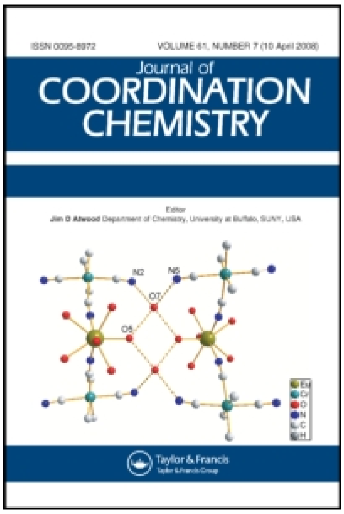


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Complexes of beryllium(II) with <i>N</i>-(2-Acetoamido) iminodiacetate and ligands containing a phosphonate group

Alfredo Mederos[a]; Felipe Brito[b]; Pedro Gili[a]; Sixto Domínguez[a]
[a] Facultad de Farmacia, Departamento de Química Inorgánica, Universidad de La Laguna (ULL), Tenerife, Canary Islands, Spain [b] Facultad de Ciencias, Centro de Equilibrios en Solución, Escuela de Química, Universidad Central de Venezuela (UCV), Caracas, Venezuela

To cite this Article Mederos, Alfredo , Brito, Felipe , Gili, Pedro and Domínguez, Sixto(2009) 'Complexes of beryllium(II) with <i>N</i>-(2-Acetoamido) iminodiacetate and ligands containing a phosphonate group', Journal of Coordination Chemistry, 62: 1, 3 — 13

To link to this Article: DOI: 10.1080/00958970802474854

URL: http://dx.doi.org/10.1080/00958970802474854

Journal of Coordination Chemistry
Vol. 62, No. 1, 10 January 2009, 3–13

Taylor & Francis
Taylor & Francis Group

Complexes of beryllium(II) with *N*-(2-Acetoamido) iminodiacetate and ligands containing a phosphonate group

ALFREDO MEDEROS†, FELIPE BRITO‡, PEDRO GILI† and
SIXTO DOMÍNGUEZ*†

†Facultad de Farmacia, Departamento de Química Inorgánica,
Universidad de La Laguna (ULL), Tenerife, Canary Islands, Spain
‡Facultad de Ciencias, Centro de Equilibrios en Solución, Escuela de Química,
Universidad Central de Venezuela (UCV), Caracas, Venezuela

(*Received 22 June 2008; in final form 20 August 2008*)

Complexes formed by beryllium(II) with *N*-(2-Acetoamido)iminodiacetic Acid (ADA, H_2L), Aminomethylphosphonic Acid (AMPA, H_2L), and (Phosphonomethyl)iminodiacetic Acid (MPDA, H_4L) were investigated in aqueous solution using potentiometric measurements. The protonation constants of the three ligands were determined at 298 K at ionic strength 0.5 M made up with $[(CH_3)_4N]Cl$. Five complexes of ADA–Be(II) were found: BeL, $[BeL_2]^{2-}$, $Be(HL)_2$, $[Be_2(OH)(HL)]^{2+}$ and $Be_3(OH)_3(HL)_3$. For the AMPA–Be(II) system we found eight species, the aforementioned, and also $[BeHL]^{+}$, $[Be(OH)_2L]^{2-}$ and $[Be_2(OH)(HL)_2]^{+}$. For the MPDA–Be(II) system we found six species: $[BeHL]^{-}$, $Be_2(OH)(HL)$, $[Be_2(OH)(H_2L)]^{+}$, $[Be_2(OH)(HL)_2]^{3-}$, $[Be_3(OH)_3(HL)_3]^{6-}$ and $Be_3(OH)_3(H_2L)_3$. The corresponding formation constants were determined at 25°C at ionic strength 0.5 M in $[(CH_3)_4N]Cl$. Theoretical calculations using density functional theory on the experimental species found in solution were carried out.

Keywords: Beryllium complexes; Phosphonate ligands; Stability constants; Theoretical calculations

1. Introduction

Beryllium and its compounds are extremely toxic. Because of its high stiffness to weight ratio, beryllium is increasingly being used in light weight metal alloys which are indispensable to today's nuclear, aerospace and electronic industries, and the effects on human health and the environment have been thoroughly evaluated [1, 2]. However, the biochemical mechanism of beryllium toxicity is not yet properly understood and largely speculative. Convincing experimental evidence is necessary since beryllium(II) [Be(II)] can affect the function of important proteins by forming a chelated complex with carboxylate, hydroxyl or amino groups in amino acids or hydroxyl amino acids. Different studies have been carried out in aqueous solutions between Be(II) and

---

*Corresponding author. Email: sdomingu@ull.es

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802474854

ligands containing functional groups such as OH, COOH, CO, NH_2, NHR and NR_2 as models for biochemical systems [3]. However, studies in aqueous solution concerning the interaction of Be(II) with molecules containing residues derived from phosphate groups, also relevant in the biochemical context, are relatively scarce [4]. For comparison purposes, this article deals with the interactions of the Be(II) ion with the ligands *N*-(2-Acetoamido)iminodiacetic Acid (ADA, H_2L) ($CONH_2$, COO^- and NR_3 groups), Aminomethylphosphonic Acid (AMPA, H_2L) (NH_2 and PO_3^{2-} groups), and (Phosphonomethyl)iminodiacetic Acid (MPDA, H_4L) (COO^-, PO_3^{2-} and NR_3 groups).

The potentiometric studies in aqueous solutions are complemented with theoretical calculations on the complex species found in solution for better understanding of their structures. Analogous theoretical calculations on hydrolysis complex species of Be(II) ion have been previously carried out [5].

2. Experimental

2.1. *Materials and methods*

Safety Note. *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. Any spillage of the beryllium solutions was washed out immediately. Established procedures for handling dangerous materials were followed rigorously in all phases of preparation and measurements.*

All common laboratory chemicals were of reagent grade, purchased from commercial sources and used without purification: $BeSO_4 \cdot 4H_2O$, ADA and MPDA, Aldrich; AMPA, $Me_4N(OH) \cdot 5H_2O$ and Me_4NCl, Sigma reagents. Carbon dioxide-free water was produced from deionized water which was distilled twice and stored under purified argon.

The potentiometric titrations were carried out using a DL50 Mettler Toledo titrator with a double junction combined glass electrode (Metler DG111) and LabX light titration software. The solutions (~22 mL) were thermostated at 298 K and paddle stirred. Solutions were freed of carbon dioxide by Ar bubbling. Standard HCl solution was prepared from Merck standard ampoules. The titrant solution [0.1 M solution of $Me_4N(OH)$] was prepared by dissolving $Me_4N(OH) \cdot 5H_2O$ and Me_4NCl and standardized with potassium biphthalate.

The cell constants E°, and the liquid junction potentials were determined according to the methods of Biedermann and Sillén [6] and Liberti and Light [7]. The experimental data were analyzed by the computer program HYPERQUAD [8] and species distribution diagrams were produced using HySS [9]. The fit of the values predicted by the model to the experimental data was estimated on the basis of the parameter σ, corresponding to the scaled sum of square differences between predicted and experimental values.

The protonation constants of ADA, AMPA and MPDA were determined through two potentiometric titrations (more than 70 experimental points each) at concentrations of 9 and 10 mM (to ADA), 5 and 10 mM (to AMPA), and 6 and 10 mM (to MPDA), covering pH values between 2 and 10.5. Similarly, hydrolysis constants of Be(II) under the conditions of the study were determined by four titrations of solutions containing only the cation. pH values between 2 and those causing precipitation of the corresponding hydroxide (~6.1 value), and concentrations between 1 and 9.5 mM, were covered.

The behavior of ADA in the presence of Be(II) was analyzed through at least three potentiometric titrations (more that 100 experimental points each) at metal concentrations ranging from 3.6 to 12 mM and ADA : Be(II) molar ratios 1 : 1 and 2 : 1, covering pH values between 2.1 and 6.0. For the AMPA–Be(II) system, five potentiometric titrations were analyzed at metal concentrations ranging from 2.7 to 9.2 mM, and AMPA : Be(II) molar ratios 1 : 1 and 2 : 1, covering pH values between 2.7 and 7.0. For the MPDA–Be(II) system, three potentiometric titrations were analyzed at metal concentrations ranging from 4.8 to 7.1 mM, and MPDA : Be(II) molar ratios 1 : 1, 2 : 1, and 1 : 2, covering pH values between 2.1 and 6.7.

2.2. *Electronic structure calculations*

Ground-state electronic structure calculations have been performed using the Density Functional Theory (DFT) method by employing the Gaussian 03 software package [10]. The hybrid density functional B3LYP was applied which consists of the nonlocal hybrid exchange functional as defined by Becke's three parameter equation and nonlocal Lee–Yang–Parr correlation functional [11]. For all calculations 6-31G(d, p), basis set was used [12]. The electronic ground-state was left to full geometry optimization without any symmetry constraint.

The density matrix in geometry optimization energy calculations was converged to a tight root mean square threshold of 10^{-8} a.u. The optimum structure with the minimum energy was verified by calculating the vibrational frequencies that result in the absence of imaginary eigenvalues.

The quantum chemical calculations have been performed on a Pentium 4 computer.

3. Results and discussion

3.1. *Hydrolysis of the Be(II) ion*

Because this work was carried out in aqueous solutions at 298 K and ionic strength $I = 0.5$ M in Me_4NCl, we studied the hydrolysis of Be(II) under these conditions by means of potentiometric measurements. The results are compared with those found at ionic strength $I = 0.5$ M in $NaClO_4$ [13] (table 1) and indicate similar hydrolytic species and values of the corresponding stability constants.

3.2. N-*(2-Acetoamido)iminodiacetic acid*

Substitution of an acetic group by a 2-acetoamide group in Nitrilotriacetic Acid (NTA) led to *N*-(2-Acetoamido)iminodiacetic ligand. The stepwise basicity constants for the various complexes are found in table 2. For comparison purposes the results for NTA are also included in table 2 (at 298 K and $I = 0.5$ M in $NaClO_4$) [14]. The decreased

Table 1. Equilibrium constants ($-\log \beta_{pq}$) for hydrolysis of Be(II), q $Be^{2+} + p$ $H_2O \leftrightarrow Be_q(OH)_p^{2q-p} + p$ H^+ ($T = 298$ K and $I = 0.5$ M in $[(CH_3)_4N]Cl$) refined with the aid of HYPERQUAD.[a]

Species (q, p)	(2, 1)	(3, 3)	(5, 6)	(6, 8)	(1, 2)	σ
$-\log \beta$	3.02 (2)	8.707 (5)	19.5 (1)	27.19 (7)	11.92 (5)	1.0
$-\log \beta^b$	3.20 (1)	8.68 (3)	18.31 (5)	25.77 (5)	11.68 (6)	

Notes: [a]Values in parentheses are SDs on the last significant figure.
[b]At 298 K and $I = 0.5$ M in $NaClO_4$ [13].

Table 2. Decimal logarithms of basicity constants ($T = 298$ K and $I = 0.5$ M in $[(CH_3)_4N]Cl$) refined with the aid of HYPERQUAD.[a]

	Ligand				
Reaction[b]	ADA (H_2L)	NTA (H_3L)[c]	AMPA (H_2L)	PHA (H_3L)[d]	MPDA (H_4L)
$L + H \leftrightarrow HL$	6.527 (4)	9.05 (1)	9.994 (3)	8.08 (1)	10.80 (1)
$HL + H \leftrightarrow H_2L$	2.07 (1)	2.38 (2)	5.496 (6)	4.80 (1)	5.68 (2)
$H_2L + H \leftrightarrow H_3L$	0.85 (4)	1.82 (5)	1.15 (1)	0.9 (1)	2.31 (2)
$H_3L + H \leftrightarrow H_4L$					1.70 (2)

Notes: [a]Values in parentheses are SDs on the last significant figure.
[b]The charges of the species have been omitted for simplicity.
[c]At 298 K and $I = 0.5$ M in $NaClO_4$ [14].
[d]At 298 K and $I = 0.5$ M in $NaClO_4$ [4b].

Table 3. Decimal logarithms of the Be(II) complex formation constants ($T = 298$ K and $I = 0.5$ M in Me_4NCl refined with the aid of HYPERQUAD[a].

	Ligand				
Reaction[b]	ADA (H_2L)	NTA[c] (H_3L)	AMPA (H_2L)	PHA[d] (H_3L)	MPDA (H_4L)
$Be + L \leftrightarrow BeL$	3.87 (1)	6.68 (3)	9.76 (5)	9.24 (1)	
$Be + HL \leftrightarrow [BeHL]$			4.45 (2)	4.53 (1)	4.65 (2)
$BeL + L \leftrightarrow [BeL_2]$	3.29 (3)		5.1 (1)	5.74 (2)	
$Be + 2HL \leftrightarrow [Be(HL)_2]$	7.16 (2)		8.17 (3)		
$Be(OH)_2 + L \leftrightarrow [Be(OH)_2L]$			7.14 (7)		
$Be_2(OH) + HL \leftrightarrow [Be_2(OH)(HL)]$	2.17 (6)		6.37 (5)		6.61 (3)
$Be_2(OH) + H_2L \leftrightarrow [Be_2(OH)(H_2L)]$					4.16 (5)
$Be_2(OH) + 2HL \leftrightarrow [Be_2(OH)(HL)_2]$			10.53 (7)		10.44 (5)
$Be_3(OH)_3 + 3HL \leftrightarrow [Be_3(OH)_3(HL)_3]$	6.4 (1)		7.2 (1)		12.37 (8)
$Be_3(OH)_3 + 3H_2L \leftrightarrow [Be_3(OH)_3(H_2L)_3]$					10.91 (6)

Notes: [a]Values in parentheses are SDs on the last significant figure.
[b]The charges of the species have been omitted for simplicity.
[c]At 298 K and $I = 0.5$ M in $NaClO_4$ [14].
[d]At 298 K and $I = 0.5$ M in $NaClO_4$ [4b].

basicity of the N atom in the NR_3 group in ADA is attributed to the electronic withdrawing effect of the 2-acetoamide group.

Analysis of the potentiometric data for experiments in which Be(II) was present was carried out taking into account both the ligand protonation constants and the stability constants for hydrolysis of Be^{2+}. The results are presented in table 3. Corresponding values for Be–NTA complexes [14] are also shown in table 3 for comparison. The lower

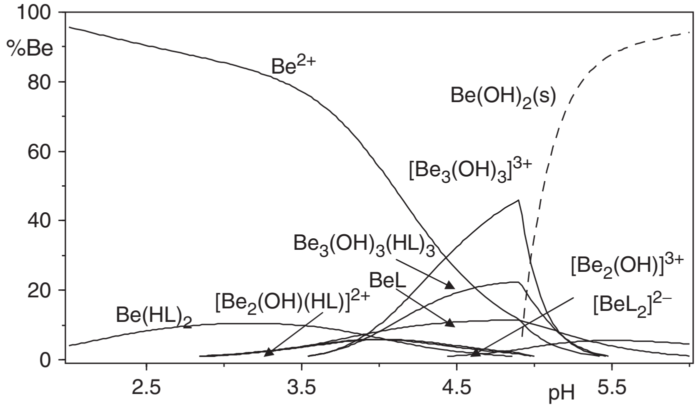
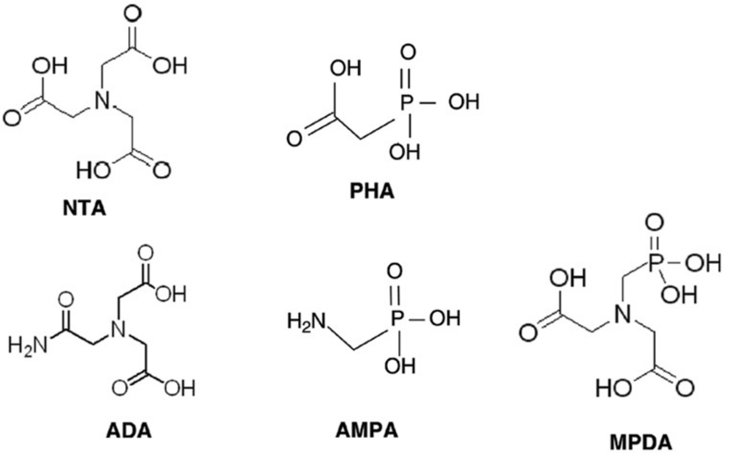


Figure 1. Distribution diagram of Be–ADA complexes as a function of pH for $C_L = C_{Be} = 10\,mM$.



Scheme 1. Structure of ligands.

basicity of N in NR$_3$ group in ADA ligand (table 2) led to lower stability constants of the BeL complex with ADA compared to NTA (table 3). Because the complexes of ADA with Be(II) are weak, a large proportion of the hydrolytic species are present (figure 1).

3.3. *Aminomethylphosphonic acid*

The stepwise basicity constants of AMPA are shown in table 1, in which for comparison purposes data are also included for Phosphonoacetic Acid (PHA) (scheme 1) [4b]. The values obtained for AMPA are in good agreement with the literature [15] at 25°C and $I = 0.1\,M$ in KNO$_3$. For PHA, the first proton is taken up preferentially by the phosphonate and the second proton by carboxylate [15]. Substitution of carboxylic group, COOH, in PHA by an amino group, NH$_2$, led to AMPA (scheme 1). As shown in table 1, first protonation of AMPA is more basic than in PHA. Therefore, it is reasonable to assume that the first proton is taken up preferentially by the more basic amino aliphatic group and the second by the phosphonate.

Analysis of the potentiometric data of the AMPA–Be(II) system was also carried out taking into account both the ligand protonation constants and stability constants of the hydrolytic species of Be(II) (table 3). Corresponding values for Be–PHA complexes [4b] are also shown in table 3 for comparison. Analysis of the data in table 3 for BeL, $[BeL_2]^{2-}$ and $[BeHL]^+$ indicate similar values of the stability constants for AMPA and PHA. It is possible that the slightly higher value for BeL in AMPA is related to the coordination of the N of the more basic amino aliphatic group to Be. Theoretical calculations in this work (vide infra) for the structure of the tetrahedral complex BeL with AMPA ligand suggest a tetrahedral Be(N, O, O, O) complex with Be–N (NH_2), Be–O ($OP(OH)_2$), B–O (OH) and BeO (OH_2), $Be(HL)(OH)(OH_2)$, with protonation of the PO_3H group. Similarly, for $[BeHL]^+$, the calculations also suggest tetrahedral Be(N, O, O, O) complex with a PO_3H_2 group.

The species distribution diagram (figure 2, molar ratio Be/L = 1/1, (a) $C_L = 1$ mM; (b) $C_L = 10$ mM), shows that the monomer complexes $[BeHL]^+$ (pH 3–5) and BeL (pH 5–7) are predominant at $C_L = 1$ mM, and when the concentration is increased (10 mM), the dimeric $[Be_2(OH)(HL)]^{2+}$ (pH 3–4) and $[Be_2(OH)(HL)_2]^+$ (pH 4–5.5) and the

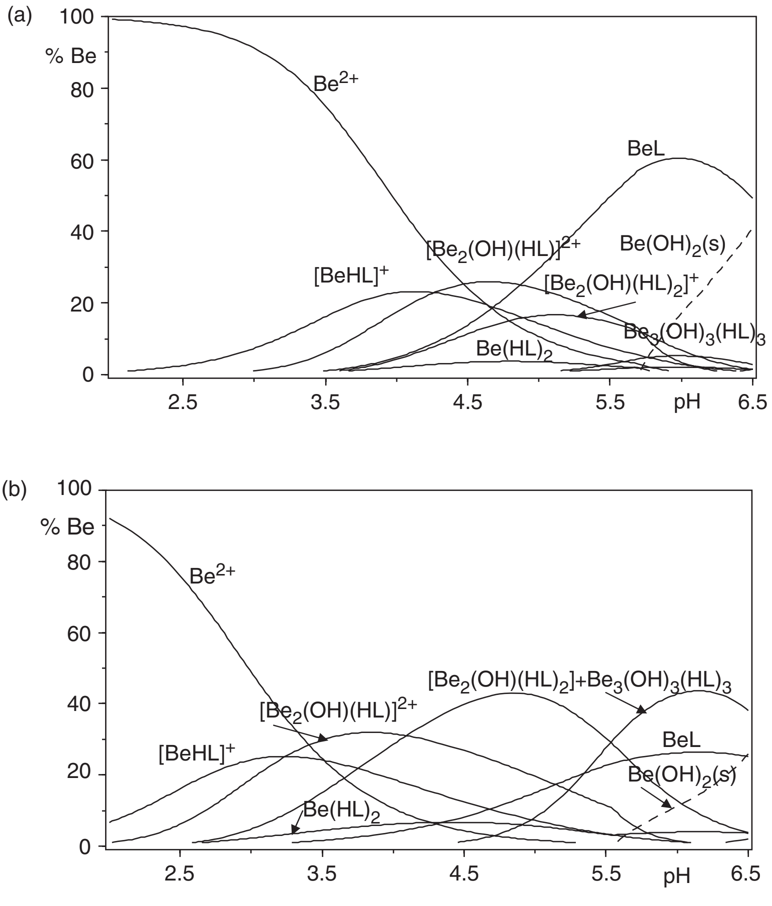


Figure 2. Distribution diagram of Be–AMPA complexes as a function of pH for (a) $C_L = C_{Be} = 1$ mM; (b) $C_L = C_{Be} = 10$ mM.

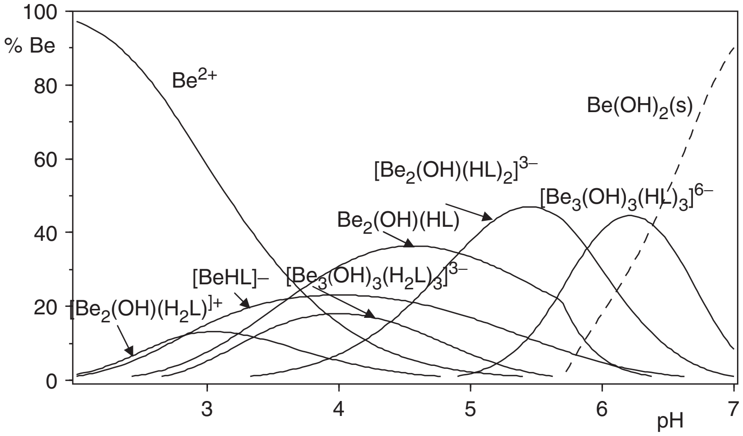


Figure 3. Distribution diagram of Be–MPDA complexes as a function of pH for $C_L = C_{Be} = 5\,mM$.

trimeric $[Be_3(OH)_3(HL)_3]$ (pH 5.5–6.5) complexes are dominant. AMPA is a good complexing agent for Be(II). However, Nitrilotripropionic and Nitriloaceticdipropionic acids are better sequestering agents for Be(II) [16].

3.4. N-*(Phosphonomethyl)iminodiacetic acid*

The stepwise basicity constants of MPDA are shown in table 1. The values obtained are in good agreement with the literature [17] at 25°C and $I = 0.1\,M$ in KNO_3. In AMPA substitution of two hydrogen atoms by two acetic groups, CH_2–COOH, led to MPDA (scheme 1). The first protonation in MPDA is more basic than for AMPA. Therefore, it is reasonable to assume that the first proton is taken up preferentially by the amino aliphatic group, more basic, and the second by the phosphonate.

The species distribution diagram (figure 3) shows that for molar ratio Be/L = 1/1 and $C_L = 5\,mM$ at pH 2–4, the dimeric complex $[Be_2(OH)(H_2L)]^+$ is dominant. In the pH range 3–5.5, the monomer $[BeHL]^-$, the trimer $[Be_3(OH)_3(H_2L)_3]^{3-}$, and dimer $Be_2(OH)(HL)$ are dominant. Dimeric $[Be_2(OH)(HL)_2]^{3-}$ and trimeric $[Be_3(OH)_3(HL)_3]^{6-}$ are dominant at pH 5–6, before precipitation of $Be(OH)_2$. $[BeL]^{2-}$ is not formed under the conditions, surely due to the low basicity of the ligand.

From the data of table 3 we can calculate formation of the trimeric species:

$$3[BeHL]^- + 3H_2O \rightleftharpoons [Be_3(OH)_3(H_2L)_3]^{3-} \quad \log K = 5.31(5).$$

Figure 3 ($C_L = C_{Be} = 5\,mM$) indicates that at pH 4 the percentage of $[BeHL]^-$ is 23% and the percentage of $[Be_3(OH)_3(H_2L)_3]^{3-}$ is 18%. If $C_L = C_{Be} = 10\,mM$, the percentages are 18 and 34%, respectively.

3.5. *Theoretical calculations*

In table 4 are given selected calculated structural parameters of the complexes studied in solution. For the system Be(II)–ADA, the obtained values for Be–O (carb) bond

Table 4. Calculated structural parameters of the complexes of Be(II) together with the energy values (a.u.).

Complex	Be–O(carb)[a]	Be–O(phos)[b]	Be–O(amide)[c]	Be–N(imine)[d]	Be–O (H_2O)[e]	Be–O(cycle)[f]	Central angles[g]	E
[Be(ADA)]	1.552, 1.556		1.703	1.863			93.9–127.7 (107.8)	−734.04
$[\mathrm{Be(HADA)}]^{+h}$	1.540, 1.622			1.867	1.720		90.6–148.5 (109.5)	−810.78
$[\mathrm{Be(ADA)_2}]^{2-}$	(1.600)			1.936			93.2–123.7 (108.8)	−1453.23
$[\mathrm{Be(HADA)_2}]$	1.562, 1612		1.671	1.895			94.2–116.2 (108.7)	−1454.40
$[\mathrm{Be_3(OH)_3(HADA)_3}]$	(1.611)		(1.810)			1.574–1.637 (1.593)	103.6–118.9 (109.2)	−2431.48
$[\mathrm{Be(AMPA)}]^{i}$		1.632		1.907	1.755, 1.490(OH)		99.5–129.1 (108.9)	−830.16
$[\mathrm{Be(HAMPA)}]^{+j}$		1.562		1.817	1.665, 1.664		101.8–115.5 (110.0)	−830.54
$[\mathrm{Be(HAMPA)_2}]$		1.571		1.826			100.6–125.8 (109.6)	−1340.89
$[\mathrm{Be_3(OH)_3(HAMPA)_3}]$		(1.605)		(1.811)		1.589–1.669 (1.627)	95.9,120.3 (109.4)	−2261.28
$[\mathrm{Be(HMPDA)}]^{-}$	1.653, 1.647	1.550		1.851			95.8–122.5 (112.3)	−1132.55
$[\mathrm{Be_2(OH)(HMPDA)_2}]^{3-k}$	1.599–1.644			1.865, 1.882	1.622, 1.652(OH)		91.5–142.7 (109.2)	−2340.76

Notes: [a] Oxygen atom of carboxylate group.
[b] Oxygen atom of phosphonate group.
[c] Oxygen atom of amide group.
[d] *N* atom of amine or imine group.
[e] Oxygen atom of water or OH bridge.
[f] Oxygen atom in cycle $\mathrm{Be_3(OH)_3}$.
[g] Central angle XBeY (X and Y are O or N atoms).
[h] This complex is really $[\mathrm{Be(HADA)(H_2O)}]^{+}$.
[i] This complex is really $[\mathrm{Be(OH)(HAMPA)(H_2O)}]$.
[j] This complex is really $[\mathrm{Be(OH)(H_2AMPA)(H_2O)}]$.
[k] This complex is really $[\mathrm{Be_2(OH)(HMPDA)_2(H_2O)}]^{3-}$.
Bond distances and angles in Å and degrees, respectively (mean values in parentheses).

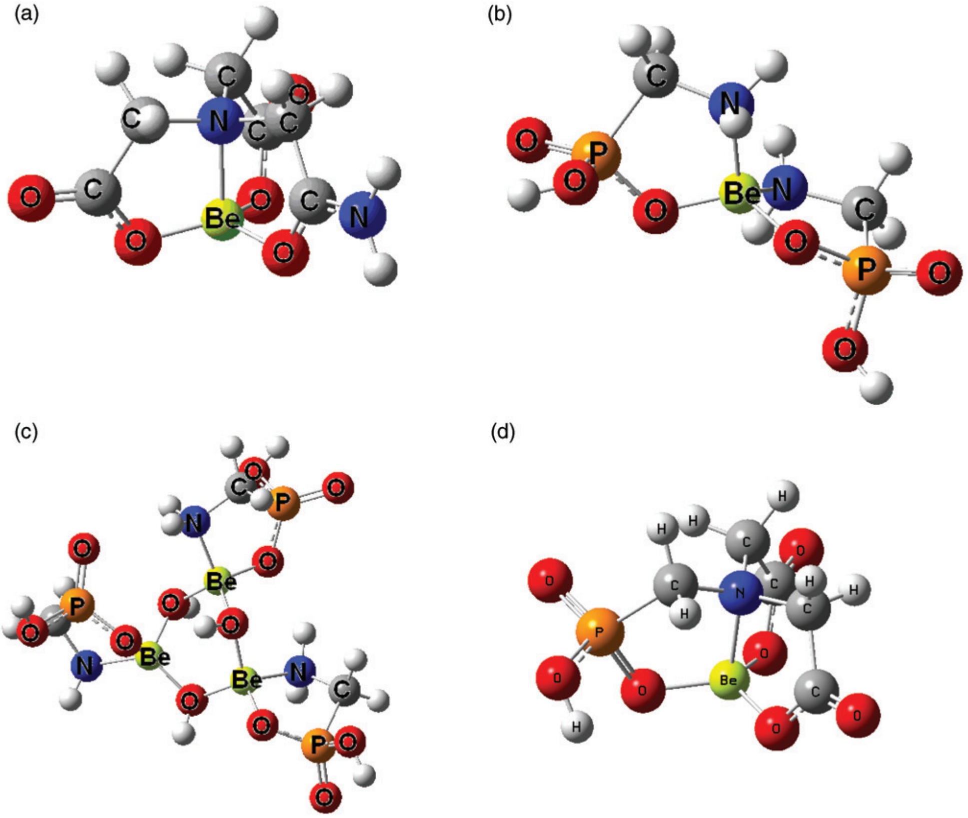


Figure 4. Optimized structures computed at the B3LYP/6-31G(d, p) level of theory. (a) [Be(ADA)]; (b) [Be(HAMPA)$_2$]; (c) [Be$_3$(OH)$_3$(HAMPA)$_3$] and (d) [Be(HMPDA)]$^-$.

distances are in excellent accord with the experimental values for Na[Be(NTP)] · 3H$_2$O [16], with the exception of [Be(ADA)$_2$]$^{2-}$, where the calculated values are higher than the experimental values. Moreover, for [Be(HADA)$_2$] species containing a proton, the calculated Be–O bond distances also are in agreement with the experimental values. This last species also has a lower energy than [Be(ADA)$_2$]$^{2-}$ (col. 9). On the other hand, the calculated Be–N bond distances are slighter larger than the experimental values. With respect to the central angle of beryllium (O–Be–N, O–Be–O), they are of the same order (average values) as the calculated values.

In [Be$_3$(OH)$_3$(HADA)$_3$], the calculated Be–O (cycle) bond distances (col. 7) are in accord with experimental values for [Be$_3$(OH)$_3$(H$_2$O)$_6$] (picrate)$_3$ · 6H$_2$O [18]. Also, the central angles of beryllium (col. 8) are in agreement with the experimental values [18]. Both calculated and experimental Be–O (H$_2$O) distances (col. 6) are longer than the Be–O (carb) and Be–O (phos) bond distances, indicating a weaker Be–O(H$_2$O) bond than Be–O(carb) and Be–O(phos), probably due to less covalent contribution.

For the system Be(II)–AMPA, no significant effects of the influence of phosphorus are observed on the Be–O bond distances. The Be–O(phos) bond distances are similar to those determined experimentally in bis(tetraphenylimidodiphosphinato)beryllium [19]. [Be(HAMPA)]$^+$ is highly symmetric and its stability constants are larger than those of the corresponding [Be(HADA)]$^+$.

Table 5. Mulliken charges obtained from population analysis (mean values in parentheses).

Complex	Be	O(carb)[a]	O(cycle)[a,b]	$O(H_2O)$[a]	O(amide)[a]	O(P)[a,c]	N[a]	P
[Be(ADA)]	0.459	(−0.426)			−0.418		−0.476	
$[Be(HADA)]^+$	0.541	(−0.450)		−0.510			−0.495	
$[Be(ADA)_2]^{2-}$	0.516	(−0.469)					−0.443	
$[Be(HADA)_2]$	0.645	(−0.508)			−0.453		−0.510	
$[Be_3(OH)_3(ADA)_3]^{3-}$	0.484	(−0.504)	−0.563					
	0.508	(−0.481)	−0.498					
	0.538	(−0.473)	−0.489					
[Be(AMPA)]	0.414	(−0.586)		−0.546			−0.610	1.148
$[Be(HAMPA)]^+$	0.524			(−0.517)			−0.622	1.196
$[Be(HAMPA)_2]$[d]	0.467					−0.539	−0.599	1.110
$[Be_3(OH)_3(HAMPA)_3]$	0.486		−0.556			−0.611	−0.597	1.117
	0.529		−0.550			−0.545	−0.634	1.099
	0.575		−0.564			−0.610	−0.587	1.104
$[Be(HMPDA)]^-$	0.470	(−0.455)				−0.589	−0.484	1.103
$[Be_2(OH)(HMPA)_2]^{3-}$	0.550	(−0.490)	−0.540[e]				−0.476	0.989
	0.483	(−0.473)					−0.487	0.998

Notes: [a] Atoms coordinated to beryllium.
[b] O (cycle) indicates bridge OH of the cycle.
[c] O(P) indicates O atom bond to P atom.
[d] This molecule is symmetrical.
[e] O of bridge in Be(OH)Be.

Figure 4 shows the optimized structures computed at the B3LYP/6-31G(d, p) level of theory: (a) [Be(ADA)]; (b) $[Be(HAMPA)_2]$; (c) $[Be_3(OH)_3(HAMPA)_3]$ and (d) $[Be(HMPDA)]^-$.

The Mulliken charges (table 5) show that the trinuclear species are asymmetric and every Be has a different positive charge. In contrast, $Be(HAMPA)_2$ is symmetric as indicated by the same values for the atomic charges of O, N, and P atoms, in addition to the same values for Be–O, Be–N, and Be–P bond distances. Complexes containing ligands with P atoms have N atoms with negative charges.

Acknowledgements

One of us (F. Brito) wishes to thank the Council of Scientific and Humanistic Development (CDCH, UCV) for financial support (Grant No. A 03-007111-2008), and the Presidency of the Government of the Canary Islands (Spain) for an invitation to the Canary Islands Awards Ceremony (30-05-2008), which, together with a research fellowship from CDCH (UCV), led to his visit to the Department of Inorganic Chemistry (ULL) in June 2008, under the Master Agreement of Scientific and Academic Collaboration between both universities.

References

[1] S. Fields. *Health Perspect.*, **109**, A474 (2001).
[2] D.N. Skilleter. *Chem. Br.*, **26**, 26 (1990).

[3] (a) A. Mederos, S. Domínguez, E. Chinea, F. Brito, S. Midollini, A. Vacca. *Bol. Soc. Chil. Quim.*, **42**, 281 (1997); (b) L. Anderighi, P. Gans, S. Midollini, A. Vacca. *Adv. Inorg. Chem.*, **50**, 109 (2000); (c) H. Schmidbaur. *Coord. Chem. Rev.*, **215**, 223 (2001); (d) A. Mederos, S. Domínguez, E. Chinea, F. Brito, F. Cecconi. *J. Coord. Chem.*, **53**, 191 (2001); (e) F. Cecconi, C.A. Ghilardi, A. Ienco, P. Mariani, C. Mealli, S. Midollini, A. Orlandini, A. Vacca. *Inorg. Chem.*, **41**, 4006 (2002).

[4] (a) A. Valle, E. Chinea, S. Domínguez, A. Mederos, S. Midollini, A. Vacca. *Polyhedron*, **18**, 3253 (1999); (b) L. Alderighi, A. Vacca, F. Cecconi, S. Midollini, E. Chinea, S. Domínguez, A. Valle, D. Dakternieks, A. Duthie. *Inorg. Chim. Acta*, **285**, 39 (1999); (c) L. Ciavatta, M. Luliano, R. Porto, P. Innocenti, A. Vacca. *Polyhedron*, **19**, 1043 (2000); (d) F. Cecconi, C.A. Ghilardi, S. Midollini, A. Orlandini. *Inorg. Chem. Commun.*, **3**, 350 (2000); (e) P. Barbaro, F. Cecconi, F. Dakternieks, S. Domínguez, A. Duthie, C.A. Ghilardi, S. Midollini, A. Orlandini, A. Vacca. *Inorg. Chem.*, **40**, 2725 (2001); (f) F. Cecconi, S. Domínguez, N. Masciocchi, S. Midollini, A. Sironi, A. Vacca. *Inorg. Chem.*, **42**, 2350 (2003).

[5] R. Martínez, F. Brito, M.L. Araujo, F. Ruette, A. Sierraalta. *Int. J. Quant. Chem.*, **97**, 854 (2004).

[6] G. Biedermann, L.G. Sillén. *Ark. Kemi*, **5**, 425 (1953).

[7] A. Liberti, I.S. Light. *J. Chem. Educ.*, **39**, 236 (1962).

[8] P. Gans, A. Sabatini, A. Vacca. *Talanta*, **43**, 1739 (1996).

[9] L. Alderighi, P. Gans, A. Ienco, D. Peters, A. Sabatini, A. Vacca. *Coord. Chem. Rev.*, **184**, 311 (1999).

[10] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Gaussian 03, Revision B.04*, Gaussian, Inc., Pittsburgh PA (2003).

[11] (a) A.D. Becke. *J. Chem. Phys.*, **98**, 5648 (1993); (b) C. Lee, W. Yang, R.G. Parr. *Phys. Rev.*, **B37**, 785 (1988).

[12] G.A. Petersson, A. Bennett, T.G. Tensfeldt, M.A. Al-Laham, W.A. Shirley, J. Mantzaris. *J. Chem. Phys.*, **89**, 2193 (1988).

[13] E. Chinea, S. Domínguez, A. Mederos, F. Brito, A. Sánchez, A. Ienco, A. Vacca. *Main Group Met. Chem.*, **20**, 11 (1997).

[14] A. Mederos, S. Domínguez, A.M. Medina, F. Brito, E. Chinea, K. Bazdikian. *Polyhedron*, **6**, 1365 (1987).

[15] M. Wozniak, G. Nowogrocki. *Talanta*, **26**, 1131 (1979).

[16] E. Chinea, S. Domínguez, A. Mederos, F. Brito, J.M. Arrieta, A. Sánchez, G. Germain. *Inorg. Chem.*, **34**, 1579 (1995).

[17] K. Sawada, W. Duan, M. Ono, K. Satoh. *J. Chem. Soc., Dalton Trans.*, 919 (2000).

[18] F. Cecconi, C.A. Ghilardi, M. Midollini, A. Orlandini, A. Mederos. *Inorg. Chem.*, **37**, 146 (1998).

[19] I. Haiduc, J. Zukerman-Schpector, E. Castellano, R. Cea-Olivares. *Heteroatom Chem.*, **11**, 244 (2000).