# Beryllium(II) Hydrolysis in 3.0 mol dm$^{-3}$ Perchlorate*

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The complex-formation equilibria in the system $Be^{II}$–$H_2O$ have been studied at 25 °C by means of e.m.f. methods, using a coulometric titration technique, in 3.0 mol dm$^{-3}$ (Na)ClO$_4$ solutions. The ranges of total beryllium(II) concentration and acidity were $80 \geqslant B \geqslant 1$ mmol dm$^{-3}$ and $2 \leqslant -\log h \leqslant 6.2$, respectively. Over the whole concentration range studied the data could be explained by assuming the equilibria (i)—(v). Previously reported information on beryllium(II) hydrolysis is

$$2Be^{2+} + H_2O \rightleftharpoons [Be_2(OH)]^{3+} + H^+ \qquad \log \beta_{21} = -3.23 \pm 0.05 \qquad (i)$$

$$3Be^{2+} + 3H_2O \rightleftharpoons [Be_3(OH)_3]^{3+} + 3H^+ \qquad \log \beta_{33} = -8.656 \pm 0.002 \qquad (ii)$$

$$5Be^{2+} + 6H_2O \rightleftharpoons [Be_5(OH)_6]^{4+} + 6H^+ \qquad \log \beta_{56} = -18.81 \pm 0.03 \qquad (iii)$$

$$6Be^{2+} + 8H_2O \rightleftharpoons [Be_6(OH)_8]^{4+} + 8H^+ \qquad \log \beta_{68} = -26.70 \pm 0.05 \qquad (iv)$$

$$Be^{2+} + 2H_2O \rightleftharpoons Be(OH)_2 + 2H^+ \qquad \log \beta_{12} = -11.09 \pm 0.04 \qquad (v)$$

reviewed and an attempt is made to correlate the data in different ionic media by using the Brønsted–Guggenheim–Scatchard specific ion interaction theory. The values of the equilibrium constants at infinite dilution derived from this approach are $\log \beta^0_{21} = -3.47 \pm 0.05$, $\log \beta^0_{33} = -8.86 \pm 0.05$, $\log \beta^0_{56} = -19.5 \pm 0.1$, and $\log \beta^0_{68} = -26.3 \pm 0.1$. Tentative structures for the polynuclear hydroxo complexes are proposed and discussed. The solubility product of α-Be(OH)$_2$(s) has been re-evaluated by using literature data and the hydrolysis constants of this study, at $I = 0$, $\log K_{s0} = -6.87 \pm 0.05$.

Several authors[1–10] have made quantitative studies of beryllium(II) hydrolysis. Kakihana and Sillen[1] carried out the first extensive study in 3.0 mol dm$^{-3}$ NaClO$_4$ at 25 °C. They established $[Be_3(OH)_3]^{3+}$ as the predominant species in the experimental range covered. The complete chemical model included $[Be_2(OH)]^{3+}$ and Be(OH)$_2$ as minor complexes. Many efforts have been made to add more chemical information to this pioneering work. The quantitative studies at 25 °C are summarized in Table 1. Carell and Olin[2] proved the validity of the Kakihana and Sillen model at high metal concentrations. Kakihana and Maeda,[8] Othaki and Kato[9] and Othaki[10] investigated solvent effects. Studies in 3.0 mol dm$^{-3}$ NaClO$_4$ solutions in deuterium oxide [9,10] showed the expected decrease in stability constants of the hydrolysis complexes. Partial substitution of water by dioxane does not introduce changes in the proposed speciation at dioxane mole fractions less than 0.1. At a mole fraction of 0.2 the complex $[Be_2(OH)_2]^{2+}$ was proposed[10] in addition to the previously established species. Changes in strength and composition of the ionic media do not introduce any modification in the (2, 1), (3, 3) model and equilibrium constants for these complexes have been reported in 0.5 mol dm$^{-3}$ NaClO$_4$,[4] 1 mol kg$^{-1}$ NaCl,[3] 3 mol kg$^{-1}$ KCl,[5] 0.1 and 2.0 mol dm$^{-3}$ KNO$_3$.[6,7]

The attempts to explain the results at higher $Z$ (average number of OH bound per Be) have been far more controversial. Mesmer and Baes[3] studied beryllium(II) hydrolysis in 1 mol kg$^{-1}$ NaCl over a large range of temperature (0, 25, 60 °C). They explained the experimental data by assuming the formation of $[Be_5(OH)_7]^{3+}$ in addition to the previously proposed species. In their later review[11] they proposed $[Be_6(OH)_8]^{4+}$ instead of $[Be_5(OH)_7]^{3+}$. The reason was a later study by Lanza and Carpeni[6] in which the (6, 8) complex was proposed at the highest degrees of hydrolysis. These authors introduced additional species, $[Be_3(OH)_4]^{2+}$, $[Be_6(OH)_8]^{4+}$, $[Be_6(OH)_9]^{3+}$, and the formation of higher polynuclear complexes prior to precipitation. Most of these have not been confirmed by other investigators. Brown *et al.*[7] explained the data obtained at low metal concentrations by incorporating the mononuclear Be(OH)$_2$ into the basic model. However, Baes and Mesmer[11] expressed doubt as to the formation of this species prior to the hydroxide precipitation.

The aims of the present study are: (*a*) to refine the experimental method and thus to obtain more precise experimental information which may be used to deduce a unique chemical model for the $Be^{2+}$–$H_2O$ system in the acidity range prior to Be(OH)$_2$(s) precipitation; (*b*) to interrelate the experimental data by a quantitative description of the medium effects by using the specific ion interaction (s.i.t.) method; and (*c*) to discuss the structural implications of the chemical model. This work is described in subsequent papers[12] where the results of some n.m.r. and Raman investigations are presented.

## Experimental

*Chemicals and Analysis.*—Beryllium(II) perchlorate solutions were prepared from Be metal of 99.999% purity. Surface-cleaned foils were dissolved by heating in a mixture of 1 mol dm$^{-3}$ HClO$_4$ and concentrated hydroiodic acid. The excess of HI was removed by adding HIO$_3$ and evaporating the I$_2$ produced. Final traces of HIO$_3$ were eliminated by coulometric reduction.

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* *Supplementary data available* (No. SUP 56683, 5 pp.): primary titration data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

No $Cl^-$, $I^-$, $IO_3^-$, $I_2$, or iron(III) contamination was detected in the final solution.

Beryllium was analyzed gravimetrically as BeO or $Be_2P_2O_7$. The results of the two methods agreed within 0.3%.

Stock solutions of $NaClO_4$ and $AgClO_4$ were prepared and analyzed as described elsewhere.[13]

*Method*.—The beryllium(II) hydrolysis equilibria were studied in a 3.0 mol dm$^{-3}$ (Na)$ClO_4$ medium. The total metal concentration ranged from 1 to 80 mmol dm$^{-3}$.

The measurements were performed as e.m.f. titrations. The acidity of the test solutions was either increased or decreased coulometrically. This technique was chosen in order to avoid local precipitation caused by the use of a strong alkaline reagent like NaOH, or the formation of beryllium(II) carbonate complexes[12] when using $NaHCO_3$ as the titrating reagent. Much care was taken to use low current densities in the experimental range where local precipitation was expected. Current densities of less than $10^{-5}$ A cm$^{-2}$ were used for the titration with total concentration of $Be^{II}$, $B = 1$ mmol dm$^{-3}$, and at $Z > 0.5$. The titration results made in two opposite senses (increasing and decreasing $[H^+]$) were the same within the (very small) experimental error. This was an indication that true equilibrium had been attained and that no local precipitation occurred in the test solutions.

The titrations were made in an oil-bath thermostatted at 25.00 ± 0.01 °C. The experiments were controlled by a microcomputer monitoring system developed at this Department.[14] Equilibrium was assumed to be established when the e.m.f. was found to be constant within 0.01 mV during 15 min. This normally took 15—30 min. The slow equilibria reported by several authors[1,3,10] were not observed in the present studies. Longer equilibration times were observed in the $[H^+]$ ranges at which hydrolysis begins. The previously proposed slow kinetics

**Table 1.** Survey of investigations of beryllium(II) hydrolysis at 25 °C

| | log $\beta_{pq}$[a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Medium | (1, 2) | (2, 1) | (3, 3) | (3, 4) | (5, 6) | (5, 7) | (6, 8) | (6, 9) | Ref. |
| 0.5 mol dm$^{-3}$ $NaClO_4$ | | −3.20 | −8.81 | | | | | | 4 |
| 3.0 mol dm$^{-3}$ $NaClO_4$ | −10.9 | −3.24 | −8.66 | | | | | | 1 |
| | −11.16 | −3.16 | −8.66 | | | | | | 8 |
| | −11.07 | −3.23 | −8.66 | | −18.84 | | −26.69 | | This work |
| 3.0 mol dm$^{-3}$ $ClO_4^-$ 'self medium' | | −3.22 | −8.66 | | | | | | 2 |
| 1 mol kg$^{-1}$ NaCl | | −3.42 | −8.907 | | | −25.33[b] | −27.46 | | 3, 11 |
| 3 mol kg$^{-1}$ KCl | | −3.18 | −8.91 | | | | | | 6 |
| 0.1 mol dm$^{-3}$ $KNO_3$ | −11.32 | −2.96 | −8.81 | | | | | | 7 |
| 2 mol dm$^{-3}$ $KNO_3$ | | −3.28 | −8.90 | −16.00 | | | −27.50 | −34.50 | 6 |

[a] For the equilibrium $p\text{Be}^{2+} + q\text{H}_2\text{O} \rightleftharpoons [\text{Be}_p(\text{OH})_q]^{(2p-q)+} + q\text{H}^+$. [b] The species (5, 7) was initially proposed, and later changed to (6, 8).

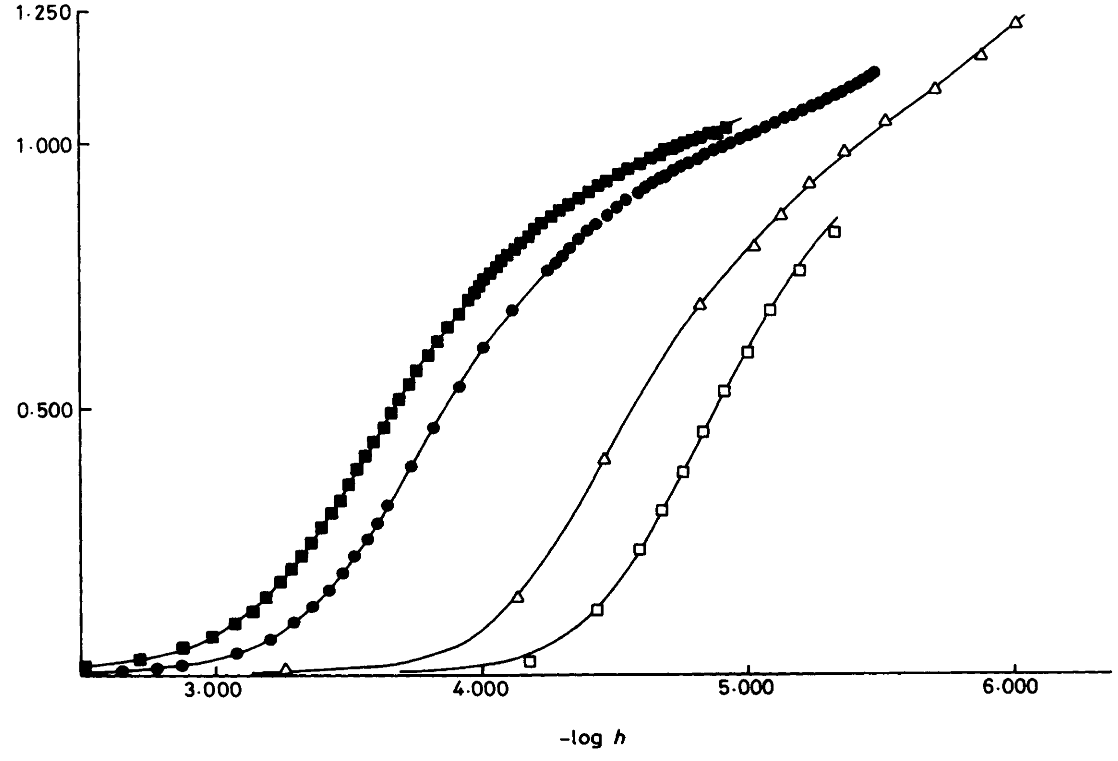

**Figure 1.** Plot of the experimental data in the form $Z$ *vs.* $-\log h$. $B$ = 80 (■), 40 (●), 3.5 (△), and 1 mmol dm$^{-3}$ (□). The theoretical curves were calculated assuming the final speciation scheme proposed in this work

at $Z > 0.5$ is probably caused by local precipitation. A preamplifier (Analog device 309 K) and a Fluke 8810 digital voltmeter were used to read the potentials. The glass electrodes used were of the type Metrohm EA 109. The constant-current circuit was provided by an Electronic Measurements C633B power supply. The reader is referred to ref. 15 for more detailed information about the experimental methodology.

The primary experimental data in the form of e.m.f. values and hydrogen ion concentrations are available as SUP 56683.

## Calculations and Results

The set of experimental data plotted in the form $Z$ *vs.* $\log h$ where $h$ is the hydrogen-ion concentration is shown in Figure 1. The data were treated in the following way. First the predominant ($p$, $q$) values and the corresponding stability constants were established by graphical methods. This model then was checked and refined by treating the whole set of data by a least-squares computer procedure.

*Graphical Treatment.*—The graphical intepretation was made by using a version of the MLAB on-line modelling computer program.[16] This program involves a matrix algebra system, and contains a graphics capability which in the present adaptation permitted the comparison of experimental and model curves in a rapid and straightforward manner. The computer-assisted graphics procedure provides an easy way of systematic hypothesis testing and combines the advantages of graphical and computer treatments.

*Evaluation of the predominant* (p, q) *values.* The set of curves of $Z$ *vs.* $-\log h$ (Figure 1) were approximately parallel for $0.2 < Z < 0.7$. The spacing along the $\log h$ axis at fixed $Z$ was constant [equation (1)]. The value of $t$ decreases for $Z < 0.2$

$$t = (\Delta \log B/\Delta \log h)_Z = 1.5 \pm 0.03 \qquad (1)$$

and increases for $Z > 0.75$. These changes were more pronounced the larger the $B$ value. There is good agreement between my experimental data and those obtained by previous authors[1,2] for $Z < 0.7$. At higher $Z$ values the discrepancies between different studies are large and reliable data at such values can be obtained only by coulometry.

A preliminary plot of the experimental data in the form $Z$ *vs.* ($\log B - 1.5 \log h$) shows that the data in the range $0.25 < Z < 0.85$ can be fitted to a single curve within the experimental error, the deviations being larger the lower the $B$ values. This indicates the predominance of polynuclear complexes of the general type $\mathrm{Be[(OH)_{1.5}Be]}_n$ in this $Z$ range.

The initial treatment of the experimental data was simplified by treating the data in the ranges $0 < Z < 0.8$ and $0.8 < Z < 1.2$ separately.

The model with $[\mathrm{Be_2(OH)}]^{3+}$ and $[\mathrm{Be_3(OH)_3}]^{3+}$ as predominant species was tested by comparing the experimental curves $y(x)_z$ ($y = \log B - \log h$, $x = \log B - 1.5 \log h$) with normalized[17] $Y(X)_Z$ functions. The agreement between experimental and the model functions was unsatisfactory.

As a consequence I tried to include an additional complex to explain the data at $Z < 0.8$. The preliminary graphical study indicated the existence of more than one $\mathrm{Be[(OH)_{1.5}Be]}_n$ 'core + links'[18] type of complex. The next term was selected to have $n = 2$. Hence, the next hypothesis to be tested was a model which included $[\mathrm{Be_5(OH)_6}]^{4+}$ in addition to the previously proposed complexes. In this case equations (2) and (3) are

$$B = b(1 + 2\beta_{21}bh^{-1} + 3\beta_{33}b^2h^{-3} + 5\beta_{56}b^4h^{-6}) \qquad (2)$$

$$Z = (\beta_{21}bh^{-1} + 3\beta_{33}b^2h^{-3} + 6\beta_{56}b^4h^{-6})/(1 + 2\beta_{21}bh^{-1} + 3\beta_{33}b^2h^{-3} + 5\beta_{56}b^4h^{-6}) \qquad (3)$$

applicable and the normalized functions are (4)—(6) where the normalized variables are given in equations (7)—(9) and $b =$

$$X = 0.5 \log v + \log(1 + 2u + 3Lv + 5v^2) \qquad (4)$$

$$Y = \log u + \log(1 + 2u + 3Lv + 5v^2) \qquad (5)$$

$$Z = (u + 3Lv + 6v^2)/(1 + 2u + 3Lv + 5v^2) \qquad (6)$$

$$u = \beta_{21}bh^{-1} \qquad (7)$$

$$v^2 = \beta_{56}b^4h^{-6} \qquad (8)$$

$$L^2 = \beta_{33}{}^2/\beta_{56} \qquad (9)$$

concentration of free $\mathrm{Be^{II}}$. A reasonably good fit was obtained between normalized and experimental functions. The calculated values for the stability contstants were: $\log \beta_{21} = -3.21 \pm 0.05$, $\log \beta_{33} = -8.65 \pm 0.03$, and $\log \beta_{56} = -18.85 \pm 0.05$.

The graphical treatment was then extended to $0.8 \leqslant Z \leqslant 1.2$, where the contribution of $[\mathrm{Be_2(OH)}]^{3+}$ can be neglected. In order to explain the data, the formation of an additional complex of general formula $[\mathrm{Be}_p\mathrm{(OH)}_q]^{(2p-q)+}$ had to be added to the model. Normalized functions $Y(X)_Z$ of general forms (10) and (11) were systematically tested with experimental functions

$$X = \log u + \log(1 + 3Lu^2 + 5u^4 + qvp^{-1}) \qquad (10)$$

$$Y = \log v + \log(1 + 3Lu^2 + 5u^4 + qvp^{-1}) \qquad (11)$$

$y(x)_Z$ as in (12) and (13). The best fit was obtained for $p = 6$ and

$$x = \log B - 1.5 \log h \qquad (12)$$

$$y = \log B - [q/(p - 1)] \log h \qquad (13)$$

$q = 8$ indicating the existence of a complex $[\mathrm{Be_6(OH)_8}]^{4+}$. The value for the stability constant obtained from the fitting parameters was $\log \beta_{68} = -26.7 \pm 0.1$.

*Numerical Data Treatment.*—Once the predominant complexes and their stability constants had been established for the whole range of experimental data studied, the final refinement of the model was performed by a least-squares method. The general least-squares minimizing program LETAGROP[19] in its version ETITR[20] was used for this purpose.

The entire set of experimental data (171 points) was treated simultaneously. Least-squares refinement of several different models was attempted in addition to the one obtained by graphical methods. All complexes previously proposed by other authors were tested but the agreement between the calculated and experimental data was always much poorer than in the present model.

The possible occurrence of mononuclear complexes was considered. Evidence for the presence of $[\mathrm{Be(OH)}]^+$ was obtained only in the titrations at lowest $B$ where at the pH values studied it accounts for, at most, 5% of the total $\mathrm{Be^{II}}$. The concentration is so small that this complex was not included in the final model. On the other hand, inclusion of $\mathrm{Be(OH)_2}$ resulted in a significant improvement of the model as judged from the least-squares refinement. Hence the entire set of data could be explained by the formation of $[\mathrm{Be_2(OH)}]^{3+}$, $[\mathrm{Be_3(OH)_3}]^{3+}$, $[\mathrm{Be_5(OH)_6}]^{4+}$, $[\mathrm{Be_6(OH)_8}]^{4+}$, and $\mathrm{Be(OH)_2}$.

A comparison of the $\log \beta_{pq}$ values obtained by graphical and numerical methods is given in Table 2. The distribution

**Table 2.** Comparison between the results (log $\beta_{pq} \pm 3\sigma$) obtained by computer-assisted graphical means and by the least-squares computer procedure LETAGROP-ETITR[20]

| Species | Graphical treatment | LETAGROP |
|---|---|---|
| $[Be_2(OH)]^{3+}$ | $-3.21 \pm 0.05$ | $-3.23 \pm 0.05$ |
| $[Be_3(OH)_3]^{3+}$ | $-8.65 \pm 0.03$ | $-8.656 \pm 0.002$ |
| $[Be_5(OH)_6]^{4+}$ | $-18.85 \pm 0.05$ | $-18.81 \pm 0.03$ |
| $[Be_6(OH)_8]^{4+}$ | $-26.65 \pm 0.1$ | $-26.70 \pm 0.05$ |
| $Be(OH)_2$ | | $-11.09 \pm 0.04$ |

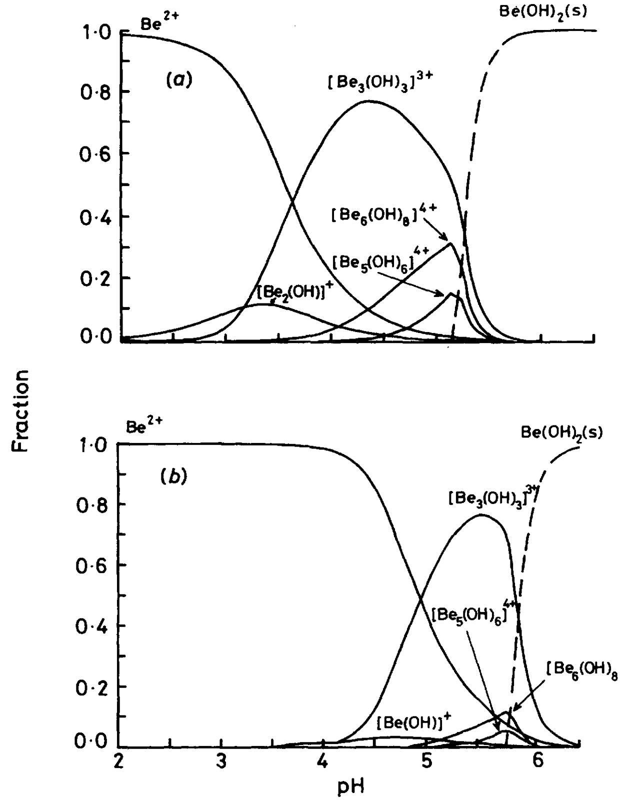

**Figure 2.** Percentage distribution of the various beryllium(II) complexes at $B$ = 0.1 (*a*) and 1 mmol dm$^{-3}$ (*b*) obtained in this work

diagrams in Figure 2 are obtained using the proposed hydrolysis model.

*Evaluation of Medium Effects.*—It has been pointed out in the Introduction that the published information about beryllium(II) hydrolysis covers a wide range of ionic media and ionic strengths. Any attempt to compare the different sets of data must take these medium effects into account. A reasonable approach is to refer the equilibrium constants to a common standard state, *e.g.* infinite dilution, by calculating the activity coefficients of the species involved in the various reactions.

Many semiempirical methods have been proposed for this purpose. The approach first outlined by Brønsted[21] and later developed by Guggenheim[22] and Scatchard[23] has been proven to be satisfactory for ionic media of moderate strength.[24—27] According to the s.i.t. approach the activity coefficient $\gamma_i$ of a single ion $i$ can be defined as in equation (14) where the Debye–Hückel term $D(I)$ is given by equation (15), in aqueous solution at $I$ = 25 °C and at 1 atm (*ca.* $10^5$ Pa) pressure. $\Sigma(i,j)$ is the summation of the specific interaction coefficients which account for the short-term interactions between the ion $i$ and those of opposite charge $j$; $m_k$ is the molality of the medium. The reader is referred to refs. 24—27 for further information on the s.i.t. approach.

**Table 3.** Application of s.i.t. to the $\beta_{21}$ determination in a perchlorate self-medium[2]

| | log $\beta_{21}$ | |
|---|---|---|
| $B$/mol dm$^{-3}$ | exptl. | corrected |
| 0.0397 | $-3.23$ | $-3.23$ |
| 0.0794 | $-3.23$ | $-3.23$ |
| 0.1589 | $-3.21$ | $-3.22$ |
| 0.3178 | $-3.21$ | $-3.23$ |
| 0.64 | $-3.18$ | $-3.22$ |
| 1 | $-3.15$ | $-3.22$ |

$$\log \gamma_i = -Z_i D(I) + \Sigma\varepsilon(i,j)m_k \qquad (14)$$

$$D(I) = 0.5109\sqrt{I}/(1 + 1.5\sqrt{I}) \qquad (15)$$

By using tabulated data on interaction coefficients[26,27] it is possible to establish a correlation between the magnitude of these coefficients for a certain ion and its size and charge. Reasonable guesses can therefore be made about the magnitude of unknown interaction coefficients by comparison with data for ions of similar characteristics. This important feature of the s.i.t. approach will be used to estimate the unknown interaction coefficients in the beryllium system.

A summary of data for beryllium(II) hydrolysis at 25 °C is given in Table 1. Three different ionic media have been used: chloride, perchlorate, and nitrate. Although the values of the stability constants are quoted for the medium in which they were determined, the values used for the s.i.t. treatment were recalculated to the molal scale for the sake of consistency.

*Evaluation of* $\beta^0_{21}$. Experimental data are available for the media 3.0 mol dm$^{-3}$ $NaClO_4$,[1,8] 3.0 mol dm$^{-3}$ perchlorate 'self-medium',[2] 0.5 mol dm$^{-3}$ $NaClO_4$,[4] 1 mol kg$^{-1}$ NaCl,[3] 3 mol kg$^{-1}$ KCl,[5] and 0.1 and 2 mol dm$^{-3}$ $KNO_3$.[6,7] The data from the self-medium study show a systematic variation of log $\beta_{21}$ with $B$. This is presumably due to changes in the medium caused by the progressive replacement of $2Na^+$ by $Be^{2+}$ and can be quantitatively accounted for by the s.i.t. method, *cf.* Table 3. The average value obtained for the equilibrium constant extrapolated to the 3.0 mol dm$^{-3}$ $NaClO_4$ reference state, log $\beta_{21} = -3.225 \pm 0.005$, agrees very well with direct experimental values obtained in 3.0 mol dm$^{-3}$ $NaClO_4$ (this work and ref. 1). The mean value for the three determinations is log $\beta_{21} = -3.23 \pm 0.01$. The value log $\beta_{21} = -3.16$ reported by Kakihana and Maeda[8] seems to be slightly larger than expected.

The interaction coefficients used are $\varepsilon(H^+, ClO_4^-) = 0.14$[26,27] and $\varepsilon(Be^{2+}, ClO_4^-) = 0.30$ estimated from previously determined interaction coefficients for different bivalent cations with perchlorate, where $\varepsilon(M^{2+}, ClO_4^-) = 0.30 \pm 0.04$.[27] From the data at 3.0 and 0.5 mol dm$^{-3}$ $NaClO_4$, $\varepsilon[Be_2(OH)^{3+}, ClO_4^-] = 0.50$, in good agreement with previously determined values for $\varepsilon(M^{3+}, ClO_4^-) = 0.52 \pm 0.06$,[26,27] and for log $\beta_{21}$ extrapolated to infinite dilution, log $\beta^0_{21} = -3.51$.

In chloride media $\varepsilon(H^+, Cl^-) = 0.12$ was employed, calculated from activity coefficient data[27] and $\varepsilon(Be^{2+}, Cl^-) = 0.17$ was estimated from the reported values[27] $\varepsilon(Mg^{2+}, Cl^-) = 0.19$, $\varepsilon(Ni^{2+}, Cl^-) = 0.17$, and $\varepsilon(Ca^{2+}, Cl^-) = 0.14$. The estimate $\varepsilon[Be_2(OH)^{3+}, Cl^-] = 0.30$ was employed, based on a comparison with previously determined interaction coefficients, $\varepsilon(Y^{3+}, Cl^-) = 0.28$, $\varepsilon(Al^{3+}, Cl^-) = 0.30$, and $\varepsilon(Cr^{3+}, Cl^-) =$

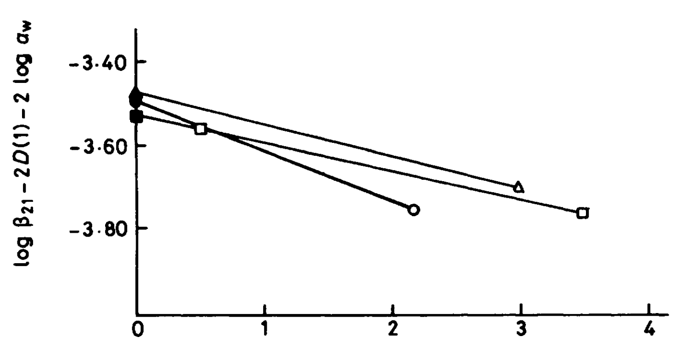

**Figure 3.** Variation of $\log \beta_{21}$ with ionic strength in chloride (△), perchlorate (□), and nitrate (○) media ($a_w$ = activity of water in the different media). Full symbols represent extrapolations to the infinite dilution standard state

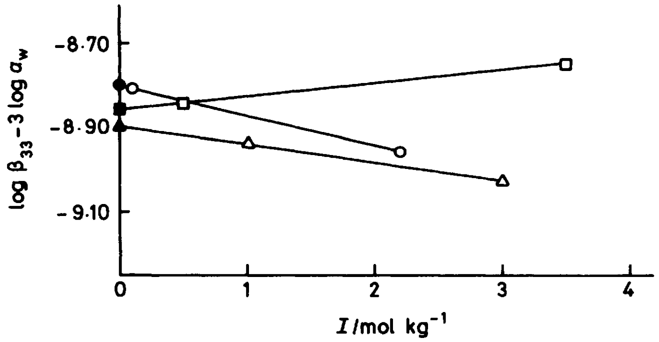

**Figure 4.** Variation of $\log \beta_{33}$ with ionic strength in chloride (△), perchlorate (□), and nitrate (○) media. See also Figure 3

0.33.[26,27] The value of $\log \beta_{21}$ extrapolated to infinite dilution from the determination in 1.0 mol kg$^{-1}$ is $-3.72 \pm 0.05$, while that extrapolated from 3.0 mol kg$^{-1}$ KCl is $-3.47 \pm 0.05$.

Two determinations are available in $KNO_3$ media. The interaction coefficients used were: $\varepsilon(H^+, NO_3^-) = 0.07$, calculated from activity data,[27] $\varepsilon(Be^{2+}, NO_3^-) = 0.16$, estimated from known interaction coefficients $\varepsilon(Mg^{2+}, NO_3^-) = 0.17$ and $\varepsilon(Zn^{2+}, NO_3^-) = 0.16$;[27] and $\varepsilon[Be_2(OH)^{3+}, NO_3^-] = 0.27$ estimated from $\varepsilon(Cr^{3+}, NO_3^-) = 0.27$.[27] From the determination in 0.1 mol dm$^{-3}$ $KNO_3$ an extrapolated value of $\log \beta^0_{21} = -3.18 \pm 0.05$ is obtained, and from 2 mol dm$^{-3}$ $KNO_3$, $\log \beta^0_{21} = -3.70 \pm 0.05$.

In Figure 3 the different extrapolations are compared by using the s.i.t. treatment. The agreement between the $\log \beta^0_{21}$ values from the three different ionic media studied is quite good, except for the values determined in 0.1 and 2 mol dm$^{-3}$ $KNO_3$ and 1 mol kg$^{-1}$ NaCl. The average value is $\log \beta^0_{21} = -3.49 \pm 0.02$; inclusion of the divergent determinations would give $\log \beta^0_{21} = -3.48 \pm 0.17$.

*Evaluation of* $\beta^0_{33}$. The species $[Be_3(OH)_3]^{3+}$ is predominant at beryllium(II) concentrations higher than 1 mmol dm$^{-3}$. As a consequence the stability constant is $\beta^0_{33}$ is less sensitive to small systematic errors in the experimental data than is $\beta^0_{21}$.

Data in $NaClO_4$ media are quite extensive. In 3.0 mol dm$^{-3}$ perchlorate $\log \beta_{33} = -8.66 \pm 0.01$ (this work and refs. 1, 2, and 8). One determination at 0.5 mol dm$^{-3}$ has also been reported, $\log \beta_{33} = -8.81$.[5] The interaction coefficients used for the calculations were $\varepsilon(H^+, ClO_4^-) = 0.14$ and $\varepsilon(Be^{2+}, ClO_4^-) = 0.30$, as before. From the s.i.t. approach, I obtain $\varepsilon[Be_3(OH)_3^{3+}, ClO_4^-] = 0.51$ in good agreement with the value (0.50) previously determined and those available in the literature for $\varepsilon(M^{3+}, ClO_4) = 0.52 \pm 0.06$.[26,27] The constant extrapolated to infinite dilution, $\log \beta^0_{33}$, is $-8.86 \pm 0.05$.

Two determinations are available in chloride media: $\log \beta_{33}$ (1 mol kg$^{-1}$ NaCl) = $-8.91$[3] and $\log \beta_{33}$ (3 mol kg$^{-1}$) = $-8.91$.[5] By using the interaction coefficients $\varepsilon(H^+, Cl^-) = 0.12$[27] and $\varepsilon(Be^{2+}, Cl^-) = 0.17$ (estimated as before), one obtains $\log \beta^0_{33} = -8.90$ and $\varepsilon[Be_3(OH)_3^{3+}, Cl^-] = 0.18$. The latter appears to be smaller than expected by comparison with $\varepsilon(M^{3+}, Cl^-) = 0.30 \pm 0.05$.[26,27] If the extrapolated constant is calculated from each separate determination by using an estimate for $\varepsilon[Be_3(OH)_3^{3+}, Cl^-] = 0.30 \pm 0.05$, consistent with previously reported data,[26,27] $\log \beta^0_{33} = -8.78 \pm 0.05$ is obtained from the data in 1 mol kg$^{-1}$ NaCl and $-8.5 \pm 0.2$ from the determination in 3 mol kg$^{-1}$ KCl.

The stability constants determined at 0.1 and 2.0 mol dm$^{-3}$ $KNO_3$ are $\log \beta_{33}$ $-8.81$[7] and $-8.90$,[6] respectively. The set of interaction coefficients used in the s.i.t. calculation are $\varepsilon(H^+, NO_3^-) = 0.07$[27] and $\varepsilon(Be^{2+}, NO_3^-) = 0.17$ obtained in the same way as before. The value obtained for $\varepsilon[Be_3(OH)_3^{3+}, NO_3^-] = 0.29$ is in good agreement with $\varepsilon(Cr^{3+}, NO_3^-) = 0.27$,[27] giving support to the previous estimate for $\varepsilon$-$[Be_2(OH)^{3+}, NO_3^-] = 0.27$. The constant extrapolated to infinite dilution, $\log \beta^0_{33} = -8.81$.

The average equilibrium constant at infinite dilution for the predominant $[Be_3(OH)_3]^{3+}$ complex is $\log \beta^0_{33} = -8.8 \pm 0.15$. A better estimate $\log \beta^0_{33} = -8.84 \pm 0.04$, is obtained if the determination in 3 mol kg$^{-1}$ KCl is neglected, *cf.* Figure 4.

*Higher polynuclear species* (5,6), (6,8). The experimental information available for the higher polynuclear hydroxo complexes is scarce. However, by using the s.i.t. approach an attempt can be made to estimate the medium effects. The interaction coefficients used are the same as in the previous calculations with the addition of $\varepsilon[Be_5(OH)_6^{4+}, ClO_4^-] = 0.80$ estimated by comparison with the experimentally determined values for $\varepsilon[Y_2(CO_3)^{4+}, ClO_4^-] = 0.80$ and $\varepsilon[Fe_4(OH)_4^{4+}, ClO_4^-] = 0.82$.[26] The value for $\log \beta_{56}$ extrapolated to the pure water reference state is $\log \beta^0_{56} = -19.5 \pm 0.1$.

Three determinations of $\beta_{68}$ in different ionic media have been reported, *cf.* Table 1. However, the three investigations differ in the model chosen to explain the data at higher values of *Z*. Consequently, no attempt has been made to correlate the different determinations. The extrapolated value obtained from the determination in 1 mol kg$^{-1}$ NaCl[3] is $\log \beta^0_{68} = -26.9 \pm 0.1$. The interaction coefficients used for $\varepsilon(Be^{2+}, Cl^-)$ and $\varepsilon(H^+, Cl^-)$ are the same as before. No reliable value for $\varepsilon(M^{4+}, Cl^-)$ is available in the literature, hence from observed trends it was assumed that $\varepsilon[Be_6(OH)_8^{4+}, Cl^-] = \varepsilon[Be_6(OH)_8^{4+}, ClO_4^-] - 0.2 \approx \varepsilon[Be_5(OH)_6^{4+}, ClO_4^-] - 0.2$. By using these parameters, $\log \beta^0_{68} = -26.8 \pm 0.1$ is obtained from the determination in 2 mol dm$^{-3}$ $KNO_3$. Finally, from the present determination in 3.0 mol dm$^{-3}$ perchlorate and taking into consideration the interaction coefficients estimated before, a somewhat higher value, $\log \beta^0_{68} = -26.3 \pm 0.1$, is obtained.

## Discussion

From the information collected it can be concluded that there is in general a good agreement between several groups of investigators that the low *Z* range can be explained by the presence of the species $[Be_2(OH)]^{3+}$ and $[Be_3(OH)_3]^{3+}$. The equilibrium constants which have been determined in media of different ionic strengths and compositions can be correlated by using s.i.t. The values extrapolated to the pure water reference state in general agree very well with one another. The exceptions are the values for $\beta_{21}$ reported in 0.1 mol dm$^{-3}$ $KNO_3$[7] and 1 mol kg$^{-1}$ NaCl.[3] In both cases the hydrolysis model proposed is not complete with respect to the mononuclear species. This is especially remarkable for the study at 0.1 mol dm$^{-3}$ $KNO_3$ where, according to my preliminary calculations, at the lowest metal concentration (0.2 mmol dm$^{-3}$ $Be^{II}$) the complex $[Be(OH)]^+$ is far more abundant than $Be(OH)_2$ and accounts for 10% of the total $Be^{II}$ in solution (see below).

The presence of the first mononuclear hydroxide complex, $[Be(OH)]^+$, is difficult to ascertain from equilibrium data. In my calculations the presence of this complex was indicated at the lowest metal concentration, and accounts for at most 5% of the total $Be^{II}$ (see Figure 2). Brown *et al.*[7] working at very low metal levels (2.5—0.3 mmol dm$^{-3}$) could not justify the inclusion of this complex in their chemical model. Schwarzenbach and Wenger[28] observed the presence of $[Be(OH)]^+$ and gave a value for the stability constant in 0.1 mol dm$^{-3}$ $NaClO_4$ at 20 °C as $\log \beta_{11} = -5.7$. I have obtained a value $\log \beta_{11} = -6 \pm 0.2$ in 3.0 mol dm$^{-3}$ $NaClO_4$ at 25 °C. By applying the s.i.t. approach, the constant obtained in 0.1 mol dm$^{-3}$ $NaClO_4$ can be extrapolated to the ionic media used in this study, $\log \beta_{11} = -6.1 \pm 0.1$. A reasonable agreement is found in spite of the temperature difference. This (1, 1) species seems to have quite a narrow range of existence in comparison with the more stable (2, 1) complex. Only extremely accurate data obtained at very low total beryllium(II) concentrations would provide a more definitive evidence.

The presence of $Be(OH)_2$ in solution is controversial. This complex was included in the chemical model proposed by Kakihana and Sillen,[1] and confirmed by others.[7,8,28] Baes and Mesmer[11] suggested that the high solubility calculated by using the equilibrium constant of Kakihana and Sillen[1] is not compatible with the values experimentally observed by Gilbert and Garrett.[29] Brown *et al.*[7] found at low metal concentration a noticeable improvement in their model when they included $Be(OH)_2$. In the present calculations the agreement between experimental and calculated data was also better when the (1, 2) complex was included. I have recalculated the solubility data of Gilbert and Garrett (see below) using my chemical model. The calculations show that the amount of (1, 2) complex formed in the pH range investigated by the authors is at most 10%. The solubility method is not sensitive enough for such relatively low concentrations. Hence, the more accurate potentiometric determinations in homogeneous solutions should give more precise information on the minor species. Five different determinations of this kind are available. Three of them in 3.0 mol dm$^{-3}$ $NaClO_4$ at 25 °C agree reasonably well (see Table 1); the average value is $\log \beta_{12} = -11.04 \pm 0.13$. The value of Kakihana and Sillen is bound to be affected by the use of $NaHCO_3$ as titrating agent, as I have already discussed. The difference between the present determination and that of Kakihana and Maeda[8] falls within the experimental error. Schwarzenbach and Wenger[28] also determined $\log \beta_{12} = -11.8$, in 0.1 mol dm$^{-3}$ $NaClO_4$ at 20 °C. By applying the s.i.t. treatment and neglecting the temperature differences, the extrapolated value for $\log \beta^0_{12} = -11.00 \pm 0.05$. Finally, Brown *et al.*[7] obtained $\log \beta_{12} = -11.32 \pm 0.01$ in 0.1 mol dm$^{-3}$ $KNO_3$. The value extrapolated to the infinite dilution standard state is $\log \beta^0_{12} = -11.02 \pm 0.05$. Thus, a very good agreement is found between the five different determinations, giving an average value for the extrapolated constant, $\log \beta^0_{12} = -11.00 \pm 0.05$, in contrast to the much lower value proposed by Baes and Mesmer.[11]

Few investigations have been made in the range where the higher polynuclear complexes exist. Kakihana and Sillen[1] first proposed the formation of $[Be_5(OH)_6]^{4+}$ in their study of beryllium(II) hydrolysis. They later rejected their hypothesis, probably because of the lack of experimental data in the range where the complex predominates. It seems that no other group of investigators has considered this complex. The existence of $[Be_6(OH)_8]^{4+}$ was initially proposed by Lanza and Carpeni.[6] Together with (3, 4) and (6, 9) species, a good agreement was found between the data collected and those calculated from the model. Recently, Baes and Mesmer[11] have corrected their initial hypothesis of formation of the (5, 7) complex, proposing (6, 8) as an equally good candidate. I have collected a fair amount of data in the range of existence of these species. The graphical and numerical treatments support the formation of (5, 6) in the same hydrogen-ion concentration range in which the (6, 8) complex occurs. The numerical value of the constant for the latter is affected by the model chosen. Hence, the values obtained in 3.0 mol dm$^{-3}$ $NaClO_4$ were chosen for the extrapolation to the infinite dilution state.

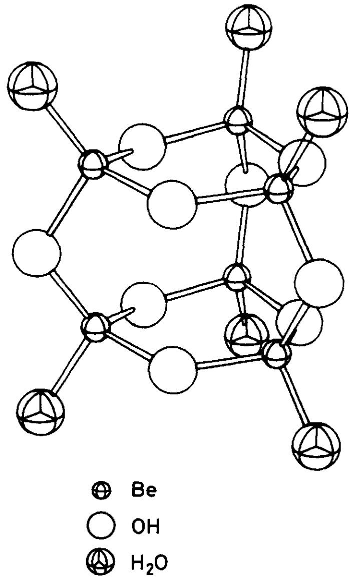

**Figure 5.** Tentative structure for the hypothetical $[Be_6(OH)_9]^{3+}$ complex, built up exclusively *via* OH bridging

As already mentioned, I have recalculated the solubility data of Gilbert and Garrett by using the present equilibrium model. Two different sets of data are available: the first obtained by studying the solubility of α-$Be(OH)_2$ in solutions at pH 4.77—5.32, the second by measuring the solubility of the same solid phase in alkaline solutions, at pH 12.29—13.86. First, the value of $\log K_{s0}$ for the reaction (16) was recalculated using the

$$Be^{2+} + 2H_2O \rightleftharpoons \alpha\text{-}Be(OH)_2 + 2H^+ \qquad (16)$$

stability constants extrapolated to the infinite dilution standard state. The best fit between the calculated and experimental data, in the form $B$ *vs.* $h$, is obtained for $\log K_{s0} = -6.87 \pm 0.05$. This value is lower than the one proposed by Baes and Mesmer,[11] $-6.65 \pm 0.05$, but in better agreement with that originally proposed by Schindler and Garrett,[30] $-6.85 \pm 0.05$.

*Tentative Structures for the* $Be^{II}$–$H_2O$ *Polynuclear Complexes.*—A careful choice of the experimental conditions and an exhaustive data treatment will in general provide accurate information about the most probable stoicheiometries of the complexes in solution. However, when selecting a chemical model one should always consider the structural soundness of the hypothesis proposed. Some inferences can be made from the known structures for the different beryllium(II) oxide and hydroxide phases.

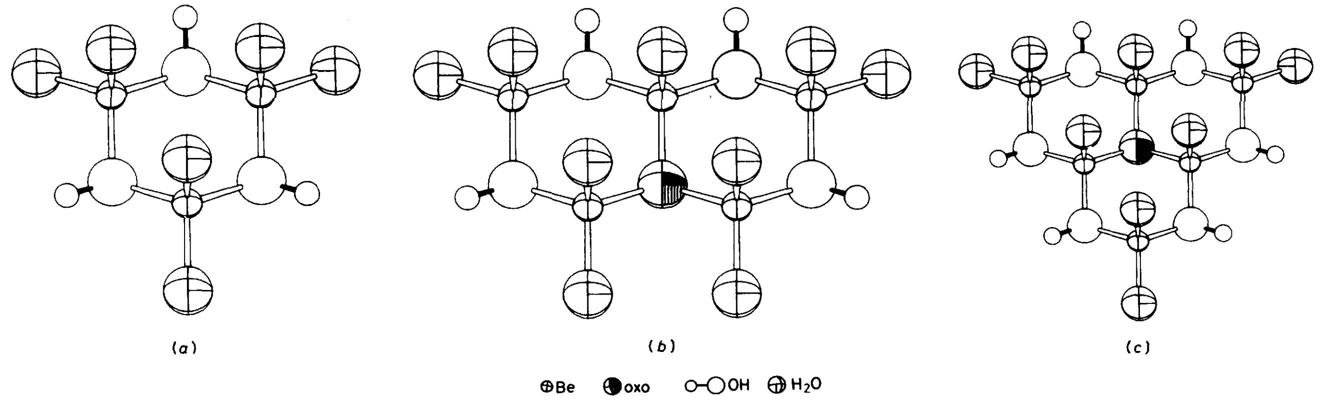

**Figure 6.** Tentative structures for the $[Be_3(OH)_3]^{3+}$ (*a*), $[Be_5O(OH)_4]^{4+} \equiv [Be_5(OH)_6]^{4+}$ (*b*) and $[Be_6O(OH)_6]^{4+} \equiv [Be_6(OH)_8]^{4+}$ (*c*) complexes. The structures are based on mixed oxo and hydroxo bridging

Three well defined solid phases have been characterized in the $Be^{II}$–$H_2O$ system at 25 °C. The first crystalline phase which appears in contact with saturated beryllium(II) solutions is α-$Be(OH)_2$(s).[11] This hydroxide crystallizes in the cristobalite structure and contains linked $Be(OH)_4$ tetrahedra where each corner is shared by two tetrahedra. It transforms with time into β-$Be(OH)_2$(s). This solid has the same structure as the ε form of $Zn(OH)_2$(s) with OH bridges between two Be atoms. A similar arrangement is found for $[Be_3(OH)_3]^{3+}$ in the solid state.[31] Finally, BeO(s) has the wurtzite structure containing $BeO_4$ tetrahedra where each corner is shared by four other tetrahedra.

One would expect that the co-ordination of Be in the polynuclear complexes in solution follows the same structural patterns. This has already been indicated for the (3, 3) complex by the $^1H$ n.m.r. study of Akitt and Duncan.[32] The formation of polynuclear species in the $Be^{II}$–$H_2O$ system can be achieved in two ways by using the same corner-sharing principles as in $Be(OH)_2$(s) and BeO(s). (*a*) *via* OH bridging. This implies the following stoicheiometric sequence: $[Be_2(OH)]^{3+}$, $[Be_3(OH)_3]^{3+}$, $[Be_5(OH)_6]^{4+}$, and $[Be_6(OH)_9]^{3+}$. A model of the resulting (6, 9) structure is shown in Figure 5. (*b*) *via* OH and O bridging. In this case the following stoicheiometries are applicable: $[Be_2(OH)]^{3+}$, $[Be_3(OH)_3]^{3+}$, $[Be_5(OH)_6]^{4+}$, and $[Be_6(OH)_8]^{4+}$. The $[Be_5(OH)_6]^{4+}$ and $[Be_6(OH)_8]^{4+}$ complexes can contain at most one oxide oxygen, to retain the tetrahedral geometry, and should be written as $[Be_5O(OH)_4]^{4+}$ and $[Be_6O(OH)_6]^{4+}$. The oxygen atom is placed at the point where the three tetrahedra meet. Models of the structures of the (3, 3), (5, 6), and (6, 8) complexes are shown in Figure 6.

At this stage it is not possible to decide which of the proposed structural hypotheses is the right one. Although the stoicheiometric information is compatible with mixed O, OH bridging, the only information available on the structure of the beryllium(II) hydroxo polynuclear complexes suggests OH bridging for the 3, 3 complex. Additional information of this kind can be obtained by using a combination of $^1H$, $^9Be$, and $^{17}O$ n.m.r. spectroscopies. Work is in progress in this direction.

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