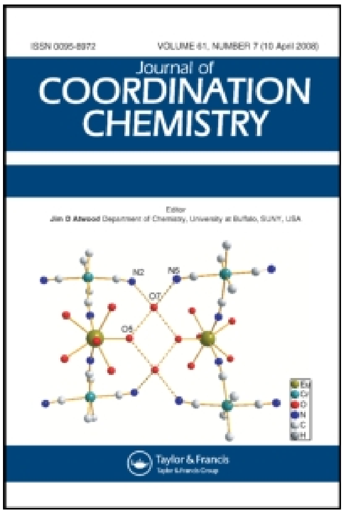

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Beryllium binding to adenosine 5′-phosphates in aqueous solution at 25°C**

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Equilibrium constants for the binding of beryllium(II) to the nucleotides: adenosine 5′–monophosphate, -diphosphate, and -triphosphate have been determined. The species formed are $[BeL]^{(z-2)-}$, $[Be(HL)]^{(z-3)-}$, $[Be_2(OH)L_2]^{(2z-3)-}$ and $[Be_3(OH)_3(HL)_3]^{(3z-6)-}$, where L^{z-} represents the fully deprotonated nucleotide. When the complex contains a protonated ligand, the protonation site is an adenosine nitrogen. Formation of these complexes is unlikely to interfere, under physiological conditions, with the functioning of the nucleotides due to the precipitation of beryllium hydroxide in the pH range 6–7.

Keywords: Beryllium; Nucleotides; Formation constants

1. Introduction

Beryllium metal is both light and strong and these properties make it the metal of choice in weight-limited applications. The metal and its oxide and other compounds are used extensively in the nuclear, aerospace and electronic industries. However, the metal and the compounds are potentially extremely toxic as exposure to airborne particles containing them can cause Chronic Beryllium Disease (CBD) [1–3].

The chemistry of aqueous solutions of beryllium(II) has been studied intensively and three reviews on this topic have been published recently [4–6]. Phosphates of adenosine are essential components in the storage, use and release of energy and most reactions involving them are either promoted or inhibited by metal ions. The ability of Be^{2+}(aq) to bind to ligands of biological interest has been studied extensively in recent years. For example, it was found that the so-called *beryllofluorides* form adducts with the

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**Dedicated to Professor Alfredo Mederos on the occasion of his retirement

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polyphosphate part of nucleotides and have a large effect on the action of important enzymes [7–9].

The magnesium ion, Mg^{2+}(aq), forms complexes such as $[Mg(ATP)]^{2-}$ and $[Mg(ADP)]^{-}$ which play a fundamental role in numerous biological processes. Since beryllium is in the same group of the periodic table as magnesium, it is expected that Be^{2+}(aq) might compete with the magnesium ion and thus affect both the speed of reactions and their quantitative outcome. The published data on complexes of nucleotides with beryllium is unsatisfactory [10–12]. We have therefore undertaken a painstaking re-investigation of the species formed by beryllium(II) and the three nucleotides: adenosine 5′-monophosphate (AMP), -diphosphate, (ADP), and -triphosphate (ATP), and the stability constants of the complexes formed. Knowledge of these stability constants is essential for understanding of many reactions in biological systems.

2. Experimental

2.1. *Materials*

Adenosine triphosphate disodium salt hydrate (>98%), ADP potassium salt dihydrate (>99%) and AMP disodium salt monohydrate (>99%) were obtained by Fluka and used without further purification. Carbon dioxide-free water was produced from deionized water which was twice distilled in a quartz apparatus and stored under purified nitrogen. An aqueous beryllium(II) stock solution was prepared and standardized as previously described [13].

2.2. *Potentiometric measurements*

Potentiometric titrations were carried out at 298 K at $0.50\,mol\,dm^{-3}$ ionic strength (made up with $NaClO_4$). The apparatus and the experimental technique have been described previously [13]. The electrodes were calibrated in terms of hydrogen ion concentration $[H_3O^+]$ and the decimal log value of K_w $(=[H_3O^+][OH^-])$ was found to be -13.69 ± 0.01. Experimental details are summarized in table 1. Stability constants were determined with the use of HYPERQUAD [14].

Table 1. Summary of experimental conditions for beryllium(II)–AMP, beryllium(II)–ADP, and beryllium(II)–ATP[a].

	AMP	ADP	ATP
Solution composition			
Total ligand concentration range/mmol dm^{-3}	2.0–4.5	1.5–2.8	1.0–2.6
Total metal concentration range/mmol dm^{-3}	1.6–3.7	0.9–3.1	1.0–3.5
pH range	2.4–6.3	2.2–7.3	2.2–5.7
Total number of data points			
Protonation	56 (2 titrations)	96 (2 titrations)	84 (2 titrations)
Beryllium complexation	342 (7 titrations)	428 (7 titrations)	425 (10 titrations)

Notes: [a]Experimental method: potentiometric; temperature: 25°C; ionic strength: $0.5\,mol\,dm^{-3}$ $NaClO_4$; method of calculation: HYPERQUAD [14].

2.3. *NMR measurements*

The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded by a Bruker AC-200 spectrometer operating at 200.130, 81.018, and 28.18 MHz and referenced to internal TMS and external 85% H_3PO_4, respectively. Downfield values of the chemical shifts are reported as positive. NMR measurements were carried out in aqueous solutions using coaxial 5 mm tubes, the inner one containing D_2O to provide a lock signal. pH values were measured using an Orion Research, model 601I apparatus, equipped with a combined glass–Ag/AgCl microelectrode (Ingold). Be^{2+} and nucleotide concentrations were varied from 50 to 150 mmol dm^{-3}.

2.4. *Electrospray mass spectra*

Electrospray mass spectra (ESMS) were obtained with a Platform II single quadruple mass spectrometer (Micromass, Altrincham. UK) using a water: acetonitrile (1 : 1) mobile phase. The spectra of aqueous solutions of 0.1 M beryllium sulphate and 0.2 M ATP disodium salt or ADP disodium salt were recorded as previously described [15].

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

3. Calculations

3.1. *Definition of the model and equilibrium constants*

Reaction (1) defines the stoichiometry of an equilibrium for binding of Be^{2+} to the nucleotide anions ATP^{4-}, ADP^{3-}, and AMP^{2-} in terms of the stoichiometric coefficients p, q and r and the charge z- on the fully deprotonated ligand.

$$p\mathrm{Be}^{2+} + q\mathrm{L}^{z-} + r\mathrm{H}^+ \rightarrow [\mathrm{Be}_p\mathrm{L}_q\mathrm{H}_r]^{(qz-2p-r)-} \tag{1}$$

A negative value of r indicates the presence of hydroxide in the complex, using the convention that $[\mathrm{OH}^-] = K_\mathrm{w}[\mathrm{H}^+]^{-1}$. The cumulative formation constant for the formation of the generic complex $[\mathrm{Be}_p\mathrm{L}_q\mathrm{H}_r]^{(qz-2p-r)-}$ is given by equation (2).

$$\beta_{pqr} = \frac{\left[[\mathrm{Be}_p\mathrm{L}_q\mathrm{H}_r]^{(qz-2p-r)-}\right]}{\left[\mathrm{Be}^{2+}\right]^p\left[\mathrm{L}^{z-}\right]^q\left[\mathrm{H}^+\right]^r} \tag{2}$$

The ensemble of all species defined by their p, q and r values is called a model of the equilibrium system. Equilibrium constants for beryllium hydrolysis were obtained previously under the same conditions of ionic strength and temperature [16]. Protonation constants and complex formation constants were derived from

Table 2. Overall formation constants of the species considered in the systems investigated ($I = 0.5\ \text{mol dm}^{-3}$ $NaClO_4$, $T = 298$ K).

	pqr	$\log \beta^{a}_{pqr}$		
Dissociation of water				
$H_2O \rightarrow H^+ + OH^-$	0 0 −1		−13.69 (1)	
Metal hydrolysis				
$2Be^{2+} + H_2O \rightarrow [Be_2OH]^{3+} + H^+$	2 0 −1		-3.20^{b}	
$3Be^{2+} + 3H_2O \rightarrow [Be_3(OH)_3]^{3+} + 3H^+$	3 0 −3		-8.68^{b}	
$5Be^{2+} + 6H_2O \rightarrow [Be_5(OH)_6]^{4+} + 6H^+$	5 0 −6		-18.31^{b}	
$6Be^{2+} + 8H_2O \rightarrow [Be_6(OH)_8]^{4+} + 8H^+$	6 0 −8		-25.77^{b}	
$Be^{2+} + 2H_2O \rightarrow Be(OH)_2 + 2H^+$	1 0 −2		-11.68^{b}	
$Be^{2+} + 2H_2O \rightarrow Be(OH)_2(s) + 2H^+$	1 0 −2		8.67^{c} (K_{sp})	
		AMP ($z = 2$)	ADP ($z = 3$)	ATP ($z = 4$)
Ligand protonation				
$H^+ + L^{z-} \rightarrow (HL)^{(z-1)-}$	0 1 1	6.02 (2)	6.10 (3)	6.21 (2)
$2H^+ + L^{z-} \rightarrow (H_2L)^{(z-2)-}$	0 1 2	9.80 (2)	10.16 (6)	10.30 (2)
$3H^+ + L^{z-} \rightarrow (H_3L)^{(z-3)-}$	0 1 3		11.8 (1)	11.91(4)
Metal complex formation				
$Be^{2+} + L^{z-} \rightarrow [BeL]^{(z-2)-}$	1 1 0	4.92 (2)	5.97 (2)	6.52 (1)
$Be^{2+} + H^+ + L^{z-} \rightarrow [Be(HL)]^{(z-3)-}$	1 1 1	8.50 (3)	9.81 (2)	10.49 (1)
$2Be^{2+} + H_2O^+ + 2L^{z-} \rightarrow [Be_2(OH)L_2]^{(2z-3)-} + H^+$	2 2 −1	7.90 (3)	8.22 (6)	10.59 (5)
$3Be^{2+} + 3H_2O^+ + 3L^{z-} \rightarrow [Be_3(OH)_3(HL)_3]^{(3z-6)-}$	3 3 0	20.0 (1)	22.8 (1)	24.9 (1)
σ(weighted residuals)		1.5	2.9	1.3
χ^2		26	37	25

Notes: [a]Values in brackets are SDs on the last significant figures.
[b]Reference [26].
[c]Reference [19].

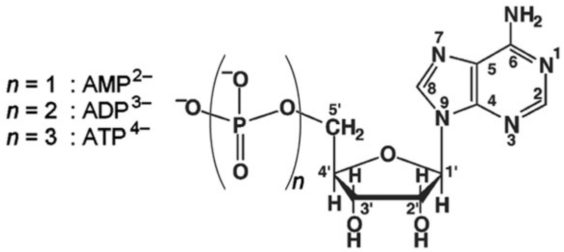
potentiometric titration data using the program HYPERQUAD [14] in which the sum of weighted, squared residuals in emf is minimized. The "best" model for each ligand was selected according to a series of hypothesis tests, described previously [17], involving the values of σ, the SD of the weighted residuals, the SDs on the equilibrium constants and χ^2, an indicator of the normality of the distribution of the residuals. Values of the stability constants and associated statistics for the selected model are given in table 2.

Species distribution diagrams were obtained using the program HYSS [18], taking into account the possibility that $Be(OH)_2$ may precipitate out of solution. The solubility product of $Be(OH)_2$ was taken from the work of Bruno [19].

4. Results and discussion

4.1. *Ligand protonation*

Values of the protonation constants of the nucleotides shown in scheme 1 obtained in the present study are given in table 2 and are in good agreement with previously published values [20–22]. The first protonation occurs mainly at the terminal phosphate group, the second proton goes mainly to the nitrogen site on adenosine, and the third proton (in ADP and ATP) goes mainly to a central phosphate group. This protonation sequence is well established [22, 23], though, as the term mainly implies, protonation of



Scheme 1. Chemical structures of the nucleotides considered in this study.

Table 3. List of complex species previously postulated, experimental conditions and decimal logarithms of the stability constants.

Reaction	T(°C)	Ionic strength	log K	Reference
$Be^{2+} + ATP^{4-} \rightarrow [Be(ATP)]^{2-}$	22	0.2M	5.01	[10]
	25	0.1M KNO_3	8.49	[11]
	25	0.1M $NaClO_4$	7.62 (5)	[12]
$Be^{2+} + (HATP)^{3-} \rightarrow [Be(HATP)]^{-}$	25	0.1M KNO_3	7.51	[11]
$Be^{2+} + OH^{-} + ATP^{4-} \rightarrow [Be(ATP)(OH)]^{3-}$	25	0.1M KNO_3	14.35	[11]
	25	0.1M $NaClO_4$	6.2 (2)	[12]
$Be^{2+} + ADP^{3-} \rightarrow [Be(ADP)]^{-}$	25	0.1M $NaClO_4$	7.23 (7)	[12]
$Be^{2+} + OH^{-} + ADP^{3-} \rightarrow [Be(ADP)(OH)]^{2-}$	25	0.1M $NaClO_4$	6.8 (1)	[12]

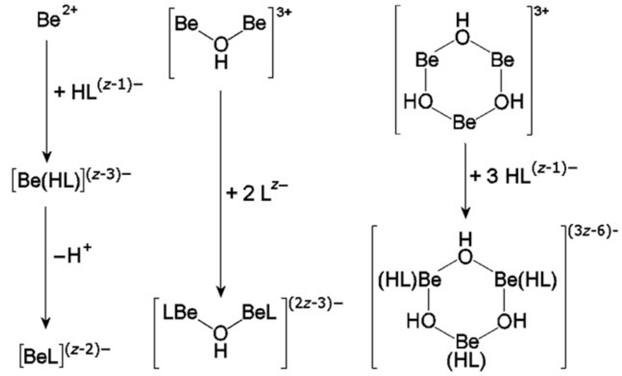
any one site is not exclusive. The protonation constant obtained by potentiometry is a macroconstant, equal to the sum of the microconstants for protonation of individual sites. The actual situation is that a tautomeric equilibrium may exist between protonated species of the same stoichiometry.

4.2. *Beryllium(II) complexes*

Previously determined values for beryllium complexes are given in table 3 showing little consistency in regard to the models chosen. Brintzinger and Fallab [10] postulated the existence of the single species $[Be(ATP)]^{2-}$, whereas other authors [11, 12] have suggested that $[Be(HATP)]^{-}$ and $[Be(OH)(ATP)]^{3-}$ are also formed. A major defect in relation to the published papers is that beryllium hydrolysis was not properly taken into account.

Analysis of our potentiometric titration data with HYPERQUAD [14] has provided a very satisfactory result. The same model applies to all three ligands, comprising the four species $[BeL]^{(z-2)-}$, $[Be(HL)]^{(z-3)-}$, $[Be_2(OH)L_2]^{(2z-3)-}$, and $[Be_3L_3)]^{(3z-6)-}$, as shown in scheme 2. Species distribution diagrams are shown in figures 1–3. The fit between observed and calculated data was excellent with this model. We conclude that other species may be present, but at such low concentration as to have negligible effect on the measured electrode potentials (p[H]); in particular, we have found no evidence for the presence of complexes with other than 1 : 1 Be : ligand ratio.

$[BeL]^{(z-2)-}$ is a straightforward complex of Be^{2+} and the deprotonated ligand. Likewise, $[Be(HL)]^{(z-3)-}$ is a complex with the protonated ligand, in which protonation occurs at an adenosine nitrogen, remote from the site of beryllium coordination, as discussed below. $[Be_2(OH)L_2]^{(2z-3)-}$ results from interaction of the hydrolyzed species



Scheme 2. Chemical model for beryllium binding to AMP, ADP and ATP.

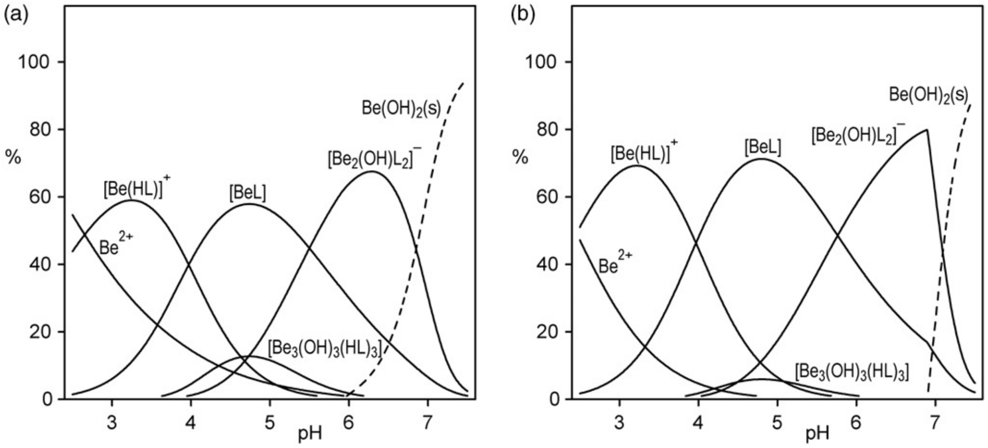


Figure 1. Speciation of beryllium(II) complexes with adenosine monophosphate ($L = AMP^{2-}$) relative to the total beryllium concentration, as a function of $-\log [H^+]$ (pH). Insoluble beryllium hydroxide is shown as $Be(OH)_2(s)$. Total concentrations: L, 1 mM, Be^{2+} (a) 1 mM, (b) 0.5 mM.

$[Be_2(OH)]^{3+}$ with two molecules of L^{z-} (scheme 2). The stoichiometry of the species $[Be_3L_3]^{(3z-6)-}$ is misleading as it is really a complex of the hydrolytic trimer $[Be_3(OH)_3]^{3+}$ and could be written as $[Be_3(OH)_3(HL)_3]^{(3z-6)-}$ (scheme 2). Similar complexes of $[Be_3(OH)_3]^{3+}$ have been identified with other ligands [13, 24]. Note that the coordination sphere of beryllium will be completed by water molecules which are not shown in the structures. Although the agreement with published stability constants is poor, we believe that the present results are correct because of the consistency of the models for AMP, ADP and ATP, not only amongst themselves, but also with the models proposed for other ligands such as oxalate, malonate, succinate [13, 24], phosphonoacetate and methylenediphosphonate [25].

The stability constants for formation of $[BeL]^{(z-2)-}$ and $[Be(HL)]^{(z-3)-}$ increase in the order AMP < ADP < ATP, that is, with the length of the polyphosphate chain and the overall charge. It is likely that Be is chelated by adjacent oxygen atoms on adjacent

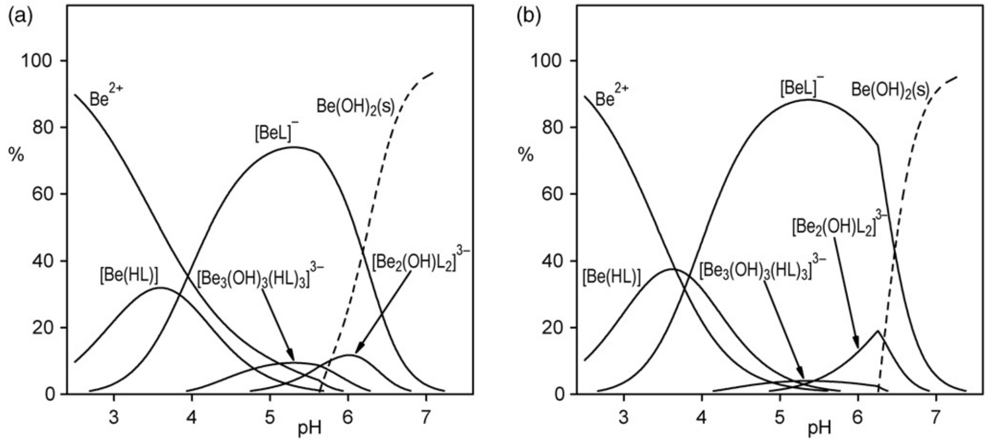


Figure 2. Speciation of beryllium(II) complexes with adenosine diphosphate ($L = ADP^{3-}$) relative to the total beryllium concentration, as a function of $-\log[H^+]$ (pH). Insoluble beryllium hydroxide is shown as $Be(OH)_2(s)$. Total concentrations: L, 1 mM, Be^{2+} (a) 1 mM, (b) 0.5 mM.

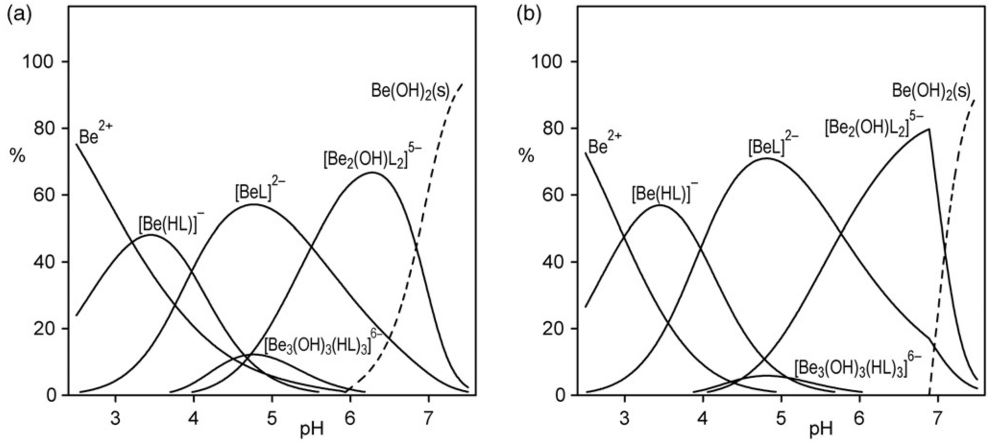


Figure 3. Speciation of beryllium(II) complexes with adenosine triphosphate ($L = ATP^{4-}$) relative to the total beryllium concentration, as a function of $-\log [H^+]$ (pH). Insoluble beryllium hydroxide is shown as $Be(OH)_2(s)$. Total concentrations: L, 1 mM, Be^{2+} (a) 1 mM, (b) 0.5 mM.

phosphate groups, as suggested for Mg complexes. The values of the stability constants are higher than the values of the corresponding Mg complexes. For example, $\log K$ for $[Mg(ATP)]^{2-}$ is 4.10 ($I = 0.10\,\mathrm{mol\,dm^{-3}}$ at 25°C) [21] and for $[Be(ATP)]^{2-}$ is 6.52. This remarkable difference corresponds to the greater Lewis acidity of Be^{2+} compared to Mg^{2+}, as indicated by the greater tendency to hydrolyze. Factors contributing to this are the fact that beryllium complexes are tetrahedral, whereas magnesium complexes are octahedral, and that Be^{2+} is much smaller than Mg^{2+}.

The stepwise protonation constants of $[BeL]^{(z-2)-}$, given in table 4, are approximately the same for all three ligands and not very different from the protonation constants of $(HL)^{(z-2)-}$, consistent with the hypothesis that this protonation step concerns mainly

Table 4. Stepwise equilibrium constants for protonation and beryllium complex formation of adenosine-5′-phosphates in 0.5M $NaClO_4$ aqueous solution at 298 K.

	log *K*		
Reaction	AMP ($z=2$)	ADP ($z=3$)	ATP ($z=4$)
$L^{z-} + H^+ \rightarrow (HL)^{(z-1)-}$	6.02 (2)	6.10 (3)	6.21 (2)
$(HL)^{(z-1)-} + H^+ \rightarrow (H_2L)^{(z-2)-}$	3.78 (3)	4.06 (7)	4.09 (3)
$(H_2L)^{(z-2)-} + H^+ \rightarrow (H_3L)^{(z-3)-}$		1.6 (1)	1.61 (7)
$Be^{2+} + L^{z-} \rightarrow [BeL]^{(z-2)-}$	4.92 (7)	5.97 (2)	6.52 (1)
$Be^{2+} + (HL)^{(z-1)-} \rightarrow [Be(HL)]^{(z-3)-}$	2.48 (3)	3.71 (2)	4.28 (1)
$[BeL]^{(z-2)-} + H^+ \rightarrow [Be(HL)]^{(z-3)-}$	3.58 (8)	3.84 (3)	3.97 (2)
$[Be_2(OH)]^{3+} + 2L^{z-} \rightarrow [Be_2(OH)L_2]^{(2z-3)-}$	4.70 (3)	5.02 (6)	7.39 (5)
$[Be_3(OH)_3]^{3+} + 3(HL)^{(z-1)-} \rightarrow [Be_3(OH)_3(HL)_3]^{(3z-6)-}$	8.32 (1)	11.1 (1)	13.2 (1)

on nitrogen of the adenine residue, probably N^1 (scheme 1), and consequently will be little affected by binding of beryllium at the phosphate end of the nucleotide. This protonation has only a small effect on beryllium binding.

Attempts to confirm the validity of the models using ESMS and NMR were not successful. As shown previously, nucleotides are prone to self-association in solutions more concentrated than about 5 mmol dm^{-3} [23]. Meaningful results could not be obtained with very dilute solutions. Measurements made on solutions at concentrations of 50 and 100 mmol dm^{-3} showed clear evidence of self-association.

5. Conclusion

The species formed by binding beryllium to the three nucleotides ATP^{4-}, ADP^{3-} and AMP^{2-} and their protonated forms $H(ATP)^{3-}$, $H(ADP)^{2-}$ and $H(AMP)^{-}$, shown in scheme 2, belong to the same model proposed for complexes of beryllium with other ligands. In particular, because of the high acidity of Be^{2+}(aq), complexes are formed at relatively low pH with the hydrolyzed species $[Be_2OH]^{3+}$ and $[Be_3(OH)_3]^{3+}$. However, under physiological conditions at pH ≈ 7.2 most of the beryllium will be in the form of the precipitate, $Be(OH)_2$, as illustrated in the speciation diagrams, figures 1–3, so it will not interfere with the functioning of the nucleotides. The precise pH at which precipitation begins depends to some extent on the ratio of total concentrations of nucleotide and beryllium ion. At pH lower than about six Be^{2+} will compete strongly with Mg^{2+} for binding to these vitally important compounds.

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