Synthesis and Crystal Structure of Zn(O3PC2H4NH2), the First Functionalized Zeolite-like Phosphonate

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The title compound was prepared by reaction of zinc nitrate, (2-aminoethyl)phosphonic acid and sodium benzoate in water in an autoclave at 180 °C, and its crystal structure shows a channel-type arrangement.

Interest in the chemistry of phosphonates has risen in recent years, notably because of the possibility of design of new three-dimensional frameworks, with applications as sorbents, catalysts, molecular sieves and photosynthetic systems. The main strategy for their preparation involves diphosphonic acids $H_2O_3P-R-PO_3H_2$, leading to pillared layered structures (PLS), as reported for zirconium[1–6] and for vanadium.[7] Moreover, we have recently demonstrated that PLS were also accessible, using (2-carboxyethyl)phosphonic acid as pillaring agent, for zinc,[8] bismuth[9] and mixed zinc and manganese arranged in specific geometry within the layers.[10]

Parallel to this, examples of tubular zeolite-like phosphonate structures were limited to our synthesis of β-Cu(O3PMe).[11] In an effort to extend the chemistry of three-dimensional open-frameworks containing channels, we felt that functionalized phosphonic acids were powerful tools for this purpose. We report in this paper, the hydrothermal synthesis and the novel structure of a functionalized three-dimensional phosphonate with a channel-type arrangement, Zn(O3PC2H4NH2) 1, assembled from zinc nitrate, (2-aminoethyl)phosphonic acid and sodium benzoate in water,† with amino ends present in the internal tubular void spaces.

In the structure of compound 1,‡ the zinc atoms are coordinated by three oxygens of three different phosphonate groups, and by the nitrogen of an additional phosphonate unit (Fig. 1). In the bc plane, the zinc atoms are nearly coplanar and arranged in 16-membered rings, constructed by corner-sharing of four ZnO3N tetrahedra and four PO3C tetrahedra. The sheet linkage of these rings results in eight-membered rings (Zn–O–P–O–Zn–O–P–O), with an arrangement very similar to that described by us in Zn(O3PC2H4CO2H)·1.5H2O[8] and Harrison in ZnPO–dab-A, a zincophosphate containing cationic 1,4-diaza-bicyclo[2.2.2]octane guests.[12] The stacking of the 16-membered rings, perfectly aligned along the a-axis, forms infinite elliptical tunnels with windows of approximate dimensions 3.6 × 5.3 Å. A remarkable feature, is the presence of the nitrogen atoms in these cavities, as two face-to-face columns parallel to the axis of the channels. The shortest distances between two nitrogens are 6.431(3) Å (within the column) and 3.650(3) Å (between two adjacent columns). The Zn–P–O inorganic layers are connected together via O–P–C–C–N links in the a unit-cell direction, to form a three-dimensional network (Fig. 2), again with channels apparent in the b direction. No guest (water, sodium or benzoic acid) was trapped in the structure.

After the recently reported pillared layered structure of Zn3(O3PC2H4CO2)2 (covalent interlayer bonding via PO3 and CO2 groups),[8] this example clearly shows that, as with diphosphonic acids, functionalized phosphonic acids can act as efficient building blocks for the self-assembly of three-dimensional open-structures. One of the key points influencing the final arrangement of the phosphonate hybrid material is the length of the R spacer in H_2O_3P-R-Z, as demonstrated by Haushalter[7] for the vanadium system (Z = PO3H2, R = (CH2)x); by increasing the number of methylene groups, one- (x = 1), two- (x = 2) and three-dimensional (x = 3) compounds were obtained. The present work highlights another way to manipulate the connectivity of the phosphonate framework, that is the choice of the Z functional end, simply by varying the
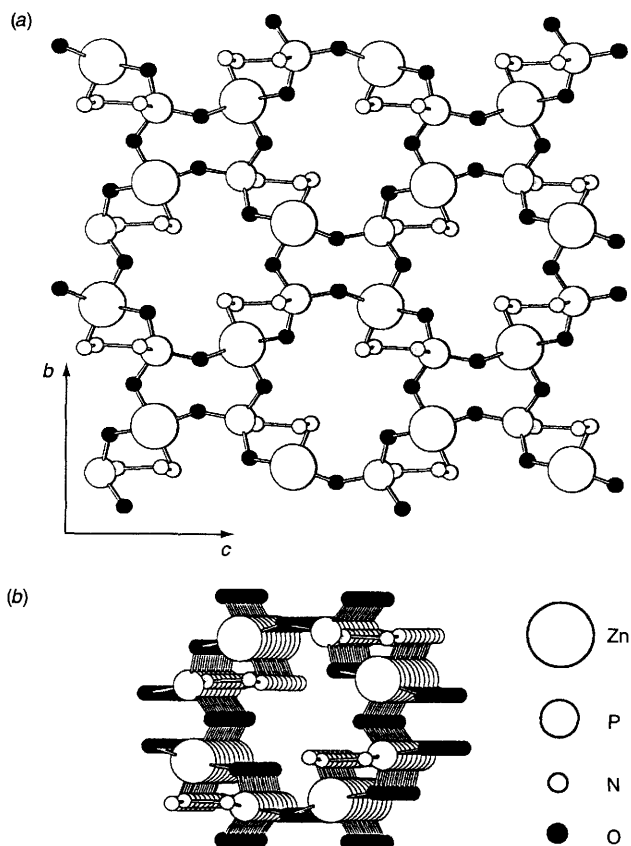

Fig. 1 (a) Schematic representation of Zn(O3P(CH2)2NH2) viewed down the a-axis, illustrating the tubular structure; (b) view of a channel. Selected interatomic distances (Å): Zn–O 1.942(2), 1.933(2), 1.955(2); Zn–N 2.027(2); P–O 1.528(2), 1.521(2), 1.534(2); P–C 1.806(1).
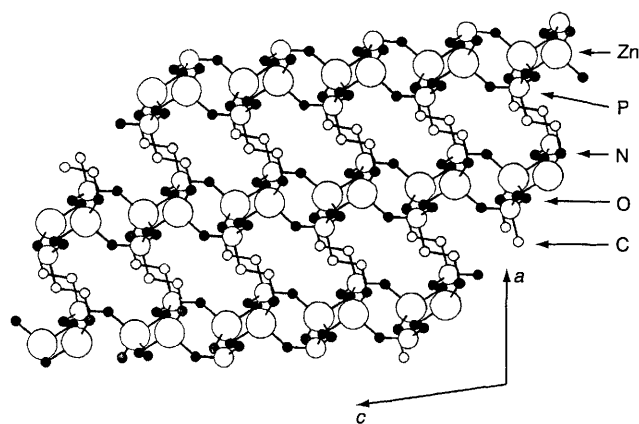
Fig. 2 View of the ac plane of Zn(O3P(CH2)2NH2), showing the connection between the Zn, P, O, N layers

number of its potential binding sites (three oxygen atoms for PO_3H_2, two oxygen atoms for CO_2H, one nitrogen atom for NH_2), that can participate to the cohesion of the network.

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Footnotes

† *Synthesis of* 1: A mixture of zinc nitrate (0.5 mmol), (2-amino-ethyl)phosphonic acid (0.5 mmol) and sodium benzoate (1.5 mmol) with water (10 ml) was placed in the PTFE cell (50% fill volume) of an autoclave, that was sealed and placed in a drying oven for 60 h at 180 °C. $Zn(O_3PC_2H_4NH_2)$ was obtained as white crystals, used for the X-ray structure determination, in 70% yield (90% yield if the concentration of the starting materials was doubled). *Selected data*: IR (KBr) v/cm^{-1} 3291 (s), 3265 and 3180 (m), 1600 (m), 1119 (s), 1060 and 1040 (vs), 1005 (s), 952 (m), 582 (m), 536 (m); TGA room temp. to 300 °C, 0%; ^{31}P MAS NMR (85 mass% H_3PO_4) δ 26.7.

‡ *Crystal data* for 1: $ZnPO_3C_2NH_6$, monoclinic, $P2_1/c$, $a = 6.434(1)$, $b = 8.4344(8)$, $c = 9.761(1)$ Å, $\beta = 99.93(2)°$, $V = 521.5(3)$ Å^3, $D_c = 2.40$ g cm^{-3}, $Z = 4$, $\mu = 50.32$ cm^{-1}, $T = 298$ K, crystal dimensions $0.07 \times 0.07 \times 0.13$ mm. Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) with ω-2θ scans. An empirical absorption correction was applied (transmission min., 0.87; max., 1.0). The structure was determined by direct methods using programs in the MOLEN package[13] on the basis of 2500 independent reflections with $I > 2\sigma(I)$ (98 parameters). All non-H atoms were defined anisotropically, $R = 0.031$, $R_w = 0.034$, max. shift/e.s.d. = 0.001, residual electron density = $-0.65/0.57$ e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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