Hydrothermal Synthesis of Single Crystals of $Mg_2[Be_3(PO_4)_3(OH)]\cdot 6H_2O$; the One-dimensionally Infinite, Chiral, Polar Polyanion $[Be_3(PO_4)_3(OH)]_n^{4n-}$

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Single crystals of $Mg_2[Be_3(PO_4)_3(OH)]\cdot 6H_2O$ are grown hydrothermally and characterized by X-ray structure analysis, which proves $BeO_3(OH)$ and PO_4 tetrahedra are linked by common corners to establish a one-dimensionally infinite, chiral, polar polyanion of composition $[Be_3(PO_4)_3(OH)]_n^{4n-}$ with nearly 1 nm diameter extending parallel to [001].

Beryllophosphates should provide ample framework structure types composed of corner-sharing tetrahedra similar to aluminosilicates.[1–6] Organic cations acting as template molecules often favour the formation of molecular sieve-like structures. $Mg_2[Be_3(PO_4)_3(OH)]\cdot 6H_2O$, however, which was formed in the presence of Et_4N^+ cations under hydrothermal conditions contains a one-dimensionally infinite polyanion as the most prominent structural feature.‡,§

The $[Be_3(PO_4)_3(OH)]_n^{4n-}$ polyanion possesses crystallographic threefold symmetry. Be is tetrahedrally coordinated by three oxygen atoms [O(1), O(2), O(3)] and one OH group which forms the common corner of three symmetrically equivalent $BeO_3(OH)$ tetrahedra (Fig. 1). These groups of three tetrahedra are stacked in the [001] direction separated by PO_4 tetrahedra inserted between the $BeO_3(OH)$ tetrahedra. The Be-centred tetrahedra are linked with PO_4 tetrahedra *via* common corners [O(1), O(2), O(3), Fig. 1]. There is no direct connection between neighbouring PO_4 groups. The P–O bond lengths are almost equal [152.6(1)–154.6(1) pm, Fig. 1] yielding an overall bonding order of 5.03 employing the method of Brown.[7] The same is true for the Be–O bonds [160.0(3)–162.8(3) pm]. The Be–OH bond is considerably longer [174.5(2) pm]. The overall bonding order for the four Be–O contacts reaches 1.97 indicating that the tetrahedral environment is well adapted to the central atoms.

The X-ray structure analysis on the layered compound $Be_2(PO_4)(OH)\cdot 2H_2O$ yielded P–O bonds in the range between 153.6(3) and 154.0(3) pm.[8] The Be–OH bonds in this beryllophosphate featuring an electrically neutral two-dimensionally infinite arrangement of corner-sharing PO_4 and $BeO_2(OH)(H_2O)$ tetrahedra are markedly short [158.7(6) and 160.3(6) pm]. The Be–O bond lengths [160.7(5)–163.3(6) pm] are similar to those of $Mg_2[Be_3(PO_4)_3(OH)]\cdot 6H_2O$.

The Be atoms in $Mg_2[Be_3(PO_4)_3(OH)]\cdot 6H_2O$ are further apart from each other [292.9(2) pm] than in $Be_2(PO_4)(OH)\cdot 2H_2O$ [282.8(7) pm]. In contrast, P and Be atoms of $Mg_2[Be_3(PO_4)_3(OH)]\cdot 6H_2O$ [278.3(3)–283.7(3) pm] are closer than in the layered beryllophosphate [284.4–285.8(5) pm]: comparable to the P···Be contact in $LiBePO_4\cdot H_2O$[3] [281(2) pm].

The $[Be_3(PO_4)_3(OH)]_n^{4n-}$ polyanions with nearly 1 nm diameter are chiral and polar. Consequently, $Mg_2[Be_3(PO_4)_3(OH)]\cdot 6H_2O$ is an electret, since the space group is $P6_3$ and there is no mechanism providing an inversion of the polarization of the polyanions without destruction of the entire crystal structure.

Each of the two crystallographically unique Mg^{2+} is situated on a threefold axis and coordinated octahedrally by three water molecules [Mg(1): O(w1), Mg(2): O(w2)] and three oxygen atoms [O(4)] stemming from the PO_4 tetrahedra (Fig. 2). The Mg–OH_2 bonds are shorter [Mg(1): 206.7(2), Mg(2): 208.5(2) pm] than the Mg–O(4) bonds [Mg(1): 212.6(2), Mg(2): 209.8(2) pm]. The overall bonding order for the Mg–O bonds is close to 2.0 for both Mg(1) and Mg(2). The coordination octahedra of Mg(1) and Mg(2) share a common face made up by three symmetrically equivalent O(4) atoms yielding a rather short Mg–Mg distance of 286.9(2) pm. The polyanions are stacked parallel to [001] in the crystal structure and are linked to each other by the Mg^{2+} cations compensating for the negative excess charge of the anionic chains (Fig. 3).

All hydrogen atoms of the two unique water molecules participate in hydrogen bonds. The hydrogen bonds involving H(21) and H(22) stemming from O(w2) are considerably stronger [O(w2)···O(3) 270.4(2), O(w2)···O(2) 271.1(2) pm] than those bonds with O(w1) acting as proton donator [O(w1)···O(1) 294.5(2), O(w1)···O(w2) 284.2(3) pm]. The OH group is not involved in hydrogen bonds similar to the OH group in the layered compound $Be_2(PO_4)(OH)\cdot 2H_2O$ which links two adjacent Be-centred tetrahedra.[8]

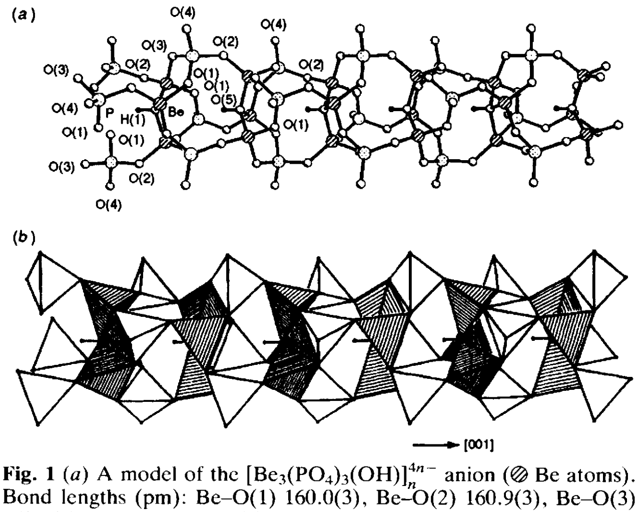

Fig. 1 (*a*) A model of the $[Be_3(PO_4)_3(OH)]_n^{4n-}$ anion (▨ Be atoms). Bond lengths (pm): Be–O(1) 160.0(3), Be–O(2) 160.9(3), Be–O(3) 162.8(3), Be–OH 174.5(2), P–O(1) 153.4(2), P–O(2) 154.6(1), P–O(3) 154.4(1), P–O(4) 152.6(1); (*b*) The $[Be_3(PO_4)_3(OH)]_n^{4n-}$ anion composed of corner-sharing tetrahedra (Be-centred tetrahedra are hatched). All O–H vectors posses the same direction and run parallel to [001].

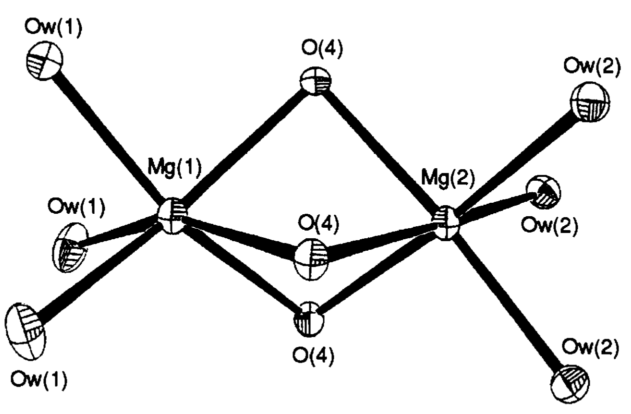

Fig. 2 Mg^{2+} cations situated on a threefold crystallographic axis compensate for the negative excess charge of the $[Be_3(PO_4)_3(OH)]_n^{4n-}$ anions. The two unique Mg^{2+} cations [Mg(1), Mg(2)] are coordinated octahedrally by three water molecules each and three oxygen atoms stemming from PO_4 tetrahedra [O(w1), O(w2), O(4)]. The coordination octahedra are linked in pairs by a common face [3 × O(4)]. Distances (pm): Mg(1)–O(w1) 206.7(2), Mg(1)–O(4) 212.6(2), Mg(2)–O(w2) 208.5(2), Mg(2)–O(4) 209.8(2), Mg(1)–Mg(2) 286.9(2).

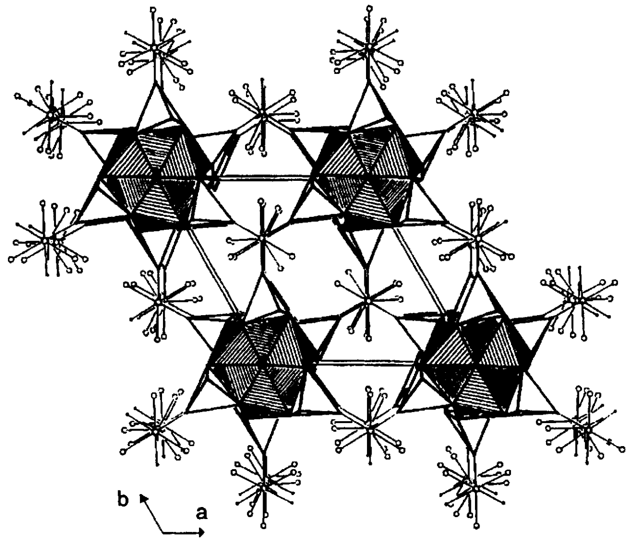

Fig. 3 Pairs of Mg-centred octahedra link the column-like $[Be_3(PO_4)_3(OH)]_n^{4n-}$ polyanions *via* the P–O(4)–Mg bonds. (Viewed parallel to [001]. Be-centred tetrahedra are hatched. Large circles represent H_2O molecules and Mg^{2+} cations, respectively).

This work has been supported by Fonds der Chemischen Industrie and by Hanns-Seidel-Stiftung with funds of Bundesministerium für Bildung und Wissenschaft.

Received, 18th July 1994; Com. 4/04394D

Footnotes

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‡ *Crystal data* for $Mg_2[Be_3(PO_4)_3(OH)]\cdot 6H_2O$. Hexagonal a = 996.3(2), c = 815.2(2) pm, V = 700.8 × 10^6 pm^3, space group $P6_3$ (No. 173). Z = 2, M_r = 485.7, D_c = 2.30 g cm^{-3}, μ = 6.1 cm^{-1} (Mo-Kα), F(000) = 492.3864 reflections of a single crystal with dimensions 0.36 × 0.36 × 0.14 mm^3 were collected on a Siemens R3m/V four-circle diffractometer (graphite-monochromated Mo-Kα radiation) in the ω-scan mode to $2\theta_{max}$ = 70°, T 295 K; a numerical absorption correction was applied. 1991 unique reflections with $|F| > 3\sigma_{|F|}$ were considered observed. All hydrogen atoms could be located and were refined with a common isotropic displacement parameter. All non-hydrogen atoms were refined anisotropically (96 parameters, SHELXTL-PLUS program package[9]). R = 0.0345, R_w = 0.0298, R_g = 0.0359; absolute configuration η = 0.9(2), $w = \sigma|F|^{-2}$, largest features in final difference Fourier synthesis +1.02/−1.43 e × 10^{-6} pm^{-3}.

§ *Selected spectroscopic data*: IR data (in KBr, cm^{-1}): 3524st, 3407st, 3348st, 3246st, 1643w, 1128st, 1208sh, 1141st, 1058m, 1027w, 985m, 797m, 760m, 680w, 663w, 541w, 500m, 428w.

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