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Identification and Structural Characterization of the Predominant Species Present in Alkaline Hydroxyberyllate Solutions

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The earliest observations that led to the discovery of the element beryllium almost exactly two centuries ago[1] focused on the "amphoteric" behavior of beryllium hydroxide: Like aluminum hydroxide, beryllium hydroxide dissolves in both strong aqueous acid and base.[2] While there is little doubt about the nature of the dicationic tetraaquoberyllium species $[Be(OH_2)_4]^{2+}$ resulting after treatment with acid,[3−8] both the old and the new literature reflect a continuous debate about the composition and structure of the compounds that appear upon treatment with base.[9,10] A plethora of stoichiometries and structures of "beryllates" have been formulated, but only the component $[Be(OH)(H_2O)_2]_3^{3+}$ could recently be identified and structurally characterized.[11]

We now report, for the first time, the identification of a hydroxyberyllate species, $[Be_4(OH)_{10}]^{2-}$, which has a highly symmetrical tetranuclear structure unprecedented in metal hydroxide chemistry (Figure 1).

In the course of our ongoing studies of beryllium complexation by biorelevant ligands,[12−16] we undertook systematic ^{9}Be NMR investigations of equilibria involving various beryllium salts in aqueous solutions as a function of pH. From the results, it appeared that in the pH range between 12 and 14 there is virtually only a single aquo/hydroxo/oxo species present in solution which is characterized by a resonance at δ 2.0 ppm (relative to the reference line of aqueous $[Be(OH_2)_4]^{2+}$, $\delta = 0$). The facts that the nature of the counterion (Na^+, K^+, etc.) has little effect on the chemical shift δ of this peak and that only a relatively sharp singlet signal is observed for the quadrupolar ^{9}Be nuclei suggested that this particular beryllate species is an independent entity in solution and possesses high symmetry.

Through careful layering of an aqueous sodium beryllate solution at pH 13.2 with acetone at 20 °C, it was possible, after allowing the solution to stand for a few weeks in a carbon dioxide free atmosphere, to isolate a solid phase as single crystals[17] which analyzed as $Na_2[Be_4(OH)_{10}](H_2O)_5$. It has been shown previously that alkali beryllate solutions strongly absorb CO_2 to give carbonato beryllate salts,[13] and therefore, it is mandatory to work with rigorous exclusion of CO_2.

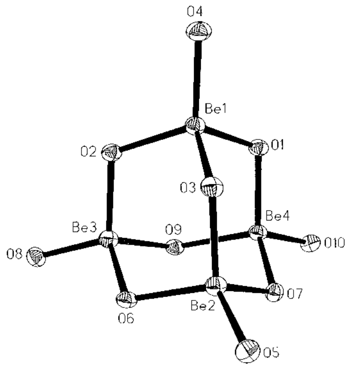

Figure 1. Molecular structure of the hydroxyberyllate dianion $[(BeOH)_4(OH)_6]^{2-}$ in the crystal lattice of $Na_2[Be_4(OH)_{10}]\cdot 5H_2O$. (ORTEP, 50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Be1−O1 1.680(2), Be1−O2 1.634(2), Be1−O3 1.630(2), Be1−O4 1.607(2), Be2−O3 1.662(2), Be2−O5 1.615(2), Be2−O6 1.648(2), Be2−O7 1.647(2), Be3−O2 1.636(2), Be3−O6 1.676(2), Be3−O8 1.587(2), Be3−O9 1.649(2), Be4−O1 1.648(2), Be4−O7 1.654(2), Be4−O9 1.660(2), Be4−O10 1.608(2); Be1−O1−Be4 116.27(9), Be1−O2−Be3 114.67(9), Be1−O3−Be2 116.13(9), Be2−O6−Be3 114.98(9), Be2−O7−Be4 116.17(9), Be3−O9−Be4 115.50(9).

A single-crystal X-ray diffraction analysis[18] of a suitable specimen of the new disodium decahydroxytetraberyllate revealed that the sole beryllate component of the lattice is a tetranuclear unit with an adamantane-type structure, which had never been considered for aqueous beryllium chemistry (Figure 1). This dianionic unit has the net formula $[(BeOH)_4(OH)_6]^{2-}$ with the beryllium atoms at the vertexes of a regular tetrahedron, six hydroxyl groups bridging the six edges of the polyhedron, and one terminal hydroxyl group attached to each of the four beryllium atoms. Each beryllium atom is thus surrounded by four OH groups which again form a tetrahedron.

These tetranuclear beryllate units are connected into layers via one set of sodium atoms (Na2, Figure 2), which are located at

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(17) *Caution*: Beryllium and its compounds are classified as extremely toxic. Appropriate precautions should be taken while handling and disposing of all contaminated material. *Preparation*: $BeSO_4(H_2O)_4$ (1.77 g, 10 mmol) is dissolved in 30 mL of desalinated water and treated with $Ba(OH)_2(H_2O)_8$ (3.15 g, 10 mmol) and NaOH (0.80 g, 20 mmol) to give a precipitate of $BaSO_4$ and $Be(OH)_2$. The slurry is stirred at 20 °C for 18 h to redissolve the beryllium hydroxide. After filtration, the solution has a pH = 13.2. It is concentrated in a vacuum to a volume of about 5 mL and carefully layered with 18 mL of acetone. After 3 weeks, a crop of colorless crystals of $Na_2[Be_4(OH)_{10}](H_2O)_5$ is obtained (0.19 g, 22.2% yield). Anal. Calcd for $Be_4\,H_{20}Na_2O_{15}$ (342.18): H, 5.89. Found: H, 5.83. ^{9}Be NMR (D_2O, 20 °C, pH 13.2; JEOL GX 400, 56.4 MHz): $\delta = 2.0$ ppm rel. to $[Be(H_2O)_4]^{2+}$.

(18) *Crystallography*: 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 $Be_4H_{20}Na_2O_{15}$: $M_r = 342.18$, colorless crystals, triclinic, $a = 7.541(1)$ Å, $b = 8.592(1)$ Å, $c = 11.179(1)$ Å, $\alpha = 109.74(1)°$, $\beta = 96.27(1)°$, $\gamma = 104.13(1)°$, space group $P\bar{1}$, $Z = 2$, $V = 646.38(13)$ Å^3, $\rho_{calcd} = 1.758$ g cm^{-3}, $F(000) = 356$; $T = -91$ °C. Data were corrected for Lorentz and polarization effects, but not for absorption [λ(Mo Kα) = 2.31 cm^{-1}]: 2522 measured reflections [$(\sin\theta/\lambda)_{max} = 0.62$ Å^{-1}]; 270 refined parameters, wR2 = 0.0623, $R = 0.0238$ for 2389 reflections with $I \geq 2\sigma(I)$ [0.0693 and 0.0321 for all data, respectively]. Residual electron densities: +0.203/−0.241. The function minimized was $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0363$, $b = 0.23$. All non- H atoms were refined with anisotropic displacement parameters. All H atoms were located and refined with isotropic displacement parameters.

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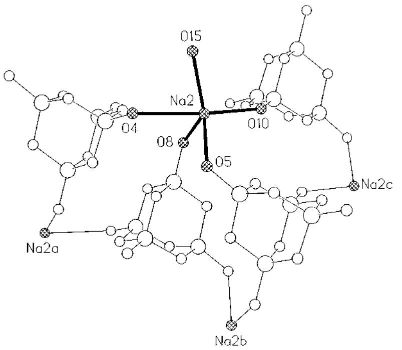

Figure 2. Coordination sphere of the first set of sodium atoms (Na2) in the layer structure of $Na_2[Be_4(OH)_{10}]\cdot 5H_2O$.

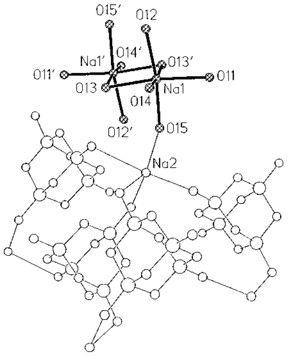

Figure 3. Environment of the second set of sodium atoms (Na1) between the layers of the structure of $Na_2[Be_4(OH)_{10}]\cdot 5H_2O$.

the four terminal (Be) hydroxyl groups. The sodium atoms Na2 are surrounded by hydroxyl groups of four different beryllate cages as part of a distorted trigonal bipyramidal coordination sphere, the fifth position of which is taken up by one of the five water molecules (O15, Figure 2).

To add to the extreme complexity of the new phase, these water molecules (O15) are linked to another set of sodium atoms (Na1, Figure 3), which appear in pairs and are coordinated by the remainder of the water molecules in edge-sharing octahedra. Through bifurcated hydrogen bonds, these double octahedra are linked into chains which lie parallel between the sodium beryllate layers containing the other type of sodium cations (Na2, above). As an integral feature of the structure, there is a network of hydrogen bonds which extends throughout the lattice and connects the two types of layers and the components of each layer. An essential element of this connectivity is the water molecules at Na1, which form bridges between the beryllate cages in neighboring layers (e.g., O12, Figure 4).

Unfortunately enough, the new beryllate species, for all its structural simplicity (Figure 1), is thus intercalated into an exceedingly complicated lattice.

The adamantane-type structure of the hydroxyberyllate component comes as a surprise not only because it had never been formulated[4] but also because the chemistry of the most closely related element zinc so far is devoid of such a building block.[19,20]

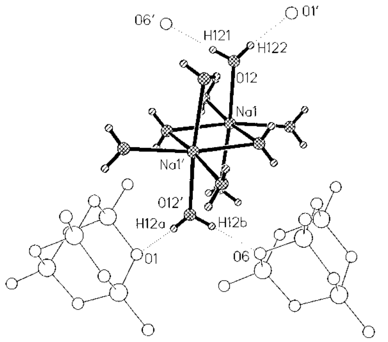

Figure 4. Exemplified hydrogen bonding in $Na_2[Be_4(OH)_{10}]\cdot 5H_2O$.

Table 1. Average Bond Lengths (in angstroms) and Bond Angles (in degrees) in $[Be_4(OH)_{10}]^{2-}$

variable	count	MP2 S_4	DFT S_4	DFT C_1	exptl
bridging O−Be bond	12	1.677	1.671	1.672	1.652
terminal O−Be bond	4	1.596	1.585	1.586	1.604
bridging O−H bond	6	0.962	0.962	0.963	0.777
terminal O−H bond	4	0.964	0.965	0.965	0.770
angle O−Be−O (terminal)	12	113.6	113.6	113.2	112.6
angle O−Be−O (internal)	12	105.0	105.0	105.5	106.2
angle Be−O−Be	6	117.8	117.8	116.8	115.6
angle Be−O−H (terminal)	4	101.9	103.4	103.6	111.7
angle Be−O−H (bridging)	12	108.5	109.2	107.2	111.6

The experimental results could be confirmed by theoretical calculations (Gaussian 94,[21] 6-31G** basis set) at both the MP2 and DFT levels.[22] S_4 symmetry was assumed for both $[Be(OH)_4]^{2-}$ and the adamantane cage as isolated species corresponding to the gas phase at MP2 level. At the DFT level, the adamantane symmetry could be lowered to C_1 and the vibrational frequencies were calculated to get an estimate of zero-point vibrations and the entropy associated with the internal vibrations of the molecules at 298 K. In a separate set of calculations, solvent effects were estimated by using the SCI−PCM[23] model which treats the solvent as a dielectric continuum with a realistic shape of the solute cavity. Any effects of specific solvation, such as H bonding, are ignored.

The calculated bond lengths and angles compare favorably with the experimental ones, except for the O−H bond lengths and Be−O−H angles, where the theoretical data are expected to be more accurate than the experimental ones (Table 1).

The energetics were estimated by calculating the change of enthalpy for the following reaction:

$$4[Be(OH)_4]^{2-} \rightarrow [Be_4(OH)_{10}]^{2-} + 6OH^-$$

The calculated ΔH values are −89 kcal/mol at the MP2 level, and −86 kcal/mol at the DFT level, thus indicating a higher stability of the proposed structure in the gas phase. Inclusion of zero-point vibrations and vibrational entropy will add an additional −24 kcal/mol (DFT), producing an overall ΔG for the reaction of −110 kcal/mol at 298 K. When solvent effects are taken into account, the ΔH becomes positive (+98 kcal/mol), but adding the vibrational and entropy terms brings the overall ΔG back to the negative side, yielding −12 kcal/mol as the solution-phase ΔG.

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Supporting Information Available: Tables listing crystal and structure refinement data, isotropic and anisotropic displacement parameters, bond lengths and angles, and a cell plot diagram for SMI4 (5 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[22] DFT: density functional theory (the B3LYP functional as implemented in Gaussian 94 was used). MP2: Møller−Plesset 2nd-order perturbation theory.

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