Studies of Metal Carbonate Equilibria. Part 15.[1] The Beryllium(II)–Water–Carbon Dioxide(g) System in Acidic 3.0 mol dm^{-3} Perchlorate Media *

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The complex-formation equilibria in the system Be^{II}–H_2O–$CO_2(g)$ have been studied by e.m.f. techniques in 3.0 mol dm^{-3} (Na)ClO_4 at 25 °C in the range $2.0 \leqslant \log h \leqslant 6.2$, where h is the free hydrogen-ion concentration. The total metal concentration, B, has been varied from 1 to 80 mmol dm^{-3} and the partial pressure of CO_2 from 0.1 to 0.97 atm. The e.m.f. data obtained can be explained by assuming, in addition to previously proposed hydrolytic species, the ternary equilibria (i)—(iv). The stability constants of the mixed complexes are as follows: $\log \beta_{331} = -8.90 \pm 0.02$,

$$3Be^{2+} + 3H_2O + CO_2(g) \rightleftharpoons [Be_3(OH)_3(CO_2)]^{3+} + 3H^+ \qquad (i)$$

$$5Be^{2+} + 6H_2O + CO_2(g) \rightleftharpoons [Be_5(OH)_6(CO)_2]^{4+} + 6H^+ \qquad (ii)$$

$$6Be^{2+} + 9H_2O + 2CO_2(g) \rightleftharpoons [Be_6(OH)_9(CO_2)_2]^{3+} + 9H^+ \qquad (iii)$$

$$Be^{2+} + 2H_2O + CO_2(g) \rightleftharpoons Be(OH)_2(CO_2) + 2H^+ \qquad (iv)$$

$\log \beta_{561} = -17.24 \pm 0.04$, $\log \beta_{692} = -29.46 \pm 0.06$, and $\log \beta_{121} = -10.4 \pm 0.1$. The Raman spectra of concentrated solutions containing the different mixed complexes have been recorded. From these results tentative structures for the mixed hydroxo–carbonato complexes are proposed and discussed. The (1,2,1), (3,3,1), and (5,6,1) complexes are suggested to possess stoicheiometries $BeCO_3$, $[Be_3(OH)_2(HCO_3)]^{3+}$, and $[Be_5(OH)_4(CO_3)]^{4+}$ respectively.

The carbonate and hydrogencarbonate (bicarbonate) ions are frequently used as reagents in preparative and analytical chemistry, particularly to dissolve sparingly soluble metal oxides and hydroxides. The carbonate system, which by and large regulates the pH of most natural water systems, may also be important for the speciation and mobility of trace metals in these systems.[2] The chemical information on the composition, structure, and bonding in the complexes formed is scarce, particularly for the mixed hydroxo–carbonato complexes. Hence, a detailed study of the mixed complex formation can give us information about the following: (*a*) the relative stability of the mixed hydroxo–carbonato complexes compared to the hydroxide complexes; (*b*) the way in which the stoicheiometry and the structures of the hydroxide complexes change upon replacement with, or insertion of, a hydrogencarbonato or a carbonato group; and (*c*) whether there is a simple mechanistic pathway for the transformation between hydroxide and carbonate complexes.

In the solid state, some minerals are known to contain both hydroxo and carbonato ligands: hydromagnesite, $Mg_5(OH)_2(CO_3)_4(H_2O)_4$;[3] dawsonite, $NaAl(OH)_2(CO_3)$;[4] malachite, $Cu_2(OH)_2(CO_3)$;[5] azurite, $Cu_3(OH)_2(CO_3)_2$;[6] and callaghanite, $Cu_8Mg_8(OH)_{24}(CO_3)_4 \cdot 8H_2O$.[7] Some mixed hydroxo-carbonato complexes have been synthesized in the solid state, *e.g.* $NH_4[Ga(OH)_2(CO_3)]$,[8] with the same composition and structure as dawsonite but where Na and Al have been replaced by NH_4 and Ga respectively. Among the cobalt(III) carbonato complexes, which have been extensively studied, solids of composition $[Co(terpy)(OH)(CO_3)] \cdot 4H_2O$[9] (terpy = 2,2′:6′,2″-terpyridyl) and $[Co_2(NH_3)_6(\mu\text{-}OH_2)(\mu\text{-}CO_3)]SO_4 \cdot 5H_2O$[10] have been reported. For Cu^{II} a solid of composition $K_{0.4}[Cu_{0.9}(OH)_2(HCO_3)] \cdot 1.66H_2O$[11] has been characterized. In the case of Be^{II}, Sengupta[12] has synthesized some salts containing the anion $[Be_4O(CO_3)_6]^{6-}$. The structure of a hexa-aminecobalt(III) salt has been determined by *X*-ray diffraction and will be reported in a forthcoming publication in this series.[13]

In aqueous solution the formation of some mixed hydroxo–carbonato complexes has been proposed, particularly at alkaline pH. There is information in the case of Be^{II},[12] Fe^{III},[14] and some lanthanides, *i.e.* Eu^{III} and Nd^{III}.[15] Quantitative information about the stoicheiometry and stability of mixed complexes has been obtained for Al^{III}[16] and U^{VI}.[17] Recently, the formation of mixed hydroxo–carbonate complexes of Zn^{II} in carbonate media has been proposed.[18] The composition and stability of mixed hydroxo–carbonato complexes of U^{IV} and Th^{IV} is currently being studied in our laboratory.

The data previously available for the Be^{II}–H_2O–CO_2 system were restricted to rather ambiguous solubility studies at alkaline pH[19–21] and semiquantitative information on the composition of beryllium(II) carbonate complexes.[12] In a previous study on the hydrolysis of Be^{II} it was observed[22] that the system behaved in a different way when the $N_2(g)$ stream was replaced by $CO_2(g)$. There is, as mentioned above, quantitative information on mixed hydroxo–carbonato complexes of Al^{III} in the neutral region prior to the precipitation of aluminium hydroxide.[16] The chemical similarities of Al^{III} and Be^{II} in aqueous solution makes it likely that mixed complexes

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* *Supplementary data available* (No. SUP 56684, 10 pp.): primary titration data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: atm = 101 325 Pa.

should be formed also for Be^{II}. The information previously obtained on beryllium(II) hydrolysis was then a useful starting point to study the three-component system.

Experimental

The Be^{II}–H_2O–$CO_2(g)$ system was investigated in a 3.0 mol dm^{-3} $(Na)ClO_4$ medium using e.m.f. titrations. The free hydrogen-ion concentration, h, in solution was measured at 25 °C by using the cell (1), in solutions of various total

$$\text{Glass electrode/Sample/Reference electrode} \qquad (1)$$

beryllium(II) concentrations, B, and analytical hydrogen-ion concentrations, H, saturated with CO_2–N_2 mixtures of different compositions, where the reference half-cell was 3.0 mol dm^{-3} $NaClO_4$/0.01 mol dm^{-3} $AgClO_4$, 2.99 mol dm^{-3} $NaClO_4$/AgCl,-Ag. In this case the Nernst equation takes the form (2) where

$$E = E_0 + 59.16 \log h + E_j \qquad (2)$$

E_0 is the standard potential of the glass electrode and E_j is the liquid junction potential as a result of the differences in $[Na^+]$ and $[H^+]$ between the sample and the reference half-cell. This can be written as in equation (3). In the medium used in

$$E_j = j_1[H^+] + j_2[Na^+] \qquad (3)$$

this study, $j_1 = -16.8$ dm^3 mV mol^{-1} and $j_2 = 7.34 \pm 0.08$ dm^3 mV mol^{-1} as determined in separate experiments. The latter value was found to be in good agreement with a previous determination, 7.2 ± 0.2 dm^3 mV mol^{-1}.[23]

During a titration the total metal concentration B and the $CO_2(g)$ partial pressure, a, were kept constant. The total acidity of the test solutions, H, was varied coulometrically. The acidity range investigated was $2.0 \leqslant -\log h \leqslant 6.2$. The total metal concentration studied was $1 \leqslant B \leqslant 80$ mmol dm^{-3}. The carbon dioxide partial pressure varied in the range $0.1 \leqslant a \leqslant 0.97$ atm.

The experimental methodology was similar to that used in the previous paper.[22] For more details the reader is referred to that paper and to ref. 23.

Chemicals and Analysis.—All chemicals were prepared and analysed as previously described.[22,23] For equilibration of the test solutions with $CO_2(g)$ of the required partial pressure, carbon dioxide–nitrogen gas mixtures were used. These were prepared and analysed by AGA SpecialGas. The uncertainty in the gas analysis (1%) was found to have very little significance in our experiments. The gas was purified and equilibrated with the solvent (3.0 mol dm^{-3} $NaClO_4$) by bubbling through a series of washing bottles containing 10% H_2SO_4, distilled water, and 3.0 mol dm^{-3} $NaClO_4$ respectively, and finally through a G-4 glass filter. The partial pressure values were corrected for the water pressure in 3.0 mol dm^{-3} $NaClO_4$.

The primary experimental data (512 points), in the form of e.m.f., H, and a values, are available as SUP 56684.

Calculations and Results

In Figure 1 a representative set of experimental data is plotted for $B = 1$ and 80 mmol dm^{-3}, at $a = 0.97$, 0.29, and 0.10 atm, in the form Z *vs.* log h, where Z is the number of OH bound to Be^{II} and defined as $(h - H + [OH^-] - [HCO_3^-] - 2[CO_3^{2-}])/B$. Similar sets of data were obtained for $B = 3$, 10, 20, and 40 mmol dm^{-3}.

The e.m.f. data at acidic pH were treated in the following way. First the predominant (p,q) values were obtained by a graphical treatment of data from experiments with CO_2–N_2 gas mixtures of the same composition (constant a), and different total metal concentrations B. The predominant r values were obtained afterwards by studying the dependence of the conditional constants K_{pq}^* on a (see below). Finally, the model obtained by graphical means was refined by treating the complete set of data by the least-squares computer program LETAGROP–ETITR.[24]

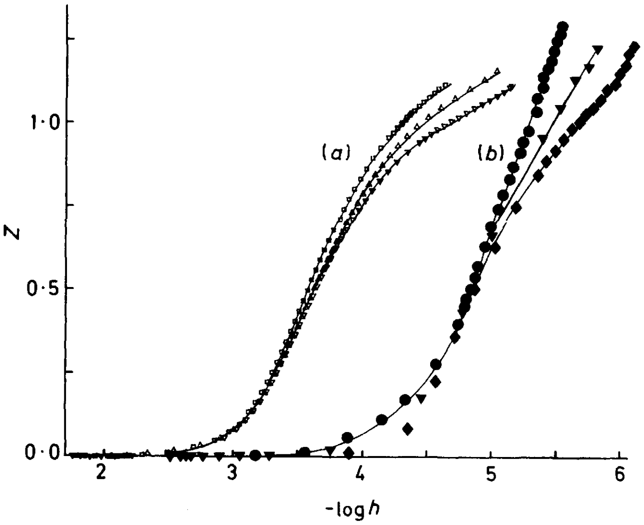


Figure 1. Plot of the experimental data in the form Z *vs.* $-\log h$ at $B = 1$ (*a*) and 80 mmol dm^{-3} (*b*) and $a = 0.10$ (▽, ◆), 0.29 (△, ▼), and 0.97 atm (□, ●). The curves were calculated with the stoicheiometric model proposed in this work

Graphical Treatment.—The predominant (p,q) values were determined in a similar way to those for the beryllium(II) hydrolysis system.[22] The same computer-assisted graphical procedure[25] was used. Basically, the same set of predominant (p,q) values as for the hydrolysis system was found. The only deviation was for the highest polynuclear complex. In the case of the ternary system, the graphical treatment gave a significantly better fit by including the (6,9) term instead of the (6,8) found in the hydrolysis system.

The majority of the constants obtained were dependent on the $CO_2(g)$ partial pressure. The predominant (p,q) values and the constants determined by the graphical treatment are summarized in Table 1.

Estimation of the r *Values; Treatment of the Conditional Constants.*—In order to evaluate the predominant r values the dependence of the conditional constants K_{pq}^* on the partial pressure of carbon dioxide, a, was studied. At each constant a, the general conditional constant of the (p,q,r) species with the same p and q coefficients but different r can be written as in equation (4). According to this equation, the function K_{pq}^* can

$$K_{pq}^* = \sum_r \beta_{pq} a^r \qquad (4)$$

be expressed as a power series of a, from which values for β_{pq} and r can be obtained, *e.g.* by standard graphical methods.

The following conclusions can be drawn from Table 1. The value of K_{21}^* shows no dependence on a, indicating the predominance of the species (2,1,0). The plot of K_{33}^* *vs.* a is linear, indicating the existence of species (3,3,0) and (3,3,1). The slope gives $\beta_{331} = (1.35 \pm 0.09) \times 10^{-9}$ mol dm^{-3} atm^{-1} and the intercept with the y axis gives $\beta_{330} = (2.23 \pm 0.15) \times 10^{-9}$

mol dm^{-3} or log $\beta_{330} = -8.65 \pm 0.03$. This is in good agreement with the value obtained in the previous hydrolysis study (log $\beta_{330} = -8.656 \pm 0.002$).[22] The plot of $K_{56}{}^*$ *vs.* a is approximately linear with a slope of unity ($r^2 = 0.9995$), indicating the coexistence of the species (5,6,0) and (5,6,1). The slope gives the value $\beta_{561} = (9.66 \pm 0.20) \times 10^{-18}$ mol^2 dm^{-6} atm^{-1} or log $\beta_{561} = -17.02 \pm 0.03$. The intercept with the y axis gives $\beta_{560} = (1.56 \pm 0.15) \times 10^{-19}$ mol^2 dm^{-6} or log $\beta_{560} = -18.8 \pm 0.1$, in good agreement with the value determined previously (log $\beta_{560} = -18.84 \pm 0.04$).[22] The plot of log $K_{69}{}^*$ against log a is also linear with a slope of approximately 2 (1.9 ± 0.1), which indicates the predominance of species (6,9,2). From the intercept we obtain log $\beta_{692} = -29.7 \pm 0.2$.

Numerical Data Treatment.—Once the most probable (p,q,r) and β_{pqr} values had been obtained by graphical means, the three-component system was checked and refined by using the least-squares procedure LETAGROP–ETITR;[24] β_{pqr} is the equilibrium constant for the reaction $p\text{Be}^{2+} + q\text{H}_2\text{O} + r\text{CO}_2\text{(g)} \rightleftharpoons [\text{Be}_p(\text{OH})_q(\text{CO}_2)_r]^{(2p-q)+} + q\text{H}^+$. The whole set of e.m.f. data corresponding to the various titrations at constant B and three different partial pressures of CO_2 was treated simultaneously.

Table 1. Summary of the predominant (p,q) values and the conditional constants log $K_{pq}{}^*$ at different a values

	a/atm			
(p,q)	0.97	0.30	0.10	3σ
2,1	−3.20	−3.22	−3.19	±0.05
3,3	−8.45	−8.59	−8.62	±0.03
5,6	−17.02	−17.53	−17.92	±0.1
6,9	−29.60	−31.03	−31.50	±0.1

Table 2. A comparison between the stability constants obtained by graphical means and by the LETAGROP–ETITR calculations. Values are given as log $\beta_{pqr} \pm 3\sigma$

Species	Graphical	LETAGROP
$[Be_2(OH)]^{3+}$	−3.20 ± 0.05	−3.23 ± 0.05
$[Be_3(OH)_3]^{3+}$	−8.65 ± 0.03	−8.66 ± 0.01
$[Be_3(OH)_3(CO_2)]^{3+}$	−8.87 ± 0.03	−8.90 ± 0.02
$[Be_5(OH)_6]^{4+}$	−18.8 ± 0.1	−18.8 ± 0.1
$[Be_5(OH)_6(CO_2)]^{4+}$	−17.0 ± 0.1	−17.24 ± 0.04
$[Be_6(OH)_9(CO_2)_2]^{3+}$	−29.7 ± 0.1	−29.46 ± 0.06
$Be(OH)_2$		−11.0 ± 0.1
$Be(OH)_2(CO_2)$		−10.4 ± 0.1

Since the beryllium(II)-hydrolysis model had already been refined,[22] we first refined only the mixed species. Several alternative models were tried and compared with the one determined by the graphical treatment (see Table 1), without any significant improvement. We obtained a better agreement by adding the (1,2,0) and (1,2,1) species to this model, corresponding to $Be(OH)_2$ and $Be(OH)_2(CO_2)$. Finally, we also refined the (2,1,0) and (3,3,0) hydroxo species which predominate at low pH. We obtained the same result as in the previous work.[22]

Hence, we concluded that the e.m.f. data collected in the acidity range $2.0 \leqslant \log h \leqslant 6.2$ can best be explained by the set of complexes and stability constants summarized in Table 2. In Figure 2 we include a distribution diagram of the different $[Be_p(OH)_q(CO_2)_r]$ species as a function of pH, for $B = 20$ mmol dm^{-3} and $a = 0.97$ atm.

Raman Measurements.—The CO_2 group in complexes of the type $[Be_p(OH)_q(CO_2)_r]^{(2p-q)+}$ may be present as $HCO_3^- \equiv (HO)CO_2^-$ or $CO_3^{2-} \equiv (HO)_2CO_2^{2-}$.

The differences in the Raman spectra of bonded hydrogencarbonate and carbonate can be used to ascertain the mode of bonding of the CO_2 groups in the mixed complexes. A large amount of information is available on the i.r. and Raman spectra of carbonato complexes,[26,27] particularly in the solid state. The main difference in the vibrational spectra of complexes containing HCO_3^- and CO_3^{2-} appears in the symmetric C–O stretching vibrations. For hydrogencarbonato complexes a band occurs in the 1 350—1 400 cm^{-1} region. In the case of carbonato complexes the doubly degenerate asymmetric E vibration at 1 350—1 400 cm^{-1} is split by up to 100 cm^{-1} upon unidentate co-ordination. The splitting increases by up to 300 cm^{-1} or more for bridged or polydentate carbonate bonding. The symmetric polarized C–O stretch at about 1 060 cm^{-1} can also be used to distinguish carbonato from hydrogencarbonato complexes.

We recorded the Raman spectra of two 0.42 mol dm^{-3} $Be(ClO_4)_2$ solutions which contained relatively large amounts of

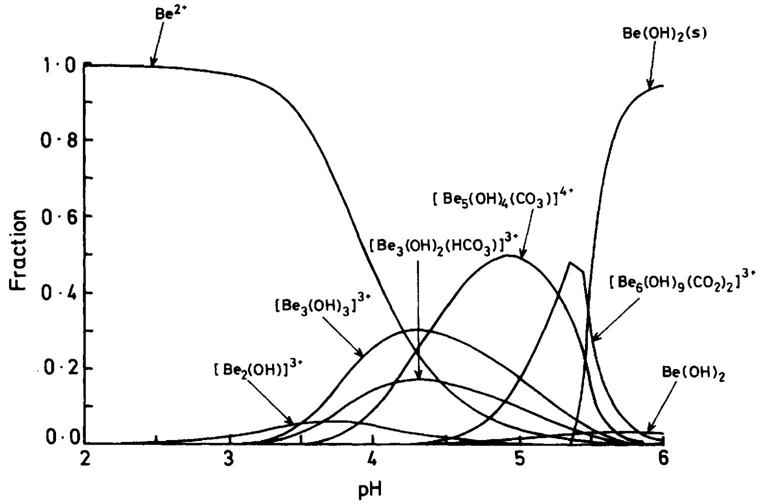


Figure 2. Distribution diagram for the species in the Be^{2+}–H_2O–$CO_2(g)$ system in the pH range investigated, calculated at $B = 20$ mmol dm^{-3} and $a = 0.97$ atm by using the SED program (I. Puigdomenech, Computer programs for drawing equilibrium diagrams, Report TRITA-OOK 3010, The Royal Institute of Technology, Stockholm, 1982)

Table 3. Raman bands of the carbonate and hydrogencarbonate groups in the region 950—1 500 cm^{-1}, in the solutions investigated (w = weak, m = medium, s = strong, br = broad, p = polarized)

Solution	Bands (cm^{-1})
1 (pH 4.59)	1 430mbr, 1 050m,p
2 (pH 3.59)	1 430w,br, 1 310m,br, 1 050m,p
0.1 mol dm^{-3} $NaHCO_3$	1 357m,br, 1 010s
0.1 mol dm^{-3} Na_2CO_3	1 068s

the predominant mixed species (3,3,1) and (5,6,1). Unfortunately, the (6,9,2) complex appears too close to the solubility limit of $Be(OH)_2(s)$ to be obtained in the high concentrations required for these kind of studies. We also recorded the spectra of solutions containing 0.1 mol dm^{-3} $NaHCO_3$ and 0.1 mol dm^{-3} Na_2CO_3, respectively. The Raman spectra were excited with a Coherent Innova 90-S argon-ion laser using the 514.5-nm line, and recorded with a DILOR RT130 triple monochromator using d.c. amplification at 4 cm^{-1} spectral bandwidth.

The beryllium solutions were equilibrated with $CO_2(g)$ at 0.97 atm. The pH at equilibrium (4.59 and 3.59 respectively) was measured by a combined glass electrode (Methrom EA121), previously calibrated in the same ionic medium. The composition of these solutions was calculated by using the set of equilibrium constants determined in this work, corrected for the change in ionic medium [3.0 mol dm^{-3} $NaClO_4$ to 0.42 mol dm^{-3} $Be(ClO_4)_2$], by applying the specific ion interaction (s.i.t.) method.[28] The set of interaction coefficients previously estimated for the hydroxo complexes (ref. 22 and references therein) was employed. We assumed the interaction coefficients of the mixed species to be related to the ones for the hydrolysis complexes in the following way: $\varepsilon[Be_3(OH)_3{}^{3+},ClO_4{}^-] = \varepsilon[Be_3(OH)_3(CO_2)^{3+},ClO_4{}^-] = 0.5$; $\varepsilon[Be_5(OH)_6{}^{4+},ClO_4{}^-] = \varepsilon[Be_5(OH)_6(CO_2)^{4+},ClO_4{}^-] = 0.8$; and $\varepsilon[Be_3(OH)_3{}^{3+},ClO_4{}^-] = \varepsilon[Be_6(OH)_9(CO_2)_2{}^{3+},ClO_4{}^-] = 0.5$. For a discussion of the dependence of the interaction coefficients on the charge and size of the complex ion the reader is referred to refs. 29 and 30.

In this way we found that almost all CO_2 in solution 1 occurred in the (5,6,1) complex, and that solution 2 contained comparable amounts of the (3,3,1) and (5,6,1) complexes, 45 and 55% respectively.

In Table 3 we have summarized the bands of interest in the Raman spectra. The most tangible difference between the Raman spectra of solutions 1 and 2 is the band at 1 310 cm^{-1} for solution 2. By comparison with the spectrum of a $NaHCO_3$ solution, this band is consistent with a symmetric C–O stretching of bonded $HCO_3{}^-$. Furthermore, Yoshida *et al.*[31] found a band in this range in the i.r. spectra of several rhodium bicarbonate complexes, for which crystal structure determinations showed that the bicarbonate group is terminal.

The band at 1 430 cm^{-1} found in the spectra of solutions 1 and 2 occurs in both unidentate bicarbonate and in polydentate carbonate complex.[26] That at 1 050 cm^{-1}, also present in the spectra of these two solutions, is assigned to the symmetric stretching of co-ordinated carbonate, slightly shifted towards lower frequencies as compared to the band at 1 068 cm^{-1} for free $CO_3{}^{2-}$ in aqueous solution. The spectrum of solution 1, in which the (5,6,1) complex dominates, then indicates that the bonded CO_2 is present as $CO_3{}^{2-}$, and consequently the formula of this complex should be written as $[Be_5(OH)_4(CO_3)]^{4+}$. Solution 2 contains in addition significant amounts of the (3,3,1) complex and the band at 1 310 cm^{-1}, which corresponds to unidentate $HCO_3{}^-$ suggests that the complex should be formulated as $[Be_3(OH)_2(HCO_3)]^{3+}$. Tentative structures of these two complexes are given in Figures 3 and 4.

Table 4. Some equilibrium constants, log K_{CO_2}, for the transition from a hydroxo to a mixed bicarbonate–carbonate complex at 25 °C in a 3.0 mol dm^{-3} perchlorate medium

Equilibrium	log K_{CO_2}	Ref.
$[Be_3(OH)_3]^{3+} + CO_2(g) \rightleftharpoons [Be_3(OH)_2(HCO_3)]^{3+}$	−0.25	This work
$[Be_5(OH)_6]^{4+} + CO_2(g) \rightleftharpoons [Be_5(OH)_4(CO_3)]^{4+}$	1.76	This work
$Be(OH)_2 + CO_2(g) \rightleftharpoons Be(OH)_2(CO_2)$	0.7	This work
$[(UO_2)_3(OH)_5]^+ + CO_2(g) \rightleftharpoons [(UO_2)_3O(OH)_2(HCO_3)]^+$	−0.20	17

Discussion

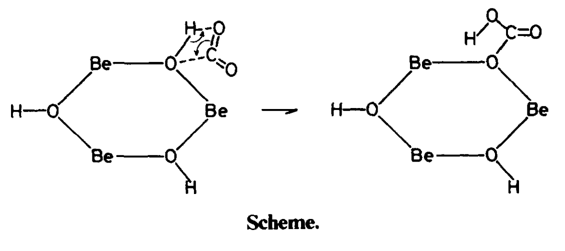
The predominant mixed complexes formed in the Be^{II}–H_2O–$CO_2(g)$ system in the acid to neutral pH range have the stoicheiometries $[Be_3(OH)_3(CO_2)]^{3+}$ and $[Be_5(OH)_6(CO_2)]^{4+}$, respectively, while the complexes $[Be_6(OH)_9(CO_2)_2]^{3+}$ and $Be(OH)_2(CO_2)$ are minor species. The most direct way to determine the chemical form of the bonded CO_2 ($HCO_3{}^-$ or $CO_3{}^{2-}$) is from spectroscopic information (Raman data in our case). However, it is well known that the binding constant of a multidentate ligand is strongly influenced by its co-ordination mode. Hence, the equilibrium constant of reactions of the type (5), where M is a metal ion and charges are omitted

$$M_p(OH)_q + CO_2(g) \rightleftharpoons M_p(OH)_q(CO_2) \qquad (5)$$

for simplicity, should indicate how the CO_2 group is bonded. Some data of this kind are given in Table 4.

The difference in log K_{CO_2} between $[Be_3(OH)_2(HCO_3)]^{3+}$ and $[Be_5(OH)_4(CO_3)]^{4+}$ is two logarithmic units, which suggests a difference in bonding of the CO_2 group between the two complexes. This is in agreement with the Raman data which indicate that $[Be_3(OH)_2(HCO_3)]^{3+}$ contains bonded bicarbonate, while $[Be_5(OH)_4(CO_3)]^{4+}$ contains bonded carbonate. The magnitude of log K_{CO_2} for $[(UO_2)_3O(OH)_2(HCO_3)]^+$ indicates a similar bonding to that in $[Be_3(OH)_2(HCO_3)]^{3+}$. The model for the structure of $[Be_3(OH)_2(HCO_3)]^{3+}$ is shown in Figure 3.

In a previous investigation[22] on the hydrolysis of Be^{II} the following stoicheiometries and structures of the predominant hydroxide complexes were proposed: $[Be_3(OH)_3]^{3+}$, $[Be_5(OH)_6]^{4+}$, and $[Be_6(OH)_8]^{4+}$. There seems to be a close relationship between these hydroxide complexes and the corresponding mixed hydroxo–carbonato complexes, indicating a possible pathway for reaction between the hydroxo complexes and $CO_2(aq)$ (the predominant form of free carbonate in the pH range investigated). This type of insertion reaction of CO_2 has been studied by Harris and co-workers[32] for other types of complexes. From their results, we propose that the transition from the hydroxide to the mixed complex (3,3,1) proceeds according to the Scheme.



Scheme.

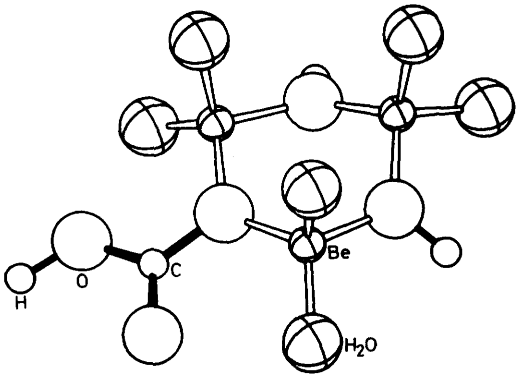


Figure 3. Proposed structure of the $[Be_3(OH)_2(HCO_3)]^{3+}$ complex

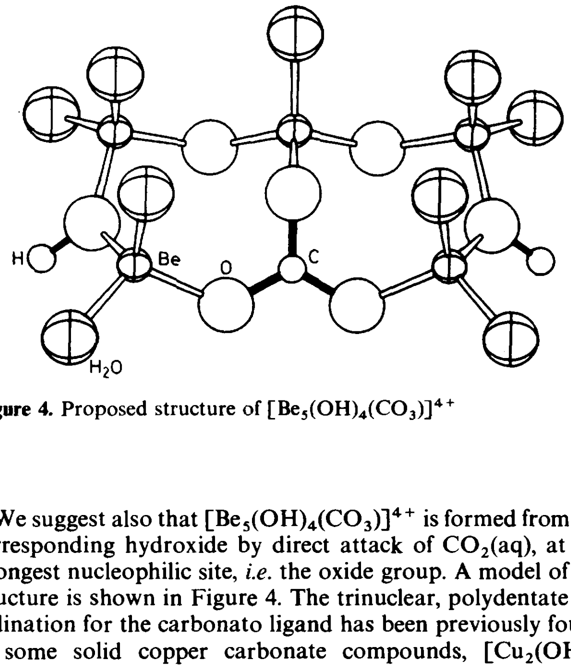


Figure 4. Proposed structure of $[Be_5(OH)_4(CO_3)]^{4+}$

We suggest also that $[Be_5(OH)_4(CO_3)]^{4+}$ is formed from the corresponding hydroxide by direct attack of $CO_2(aq)$, at the strongest nucleophilic site, *i.e.* the oxide group. A model of the structure is shown in Figure 4. The trinuclear, polydentate co-ordination for the carbonato ligand has been previously found in some solid copper carbonate compounds, $[Cu_2(OH)_2(CO_3)_2]^{2-}$ [33] and $Tl_2Cu(CO_3)_2$.[34]

In the case of the minor species (6,9,2) and (1,2,1) it is less straightforward to decide the mode of bonding of the CO_2 groups. For the (6,9,2) complex we have no additional information (log K_{CO_2} or spectroscopic data) which could give us an idea about the structure. No direct uptake of CO_2 in the form of carbonate is possible in $[Be_6O(OH)_6]^{4+}$, *cf.* Figure 6 of ref. 22, for geometrical reasons. Replacement of two H_2O in the co-ordination sphere of Be by a chelating CO_3^{2-} is geometrically possible, but obviously not energetically. The complex $[Be_6(OH)_9(CO_2)_2]^{3+}$ might have a structure similar to the one proposed previously for $[Be_6(OH)_9]^{3+}$,[22] where two of the OH^- groups bridging the $Be_3(OH)_3$ rings are replaced by HCO_3^- and/or CO_3^{2-}. For $Be(OH)_2(CO_2)$, log $K_{CO_2} = 0.7$. This complex appears at pH values (≥ 6) where carbonate rather than bicarbonate complexes are more likely to be formed and therefore we propose $BeCO_3$ as the most probable.

The same kind of comparisons can be made with the help of the information available on the Al^{III}–H_2O–$CO_2(g)$ system,[16] although the mixed complexes cannot be related to the hydroxo complexes by the insertion of a CO_2 molecule. However, the difference in magnitude between the constants for the transitions from the (2,2,0) to the (2,4,1) and from the (3,5,0) to the (3.6.1) species suggests differences in bonding. The large value (6.5) of log K for reaction (6) indicates that the carbonate ion is chelated, which is compatible with the structure proposed by Öhman and Forsling.[16] In the case of $[Al_3(OH)_5(CO_2)]^{4+}$

$$\underset{(2,4,0)}{[Al_2(OH)_2]^{4+}} + CO_3^{2-} \rightleftharpoons \underset{(2,4,1)}{[Al_2(OH)_2(CO_3)]^{2+}} \quad (6)$$

$$\underset{(3,4,0)}{[Al_3(OH)_4]^{5+}} + HCO_3^- \rightleftharpoons \underset{(3,5,1)}{[Al_3(OH)_4(HCO_3)]^{4+}} \quad (7)$$

the value of log K for the transition (7) is smaller (0.6) indicating the presence of bonded HCO_3^-, terminal or bridging.

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