O(33)	12828(7)	19000(6)	6004(7)	25(2)
Zn(11)[a]	8708(2)	19562(2)	3019(2)	26(1)	O(34)	14247(9)	19994(7)	4501(8)	34(3)
Zn(12)[a]	6245(2)	25725(2)	2928(2)	21(1)	O(35)	12852(8)	21309(6)	5764(8)	27(2)
Zn(11A)[b]	7097(4)	19162(4)	2987(4)	26(2)	O(36)	14573(8)	20199(6)	6839(7)	24(2)
Zn(12A)[b]	4817(5)	25040(4)	2905(5)	38(2)	O(37)	7219(8)	24392(7)	-682(7)	28(2)
P(1)	8603(3)	19975(2)	5119(3)	13(1)	O(38)	5592(7)	23982(6)	937(7)	23(2)
P(2)	11923(3)	18579(2)	5465(3)	12(1)	O(39)	7898(8)	24073(6)	1472(8)	31(3)
P(3)	4820(3)	24764(2)	752(3)	15(1)	O(40)	12183(8)	17578(6)	5217(7)	27(2)
P(4)	6717(3)	23602(2)	5482(2)	11(1)	O(41)[a]	7664(11)	20455(9)	2896(9)	24(3)
P(5)	6496(3)	26452(2)	5026(2)	13(1)	O(42)[a]	5798(12)	24343(10)	2968(10)	27(3)
P(6)	11689(3)	21444(2)	5885(2)	11(1)	O(100)	11669(22)	17698(39)	-2115(35)	295(21)
P(7)	8235(3)	24988(2)	1932(2)	13(1)					
P(8)	7712(3)	25312(2)	-977(2)	15(1)	Free amine				
P(9)	5209(3)	20275(2)	3972(2)	13(1)	N(8)	9364(9)	22614(7)	1366(8)	22(3)
P(10)	5670(3)	19842(2)	6869(2)	11(1)	N(7)	9281(10)	22613(8)	4850(11)	36(3)
O(1)	9034(9)	25307(7)	6527(8)	38(3)	C(12)	9913(13)	22904(10)	2232(11)	33(4)
O(2)	6784(7)	24232(6)	6347(7)	25(2)	C(11)	9370(12)	22554(9)	3110(12)	24(3)
O(3)	7370(7)	25528(6)	8027(6)	22(2)	C(10)	9881(11)	22901(10)	3988(11)	28(3)
O(4)	7145(7)	26364(6)	5901(7)	24(2)	N(6)	8920(10)	17559(8)	9535(10)	34(3)
O(5)	11306(7)	20820(6)	6698(7)	22(2)	N(5)	8961(10)	17637(8)	6039(8)	28(3)
O(6)	10982(7)	18614(6)	6105(7)	22(2)	C(9)	8364(12)	17826(9)	8664(11)	27(3)
O(7)	9924(7)	19544(6)	7934(6)	22(2)	C(8)	8920(13)	17503(10)	7809(14)	36(4)
O(8)	9145(9)	20064(7)	6038(8)	32(3)	C(7)	8437(12)	17940(9)	6941(10)	28(3)
O(9)	11106(8)	21230(6)	4974(7)	28(2)					
O(10)	11755(7)	19128(6)	4528(7)	25(2)	Bonded amine				
O(11)	9373(7)	19854(7)	4306(7)	21(2)	N(4)	10536(9)	15959(8)	3043(9)	30(3)
O(12)	10971(7)	20420(6)	2882(6)	19(2)	N(3)	8146(15)	18170(13)	2972(14)	76(5)
O(13)	7372(8)	29120(6)	-345(7)	31(3)	C(6)	10766(15)	16934(12)	3062(13)	53(5)
O(14)	6452(8)	27529(6)	1157(7)	26(2)	C(5)	9875(34)	17464(27)	3411(30)	153(15)
O(15)	5325(8)	25734(6)	789(8)	33(3)	C(4)[a]	8916(27)	17521(21)	3362(23)	68(9)
O(16)	7320(7)	25692(6)	1916(6)	19(2)	C(4A)[b]	9345(31)	17481(26)	2611(29)	14(9)
O(17)	5994(7)	19472(7)	4012(6)	24(2)	N(2)[a]	5441(14)	26936(12)	2828(12)	27(4)
O(18)	7927(7)	19111(6)	5099(7)	20(2)	N(2A)[b]	4988(33)	26564(27)	2905(28)	27(9)
O(19)	5717(7)	18982(6)	6242(7)	21(2)	N(1)	3033(9)	29262(8)	2863(15)	30(3)
O(20)	6451(8)	17482(6)	4702(6)	24(2)	C(3)	4216(18)	26819(14)	2863(15)	66(6)
O(21)	10675(7)	26224(6)	-31(6)	20(2)	C(2)	3705(22)	27622(17)	3274(20)	87(8)
O(22)	9152(8)	25405(7)	1444(7)	29(2)	C(1)	3484(29)	29224(25)	2606(27)	136(12)
O(23)	10413(7)	23910(6)	185(7)	22(2)					

[a]Disordered atoms with site occupancy factor (SOF) = 0.689. [b]Disordered atoms with site occupancy factor (SOF) = 0.311.

rings. The position of the bonded amine molecule causes the channels to be marginally different in shape and dimensions [(5.7 × 7.5 Å) and (5.6 × 8.1 Å)] as shown in Fig. 2. Along the *a* axis, however, the two types of amine molecules occupy distinctly different channels. The bonded amine sits in the middle of an eight-membered channel (5.1 × 5.9 Å), whereas the free amine occupies an elliptical ten-membered channel (7.9 × 7.0 Å) (atom–atom contact distances not including the van der Waals radii) as shown in Fig. 3. The free water molecule is also located in the ten-membered channel containing the free amine (Fig. 3). Solids in which different amine molecules occupy different channels are known.[11] Zinc phosphate **I** is, however, different and unique in two respects. First, the same amine occupies two different channels and second, there are two types of amine molecules, free and bonded, each present in a separate channel in one of the directions. The presence of different types of amines is also reflected in the shapes of the eight- and ten-membered channels along the *a* axis. These channels are reminiscent of those found in aluminosilicate zeolites.[12] The framework density (FD, number of tetrahedral atoms per 1000 Å^3)[8] of **I** is 16.6, a value in the middle range of FD values, indicating a degree of openness comparable to aluminophosphates and aluminosilicates.[12]

Of the 42 oxygen atoms in the asymmetric unit, eight (*ca.* 20%) make a trigonal connection with two Zn atoms and one P atom forming a three-membered ring, two are terminal oxygens (water molecules) and the remainder of the oxygens form Zn–O–P linkages. The three-coordinated oxygen atoms result in the formation of three-membered rings in this material. Furthermore, these three-coordinated oxygen atoms lead to the formation of short Zn–O–Zn linkages in the material's framework, the third coordination always being to a P atom. Such trigonal coordination of oxygen atoms in Zn–O–Zn bridges is a consequence of the electrostatic valence requirement of the bridging oxygen atoms. Thus, it can not be concluded that the presence of three-coordinate oxygen bridges will give rise to more dense frameworks. Other examples of such electrostatic valence requirements of oxygen have been reported in the literature.[10,13–15] Trigonal and tetrahedral coordination of oxygen atoms observed in such structures[10,13–15] suggests that bridges occur when divalent

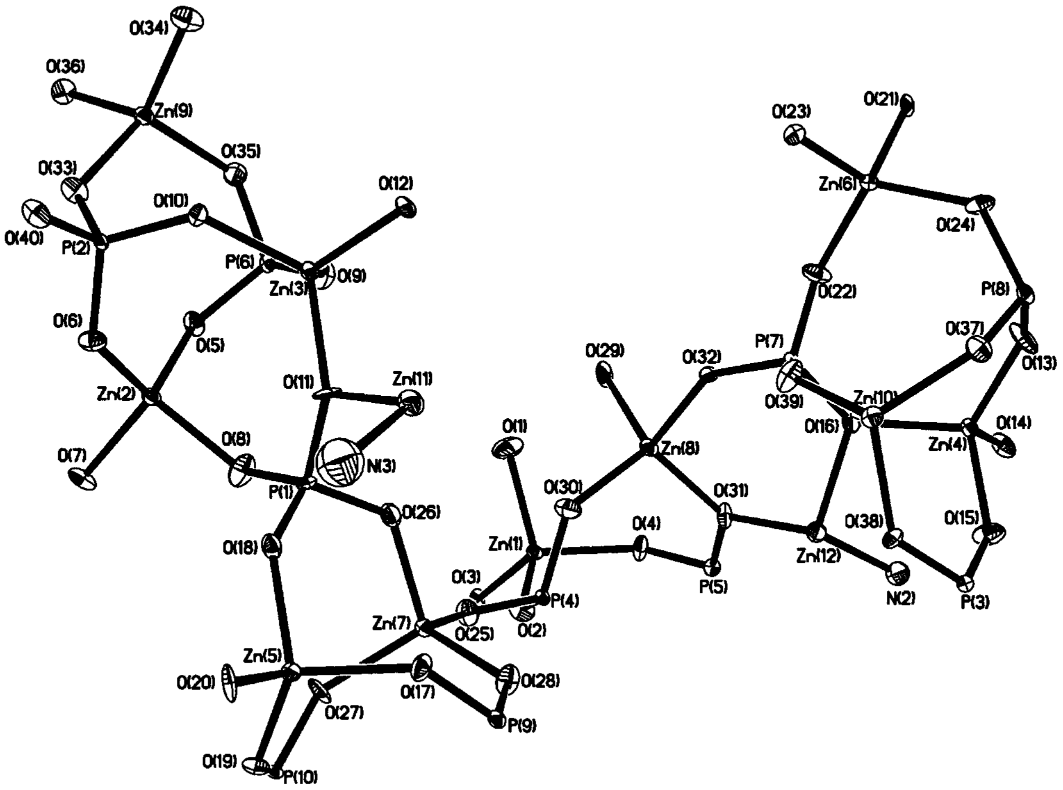

Fig. 1 ORTEP plot of the framework of $[NH_3(CH_2)_3NH_3]_2[NH_3(CH_2)_3NH_2]_2[Zn_{12}(OH_2)_2(PO_4)_{10}]\cdot H_2O$ **I**; the thermal ellipsoids are given at 50% probability. The zinc atoms Zn(11) and Zn(12) are disordered (the disordered positions are not shown).

tetrahedral atoms are present. It may be expected that the presence of such features in the zinc phosphate system would lead to novel open-framework architectures that have no structural counterparts in aluminosilicates or aluminophosphates.

The bond distances and angles in **I** show typical values with Zn–O bond distances in the range 1.867–2.12 Å (av. 1.956 Å) and O–Zn–O bond angles in the range 98.5–132.3° (av. 109.7°), similar to values found in similar structures.[4,5,10,15] P–O distances and O–P–O angles also occur in the expected

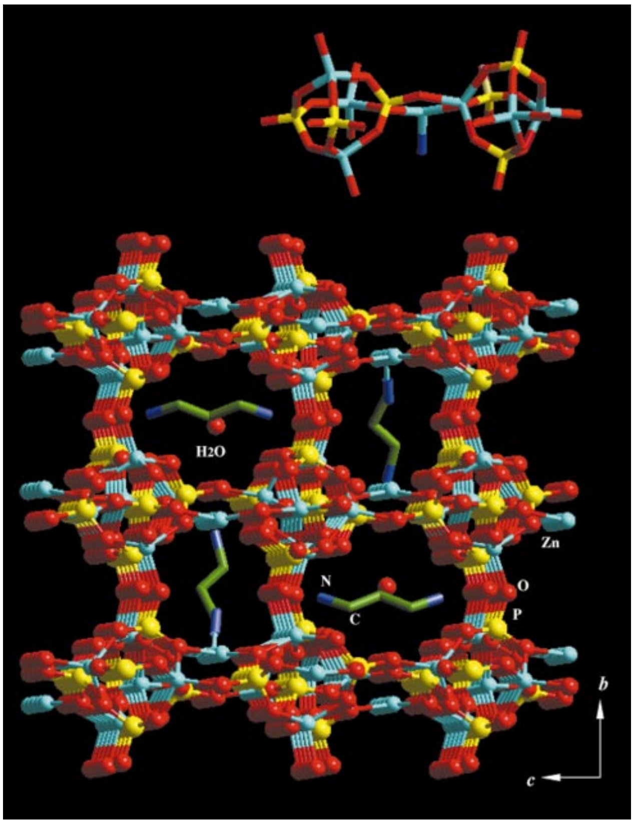

Fig. 2 Structure of $[NH_3(CH_2)_3NH_3]_2[NH_3(CH_2)_3NH_2]_2$-$[Zn_{12}(OH_2)_2(PO_4)_{10}]\cdot H_2O$ **I** along the [100] direction showing the different channels. The bonded and free amine molecules occupy different channels. Note that the water molecules (not bound to Zn center) also occupy the ten-membered channel along with the free amine. The inset shows the spherical building block.

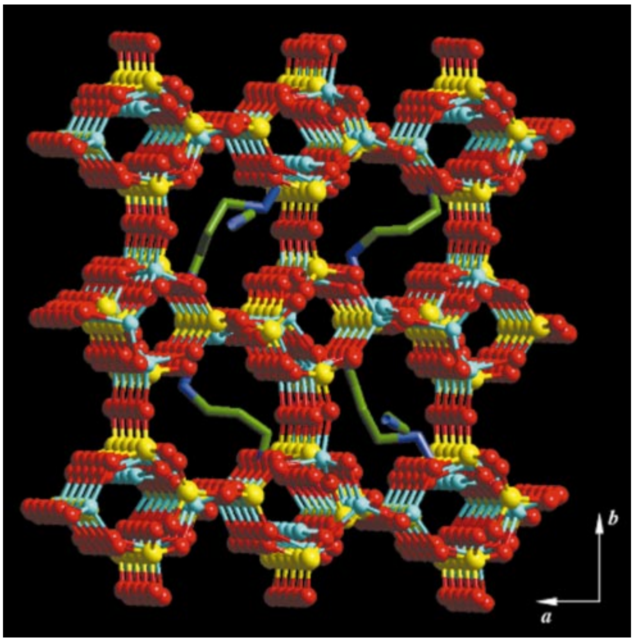

Fig. 3 Structure of $[NH_3(CH_2)_3NH_3]_2[NH_3(CH_2)_3NH_2]_2$-$[Zn_{12}(OH_2)_2(PO_4)_{10}]\cdot H_2O$ **I** along the [001] direction showing the channels. Note that both bonded and free amine molecules occupy the same channels (free amine molecules are situated at the center of the channels). Water molecules are omitted for clarity.

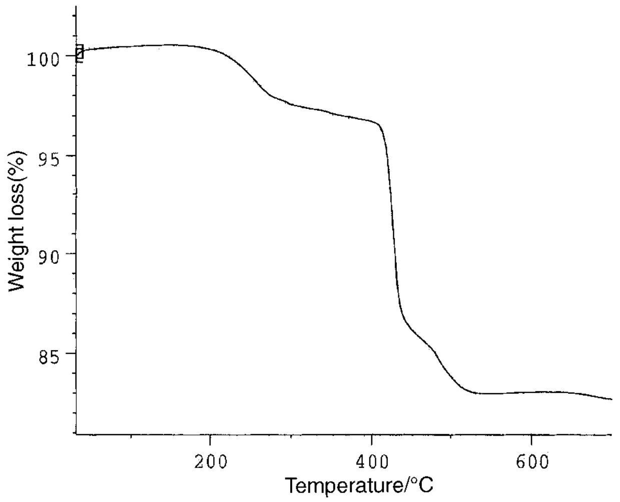

Fig. 4 Thermogravimetric analysis of $[NH_3(CH_2)_3NH_3]_2$-$[NH_3(CH_2)_3NH_2]_2[Zn_{12}(OH_2)_2(PO_4)_{10}]\cdot H_2O$ **I** in flowing nitrogen at 5 °C min^{-1}.

range. The longest Zn–O/N distance and the largest O–Zn–O/N angle are found for oxygens involved in three-coordination and nitrogen atoms bonded to Zn. Two of the zinc atoms [Zn(11) and Zn(12)], are disordered and bound to a water molecule [terminal oxygen, O(41) and O(42)] in the structure, as found in other zinc phosphate materials.[10] The water molecules O(41) and O(42) have the same occupancies as those of Zn(11) and Zn(12) to which they are attached (Table 3); we have not been able to identify the other disordered position of the water molecules from the difference Fourier maps.

As typical of many open-framework structures, the zinc phosphate structure **I** also possesses a large number of hydrogen bond interactions. Selected important hydrogen bond interactions are: O(6)···H(1) 2.128(1) Å, O(6)···H(1)–N(5) 163.3(2)°; O(28)···H(11) 2.065(1) Å, O(28)···H(11)–N(6) 159.9(1)°; O(30)···H(13) 1.906(1) Å, O(30)···H(13)–N(7) 157.6(1)° and indicate the occurrence of extensive hydrogen bond interactions involving the free amine and the framework oxygens. Similar hydrogen bond interactions have been observed in many open-framework phosphates.[1,2,4,10]

Thermogravimetric analysis (TGA) carried out under a nitrogen atmosphere indicated three mass losses in the range 25–700 °C (Fig. 4). The first mass loss of 2.6% around 250 °C corresponds to the loss of adsorbed, free as well as bound water molecules (calc. 2.8%). The second mass loss with a broad tail amounts to a total loss of 14.4% in the range 400–500 °C and corresponds to the loss of the bound and free amine molecules (calc. 15.6%). The decomposed sample was found to be poorly crystalline (powder XRD) and corresponds to a dense zinc phosphate, $Zn_2P_2O_7$ (JCPDS: 43-0488), indicating destruction of the framework structure upon loss of the amine.

Conclusion

The present study establishes the structure of an interesting zinc phosphate where the amine simultaneously performs two roles, that of a metal ligand and of a space-filling or structure directing molecule. Such a structure has not been encountered in any open-framework materials reported hitherto. It is possible that the structure of **I** and of the zinc phosphate where the amine acts as a structure-directing ligand,[4] are intermediate structures that occur between three-dimensional open-framework phosphates and a starting 'precursor' chain phosphate. The observation of such structures points to the need to investigate the role of the amines in the formation of open-framework structures more closely, and to explore the varieties of structures that may exist wherein the amine plays different roles.

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