**Ligand Redistribution Equilibria in Aqueous Fluoroberyllate Solutions**

Michael Schmidt, Hubert Schmidbaur

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Z. Naturforsch. 53 b, 1294–1300 (1998); received July 17, 1998

Fluoroberyllates, Beryllium Fluoride, Ligand Redistribution, NMR Data

The composition of aqueous fluoroberyllate solutions has been studied by \(^{9}\)Be and \(^{19}\)F NMR spectroscopy for various ratios of the beryllium and fluorine concentrations, and at different pH values. The equilibrium constants have been determined for the ligand exchange processes, which involve the species \([\text{Be(OH)}_2\text{OH}]^{2+}\), \([\text{BeF(OH)}_2\text{OH}]^{2+}\), \([\text{BeF}_2\text{(OH)}_2\text{OH}]^{2-}\), \([\text{BeF}_3\text{(OH)}_3\text{OH}]^{3-}\), and \([\text{BeF}_4\text{(OH)}_4\text{OH}]^{4-}\). These equilibria are shifted towards \([\text{BeF}_4\text{(OH)}_4\text{OH}]^{4-}\) at high pH. No polynuclear fluoroberyllates have been detected. The fluoride exchange between the individual species is slow on the NMR time scale at room temperature, and separate sharp signals with the expected multiplicity are therefore recorded. Calculated \(^{9}\)Be chemical shifts are in good agreement with experimental data.

**Introduction**

Beryllium fluoride \(\text{BeF}_2\) is known to dissolve readily in water. The solutions are assumed to contain largely the neutral, undissociated dihydrate \(\text{BeF}_2\text{(OH)}_2\) which is involved in strong hydrogen bonding with the aqueous environment \([1]\). Results of more recent electrochemical studies have shown, however, that there is significant ligand redistribution of the fluoride and water ligands to give ionic species \([2-5]\). These conclusions were supported in a \(^{19}\)F NMR study, which showed the presence of three major components, \([\text{F}_2\text{Be(OH)}_2\text{OH}]^{\text{2+}}\), \([\text{F}_2\text{Be(OH)}_2\text{OH}]^{\text{2+}}\), and \([\text{FBe(OH)}_2\text{OH}]^{\text{3+}}\), after equilibration in pure water at room temperature \([6-10]\). Three separate resonances with a well resolved \(^{19}\)F-\(^{9}\)Be coupling pattern were observed under these conditions indicating that there is only very slow ligand exchange between these components (on the NMR time scale). Some minor resonances in the spectra could not be identified unequivocally, and assignments to multinuclear species remained at best tentative.

In recent studies in our own laboratory on beryllium hydroxide and hydroxyberyllates we have discovered several novel poly(hydroxy)polyberyllate anions, the existence of which had not been considered in all previous investigations \([11,12]\). Most surprisingly it was found that tetra(hydroxy)beryllate dianions, \([\text{Be(OH)}_4]^{2-}\), undergo spontaneous condensation even in strongly basic solutions to give hydrated hydroxide anions \([\text{HO-H-OH}]^-\) and multinuclear hydroxyberyllates, like \([\text{Be}_2\text{(OH)}_7]^{13-}\) and \([\text{Be}_4\text{(OH)}_{10}]^{25-}\).

The close relationship between hydroxy- and fluoro-beryllates prompted us to resume NMR spectroscopic studies on fluoroberyllates in order to draw a more quantitative picture of the ligand exchange equilibria in aqueous solutions. Together with \(^{19}\)F NMR spectra, \(^{9}\)Be NMR spectra were expected to contribute significantly to a better understanding of the nature of the species in solution. The investigations were to be extended to mixtures with \(\text{Be}:\text{F}\) ratios other than 1:2, and to pH values other than neutral, in order to follow the equilibria into realms of different stoichiometry.

**Results**

*Aqueous beryllium fluoride solutions*

Aqueous solutions of \(\text{BeF}_2\) (pH 4.5) at 20°C and at low concentrations (Experimental Part) show \(^{9}\)Be and \(^{19}\)F NMR spectra as presented in Fig. 1a, b. The three quartet (1:1:1:1) resonances in Fig. 1b are readily assigned to three components of an equilibrium represented by eq. (1). This spectrum is in agreement with previous reports and assignments \([6]\). The chemical shifts show a systematic
Table I. Chemical shifts and coupling constants of the beryllium fluoride species.

<table>
<thead>
<tr>
<th>Species</th>
<th>δ (ppm)</th>
<th>$^{19}$F–Be [Hz]</th>
<th>δ (ppm)</th>
<th>δ_{theo} (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{BeF}_3]^{2-}$</td>
<td>-87.71</td>
<td>-87.41</td>
<td>33.6</td>
<td>-0.34</td>
</tr>
<tr>
<td>$[\text{BeF}_3(\text{H}_2\text{O})]^{-}$</td>
<td>-90.22</td>
<td>-88.81</td>
<td>36.3</td>
<td>-0.13</td>
</tr>
<tr>
<td>$\text{BeF}_2(\text{H}_2\text{O})_2^{-}$</td>
<td>-92.65</td>
<td>-91.11</td>
<td>39.3</td>
<td>0.17</td>
</tr>
<tr>
<td>$[\text{BeF}(\text{H}_2\text{O})_3]^+$</td>
<td>-95.55</td>
<td>-93.98</td>
<td>41.2</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Fig. 1. $^9$Be NMR spectrum (a) and $^{19}$F NMR spectrum (b) of an aqueous solution of BeF$_2$ (0.25 mole/l).

decrease with the growing number of fluorine substituents at the beryllium atom (Table I).

$2\text{BeF}_2(\text{H}_2\text{O})_2 \rightleftharpoons [\text{BeF}(\text{H}_2\text{O})_3]^+ + [\text{BeF}_3(\text{H}_2\text{O})]^-$ \hspace{1cm} (1)

The $^9$Be NMR spectrum (Fig. 1a) has four lines of almost equal separations, but very different intensities. As elucidated in the following experiments with other stoichiometries, this spectrum is explained as a superposition of a 1:1 doublet, a 1:2:1 triplet and a 1:3:3:1 quartet signal (Figure 1a), assigned to the three species already identified in the $^{19}$F NMR spectrum (eq. (1)).

The two spectra are therefore providing consistent information regarding the nature of aqueous BeF$_2$ solutions. From the relative intensities of the fluorine and beryllium signals an equilibrium constant and a reaction enthalpy for eq. (1) can be calculated. The data obtained are included in Tables II and III below.
Table II. Calculated and published equilibrium constants $K_1$, $K_2$, $K_3$, and $K_4$.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1$</td>
<td>$(1.25 \pm 0.24) \times 10^{-1}$</td>
<td>$(8.0 \pm 2) \times 10^{-2}$</td>
<td>$(0.37 \pm 0.02) \times 10^{-1}$</td>
</tr>
<tr>
<td>$K_2$</td>
<td>$(4.38 \pm 0.95) \times 10^{-4}$</td>
<td>$(1.1 \pm 0.5) \times 10^{-2}$</td>
<td>$(1.63 \pm 0.06) \times 10^{-4}$</td>
</tr>
<tr>
<td>$K_3$</td>
<td>$(2.29 \pm 0.57) \times 10^{-4}$</td>
<td>$(2.2 \pm 2) \times 10^{-3}$</td>
<td>$(1.73 \pm 0.06) \times 10^{-4}$</td>
</tr>
<tr>
<td>$K_4$</td>
<td>$(2.31 \pm 0.73) \times 10^{-5}$</td>
<td>$(1 \pm 1) \times 10^{-3}$</td>
<td>$(1.26 \pm 0.02) \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Table III. Equilibrium constants $K_A$, $K_B$, $K_C$ and free enthalpies $\Delta G^\circ$.

<table>
<thead>
<tr>
<th>$[F]/[Be]$</th>
<th>$K_A$</th>
<th>$K_B$</th>
<th>$K_C$</th>
<th>$\Delta G^\circ$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.00</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3.00</td>
<td>0.037</td>
<td>—</td>
<td>—</td>
<td>8.17</td>
</tr>
<tr>
<td>2.50</td>
<td>0.033</td>
<td>—</td>
<td>—</td>
<td>8.45</td>
</tr>
<tr>
<td>2.00</td>
<td>—</td>
<td>0.041</td>
<td>—</td>
<td>7.91</td>
</tr>
<tr>
<td>1.33</td>
<td>—</td>
<td>0.061</td>
<td>—</td>
<td>6.93</td>
</tr>
<tr>
<td>1.00</td>
<td>—</td>
<td>0.055</td>
<td>—</td>
<td>7.19</td>
</tr>
<tr>
<td>0.67</td>
<td>—</td>
<td>—</td>
<td>0.128</td>
<td>5.09</td>
</tr>
</tbody>
</table>

With increasing pH (generated by addition of KOH to the solution) the signals for all three species decrease in intensity and a resonance of a new species grows, which is readily identified as $[\text{BeF}_4^{2-}]$ by the quintet multiplicity (1:4:6:4:1) of the $^9\text{Be}$ signal (Fig. 2a) and the 1:1:1:1 quartet $^{19}\text{F}$ resonance (Fig. 2b). These results show that with an increase of the hydroxide ion concentration a redistribution of the fluoride, hydroxide and water ligands is induced which leads to $[\text{BeF}_4^{2-}]$ as the only fluoroberyllate species. This process is accompanied by the precipitation of $\text{Be(OH)}_2$ [Scheme 1].

Aqueous fluoroberyllate solutions

Solutions with $\text{Be}/\text{F}$ ratios other than 1:2 were prepared by treating aqueous solutions of $\text{BeF}_2$ with various amounts of $\text{NaF}$ or $\text{BeSO}_4$. The $^{19}\text{F}$ and $^9\text{Be}$ NMR spectra are shown in Figures 3a, b. It is obvious that addition of $\text{F}^-$ leads to the appearance and gradual increase of the concentration of tetrafluoroberyllate dianion on the expense of mono-, di- and trifluoroberyllate species originally present exclusively in aqueous $\text{BeF}_2$ solutions (Fig. 1a, b). Equations (2) - (8) in Scheme 1 can be used to describe the relation between the individual components.

The chemical shift data and coupling constants for the four $\text{Be}/\text{F}$ complexes are summarized in Table I. A small range is given for each $\delta$ value to indicate the spread of the data due to concentration and counterion effects. Whereas the experimental $^9\text{Be}$ NMR data could be confirmed by theoretical calculations (Turbomole [13]) the experimental $^{19}\text{F}$
clusively, and no septet multiplicity as expected for $^{19}$F bridging two $^9$Be nuclei could be detected. Conversely, the $^9$Be resonances showed no conspicuous smaller splitting likely to occur for bridging $^{19}$F.

Therefore, contrary to the chemistry of hydroxyberyllates, the fluoroberyllates show no condensation with elimination of fluoride anions to give Be-F-Be bridging in aqueous solution over a large pH range (Scheme 1).

**Experimental**

*General:* Beryllium and its compounds are generally to be considered as highly toxic. Therefore all necessary precautions should be taken against any contamination of the environment. The reactions were carried out in pure, fully desalinated water. BeF$_2$ was commercially available and of p. a. grade. Standard equipment and instrumentation was used throughout. Jeol LA400; $^9$Be NMR: external standard $\text{[Be(H_2O)_4]}^{2+}$ ($\delta = 0.0$ ppm); $^{19}$F NMR: external standard TFA ($\delta = 0$ ppm).

The aqueous solution of BeF$_2$ (0.25 mole/l) was treated with NaF or BeSO$_4$$\cdot$4H$_2$O to obtain different $[\text{F}^-]/[\text{Be}^{2+}]$ ratios. pH values between 1.5 and 13.6 were adjusted by addition of KOH or a 50% aqueous solution of HF. Normalized integrals of the $^{19}$F NMR signals are shown in Fig. 3a.
Fig. 3a. $^{19}$F NMR spectra of aqueous solutions of BeF$_2$ (0.25 mole/l) with different $[\text{F}^-]/[\text{Be}^{2+}]$ ratios.

Table IV. Normalized integrals of the $^{19}$F NMR signals shown in Fig. 3a.

<table>
<thead>
<tr>
<th>$[\text{F}^-]/[\text{Be}]$</th>
<th>$I_1$</th>
<th>$I_3$</th>
<th>$I_2$</th>
<th>$I_1$</th>
<th>$I_4/I_3$</th>
<th>$I_3/I_2$</th>
<th>$I_2/I_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.00</td>
<td>0.422</td>
<td>0.422</td>
<td>1.000</td>
<td>0.100</td>
<td>4.586</td>
<td>1.642</td>
<td>0.018</td>
</tr>
<tr>
<td>3.00</td>
<td>0.391</td>
<td>2.293</td>
<td>0.500</td>
<td>0.171</td>
<td>3.177</td>
<td>1.102</td>
<td>0.189</td>
</tr>
<tr>
<td>2.50</td>
<td>0.045</td>
<td>0.821</td>
<td>0.500</td>
<td>0.055</td>
<td>1.642</td>
<td>0.055</td>
<td>0.045</td>
</tr>
<tr>
<td>2.00</td>
<td>1.080</td>
<td>5.154</td>
<td>1.000</td>
<td>0.210</td>
<td>5.154</td>
<td>0.210</td>
<td>0.043</td>
</tr>
<tr>
<td>1.33</td>
<td>0.333</td>
<td>7.817</td>
<td>11.032</td>
<td>0.043</td>
<td>0.709</td>
<td>0.043</td>
<td>0.043</td>
</tr>
<tr>
<td>1.00</td>
<td>0.333</td>
<td>18.390</td>
<td>56.223</td>
<td>0.018</td>
<td>0.327</td>
<td>0.018</td>
<td>0.018</td>
</tr>
<tr>
<td>0.67</td>
<td>0.500</td>
<td>3.177</td>
<td></td>
<td>0.157</td>
<td></td>
<td></td>
<td>0.157</td>
</tr>
</tbody>
</table>

**Calculation of Equilibrium Constants**

*Calculation of $K_A$ and $K_B$*

$K_A$ and $K_B$ can be obtained from the normalized integrals (Table IV) of the $^{19}$F NMR signals shown in Fig. 3a.

*Calculation of $K_C$*

$$K_C = \frac{K_4}{K_3} = \frac{[\text{BeF}_2][\text{Be}^{2+}]}{[\text{BeF}^+]^2}$$

For the determination of $K_C$, $[\text{Be}^{2+}]$ has to be calculated:
Fig. 3b. $^9$Be NMR spectra of aqueous solutions of BeF$_2$ (0.25 mole/l) with different $[F^-]/[Be^{2+}]$ ratios.

$c$(BeF$_2$) = $[BeF_2]$
$c$(BeF$^+$) = $[BeF^+]$
$c$(Be$^{2+}$) = $[Be^{2+}]$

$c_0$(BeF$_2$) and $c_0$(Be$^{2+}$) are representing the initial concentrations ($t = 0$).

I. Balance of beryllium:

$c_0$(Be$^{2+}$) = $c$(BeF$_2$) + $c$(BeF$^+$) + $c$(Be$^{2+}$)
$c_0$(Be$^{2+}$) = $c_0$(BeF$_2$) + $c_0$(BeSO$_4$)

II. Balance of fluorine:

$c_0$(F$^-$) = 2$c$(BeF$_2$) + $c$(BeF$^+$) + $c$(F$^-$)
$c_0$(F$^-$) = 2$c_0$(BeF$_2$)

For $c$(F$^-$) = 0:

$c_0$(F$^-$) = 2$c$(BeF$_2$) + $c$(BeF$^+$)
\[c$(BeF$^+$) = $\frac{c_0$(F$^-$)}{2c$(BeF_2)$ + 1} = $\frac{c_0$(F$^-$)}{2S + 1} \text{ with } S = \frac{c$(BeF$_2$)}{c$(BeF^+)$}
\[c$(BeF$_2$) = $\frac{c_0$(F$^-$)}{2 + \frac{c$(BeF^+)$}{c$(BeF_2)$}} = $\frac{c_0$(F$^-$)}{2 + \frac{1}{S}} \text{ with } S = \frac{c$(BeF$_2$)}{c$(BeF^+)$}
\[c$(Be^{2+}) = c_0$(Be$^{2+}$) - $c$(BeF$_2$) - $c$(BeF$^+$)
Calculation of $K_1$

$$K_1 = \frac{[\text{BeF}_3^-][\text{F}^-]}{[\text{BeF}_4^{2-}]} = \frac{[\text{BeF}_3^-]^2}{[\text{BeF}_4^{2-}]}$$

Balance of fluorine:

$$4c_0(\text{BeF}_4^{2-}) = 4c(\text{BeF}_4^{2-}) + 3c(\text{BeF}_3^-) + c(\text{F}^-)$$

$$c(\text{BeF}_3^-) = c(\text{F}^-)$$

$$c_0(\text{BeF}_4^{2-}) = c(\text{BeF}_4^{2-}) + c(\text{BeF}_3^-)$$

$$c(\text{BeF}_4^{2-}) = \frac{c_0(\text{BeF}_4^{2-})}{1 + \frac{c(\text{BeF}_4^{2-})}{c(\text{BeF}_3^-)}} = \frac{c_0(\text{BeF}_4^{2-})}{1 + \frac{1}{R}}$$

with $R = \frac{c(\text{BeF}_4^{2-})}{c(\text{BeF}_3^-)}$

$$c(\text{BeF}_3^-) = \frac{c_0(\text{BeF}_4^{2-})}{c(\text{BeF}_4^{2-}) + 1} = \frac{c_0(\text{BeF}_4^{2-})}{R + 1}$$

with $R = \frac{c(\text{BeF}_4^{2-})}{c(\text{BeF}_3^-)}$

Calculation of $K_2$, $K_3$ and $K_4$

Due to the relationship between $K_1$ and $K_A$, $K_B$ or $K_C$ the equilibrium constants $K_2$, $K_3$ and $K_4$ can be calculated:

$$K_A = \frac{K_2}{K_1} \Rightarrow K_2 = K_A K_1$$

$$K_B = \frac{K_3}{K_2} \Rightarrow K_3 = K_B K_2$$

$$K_C = \frac{K_4}{K_3} \Rightarrow K_4 = K_C K_3$$

Free enthalpy calculations: $\Delta G^0 = -RT \ln K$

Acknowledgement

The authors are grateful to Professor P. Pyykkö and Dr. D. Sundholm, University of Helsinki (Finland), for their assistance with the chemical shift calculations, and to DAAD for travel grants.