Beryllium(II) Complexes of the Kläui Tripodal Ligand Cyclopentadienyltris(diethylphosphito-*P*)cobaltate(−)

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The interactions of the beryllium(II) ion with the cyclopentadienyltris(diethylphosphito-*P*)cobaltate monoanion, L^-, have been investigated, in aqueous solution, by synthetic methods, potentiometry, ESMS, and ^1H, ^{31}P, and ^9Be NMR spectroscopy. L^- has been found able to displace either two or three water molecules in the beryllium(II) coordination sphere, to form mononuclear, dinuclear, and trinuclear derivatives, in which the metal ion is pseudotetrahedrally coordinated. The species $[BeL(H_2O)]^+$ and $[Be_2L_2(\mu\text{-}OH)]^+$ have been identified in solution while complexes of formula BeL_2 and $[Be_3L_4](ClO_4)_2$ have been isolated as solid materials. The species $[BeL(OPPh_2)]^+$, closely related to $[BeL(H_2O)]^+$, has been characterized in acetone solution and isolated as tetraphenylborate salt. The structure of the unusual trimeric complex $[Be_3L_4]^{2+}$ has been elucidated by an unprecedented 2D $^9Be-^{31}P$ NMR correlation spectrum showing the presence of a single central beryllium nucleus and two equivalent terminal beryllium nuclei. The three beryllium centers are held together by four cobaltate ligands, which display two different bonding modes: two ligands are terminally linked with all the three oxygen donors to one terminal beryllium, and the other two bridge two metal centers, sharing the oxygen donors between central and terminal beryllium atoms.

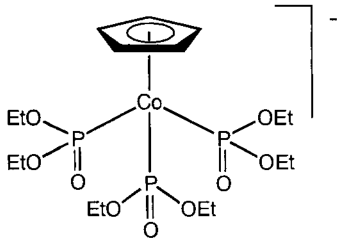
Introduction

Modern beryllium chemistry is focused mainly on the equilibria of aqueous solutions containing the beryllium(II) ion and ligands of biological relevance.[1] Few papers have so far considered the interactions of this toxic metal with molecules bearing the phosphoryl function, even though the affinity of phosphate to beryllium(II) is well-known.[2] Recently the formation of beryllium(II) complexes of ATP and ADP has been investigated through NMR[3,4] and the ability of ferritine, a phosphate-containing protein, to sequester a large amount of beryllium(II) has been studied.[5]

Only few examples of beryllium(II) chelation by tripodal ligands had been previously reported.[6]

We now report on the interactions of beryllium(II) with the Kläui ligand cyclopentadienyltris(diethylphosphito-*P*)cobaltate(−), L^- (Scheme 1),[7] as a model of beryllium(II) complexes with chelating ligands containing the phosphoryl functionality.

Scheme 1



Characterization of the speciation of the beryllium complexes present in aqueous solution was achieved using potentiometry, electrospray mass spectrometry, and multinuclear magnetic resonance spectroscopy. The species $[BeL(H_2O)]^+$ and $[LBe(OH)BeL]^+$ have been observed in aqueous solution whereas the complexes $[BeL(OPPh_3)](BPh_4)$, BeL_2, and $[Be_3L_4](ClO_4)_2$ have been isolated. This latter compound is a new trimeric species of beryllium containing both terminal and bridging L^- and has been characterized by $^9Be-^{31}P$ heteronuclear multiple quantum coherence spectroscopy, which is unprecedented in the literature.

Experimental Section

General Information. All reagents and solvents were commercial products of analytical grade and were used without any further

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purification. $Be(ClO_4)_2{\cdot}4H_2O$[6a] and $NaL{\cdot}H_2O$[8] were prepared according to literature procedures. All operations were carried out in a dry nitrogen atmosphere.

Preparation of [BeL(OPPh$_3$)]BPh$_4$. A solution of $NaL{\cdot}H_2O$ (0.290 g, 0.50 mmol) dissolved in acetone (20 mL) was added with continuous stirring to a solution of $Be(ClO_4)_2{\cdot}4H_2O$ (0.140 g, 0.50 mmol) in acetone (10 mL). Solid $NaBPh_4$ (0.170 g, 0.50 mmol) was added to the resulting solution, to which then was added diethyl ether (30 mL). After 2 days thin pale yellow crystals were filtered off, washed with a mixture of acetone/diethyl ether (30/70 in volume) and then with diethyl ether, and dried in a stream of nitrogen (0.390 g, 68% yield). Anal. Calcd for $C_{59}H_{70}BBeCoO_{10}P_4$: C, 62.06; H, 6.18; P, 10.85. Found: C, 61.85; H, 6.10; P, 10.90.

Preparation of BeL$_2$. A solution of $NaL{\cdot}H_2O$ (0.575 g, 1.00 mmol) in H_2O (40 mL) was slowly added, at 323 K, to a solution of $BeSO_4{\cdot}4H_2O$ (0.180 g, 0.50 mmol) in H_2O (5 mL). The oil which separated was extracted with 30 mL of dichloromethane. The solution was treated with anhydrous $CaCl_2$, with continuous stirring, overnight. The mixture was filtered and the dichloromethane evaporated to give a yellow powder, which was recrystallized from THF/diethyl ether to give a microcrystalline compound (0.790 g, yield 78%). Anal. Calcd for $C_{34}H_{70}BeCo_2O_{18}P_6$: C, 37.82, H, 6.53. Found: C, 37.75; H, 6.60.

Preparation of [Be$_3$L$_4$](ClO$_4$)$_2$. A solution of $NaL{\cdot}H_2O$ (0.580 g, 1.00 mmol) in H_2O (40 mL) was slowly added, at 323 K, to a solution of $Be(ClO_4)_2{\cdot}4H_2O$ (0.280 g, 0.75 mmol) in H_2O (10 mL) with continuous stirring. An oily material slowly separated after the mixture was cooled to room temperature and held in air, overnight. The microcrystalline material was filtered, washed with water, and dried in air (2.0 g, 82% yield). Anal. Calcd for $C_{68}H_{140}Be_3Cl_2Co_4O_{44}P_{12}$: C, 34.50; H, 5.96; Co, 9.96; Be, 1.14. Found: C, 34.80; H, 6.10; Co, 9.85; Be, 1.15.

Preparation of [Be$_3$L$_4$](ClO$_4$)$_2$·Et$_2$O Crystals for X-ray. The above complex (0.781 g, 0.33 mmol) was dissolved in THF (10 mL), and diethyl ether (30 mL) was added. The solution was put into a freezer, and after 2 days well-shaped pale yellow crystals were obtained. The supernatant solution was decanted, and the crystals were washed with diethyl ether. Crystals must be kept in the presence of diethyl ether.

Potentiometric Measurements. Emf determination of the equilibrium constants was carried out at 298 K. The ionic strength of the test solutions was held constant at 0.50 mol dm^{-3} using $[(CH_3)_4N]Cl$. This electrolyte was chosen because the tetramethylammonium ion does not show any tendency to associate with the ligand. The potentiometric apparatus and the experimental technique have previously been described.[9] The potentiometric titrations were performed by adding a 0.1 mol dm^{-3} solution of $[(CH_3)_4N](OH)$ to solutions, acidified with HCl, containing either the ligand (in the deprotonation experiments) or the beryllium sulfate and the ligand (in the complex formation experiments). The glass electrode was calibrated in terms of proton concentration $[H_3O^+]$, using the Gran procedure,[10] and the log value of the ionic product of water, K_w, determined for this system was −13.72. Two titrations (106 data points in the pH range 2.9−7.3) with ligand concentration close to 2 mM and known concentrations of sodium ion were used to determine simultaneously the protonation constant of the anion L^- and the formation constant of the sodium complex NaL. The complex formation potentiometric experiments consisted of three titrations (190 data points in the pH range 2.7−8.1): the concentrations of metal and ligand were in the range 1.4−2.1 and 1.5−2.1 mM, respectively, the ligand to beryllium molar ratio being in the range 1:1−1.7:1.

NMR Spectra. NMR spectra were recorded in 5 mm tubes, at 295 K, on Bruker Avance DRX-500 or AC-200 spectrometers operating at 500.132 or 200.13 MHz (^{1}H), 202.47 or 81.015 MHz (^{31}P), and 70.27 or 28.12 MHz (^{9}Be), respectively. ^{1}H chemical shifts are relative to external TMS; ^{31}P chemical shifts are relative to external 85% H_3PO_4 in H_2O; ^{9}Be chemical shifts are relative to external 0.1 M $BeSO_4$ in D_2O. Downfield values of the chemical shifts are reported as positive. 2D ^{9}Be−^{31}P NMR correlations were recorded using a pulse sequence suitable for phase-sensitive representations using TPPI. A modified HMQC sequence was employed with ^{9}Be detection and no decoupling during acquisition: 256 increments of 500 data points (with 32 scans each) were collected covering the full range in both dimensions, with a relaxation delay of 500 ms.[11] The value of pD was adjusted using minimum volumes of either concentrated D_2SO_4 or NaD; the pD values were measured using a Radiometer PHM210 equipped with a combined glass Ag/AgCl microelectrode (INGOLD); the values were corrected according to the relationship pD = pH + 0.40,[12] where pH is the pH meter reading, calibrated using standard aqueous buffer solutions.

Table 1. Protonation Constants for the Ligand Cyclopentadienyltris(diethylphosphito-*P*)cobaltate and Stability Constants for Sodium and Beryllium(II) Complexes (T = 298 K, I = 0.5 mol dm^{-3} NMe$_4$Cl)[a]

reaction	log *K* this work	log *K* ref 14[b]	log *K* ref 14[c]
$L^- + H^+ \leftrightarrows HL$	5.87(5)	5.58	8.82
$L^- + Na^+ \leftrightarrows NaL$	2.6(1)	1.98	4.1
$Be^{2+} + L^- \leftrightarrows [BeL]^+$	7.67(4)		
$2Be^{2+} + 2L^- \leftrightarrows [Be_2L_2(\mu\text{-}OH)]^+ + H^+$	11.0(1)		
$[Be_2(\mu\text{-}OH)]^{3+} + 2L^- \leftrightarrows [Be_2L_2(\mu\text{-}OH)]^+$	14.2(1)		

[a] Values in parentheses are standard deviations on the last significant figure. [b] T = 298 K, aqueous solution, I = 0.10 mol dm^{-3} NMe$_4$Cl. [c] T = 298 K, 95% methanol/water, I = 0.10 mol dm^{-3} NMe$_4$Cl.

ESMS Spectra. Electrospray mass spectra were obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, U.K.) using a water/acetonitrile (1:1) mobile phase. Water solutions (0.1 mM) of the complexes were injected directly into the spectrometer via a Rheodyne injector equipped with a 50 μL loop. A Harvard 22 syringe pump delivered the solutions to the vaporization nozzle of the electrospray ion source at a flow rate of 10 μL min $^{-1}$. Nitrogen was used both as a drying gas and for nebulization with flow rates of approximately 200 and 20 mL min^{-1}, respectively. Pressure in the mass analyzer region was usually about 4×10^{-5} mbar. Typically 10 signals averaged spectra were collected.

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 the syntheses and measurements.*

Results and Discussion

Determination of Equilibrium Constants. The basicity constants of the ligand L^- have been determined together with the stability constant of the sodium complex NaL, with the aid of the HYPERQUAD computer program.[13] The refined values, shown in Table 1, are in satisfactory agreement with the values previously reported,[14] considering the different conditions of ionic strength used.

The stability constants of the beryllium(II) complexes of L^- were also refined using HYPERQUAD.[13] The potentiometric data were analyzed taking into account the ligand protonation constant, the stability constant of NaL, and the equilibrium constants of the beryllium(II) ion hydrolysis.[15] On this basis a model for the equilibria occurring under the experimental

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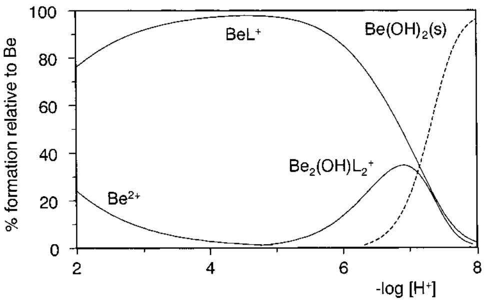

Figure 1. Calculated species distribution for beryllium(II)−cyclopentadienyltris(diethylphosphito-*P*)cobaltate(−){L} complexes as a function of pH. $C_{\mathrm{Be}} = 0.2$ M and $C_{\mathrm{L}} = 0.2$ M.

conditions was established. The complex species $[\mathrm{BeL}]^+$ and $[\mathrm{Be_2L_2}(\mu\text{-OH})]^+$ were found to be present in this system; the results of the equilibrium analysis are reported in Table 1. The stability constant of the species $[\mathrm{BeL}]^+$ (log $K = 7.67$) can be compared with those of the complexes $[\mathrm{Be(NTA)(H_2O)}]^-$ (log $K = 6.68$)[6a] and $[\mathrm{Be(NTP)(H_2O)}]^-$ (log $K = 9.23$),[6a] where NTA^{3-} and NTP^{3-} are the tripodal ligands nitrilotriacetate and nitrilotripropionate, respectively. Since in the latter complexes the ligands are tetracoordinated to the metal center, forming five- and six-membered chelate rings, respectively, it appears likely that our complex has the formulation $[\mathrm{BeL(H_2O)}]^+$, with L^- acting as a tridentate ligand. The value of the stability constant of $[\mathrm{BeL}]^+$ is remarkably smaller than that of the complex $[\mathrm{Be(mdp)}]^{2-}$ (mdp = methylene diphosphonate) (log $K = 13.7$),[16] suggesting that the phosphonate group has a higher affinity to beryllium than the present phosphito moiety. The other complex $[\mathrm{Be_2L_2}(\mu\text{-OH})]^+$ appears to be of remarkable interest, being a rare example of a derivative of the well-known beryllium hydrolysis species[1,17] $[\mathrm{Be_2(H_2O)_6}(\mu\text{-OH})]^{3+}$.

Figure 1 shows the distribution diagram for the complex species calculated using the program HYSS.[18] The beryllium complexation is ca. 100% at low pH values; the hydroxylate dimer occurs at pH 4.8−6.2, after which precipitation of $\mathrm{Be(OH)_2}$ occurs.

The anion L^- has been previously found to form both $[\mathrm{ML}^+]$ and $\mathrm{ML_2}$ complexes with divalent metal ions in methanol−water solution;[14] the relative stability constants cannot be compared with those of the beryllium complexes in water because of the different experimental conditions.

ESMS Spectra. The ESMS spectra of the system $\mathrm{BeSO_4}$/NaL (molar ratio 1:1) were recorded at cone voltages 20, 40, 60 V. Two 1.5 mM water solutions of the system, with pH = 3.99 and 6.39, respectively, were diluted with acetonitrile to give 1:1 mixtures of acetonitrile/water. The spectra of the two solutions appear substantially similar, and there are only minor variations between the spectra collected at different voltages. The positive ion ESMS spectra essentially consist of peaks at $m/z = 544$, 562, and 1105, attributable respectively to the monocharged species $[\mathrm{BeL}]^+$, $[\mathrm{BeL(H_2O)}]^+$, and $[\mathrm{Be_2L_2}(\mu\text{-OH})]^+$. In each case there is excellent agreement between calculated and observed isotopic peak patterns. At cone voltage = 20 V the peak at $m/z = 562$ (100%) is the most abundant followed by the peak at 1105 (2%). When the cone voltage increases, the intensities of the peaks due to $[\mathrm{BeL}]^+$ and $[\mathrm{Be_2L_2}(\mu\text{-OH})]^+$ increase whereas that of $[\mathrm{BeL(H_2O)}]^+$ decreases; as a matter of fact with cone voltage = 60 V we observe the following relative intensities: $m/z = 562$ (100%), 544 (55%), and 1105 (16%).

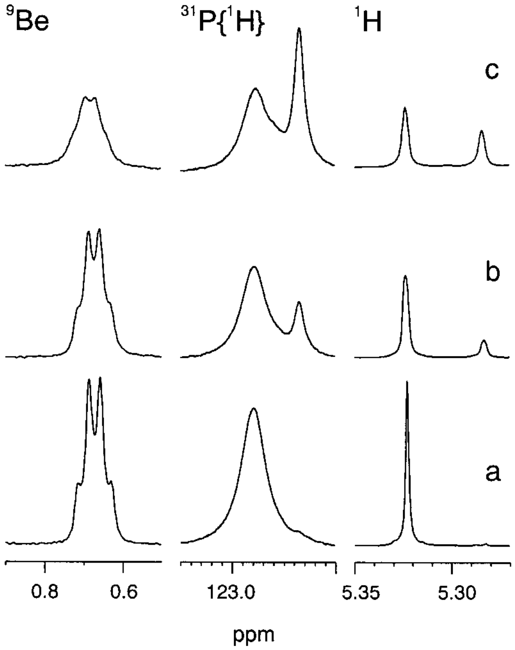

Figure 2. ^{9}Be, ^{31}P{^{1}H}, and ^{1}H ($\mathrm{C_5H_5}$ region) NMR spectra ($\mathrm{D_2O}$, $C_{\mathrm{Be}} = 0.1$ mol dm^{-3}, 295 K) of the system $\mathrm{BeSO_4}$/NaL (molar ratio 1:1) at different pD values (a, pD = 4.17; b, pD = 5.46; c, pD = 6.10).

The negative ion ESMS spectra substantially agree with the above results showing peaks at $m/z = 640$, 658, 1201, and 1219 attributable to the ion pair monocharged species $\{[\mathrm{BeL}]\cdot(\mathrm{SO_4})\}^-$, $\{[\mathrm{BeL(H_2O)}]\cdot(\mathrm{SO_4})\}^-$, $\{[\mathrm{Be_2L_2}(\mu\text{-OH})]\cdot(\mathrm{SO_4})\}^-$, and $\{[\mathrm{Be_2L_2(OH)(H_2O)}]\cdot(\mathrm{SO_4})\}^-$.

Even if we do not know the exact value of the pH of the mixture entering the mass spectrometer and even though there is not a direct correlation between peak intensity and the concentration of the species in solution, the ESMS results appear to be substantially consistent with the potentiometry data.

NMR Spectra. Workup of aqueous solutions containing equimolar amounts of $\mathrm{BeSO_4 \cdot 4H_2O}$ and NaL did not allow the isolation of any identifiable compound. The NMR spectra of the system $\mathrm{Be(SO_4) \cdot 4H_2O}$/NaL ($\mathrm{D_2O}$ solution, $C_{\mathrm{Be^{2+}}} = C_{\mathrm{L^-}} = 0.05$ mol dm^{-3}, 295 K), recorded at different pH values, are shown in Figure 2. At pD = 4.17 (the natural value) the ^{9}Be and the ^{31}P{^{1}H} spectra, with a quartet at 0.67 ppm ($^2J_{\mathrm{P-Be}} = 2.3$ Hz) and a broad singlet at 122.8 ppm, respectively, are consistent with the presence of the tetrahedal complex $[\mathrm{LBe(H_2O)}]^+$, as previously indicated by potentiometry. A similar ^{9}Be spectrum was previously reported for the complex $[\mathrm{L^\circ Be(H_2O)}]^{2+}$, where the tripodal phosphine oxide L° (L° = tris(2-diphenylphosphorylmethyl)amine) acts as a tridentate ligand.[6b] The broadness of the signal in the ^{31}P{^{1}H} spectrum is most likely due to the presence of the quadrupolar cobalt nucleus and prevents the observation of ^{31}P to ^{9}Be coupling. The ^{1}H NMR spectrum {Figure 2 ($\mathrm{C_5H_5}$ region)} also agrees well with the above results. When pD is increased, the ^{1}H and ^{31}P spectra (Figure 2) indicate that a new species occurs, whose amount gradually increases, whereas the amount of $[\mathrm{BeL(H_2O)}]^+$ decreases, until precipitation of beryllium hydroxide occurs. The ^{1}H NMR spectra in the ethyl region well agree with the above results. The spectra of NaL, recorded under the same conditions

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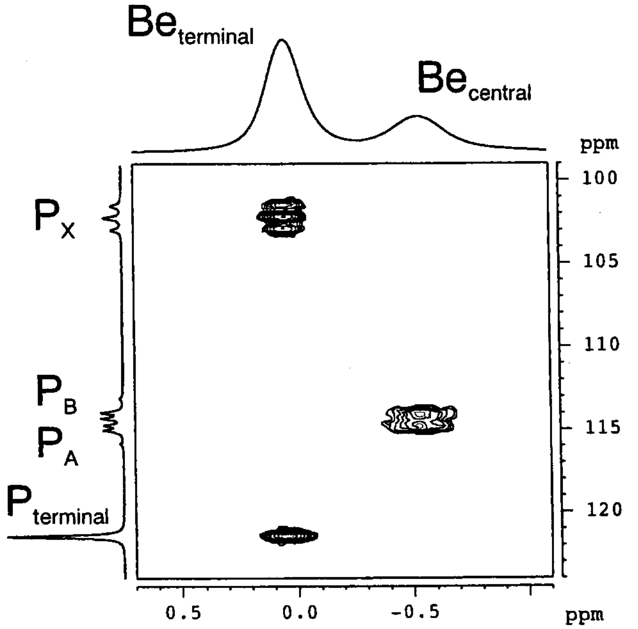

Figure 3. 2D ^{9}Be−^{31}P NMR correlation of $(Be_3L_4)(ClO_4)_2\cdot Et_2O$ (acetone-d_6, 295 K, 70.27 MHz).

of pD, do not show any signals which could be attributed to free L^-. Therefore, on the basis of potentiometric and ESMS results we assign the new complex as the dimeric $[Be_2L_2(\mu\text{-}OH)]^+$ species. The corresponding ^{9}Be resonance (Figure 2) gradually broadens as the pD increases, suggesting an exchange process (eq 1) which appears to be fast only in the case of the

$$2[BeL(H_2O)]^+ + OH^- \leftrightarrows [Be_2L_2(\mu\text{-}OH)]^+ + 2H_2O \quad (1)$$

^{9}Be NMR, due to the very small $\Delta\nu$ between the ^{9}Be signal of the two species. Although we had no success in the isolation of $[BeL(H_2O)]^+$, a closely related derivative was isolated from an organic solution. Indeed the reaction of $Be(ClO_4)_2\cdot 4H_2O$ with equimolar amounts of NaL and $OPPh_3$ in acetone/ethanol and in the presence of $NaBPh_4$ allowed the isolation of crystals of $[BeL(OPPh_3)]BPh_4$. In dichloromethane solution the ^{9}Be spectrum shows a doublet of quartets at 0.58 ppm ($^2J_{P(L)-Be} = 2.85$ Hz, $^2J_{P(OPPh_3)-Be} = 3.6$ Hz) while the ^{31}P spectrum comprises a broad singlet at 120.35 ppm (L) and a sharp 1:1:1:1 quartet at 41.1 ppm ($OPPh_3$, $^2J_{P-Be} = 2.85$ Hz). This clearly indicates that beryllium is coordinated by the three PO groups of L and the PO moiety of the phosphine oxide ligands. The sharpness of the ^{9}Be signal is consistent with a regular tetrahedral geometry. Again the broadness of the ^{31}P resonance of L^-, due to the presence of the cobalt nucleus, prevents the observation of any ^{31}P (L) to ^{9}Be coupling.

When $Be(SO_4)\cdot 4H_2O$ and NaL are allowed to react in aqueous solution, in the molar ratio 1:2, an oily material separates which can be extracted in dichloromethane. The oil analyzes as BeL_2. The room temperature ^{9}Be and ^{31}P NMR spectra of this material, in dichloromethane solution, show a broad singlet at −0.68 ppm, and two very broad resonances centered at ca. 120 and 94 ppm, respectively. Decreasing the temperature causes the ^{9}Be resonance to broaden, due to the enhancement of the quadrupolar effect, whereas the ^{31}P signals sharpen to give, at 223 K, a doublet at 118.9 ppm (2P, $^2J_{PP} = 136$ Hz) and a triplet at 94.5 ppm (1P). These data are consistent with a distorted tetrahedral geometry around the beryllium ion, with the tripodal phosphite acting as a bidentate ligand. It is likely that at room temperature the exchange between the two coordinated arms and the one uncoordinated arm of L^- is fast enough to affect the ^{31}P spectra. The complex BeL_2 is only sparingly soluble in water (ca. 10^{-3} mol dm^{-3}), and the ^{1}H, ^{31}P, and ^{9}Be NMR spectra of such solutions do not contain any signal attributable to BeL_2. On the contrary these spectra show the same signals as for of the system $BeSO_4\cdot 4H_2O$/NaL (molar ratio 1:1) under the same concentration and pH conditions, together with the resonances of the free L^- ligand. The ratio of free ligand to coordinate ligand appears to be close to 1:1.

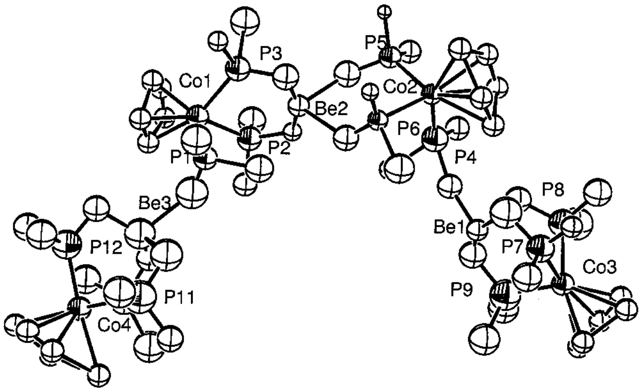

Figure 4. Perspective view of the complex cation $(Be_3L_4)^{2+}$. ORTEP drawing with 30% ellipsoids.[22] Ethylic chains have been omitted for the sake of clarity.

Finally, we have found that, when a solution of $Be(ClO_4)_2\cdot 4H_2O$ in water is treated with NaL, a microcrystalline material precipitates, which can be recrystallized from THF/diethyl ether to afford well-shaped crystals of $(Be_3L_4)(ClO_4)_2\cdot Et_2O$ in 82% yield. The reaction is quantitative if the stoichiometric metal-to-ligand ratio (3:4) is used. The 2D ^{9}Be−^{31}P NMR correlation spectrum of the complex in acetone-d_6 solution is reported in Figure 3 with the corresponding monodimensional spectra reported as projections. The ^{9}Be spectrum shows the presence of two nonequivalent Be centers in a 2:1 ratio (broad singlets at 0.04 and −0.53 ppm, respectively), while the ^{31}P{^{1}H} spectrum shows two broad, separated resonance patterns: a singlet (121.46 ppm, 6P) and an ABX spin system (δ_A 114.85 ppm, 2P; δ_B 114.07 ppm, 2P; δ_X 102.22 ppm, 2P; $^2J_{AB} = 177$ Hz, $^2J_{AX} = 147$ Hz, and $^2J_{BX} = 146$ Hz).[19] Again, no J_{P-Be} couplings are apparent in the ^{31}P{^{1}H} spectrum due to the broadening effect of the quadrupolar Co nuclei. The NMR data are consistent with the X-ray diffraction study results (vide infra). Particularly, the ^{9}Be spectrum shows the compound to be a trinuclear metal complex containing two equivalent (terminal) beryllium nuclei and one single beryllium (central). The ^{9}Be NMR line width is consistent with unsymmetrical four coordinated beryllium ions. The ^{31}P{^{1}H} spectrum shows the presence of two different kinds of L^- ligands. The singlet resonance is attributed to two equivalent tridentate terminal ligands, each one bonded to one of the terminal beryllium ions. The ABX spin system is attributed to two equivalent bridging ligands bonded to the terminal beryllium by one phosphite (P_x), and to the central beryllium by two phosphites (P_A and P_B). The magnetical nonequivalence of P_A and P_B is consistent with the unsymmetrical arrangement of the P_X−O−Be−$L_{terminal}$ unit with respect to P_A and P_B found in the solid state (vide infra). These attributions are confirmed by the 2D ^{9}Be−^{31}P NMR correlation showing the coupling of the terminal Be ion with P_X and with the phosphorus atoms belonging to the terminal L ligand, and the coupling of the central beryllium with P_A and

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(19) Data obtained from computer simulation using the program gNMR ver 4.1.0, IvorySoft 1995−1999, Cherwell Scientific Publishing.

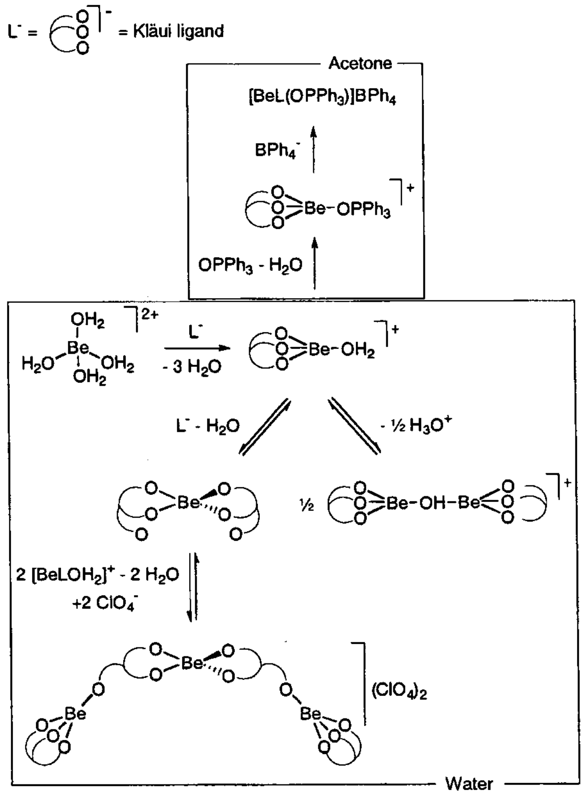
P_B only (Figure 3). Besides this simple case, the 2D ^{9}Be−^{31}P NMR correlation proved to be a useful tool to elucidate the structure and/or the composition of more complex beryllium- and phosphorus-containing compounds.

The molecular structure of the trimeric complex $(Be_3L_4)(ClO_4)_2 \cdot Et_2O$ was carried out from single-crystal diffractometric data. However, owing to the poor quality of the data[20] we consider the structure useful only to determine atom connectivity. The molecular structure consists of polynuclear cations where three beryllium atoms are linked together with four cobaltate ligands (Figure 4), perchlorate anions and diethyl ether molecules interspersed in the lattice. These results agree well with the model from the NMR spectra. Indeed the tridentate oxygen-donating ligands display two different bonding modes. Two ligands are terminally linked to one beryllium atom while the other two bridge two beryllium atoms. In this context it is interesting to note that, while there are many examples of L^- ligands terminally coordinated,[7] very few examples of this tripodal ligand acting in a bridging mode have been so far reported.[21]

Concluding Remarks

The chemistry of the system beryllium(II)−Kläui tripod system is summarized in Scheme 2. The results of this study show the remarkable affinity of the beryllium(II) ion toward the PO functionalities. As a matter of fact in aqueous solution the Kläui ligand can replace three water molecules in the beryllium coordination sphere to give stable complexes. Also the presence of six-membered rings appears to be an important factor in stabilization of the chelation.[1] The formation of an unusual derivative of the minor hydrolytic species $[Be_2(H_2O)_6(\mu\text{-OH})]^{3+}$ is probably favored by the tridenticity of L^-. Bidentate ligands have been previously found to allow the formation of derivatives of the major species $[Be_3(H_2O)_6(\mu\text{-OH})_3]^{3+}$.[1] It is noteworthy that the beryllium(II) ion differentiates itself from the other divalent ions of the IIA group because of its capability to form "covalent bonds", with quite electronegative donor groups such as F^-, −CO, and −PO, in aqueous solution.

Scheme 2



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Supporting Information Available: X-ray crystallographic file in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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(20) Nothwithstanding repeated attempts, the extreme volatility of the solvent caused the data collections to be particularly difficult. The crystals, sealed in a glass capillary, in the presence of diethyl ether, collapse within a few hours. The results of the refinements of five data collections carried out on different samples were fully comparable, but the *R* indices could not lower below 16%. Crystal data: triclinic, $P\bar{1}$, $a = 22.719(8)$ Å, $b = 19.648(7)$ Å, $c = 14.758(5)$ Å, $\alpha = 96.30(5)°$, $\beta = 82.48(5)°$, $\gamma = 107.93(5)°$, $Z = 2$.

(21) (a) Goldberg, I.; Shinar, H.; Navon, G.; Kläui, W. *J. Inclusion Phenom.* **1987**, *5*, 181. (b) Kläui, W.; Müller, A.; Eberspach, W.; Boese, R.; Goldberg, I. *J. Am. Chem. Soc.* **1987**, *109*, 164. (c) Kläui, W.; Asbahr, H.-O.; Schramm, G.; Englert, U. *Chem Ber.* **1997**, *130*, 1223.

(22) Johnson, C. K. *ORTEP, Rep. ORNL-5138*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976; as modified by Zsolnai, L., and Pritzkov, H.; Heidelberg University: Germany, 1994.