

Ternary Metal Complexes. 1. The Be(II)–F[−]–H₂O System

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Oxide, hydroxide and fluoride are all excellent bridging ligands. Bridged species formed with the first two ligands are legio both in the solid state and in solution, while fluoride mainly seems to form bridges in the solid state. The formation of complexes containing bridging fluoride requires the formation of a polynuclear species Be_pF_q^{2p−q}, or Be_pF_q(OH)_r^{2p−(q+r)}. The formation of the first type of complex gives direct evidence (in the absence of metal–metal bonding) of the presence of bridging fluoride(s), while the formation of the ternary complex requires additional non-thermodynamic information to establish the presence of fluoride bridges. Such information may be provided by the spin–spin coupling pattern between ¹⁹F and ⁹Be. For a fluoride bonded to a single Be the ¹⁹F NMR signal will be a quartet, owing to coupling between the two nuclei. For a bridging fluoride spin–spin coupling to two Be is expected to result in a septet for the ¹⁹F signal.

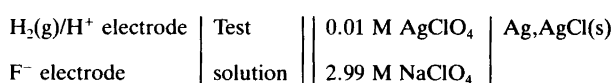
Previous investigations of the Be(II)–F[−] system, cf. Mesmer and Baes,¹ Bond and Hefter² and references cited therein, indicate that only mononuclear complexes BeF_n^{2−n}, *n* = 1–4, are formed. There is no evidence for the formation of ternary complexes of the type Be_pF_q(OH)_r^{2p−(q+r)} in the literature. However, Soboleva *et al.*³ report the formation of the ternary complexes Be(OH)F(aq) and Be(OH)₂F[−] in hydrothermal systems at a temperature in the range 150–300 °C. Previous experimental studies have been made in concentration ranges in which the formation of polynuclear complexes are not favoured. We therefore decided to reinvestigate the system under conditions for which the possible formation of polynuclear, ternary complexes should be facilitated. Our experiments have been made at 25.00 °C in a 3 M NaClO₄ ionic medium, and cover concentration ranges 20 < [Be]_{tot} < 100 mM, 1 < [F]_{tot} < 75.4 mM and 4.08 < −log [H⁺] < 5.17. The experimental information was obtained from EMF data using H⁺- and F[−]-selective electrodes and from ¹⁹F and ⁹Be NMR measurements.

Experimental

Chemicals used. All chemicals used were of analytical grade; they were prepared (NaClO₄) and analyzed using standard methods.

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EMF measurements. The EMF of cells of the following type was measured:



The *E*₀ values of the hydrogen electrode and the total initial acidity *H*₀ of the Be(II) solution in the cell were determined coulometrically using a Gran plot; the procedure has been described previously, e.g. by Bruno.⁴ The *E*₀ value of the fluoride electrode was determined in a separate experiment, also using a Gran titration procedure. The titrant was a solution of a known concentration of fluoride in a 0.01 M bicarbonate/carbonate buffer and 3 M NaClO₄. After the pH is defined by the buffer, the concentration of F[−] is equal to the total concentration of added NaF. The experimental EMF data are plotted in Fig. 1 and can be obtained from one of the authors (R.A.).

NMR measurements. The NMR measurements were made using a Bruker AM 400 instrument on some selected test solutions for which the concentrations of the various complexes were assumed to be known from the EMF data.

¹⁹F (⁹Be) NMR chemical shifts are given in ppm towards higher frequency from an external standard of CF₃COOH [5 M Be(ClO₄)₂ solution in water]. Some typical NMR parameters are as follows: ¹⁹F (⁹Be) spectral window 20 (1) kHz; pulse width 5 (20) μs, ca. 45° (90°) pulse; pulse repetition time ca. 0.5 s (15 s); digital resolution 1.2 (0.1) Hz per point. Some ¹⁹F NMR shifts and coupling constants for the investigated species are given later in Table 2, and a typical ¹⁹F NMR spectrum is shown in Fig. 3. The assignment of the peaks was made by measuring the peak integrals and comparing these with the concentrations expected from the EMF data.

Interpretation of the experimental data. From the measured concentrations of [H⁺] and the known total concentrations of Be(II) and fluoride it is in principle possible to deduce the composition of the complexes formed and their equilibrium constants, cf. Rossotti and Rossotti.⁵ However, within the concentration ranges investigated in this study it turned out to be impossible to obtain a unique chemical model by using EMF data alone. We could have extended the EMF

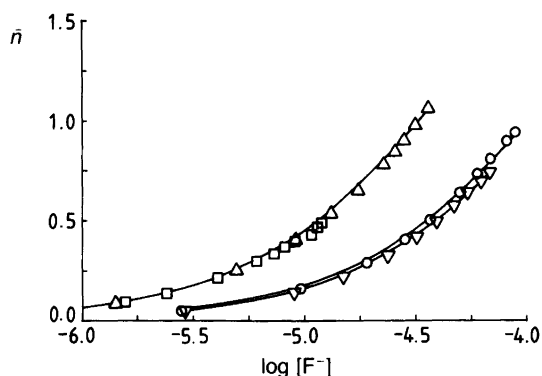
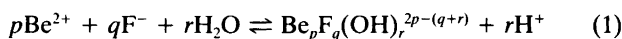


Fig. 1. $\bar{n}(F^-)$ as a function of $-\log [F^-]$. The full-drawn curves have been calculated using the equilibrium constants determined in this study and the hydrolysis constants of Bruno.⁴ □, 20 mM Be, pH 4.23–4.48; △, 30 mM Be, pH 4.13–4.61; ○, 80 mM Be, pH 4.6–5.17; ▽, 100 mM Be, pH 4.59–5.06.

part, but preferred to use auxiliary information from the NMR investigations to establish the composition of the predominant species, i.e. BeF^+ , BeF_2 , $Be_3(OH)_3F^{2+}$ and $Be_3(OH)_3F_2^+$. It was then possible to refine the equilibrium constants using the least-squares program LETAGROP,^{6,7} with either $\log [H^+]$ or $\log [F^-]$ as the error-carrying variable. Both methods gave the same chemical model and essentially the same values of the stability constants; the largest difference was found for the species (3, 2, -3), where the numbers are the stoichiometric coefficients (p, q, r) in eqn. (1).



The final model selected and the equilibrium constants are given in Table 1. The constants are the averages of the refinements using the two different error-carrying variables; the uncertainties are estimated standard deviations. Fig. 1 indicates the agreement between the experimental data in the form \bar{n}_F vs. $-\log [F^-]$ and the corresponding

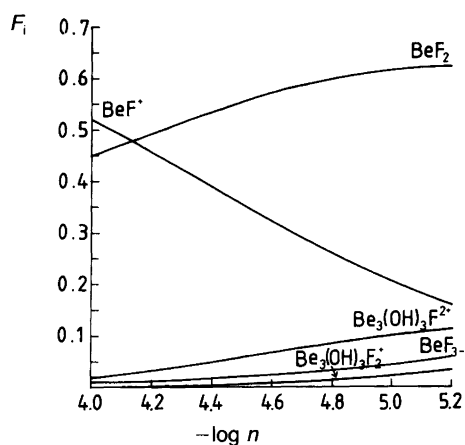


Fig. 2. Distribution of Be(II) among the different complexes as a function of $-\log h$. $[Be(II)] = 0.0720$ M, $[F^-]_{tot} = 0.0678$ M.

Table 1. Equilibrium constants for the species formed in the Be(II)– F^- – H_2O system.^a

Reaction	log K	Remarks
$Be^{2+} + F^- \rightleftharpoons BeF^+(aq)$	5.21 ± 0.03 5.12 ± 0.15^b	This work Ref. 1 ^c
$Be^{2+} + 2F^- \rightleftharpoons BeF_2(aq)$	9.57 ± 0.03 9.58 ± 0.15^b	This work Ref. 1 ^c
$3Be^{2+} + 3H_2O + F^- \rightleftharpoons Be_3(OH)_3F^{2+}$	-4.18 ± 0.06	This work
$3Be^{2+} + 3H_2O + 2F^- \rightleftharpoons Be_3(OH)_3F_2^+$	-0.67 ± 0.24	This work

^aIonic medium: 3 M $NaClO_4$; temperature 25 °C. ^bThe uncertainties are obtained by including the estimated uncertainty of ± 0.06 in the specific ion interaction term ϵ .^{8,9} ^cThe data have been recalculated from 1 mol kg^{-1} $NaClO_4$ (Ref. 1) to 3 M $NaClO_4$ using the specific ion interaction theory.^{8,9}

values calculated from the selected model. The EMF experiments have only been extended to fairly low fluoride concentrations; the average number of fluorides per beryllium, \bar{n}_F , is only slightly above one. Hence precise values cannot be expected for the species (1, 3, 0) (Fig. 2). The value of this constant was therefore taken from Mesmer and Baes,¹ recalculated to 3 M $NaClO_4$ using the specific ion interaction theory (*vide infra*), and was used as a fixed parameter in the least-squares refinements. The equilibrium constants for the binary hydroxide species ($p, 0, r$) were taken from Bruno⁴ and were also kept constant in the refinement.

Results and discussion

The equilibrium constants of the mononuclear fluoride complexes BeF^+ and $BeF_2(aq)$ from the present study agree very well with the corresponding constants determined by Mesmer and Baes¹ after recalculation to a common ionic medium. This was made by using the specific ion interaction theory,^{8,9} and the values thus obtained are also given in Table 1. The magnitude of the standard deviations, and the good agreement of the mononuclear fluoride constants with the previous determination, indicate that both the precision and the accuracy of the present study are satisfactory. Additional support for the proposed model is obtained by a comparison of the stoichiometry of the ternary beryllium complexes. Bruno *et al.*¹⁰ identified $Be_3(OH)_3(CO_3)_3^{3-}$ in solution, while Faure *et al.*¹¹ identified $Be_3(OH)_3(pic)_3$, where pic is picolinate, by an X-ray single-crystal structure determination. Both these studies indicate that the “ $Be_3(OH)_3$ ” core has a large chemical stability.

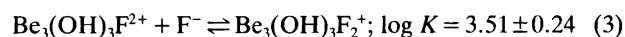
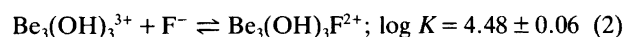
There are large differences in chemical shift between the various complexes formed (cf. Table 2), and both the ^{19}F and the 9Be NMR spectra are governed by slow exchange on the actual timescales. Hence, it is straightforward to identify any new complexes that appear and to determine

Table 2. ^{19}F NMR chemical shifts (δ) and ^9Be – ^{19}F spin–spin coupling constants $^1J(^9\text{Be}$ – $^{19}\text{F})$ for the various complexes formed in the $\text{Be}(\text{II})$ – F^- – H_2O system.^a

Species	^{19}F chemical shift/ppm ^b	$^1J(^9\text{Be}$ – $^{19}\text{F})/\text{Hz}^c$
BeF^+	–98.0	42.2
BeF_2	–95.8	39.7
BeF_3^-	–94.6	37.3
$\text{Be}_3(\text{OH})_3\text{F}^{2+}$	≈ –88.6	≈ 35
$\text{Be}_3(\text{OH})_3\text{F}_2^+$	≈ –89.2	≈ 34

^aIonic medium: 3 M NaClO_4 ; temperature 25 °C. ^bThe chemical shifts are given in ppm toward higher frequency from external trifluoroacetic acid. The shifts vary somewhat depending on the composition of the solution. ^cThe coupling constants vary slightly depending on the composition of the solution.

their concentrations from the corresponding peak integrals. This method probably offers the most precise way to determine the speciation and equilibrium constants in this system. All ^{19}F signals are quartets, indicating that no bridging fluorides are present in ternary complexes. The fluoride seems to be bonded in a terminal fashion to the bridging Be atom(s). It is interesting to observe that the binding constants for reactions (2) and (3) are only about a factor of



ten smaller than the corresponding stepwise constants for the formation of BeF^+ and $\text{BeF}_2(\text{aq})$, even when a correction is made for the larger statistical factor for the binding of the fluoride in the ternary complexes.

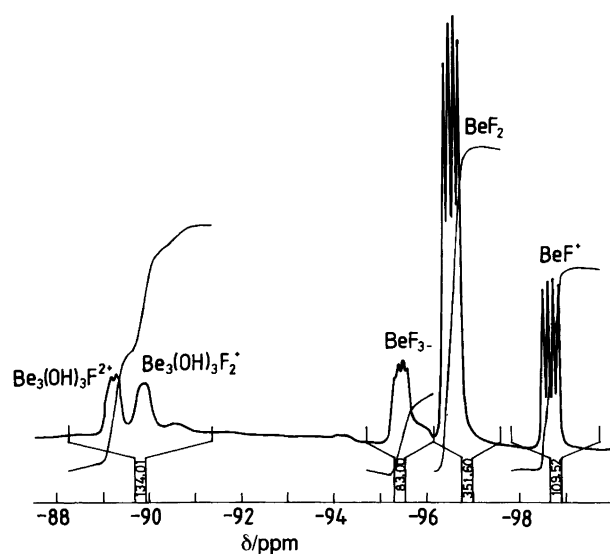


Fig. 3. 376.5 MHz ^{19}F NMR spectra of a solution containing 0.0720 M beryllium and 0.0678 M fluoride; pH 5.17; temperature: 25 °C.

The data of Soboleva *et al.*³ refer to such high temperatures that an extrapolation to 25 °C seems difficult; however, in this case one also observes the formation of ternary complexes. These are mononuclear, owing to the low total concentrations of beryllium in this solubility study; $[\text{Be}]_{\text{tot}} < 10^{-3}$ M for most of the experimental data. A high temperature also seems to promote the formation of mononuclear species.¹² This exploratory study has established the composition and the stability constants of the main ternary complexes present in the $\text{Be}(\text{II})$ – H_2O – F^- system. However, as can be seen from Fig. 3, there are some additional species formed besides the predominant BeF^+ , $\text{BeF}_2(\text{aq})$, $\text{Be}_3(\text{OH})_3\text{F}^{2+}$ and $\text{Be}_3(\text{OH})_3\text{F}_2^+$. The reason for the difficulty in interpreting the EMF data alone is probably the simultaneous presence of several complexes of comparable concentrations. This fact is used as an advantage in the NMR study, and a combination of the two methods leads more quickly to a unique chemical model than does each method alone.

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