Thermodynamic and Multinuclear NMR Study of Beryllium(II) Hydrolysis and Beryllium(II) Complex Formation with Oxalate, Malonate, and Succinate Anions in Aqueous Solution

Lucia Alderighi[a], Antonio Bianchi[a], Alfredo Mederos[b], Stefano Midollini[c], Agustin Rodriguez[b], and Alberto Vacca*[a]

Dipartimento di Chimica, Università degli Studi di Firenze[a],
Via Maragliano 77, I-50144 Firenze, Italy
Fax: (internat.) + 39-055/354845
E-mail: vacsab@chim1.unifi.it

Departamento de Química Inorgánica, Universidad de La Laguna[b],
E-38200 La Laguna, Tenerefe, Canary Islands
Fax: (internat.) +34-22/603634
E-mail: amederos@ull.es

I.S.S.E.C.C., Consiglio Nazionale delle Ricerche[c],
Via J. Nardi 39, I-50132 Firenze, Italy
Fax: (internat.) +39-055/2478366
E-mail: midolla@cacao.issecc.fi.cnr.it

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The hydrolysis of beryllium(II) and its complexation by oxalate, malonate, and succinate in 0.5 mol dm^{-3} $NaClO_4$ aqueous solution at 298 K has been studied by means of potentiometric (pH-metric), microcalorimetric, and multinuclear NMR-spectroscopic measurements. The protonation properties of the three ligands have also been investigated by potentiometry and microcalorimetry under the same experimental conditions. Thermodynamic results are consistent with a previously proposed chemical model for beryllium(II) hydrolysis, involving the species $[Be_2OH]^{3+}$, $[Be_3(OH)_3]^{3+}$, $[Be_5(OH)_6]^{4+}$, $[Be_6(OH)_8]^{4+}$, and $Be(OH)_2$. Complex formation of beryllium(II) with the dicarboxylate ligands is invariably promoted by favourable entropic contributions ($\Delta S° > 0$), while the enthalpic terms are always unfavourable ($\Delta H° > 0$). Malonate forms by far the most stable complexes owing to a more favourable (less endothermic) enthalpic contribution. These data reflect the fitting of the "bites" of the ligands with the stereochemically required tetrahedral coordination geometry about the metal ion, as well as the ligand preorganization.

Introduction

Beryllium is the most toxic non-radioactive element[1][2]. However, in spite of its particular toxicity, which to a large extent prevents the expansion of its applications, there is an increasing demand for beryllium, principally associated with the major use of this light metal in the nuclear, aerospace, and electronics industries[1][2][3]. The most notable biochemical effects resulting from beryllium contamination in mammalians include permanent cell modification, alteration of DNA replication, interference in enzymatic reactions, and impairment of cell division[1][2][3]. Nevertheless, there is not yet a clear rationalization of the relationships between beryllium toxicity and the chemical species formed in biological and environmental systems, principally because this depends very much on the particular tissue or cell type exposed to contamination, and because the actual speciation of the poisoned systems is still rather an obscure area.

The solution chemistry of Be^{2+} coordination compounds has been the subject of a limited number of studies, which have been included in two recent chemical databases[4]. The paucity of data is most likely attributable to the high toxicity exhibited by the metal ion and its complexes. In several cases, the results obtained appear to be inconsistent because of the different experimental conditions employed and, where considered, the disparate chemical models proposed for Be^{2+} hydrolysis[4].

Recently, some of us commenced a re-examination of Be^{2+} hydrolysis and Be^{2+} interaction with naturally occurring ligands by means of pH-metric measurements and NMR spectroscopy[5][6][7][8]. In one of these studies, which was concerned with the determination of equilibrium constants for the coordination of oxalate and malonate anions[8], a rational approach to the synthesis of beryllium complexes in water was also developed, leading to the isolation of crystalline $K_3[Be_3(OH)_3(oxalate)_3]\cdot 3\ H_2O$ and $K_3[Be_3(OH)_3(malonate)_3]\cdot 6\ H_2O$ and, furthermore, to the determination of the crystal structure of the latter compound.

In the present paper, we complete a first set of thermodynamic data for the coordination chemistry of beryllium

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ion with dicarboxylate ligands in aqueous solution, integrating the previously determined equilibrium constants for oxalate and malonate complexes[8] with new stability data for succinate and the enthalpy changes determined microcalorimetrically for the formation of beryllium complexes with the three ligands. Naturally, the hydrolysis of Be^{2+} and the protonation of the ligands have also been the subject of microcalorimetric investigations.

Results and Discussion

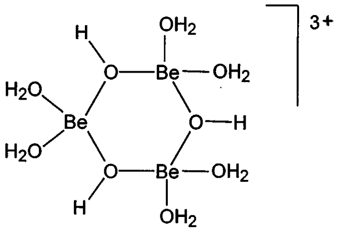
Be^{2+} Hydrolysis

The microcalorimetric determination of the complexation enthalpies of beryllium(II) in aqueous solution necessarily requires knowledge of the enthalpy changes associated with formation of the species produced upon Be^{2+} hydrolysis. Hence, the complexation experiments were preceded by a calorimetric study of beryllium(II) hydrolysis.

The $[Be(H_2O)_4]^{2+}$ cation exists only in very acidic solutions. In less acidic media, several polynuclear hydrolytic species are formed: in the most recent investigations (performed in 3.0 mol dm^{-3} $NaClO_4$[9] and in 0.5 mol dm^{-3} $NaClO_4$[6]) the species $[Be(OH)_2]$, $[Be_2OH]^{3+}$, $[Be_3(OH)_3]^{3+}$, $[Be_5(OH)_6]^{4+}$, and $[Be_6(OH)_8]^{4+}$ were identified, with the $[Be_3(OH)_3]^{3+}$ cation predominating over almost all of the pH range up to the precipitation of $Be(OH)_2$, which takes place at pH > 5. In solution, tetracoordination of Be^{2+} is preserved by coordinated water molecules, and tetrahedral arrangements are also to be expected for the species formed upon hydrolysis. Tentative structures for these polynuclear hydrolytic species have been suggested previously[9]; in particular, a cyclic structure for $[Be_3(OH)_3(H_2O)_6]^{3+}$, already indicated by a ^{1}H-NMR study[10], has been corroborated by a recent X-ray investigation[11]. The cyclic arrangement of this trimeric unit, where water molecules are replaced by bidentate ligands, has also been found in some crystalline complexes[8][12][13].

The equilibrium model and the values of the equilibrium constants for the hydrolysis of beryllium(II) were taken from a previous work[6]. The species formed in appreciable amounts in 0.5 mol dm^{-3} $NaClO_4$ solution at 298 K and the relevant thermodynamic data are listed in Table 1. In spite of various experimental modifications, it was not possible to obtain appreciable formation of the soluble species $[Be(OH)_2]$ in the microcalorimetric experiments. Therefore, the corresponding formation enthalpy was not determined.

Scheme 1



The enthalpy changes determined in the present study for $[Be_2OH]^{3+}$, $[Be_3(OH)_3]^{3+}$, and $[Be_6(OH)_8]^{4+}$ are in good agreement with those quoted in previous reports[14], while no reference values could be found in the literature for $[Be_5(OH)_6]^{4+}$ [4].

It is worthy to note that the formation of these species is promoted by both favourable enthalpic and entropic contributions. The thermodynamic data reported in Table 1 can be interpreted in terms of metal-to-OH^- bonding interactions and solvation/desolvation equilibria. The reaction between Be^{2+} and OH^--solvated ions gives rise to considerable charge neutralization, resulting in the release of water molecules from the interacting species. This desolvation process is accompanied by an entropy gain, due to the increasing number of species, and by an enthalpy loss, owing to the cleavage of $Be^{2+}-OH_2$ bonds. This entropy gain seems to be the main contribution to the favourable entropic terms observed in the formation of the hydrolytic species, while the favourable formation enthalpies are most likely attributable to contributions deriving from strong covalent bonding interactions between Be^{2+} and OH^- ions, which are only partly cancelled out by the desolvation enthalpy loss.

The balance of these opposing contributions leads to almost constant increments per OH^- group in the enthalpic and entropic terms ($-\Delta H° = 31 \pm 4$ kJ mol^{-1}, $\Delta S° = 97 \pm 10$ J K^{-1} mol^{-1}) for the formation of the hydrolytic species, which is reflected by the almost steady increase of the species stability ($-\Delta G°$) with the number of bonded OH^- groups (Figure 1).

Protonation of the Ligands

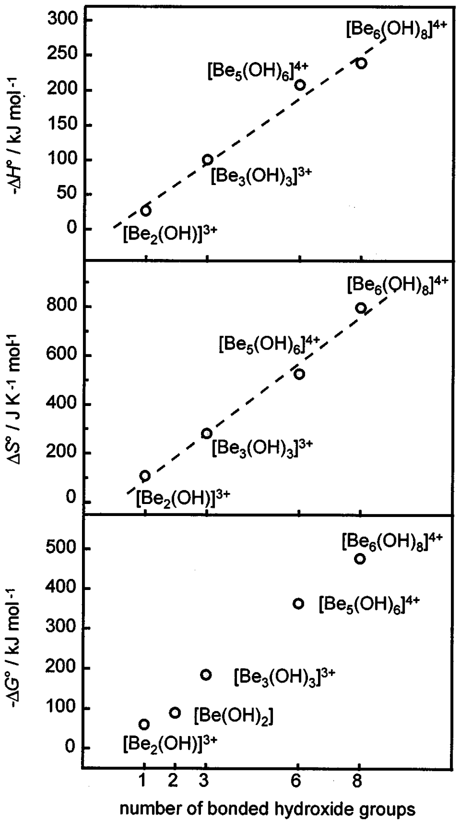
Table 2 reports the thermodynamic functions for the protonation of the three ligands investigated. There is a good

Table 1. Thermodynamic parameters for the formation of hydrolytic Be^{2+} species, determined in 0.50 mol dm^{-3} $NaClO_4$ at 298.1 ± 0.1 K[a]

reaction	log K[b]	$-\Delta G°$[b] [kJ mol^{-1}]	$-\Delta H°$ [kJ mol^{-1}]	$\Delta S°$ [J K^{-1} mol^{-1}]
$2\,Be^{2+} + OH^- \rightarrow [Be_2(OH)]^{3+}$	10.49(1)	59.87(8)	27(2)	111(7)
$3\,Be^{2+} + 3\,OH^- \rightarrow [Be_3(OH)_3]^{3+}$	32.39(3)	184.9(2)	100.8(4)	282(1)
$5\,Be^{2+} + 6\,OH^- \rightarrow [Be_5(OH)_6]^{4+}$	63.83(5)	364.3(3)	208(3)	523(10)
$6\,Be^{2+} + 8\,OH^- \rightarrow [Be_6(OH)_8]^{4+}$	83.75(5)	478.0(3)	239(2)	802(7)
$Be^{2+} + 2\,OH^- \rightarrow Be(OH)_2$	15.70(6)	89.6(3)	–	–

[a] Values in parentheses are standard deviations in the last significant figure. – [b] Values taken from ref.[6].

Figure 1. Thermodynamic functions for the formation of hydrolytic species as a function of the number of hydroxide groups bonded to Be^{2+}; the dashed lines are obtained by linear least-squares regression of the reported values, the correlation coefficients being > 0.99



general agreement with previously reported values[4], in spite of the rather different conditions of temperature and/or ionic strength used in the various investigations. The well-known increase in basicity observed in the series oxalate < malonate < succinate, as a consequence of the increasing length of the aliphatic chain, appears to be accompanied by a corresponding increase of the enthalpic contribution, while the entropic terms do not show any particularly evident trend.

Complex Formation

The thermodynamic parameters for the complexation of Be^{2+} by oxalate, malonate, and succinate are listed in Table 3.

In a previous paper, dealing with the determination of the stability constants of beryllium(II) complexes with oxalate and malonate[8] under the same experimental conditions as in the present study, it was noted that malonate complexes are significantly more stable than their oxalate counterparts. This enhanced stability can be ascribed to the formation of 6-membered chelate rings in the malonate complexes, which, compared to the 5-membered chelate rings formed by oxalate, produce less distortion in the preferred tetrahedral coordination geometry around the beryllium ion. As a matter of fact, in the molecular structures of the complexes $[Be(malonate)_2]^{2-}$[15], $[Be_3(OH)_3(malonate)_3]^{3-}$[8], $[Be(salicylate)_2]^{2-}$[16], and $[Be(acac)_2]$[17], which all feature 6-membered chelate rings, the O−Be−O bite angles imposed by the ligands range between 104.3(7) and 109.3(2)°, comparing well with the angles in an ideal tetrahedron (109.5°), while the corresponding bite angles in the 5-membered chelate rings formed by oxalate in the crystal structure of $[Be(oxalate)_2]^{2-}$ [99.6(2) and 99.7(2)°][18] deviate considerably from this value. More recently, it has been shown that the bite angles [109.1(1), 110(1)°] in the unique example of 7-membered chelate rings seen in the crystal structure of $[Be(\textit{o}\text{-phthalate})_2]^{2-}$ are also very similar to the ideal tetrahedral angle, with the Be−O distances falling within the range exhibited by related compounds, and the phthalate anion not showing any structural anomalies[19]. Furthermore, in an earlier paper, it was noted that phthalate and oxalate have comparable abilities in forming [BeL] and $[BeL_2]^{2-}$ complexes[20]. On the other hand, the complexes formed by Be^{2+} with succinate, which can in principle involve 7-membered chelate rings, are largely less stable than the corresponding species formed with malonate and oxalate (Table 3), although the difference in stability between the [BeL] complexes of oxalate and succinate is not as large as in the case of the $[BeL_2]$ and $[Be_3(OH)_3L]^+$ species. Probably as a result of this reduced stability, in the case of succinate the $[Be_3(OH)_3L_3]^{3-}$ (L = dicarboxylate ligand)

Table 2. Thermodynamic parameters for the protonation of oxalate, malonate, and succinate, determined in 0.50 mol dm^{-3} $NaClO_4$ at 298.1 ± 0.1 K[a]

reaction	log *K*	$-\Delta G°$ [kJ mol^{-1}]	$-\Delta H°$ [kJ mol^{-1}]	$\Delta S°$ [J K^{-1} mol^{-1}]
L = oxalate				
$L^{2-} + H^+ \rightarrow HL^-$	3.64(1)[b]	20.76(6)[b]	−4.7(1)	85.3(6)
$HL^- + H^+ \rightarrow H_2L$	1.00(1)[b]	5.7(6)[b]	−4.6(1)	35(7)
L = malonate				
$L^{2-} + H^+ \rightarrow HL^-$	5.054(2)[b]	28.84(1)[b]	−2.3(2)	104.5(6)
$HL^- + H^+ \rightarrow H_2L$	2.51(2)[b]	14.3(1)[b]	1.7(3)	42(2)
L = succinate				
$L^{2-} + H^+ \rightarrow HL^-$	5.041(3)	28.77(2)	1.5(8)	91(3)
$HL^- + H^+ \rightarrow H_2L$	3.908(3)	22.30(2)	6.2(8)	54(3)

[a] Values in parentheses are standard deviations in the last significant figure. − [b] Values taken from ref.[8].

Table 3. Thermodynamic parameters for the complexation of Be^{2+} by oxalate, malonate, and succinate anions, determined in 0.50 mol dm^{-3} $NaClO_4$ at 298.1 ± 0.1 K[a]

reaction	log K	$-\Delta G°$ [kJ mol^{-1}]	$-\Delta H°$ [kJ mol^{-1}]	$\Delta S°$ [J K^{-1} mol^{-1}]
L = oxalate				
$Be^{2+} + L^{2-} \rightarrow [BeL]$	3.47(2)[b]	19.8(1)[b]	−19.5(3)	132(1)
$[BeL] + L^{2-} \rightarrow [BeL_2]^{2-}$	1.77(7)[b]	10.1(4)[b]	−31(1)	138(3)
$Be^{2+} + 2L^{2-} \rightarrow [BeL_2]^{2-}$	5.24(7)[b]	29.9(4)[b]	−49(2)	263(6)
$[Be_3(OH)_3]^{3+} + L^{2-} \rightarrow [Be_3(OH)_3L]^+$	3.78(7)[b]	21.7(4)[b]	−10.9(8)	109(3)
$[Be_3(OH)_3]^{3+} + 3L^{2-} \rightarrow [Be_3(OH)_3L_3]^{3-}$	8.3(1)[b]	47.7(8)[b]	−28(1)	254(6)
L = malonate				
$Be^{2+} + L^{2-} \rightarrow [BeL]$	5.36(2)[b]	30.6(1)[b]	−10.53(6)	138.0(5)
$[BeL] + L^{2-} \rightarrow [BeL_2]^{2-}$	3.85(1)[b]	21.91(5)[b]	−5.19(8)	91.2(4)
$Be^{2+} + 2L^{2-} \rightarrow [BeL_2]^{2-}$	9.21(2)[b]	52.50(8)[b]	−15.82(8)	229.2(5)
$[Be_3(OH)_3]^{3+} + L^{2-} \rightarrow [Be_3(OH)_3L]^+$	5.26(7)[b]	30.1(4)[b]	−8.4(8)	129(3)
$[Be_3(OH)_3]^{3+} + 3L^{2-} \rightarrow [Be_3(OH)_3L_3]^{3-}$	12.84(6)[b]	73.3(3)[b]	−18.8(8)	309(3)
L = succinate				
$Be^{2+} + L^{2-} \rightarrow [BeL]$	3.04(1)	17.34(4)	−21.1(1)	129(5)
$[BeL] + L^{2-} \rightarrow [BeL_2]^{2-}$	1.0(2)	6(1)	−15(1)	69(5)
$Be^{2+} + 2L^{2-} \rightarrow [BeL_2]^{2-}$	4.1(2)	23.1(1)	−36(1)	198(5)
$[Be_3(OH)_3]^{3+} + L^{2-} \rightarrow [Be_3(OH)_3L]^+$	2.03(6)	11.6(3)	−42(1)	181(3)

[a] Values in parentheses are standard deviations in the last significant figure. − [b] Values taken from ref.[8].

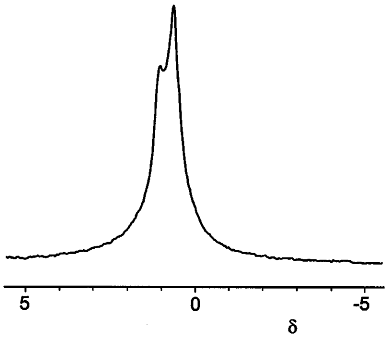
complex is not formed in appreciable amounts, at least under our experimental conditions, and its presence was not detected by means of the techniques employed in this study. Conversely, in a previous paper[21], the stability constant of this species was reported, together with that for the formation of the complex $[Be_3(OH)_3(HL)]^{2+}$ (L = succinate), containing the monoprotonated form of the ligand. In view of this report, we performed some experimental work aimed at identifying these two species in our systems, but no evidence of their formation was obtained.

Considering the low stability of the Be^{2+} complexes with succinate, a doubt arose concerning the possible monodentate coordination of the dicarboxylate anion. Nevertheless, this type of coordination should, in principle, favour the formation of complexes with the monoprotonated form of the ligand, although as mentioned above, such complexes were not detected in our experiments. In order to assess the ability of dicarboxylate ligands to bind Be^{2+} through a single carboxylate group, we also investigated the Be^{2+}/acetate system by both potentiometric and NMR techniques. The results indicated that, at least under our experimental conditions, the formation of acetate complexes is not appreciable. As a matter of fact, the ^{9}Be-NMR spectra of aqueous solutions of the system $BeSO_4/CH_3COOH$ (molar ratio 1:4) at various pH values fully resemble those of $BeSO_4$[22], indicating that acetate does not significantly coordinate the Be^{2+} ion.

On the basis of this evidence, it seems reasonable to assume that, in accordance with the behaviour of oxalate and malonate, succinate also acts as bidentate ligand towards Be^{2+}, and consequently its complexes can be formulated as $Be(succinate)(H_2O)_2$, $[Be(succinate)_2]^{2-}$, and $[Be_3(OH)_3(succinate)(H_2O)_4]^+$, where water molecules preserve the Be^{2+} tetrahedral coordination geometry.

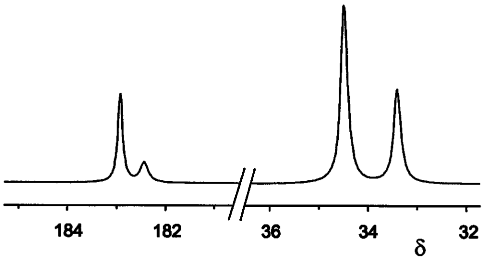
Evidence of a weak coordination of Be^{2+} by succinate comes from ^{9}Be-NMR spectra. Indeed, the ^{9}Be spectra of aqueous solutions containing $BeSO_4$ and succinic acid in a molar ratio of 1:2 in the pH range of 4−6, before the occurrence of $Be(OH)_2$ precipitation, show a signal at $\delta = 1.05$ overlapping the broad resonance due to $[Be_3(OH)_3(H_2O)_6]^{3+}$ at $\delta = 0.7$ (Figure 2). The new resonance must be attributed to a succinate−beryllium complex, probably the $[Be(succinate)(H_2O)_2]$ species. Accordingly, the corresponding $^{13}C\{^1H\}$ spectrum shows in both the CH_2 and COO regions a signal due to the uncoordinated ligand (these bands have been assigned by comparison with the spectra of free succinic acid under the same pH conditions) and a less intense resonance attributable to coordinated succinate (Figure 3).

Figure 2. $^9Be\{^1H\}$-NMR spectrum of an aqueous solution containing 0.2 mol dm^{-3} $BeSO_4$ and 0.4 mol dm^{-3} succinate at pH = 5.90



Therefore, assuming the bidentate coordination of succinate, in the absence of direct structural information on Be^{2+} derivatives with this ligand, it seems reasonable to assume that no special strain is accumulated in the 7-membered chelate rings of such complexes compared to the analogous chelate rings in $[Be(o\text{-phthalate})_2]^{2-}$. The principal reason for the lower stability of the succinate complexes might have its origins in the greater flexibility of this rather long ligand, which necessitates a considerable organization to achieve the coordinative conformation. Similar structural changes

Figure 3. $^{13}C\{^1H\}$-NMR spectrum of an aqueous solution containing 0.2 mol dm^{-3} $BeSO_4$ and 0.4 mol dm^{-3} succinate at pH = 5.90



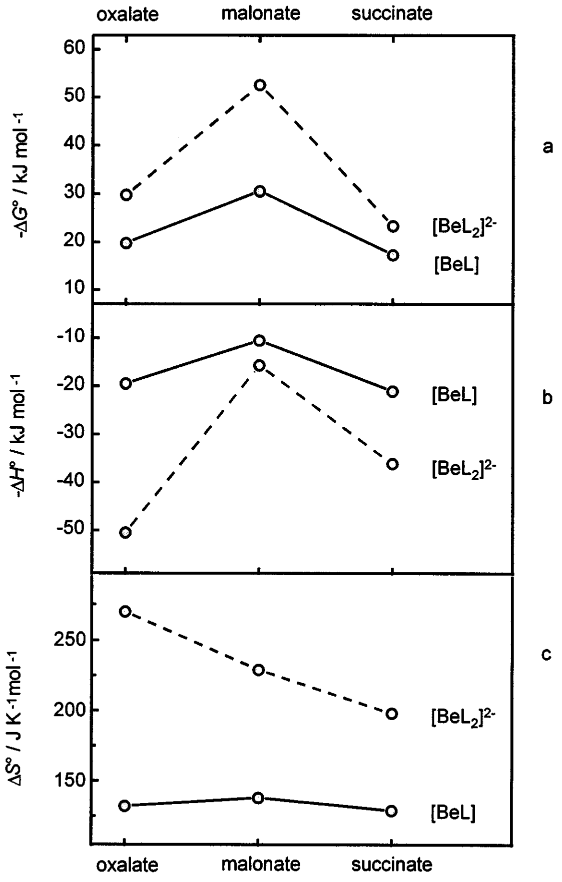
are not necessary for the rigid and preorganized *o*-phthalate ligand.

Considering the thermodynamic results reported here, different reasons can be advanced to account for the lower stability of beryllium complexes with oxalate and succinate compared to those with malonate: inadequate ligand-binding bite in the case of oxalate and considerable reorganization of ligand structure upon coordination of succinate.

As shown in Table 3, the stability of the Be^{2+} complexes with oxalate, malonate, and succinate is invariably determined by favourable entropic contributions, with the enthalpic terms always being unfavourable. This behaviour is typical of reactions between oppositely charged partners, in which charge neutralization and associated desolvation effects are of major importance. Nevertheless, energetic effects due to non-optimal matching between the stereochemical requirements of the ligand and metal ion and ligand conformational changes required for coordination also have to be taken into account. Considering the $-\Delta G°$ values obtained for [BeL] and $[BeL_2]^{2-}$, it appears that malonate forms by far the most stable complexes, as depicted in Figure 4a, as a consequence of the most favourable enthalpic contribution (less endothermic) shown in Figure 4b. The entropic contributions are very similar for the three [BeL] complexes, while in the case of $[BeL_2]^{2-}$ a greater $\Delta S°$ value favours the formation of the bis(oxalate) complex (Figure 4c).

It is noteworthy that the equilibrium constants for the binding of oxalate to Be^{2+} and $[Be_3(OH)_3]^{3+}$ are very similar, as is also the case for malonate. This is de facto due to a compensation between the enthalpic and entropic terms (Table 3), the reaction of these ligands with the trinuclear $[Be_3(OH)_3]^{3+}$ species being less endothermic than the analogous reaction with Be^{2+}. The presence of OH^- anions in $[Be_3(OH)_3]^{3+}$ produces a partial neutralization of charge on the metal ion, weakening the $Be-OH_2$ bonds, and hence the replacement of these coordinated water molecules by the ligands becomes less expensive from an enthalpic point of view. On the other hand, similar features are not operative in the succinate complexes, where a very unfavourable enthalpic contribution reduces the stability of the $[Be_3(OH)_3(succinate)]^+$ species, the formation of which is accompanied by the largest entropic gain for this type of reaction.

Figure 4. Plot of the thermodynamic functions $\Delta G°$ (a), $\Delta H°$ (b), and $\Delta S°$ (c) in relation to the cumulative formation of [BeL] and $[BeL_2]^{2-}$, where L = oxalate, malonate, and succinate



Since no anomalies are observed in the thermodynamic parameters for the formation of [BeL] (L = oxalate, malonate, succinate) complexes, it seems that the peculiar enthalpic and entropic terms for the formation of $[Be_3(OH)_3(succinate)]^+$ are not attributable to a special binding mode of succinate, but most likely to a loosening of the complex structure, which might originate from the hindrance brought about by the bulkier ligand, producing weakening of the binding interaction within the complex and increasing the disorder of its structure. As a matter of fact, we did not observe the addition of more than one dicarboxylate ligand in the case of succinate.

Conclusion

On the basis of the thermodynamic data obtained in this work concerning the solution chemistry of Be^{2+}, including metal ion hydrolysis and coordination equilibria with oxalate, malonate, and succinate ligands, the following points can be made:

1. Calorimetric data are consistent with a chemical model for Be^{2+} hydrolysis involving the species $[Be_2OH]^{3+}$, $[Be_3(OH)_3]^{3+}$, $[Be_5(OH)_6]^{4+}$, and $[Be_6(OH)_8]^{4+}$.

2. Considering a homogeneous series of chelating ligands containing the same binding groups, such as that constituted by oxalate, malonate, and succinate as investigated here, there is a distinct selectivity for the binding of Be^{2+} species by those ligands capable of forming 6-membered chelate rings.

3. Chelation of Be^{2+} ions is promoted by favourable entropic terms ($\Delta S^\circ > 0$), the unfavourable enthalpic contributions ($\Delta H^\circ > 0$) reflecting the fitting of ligand binding bites with the stereochemically required tetrahedral coordination geometry about the metal ion, as well as ligand preorganization.

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Experimental Section

Caution: In view of the extreme toxicity of beryllium compounds all experimental work was carried out in a well-ventilated fume cupboard used exclusively for this work. Established procedures for handling dangerous materials were followed rigorously at all stages of the preparations and measurements.

General Remarks: High-purity oxalic, malonic, and succinic acids were purchased from Merck. Be^{2+} stock solutions (0.02 mol dm^{-3}) were prepared by reacting metallic Be (Aldrich, 99.99% purity) with a slight excess of $HClO_4$. Be^{2+} and free acid concentrations were checked periodically by means of standard methods.

All potentiometric (pH-metric) measurements ($pH = -\log[H^+]$) used for the determination of ligand protonation and metal ion complexation constants were performed in 0.5 mol dm^{-3} $NaClO_4$ at 298.1 ± 0.1 K using the apparatus described previously[8]. The combined Ingold 405 S7/120 electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO_2-free NaOH solutions and determining the equivalent point by Gran's method[23]. This allows one to determine the standard potential E° and the ionic product of water [$pK_w = 13.69(1)$ at 298 K in 0.5 mol dm^{-3} $NaClO_4$]. In the complex formation experiments care was taken to verify the attainment of equilibrium after each titrant addition: a few minutes were necessary to reach constant emf readings. The potentiometric data were analysed using the computer program HYPERQUAD[24]. Experimental details of the potentiometric measurements are given in Table 4.

Table 4. Summary of experimental conditions for the beryllium−succinate system

Solution composition	
$[T_L]$ range [mol dm^{-3}]	0.003−0.010
$[T_M]$ range [mol dm^{-3}]	0.003−0.004
I [mol dm^{-3}], electrolyte	0.50, $NaClO_4$
pH range	3.0−6.0
Experimental method	pH titration, calibrated in concentration
T [°C]	25
Total number of data points	
Protonation	103 (2 titrations)
Beryllium complexation	387 (5 titrations)
Method of calculation	HYPERQUAD[24]
Protonation constants	
(ligand = H_2L, errors as σ)	
log β (HL)	5.041 ± 0.003
log β (H_2L)	8.950 ± 0.003
Stability constants	
log β ([BeL])	3.04 ± 0.01
log β ($[BeL_2]^{2-}$)	4.1 ± 0.2
log β ($[Be_3(OH)_3L]^+$)	−6.65 ± 0.06

The enthalpies of reaction were determined in 0.5 mol dm^{-3} $NaClO_4$ solution by means of an automated system consisting of a Thermometric AB thermal activity monitor (model 2277) equipped with perfusion-titration device and a Hamilton pump (model Microlab M) coupled with a 0.250-cm^3 gas-tight Hamilton syringe (model 1750 LT). The measuring vessel was housed in a 25-dm^3 thermostatted water bath, which was maintained at the chosen temperature within $\pm 2 \cdot 10^{-4}$ K. The microcalorimeter was checked by determining the enthalpy of reaction of strong base (NaOH) with strong acid (HCl) solutions. The value of −56.7(2) kJ mol^{-1} obtained was in agreement with literature values[4]. The protonation enthalpies of the ligands were determined as previously reported for other compounds[25]. In a typical complexation experiment, a solution containing the disodium salt of the ligand (0.08 mol dm^{-3}, ionic strength adjusted to 0.5 mol dm^{-3} by $NaClO_4$) was added in successive steps (15 μl) to acidic solutions of Be^{2+} (0.02 mol dm^{-3}, ionic strength adjusted to 0.50 mol dm^{-3} by $NaClO_4$, 1.5 cm^3) until a 1:1 metal-to-ligand molar ratio was reached. The complexation experiments were set up in such a way so as to produce a change of solution pH in the calculated range of ca. 3.7−5.0. Corrections for the heats of dilution were applied. At least three titrations (about 110 data points) were performed for each system. The corresponding enthalpies of reaction were determined from the calorimetric data by means of the AAAL program[26].

^{9}Be- and ^{13}C-NMR spectra were recorded with a Bruker AC 200 spectrometer at 28.18 MHz and 50.32 MHz, respectively. Chemical shifts are quoted with respect to external 0.10 mol dm^{-3} $BeSO_4$ in H_2O for ^{9}Be and external TMS for ^{13}C. All measurements were carried out in aqueous solutions, in the pH range of 2.3−6.0, using a coaxial inner tube containing D_2O to provide a lock signal.

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[1] D. N. Skilleter, *Chem. Br.* **1990**, *26*, 26−30.
[2] O. Kumberger, H. Schmidbaur, *Chem. Unserer Zeit* **1993**, *6*, 310−316.
[3] C. Y. Wong, J. D. Woollins, *Coord. Chem. Rev.* **1994**, *130*, 243−273 and references therein.
[4] K. J. Powell, L. D. Pettit, *IUPAC Stability Constants Database − SC-Database*, Academic Software, Otley (U.K.), **1997**. − R. M. Smith, A. E. Martell, *NIST Critically Selected Stability Constants of Metal Complexes Database*, Version 4.0, U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899 (U.S.A.), **1997**.
[5] E. Chinea, S. Dominguez, A. Mederos, F. Brito, J. M. Arrieta, A. Sánchez, G. Germain, *Inorg. Chem.* **1995**, *34*, 1579−1587.
[6] E. Chinea, S. Dominguez, A. Mederos, F. Brito, A. Sánchez, A. Ienco, A. Vacca, *Main Group Met. Chem.* **1997**, *20*, 11−17.
[7] A. Mederos, S. Dominguez, E. Chinea, F. Brito, S. Midollini, A. Vacca, *Bull. Soc. Chil. Quim.* **1997**, *42*, 281−295.
[8] P. Barbaro, F. Cecconi, C. A. Ghilardi, S. Midollini, A. Orlandini, L. Alderighi, D. Peters, A. Vacca, E. Chinea, A. Mederos, *Inorg. Chim. Acta* **1997**, *262*, 187−194.
[9] J. Bruno, *J. Chem. Soc., Dalton Trans.* **1987**, 2431−2437.
[10] J. W. Akitt, R. H. Duncan, *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 2212−2220.
[11] F. Cecconi, C. A. Ghilardi, S. Midollini, A. Orlandini, A. Mederos, *Inorg. Chem.* **1998**, *37*, 146−148.
[12] P. R. Faure, F. Bertin, H. Loiseleur, T. D. Germaine, *Acta Crystallogr.* **1974**, *B30*, 462−467.
[13] Y. Sohrin, M. Matsui, Y. Hata, H. Hasegawa, H. Kokusen, *Inorg. Chem.* **1994**, *33*, 4376−4383.
[14] B. Carell, A. Olin, *Acta Chem. Scand.* **1962**, *16*, 2357−2364. − R. E. Mesmer, C. F. Baes, *Inorg. Chem.* **1967**, *6*, 1951−1960.
[15] G. Duc, R. Faure, H. Loiseleur, *Acta Crystallogr.* **1978**, *B34*, 2115−2118.
[16] H. Schmidbaur, O. Kumberger, *Chem. Ber.* **1993**, *126*, 3−9.
[17] S. Onuma, S. Shibata, *Acta Crystallogr.* **1985**, *C41*, 1181−1183.
[18] M. Jaber, R. Faure, H. Loiseleur, *Acta Crystallogr.* **1978**, *B34*, 429−431.
[19] M. Schmidt, A. Bauer, H. Schmidbaur, *Inorg. Chem.* **1997**, *36*, 2040−2043.

[20] H. J. De Bruin, D. Kairaitis, R. B. Temple, *Aust. J. Chem.* **1962**, *15*, 457−466.
[21] G. Duc, F. Bertin, G. Thomas-David, *Bull. Soc. Chim. Fr.* **1977**, 645−648.
[22] S. Midollini, unpublished results.
[23] G. Gran, *Analyst* **1952**, *77*, 661−671.
[24] P. Gans, A. Sabatini, A. Vacca, *Talanta* **1996**, *43*, 1739−1753.
[25] A. Bianchi, B. Escuder, E. Garcia-España, S. V. Luis, V. Marcelino, J. F. Miravet, J. A. Ramírez, *J. Chem. Soc., Perkin Trans. 2* **1994**, 1253−1259. − R. Cini, G. Giorgi, D. Masi, A. Sabatini, A. Vacca, *J. Chem. Soc., Perkin Trans. 2* **1991**, 765−771.
[26] A. Vacca, *AAAL program*, University of Florence, **1996**.

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