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The Novel Binuclear Hydroxyberyllate Species $[Be_2(OH)_7]^{3-}$ and the Hydroxide Hydrate Anion $[H_3O_2]^-$ as Components of Beryllate Equilibria

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It is known from elementary textbook chemistry that beryllium hydroxide, $Be(OH)_2$, is to be classified as amphoteric, meaning that it can be dissolved readily in both aqueous acid and base.[1] While there is general agreement about the nature of the species that appear in acid solution,[2−8] mainly $[Be(H_2O)_4]^{2+}$ and $\{[Be(OH)(H_2O)_2]_3\}^{3+}$, the knowledge about the equilibria established with base is very limited. A large number of polynuclear aquo/hydroxo/oxo beryllate anions have been proposed,[9,10] but for a long time none of these has been identified unequivocally or structurally characterized.

The older literature postulates simple $[Be(OH)_4]^{2-}$ as the dominating species of strongly alkaline solution (pH 12−14).[1−6,9,10] Precipitates with various counterions have been formulated, among which a calcium salt, $Ca[Be(OH)_4]$, in particular was the subject of several studies.[9,10] It was crystallized in the form of various hydrates, but the structures could not be determined.

In the course of our own investigations in the inorganic and bioinorganic chemistry of beryllium[11] we have recently discovered that the beryllate crystallized from sodium hydroxide solutions at pH 13.2 is in fact not derived from the simple $[Be(OH)_4]^{2-}$ dianion, but contains a tetranuclear dianion $[Be_4(OH)_{10}]^{2-}$ with an adamantane type structure.[12] This observation is proof that condensation of the tetrahydroxyberyllate dianion with partial liberation of hydroxide anions is a relevant process even in strongly alkaline medium, and this result has been confirmed by state-of-the-art theoretical calculations.[12]

When working with the calcium system we discovered a dinuclear species, which must be considered the first step of the condensation which eventually leads to the adamantane cage and to more highly condensed beryllates and, finally, beryllium hydroxide.

In an attempt to repeat earlier work,[9,10] but with several variations in the precipitation and crystal growth techniques,[13] we obtained a colorless product which analyzed as a sesquihydrate of $Ca[Be(OH)_4]$. Further structural investigation of single crystals[14] has shown, however, that this trigonal phase contains in fact the anions $[Be_2(OH)_7]^{3-}$ (Figure 1) associated with hydrated calcium cations and, even more surprising, hydroxide hydrate anions $[HO-H-OH]^-$ (Figure 2). It should be noted that this stoichiometry is the same as that of $Ca[Be(OH)_4](H_2O)_{3/2}$ and that both can be related by eq 1.

$$\{Ca[Be(OH)_4]\}_2(H_2O)_3 \rightleftharpoons [Ca^{2+}]_2[Be_2(OH)_7]^{3-}[H_3O_2]^-(H_2O)_2 \quad (1)$$

In the dinuclear beryllate trianion the two beryllium atoms are bridged by a hydroxide anion with an angle $Be-O6-Be' = 137.7(3)°$. The hydrogen atom H6 is coplanar with the $Be-O6-Be'$ group as imposed by local C_2 symmetry. The two beryllium atoms are in a tetrahedral environment of oxygen atoms with O6 as the common vertex.

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(13) **CAUTION!** Beryllium and its compounds are classified as extremely toxic. Appropriate precautions should be taken while handling and disposing of all contaminated material. **Preparation.** The reactions were carried out in a CO_2-free atmosphere and in pure, fully desalinated water. Starting materials were commercially available and of p.a. quality. $BeSO_4{\cdot}4H_2O$ (1.77 g, 10.0 mmol) was dissolved in 30 mL of water. Addition of 3.15 g of $Ba(OH)_2{\cdot}8H_2O$ (10.0 mmol) and 1.6 g of NaOH (40 mmol) led to the immediate precipitation of $BaSO_4$ and of gelatinous $Be(OH)_2$. The reaction mixture was stirred at room temperature for 15 h, during which time $Be(OH)_2$ redissolved. The suspension was filtered and the resulting clear solution (pH 13.5−14) concentrated under reduced pressure to a volume of 8 mL. Dropwise addition of an aqueous solution of $CaCl_2$ (0.28 g, 2.5 mmol in 7 mL of water) resulted in an immediate precipitation of a colorless microcrystalline solid. Slow interdiffusion of the concentrated aqueous sodium beryllate solution and an aqueous $CaCl_2$ solution through a "buffer layer" of pure water gave single crystals of $Ca_2\{[Be_2(OH)_7][H_3O_2]\}{\cdot}2H_2O$ within 4 weeks suitable for structure determination (dec >250 °C, 0.32 g, 1.1 mmol, 88.8% yield). Anal. Calcd for $Ca_2\{[Be_2(OH)_7][H_3O_2]\}{\cdot}2H_2O$ (288.29): H, 4.90; Ca, 27.8. Found: H, 5.15; Ca, 27.5. ^{9}Be NMR (D_2O, 20 °C): $\delta = 2.1$ ppm, s, relative to $[Be(OH)_4]^{2+}$.

(14) **Crystal Structure Determination.** The sample was mounted in a glass capillary on an Enraf Nonius CAD4 diffractometer and used for measurements of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Graphite-monochromated Mo Kα radiation was used. The structure was solved by direct methods and refined by full-matrix least-squares calculations on F^2. **Crystal Data for** $\mathbf{Be_2Ca_2O_{11}H_{14}}$: $M_r = 228.29$, colorless crystals, trigonal, $a = b = 9.653(1)$ Å, $c = 9.135(1)$ Å, space group $P3_221$ (No. 154), $Z = 3$, $V = 737.16(13)$ Å^3, $\rho_{calc} = 1.948$ g cm^{-3}, $F(000) = 450$; $T = 21$ °C. Data were corrected for Lorentz and polarization but not for absorption effects [μ(Mo Kα) = 12.02 cm^{-1}]; 6365 measured and 1069 unique reflections [$R_{int} = 0.0259$, $(\sin\theta/\lambda)_{max} = 0.62$ Å^{-1}]; 96 refined parameters, wR2 = 0.0688, R1 = 0.0280 for 1048 reflections used for refinement. Residual electron densities: +0.63/−0.40. The function minimized was $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0560$, $b = 0$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located and refined with isotropic contributions, except for one H atom of one of the H_2O bridges between the Ca atoms. Refinement in the enantiomorphous space group $P3_121$ (No. 152) was not successful. Important interatomic distances and angles are shown in the corresponding figure captions.

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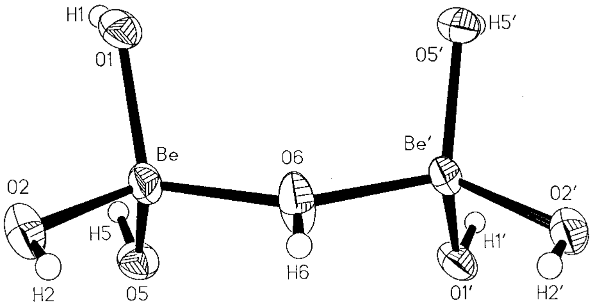

Figure 1. Molecular structure of the hydroxyberyllate trianion $[\mathrm{Be_2(OH)_7}]^{3-}$ in the crystal lattice of $\mathrm{Ca_2[Be_2(OH)_7][H_3O_2]\cdot 2H_2O}$ (ORTEP, 50% probability ellipsoids): Be−O1 1.639(3) Å, Be−O2 1.633(3) Å, Be−O5 1.611(3) Å, Be−O6 1.662(3) Å; O1−Be−O6 109.2(2)°, O6−Be−O5 108.9(2)°, O6−Be−O2 109.8(2)°; Be−O6−Be′ 137.7(3)°.

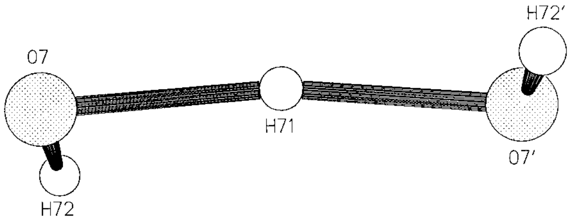

Figure 2. $[\mathrm{H_3O_2}]^-$ in the crystal lattice of $\mathrm{Ca_2[Be_2(OH)_7][H_3O_2]\cdot 2H_2O}$ (arbitrary radii): O7−H71 1.325(10) Å, O7−H72 0.80(3) Å; O7−H71−O7′ 170.5(6)°, H71−O7−H72 90(3)°.

The calcium atoms (related by the 3_2 screw axis) are in a distorted pentagonal bipyramidal environment of seven oxygen atoms, two of which are part of water molecules. In and between their helical strings the calcium-centered polyhedra share edges. O5 bridges a calcium and a beryllium atom.

The remaining independent type of oxygen atom (O7) constitutes the heavy atom domain of the anion [H−O−H−O−H]⁻, the hydrogen atoms of which have been localized and refined (local C_2 symmetry). There is ample precedent for the existence of this hydroxide hydrate species, which was the subject of theoretical scrutiny again only very recently.[1,15,16] The two oxygen atoms (O7/O7′) of the $[\mathrm{O_2H_3}]^-$ anion are not part of the coordination polyhedra of beryllium or calcium, but are engaged in hydrogen bonding.

The present results show that the condensation of $[\mathrm{Be(OH)_4}]^{2-}$ dianions with extrusion of $\mathrm{OH^-}$ anions (eq 2) is an energetically balanced process even for cases where the $\mathrm{OH^-}$ anion liberated is taken on only by a water molecule to give the hydrogen-bonded species $[\mathrm{O_2H_3}]^-$. Extrusion of four additional hydroxide anions between two of the $[\mathrm{Be_2(OH)_7}]^{3-}$ anions will then lead to the $[\mathrm{Be_4(OH)_{10}}]^{2-}$ dianion discovered in the sodium hydroxide solution,[12] probably via a chain and a ring of four vertex-sharing tetrahedra. This condensation appears to be governed by the nature and concentration of the counterions and the hydroxide concentration.

$$4[\mathrm{Be(OH)_4}]^{2-} \underset{+2\mathrm{OH}}{\overset{-2\mathrm{OH}^-}{\rightleftharpoons}} 2[\mathrm{Be_2(OH)_7}]^{3-} \underset{+4\mathrm{OH}^-}{\overset{-4\mathrm{OH}^-}{\rightleftharpoons}} [\mathrm{Be_4(OH)_{10}}]^{2-} \tag{2}$$

It should be noted that this realm of beryllium hydroxide chemistry resembles that of silicic acids, but with the essential difference that in condensed silicic acids the silicon atoms are bridged by oxide units while the beryllium atoms in polyberyllates are bridged by hydroxide units. The acidity of OH groups bridging two silicon(4+) atoms is much more enhanced than that of OH groups bridging beryllium(2+) atoms, such that in silicic acids bridging is always accompanied by complete deprotonation of the bridging oxygen atoms.

Beryllium hydroxide and various condensed beryllates are thus to be considered as components of very sensitive equilibria which can be influenced drastically by even minor adjustments of the conditions in solutions and in crystal lattices. While ^{9}Be NMR spectroscopy of fluoroberyllate solutions is extremely helpful in studying the corresponding equilibria of $\mathrm{Be^{2+}/F^-}$ systems,[17] this unfortunately is not true for the $\mathrm{Be^{2+}/OH^-}$ system, probably owing to more rapid ligand and proton exchange (via hydrogen bonds) and smaller chemical shift differences. Although for different reasons, this is also true for mass spectrometry studies. The challenge therefore remains to isolate and structurally characterize the individual species as components of well-defined salts or inclusion compounds.

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Supporting Information Available: Tables listing crystal and structure refinement data, isotropic and anisotropic displacement parameters, and bond lengths and angles and a figure showing the environment of the calcium atoms (5 pages). Ordering information is given on any current masthead page.

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