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Complexation of Beryllium(II) Ion by Phosphinate Ligands in Aqueous Solution. Synthesis and XRPD Structure Determination of Be[(PhPO$_2$)$_2$CH$_2$](H$_2$O)$_2$

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Two bifunctional ligands, phenyl(carboxymethyl)phosphinate (ccp^{2-}) and *P*,*P′*-diphenylmethylenediphosphinate (pcp^{2-}), have been tested as chelating agents of beryllium(II). Both ligands have the same charge and a similar chelating structure, but whereas the 1:1 adduct of pcp^{2-}, Be(pcp)(H$_2$O)$_2$, could be isolated as a white powder, no pure compound could be isolated from solutions containing beryllium(II) and ccp^{2-}. Instead, the solutions were examined by means of potentiometry and ^{9}Be NMR spectroscopy. Analysis of the potentiometric titration data with the program HYPERQUAD suggested the formation of the complex species BeL, [BeHL]$^+$, [BeL$_2$]$^{2-}$, and [BeHL$_2$]$^-$ (L = ccp). The formation constants for these species were determined at 25 °C and $I = 0.5$ mol dm^{-3} NaClO$_4$. The ^{9}Be NMR spectra are consistent with this model. The formation constants found for the ccp^{2-} complexes are lower than those reported for related phosphonate ligands. However, the effective stability constant (which gives a better indication of the intrinsic coordinating capacity of the ligand at a particular pH) of the complex [Be(ccp)$_2$]$^{2-}$ at pH < 4 is greater than the effective constants of the corresponding phosphonoacetate and methylenediphosphonate complexes. The structure of Be(pcp)(H$_2$O)$_2$ was determined by X-ray powder diffraction methods and consists of discrete molecules interconnected by an extended 2D network of hydrogen bonds, resulting in a stacking of *double* layers with a polar core and a lipophilic surface. Crystal data: C$_{13}$H$_{16}$BeO$_6$P$_2$, fw 339.21, monoclinic $P2_1/c$, $a = 16.174(1)$ Å, $b = 8.979(1)$ Å, $c = 10.929(1)$ Å, $\beta = 90.398(9)°$, $V = 1587.2(3)$ Å^3, $Z = 4$.

Introduction

The toxicity of beryllium and beryllium compounds is well-known, and the effects on human health and the environment have been evaluated thoroughly.[1,2] However, although the pathology of beryllosis is well documented,[3] the biochemical mechanism of beryllium toxicity is not yet properly understood. It is speculated, without convincing experimental evidence, that the beryllium(II) ion can affect the function of important proteins by forming a chelated complex with a hydroxy group of a hydroxy amino acid and a nearby carboxylate group of a carboxylic amino acid.[2] This hypothesis has stimulated a number of studies of the complexes formed in aqueous solutions between beryllium(II) and ligands containing functional groups such as OH, COOH, and CO as models for the biochemical systems.[4,5] Relatively few investigations have been reported concerning the interaction of the beryllium ion with molecules containing residues deriving from phosphate groups though these are clearly relevant in the biochemical context.[6,7]

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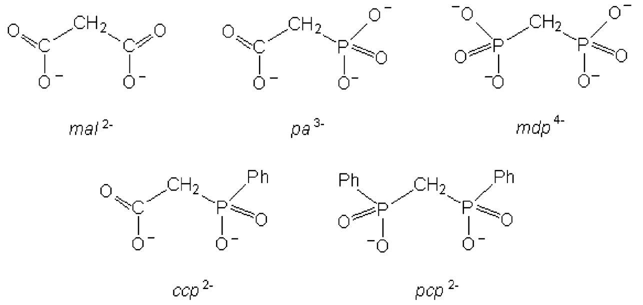
Chart 1

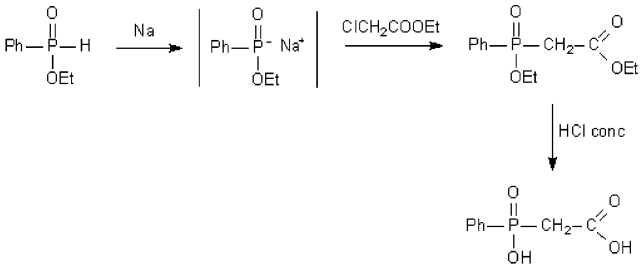


In the course of our recent investigations of the coordination chemistry of beryllium in aqueous solution, we found that bidentate ligands containing carboxylate and/or phosphonate groups form stable complexes with the beryllium(II) ion. Six-membered chelate rings, such as those formed by malonate, mal^{2-}, phosphonoacetate, pa^{3-}, and methylenediphosphonate, mdp^{4-} (Chart 1), are more favored than five- or seven-membered rings; the phosphonate group is better than carboxylate in regard to coordinating capacity.[7-9]

This paper concerns the interactions of the beryllium(II) ion with the two bidentate ligands phenyl(carboxymethyl)phosphinate (ccp^{2-}) and *P*,*P*′-diphenylmethylenediphosphinate (pcp^{2-}), shown in Chart 1. These ligands both contain a phosphinate group, $-CH_2(Ph)PO_2$; the second donor site is either a carboxylate group (ccp^{2-}) or a second phosphinate group (pcp^{2-}).

In the case of ccp^{2-}, a series of beryllium(II) complexes have been characterized in solution by means of potentiometry and NMR spectroscopy, but with pcp^{2-}, an insoluble compound was obtained which was found by X-ray powder diffraction (XRPD) studies to contain mononuclear chelate complexes interacting via an extended network of strong hydrogen bonds. By contrast, first-row transition metal ionsform polymeric mixed inorganic−organic complexes with pcp^{2-}.[10]

Scheme 1



Experimental Section

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.*

Materials and Methods. Solvents were freshly distilled under nitrogen from the appropriate drying agents immediately before use. The *P*,*P*′-diphenylmethylenediphosphinic acid, H$_2$pcp, was prepared according to a previously reported method.[11] H$_2$ccp was synthesized by the reaction in Scheme 1 rather than by the previously reported procedure.[12]

Ethylphenylphosphinate, ethylchloroacetate, and phenylphosphinic acid (Aldrich) were used as supplied. The IR spectra were recorded with a Perkin-Elmer 1600 FTIR spectrometer. Thermogravimetric analyses were performed with the aid of a Perkin-Elmer TG7 instrument, under dynamic N_2 flow.

Preparation of EtO(O)CCH$_2$P(Ph)(O)OEt. Small pieces of metallic sodium (0.8 g, 35 mmol) were added in 1 h to a solution of ethylphenylphosphinate (5.27 g, 31 mmol) in 100 mL of diethyl ether, at 273 K, with continuous stirring, under an atmosphere of dry nitrogen. The resulting pale yellow mixture was stirred at room temperature for 0.5 h and then refluxed for 2 h. The sodium excess was filtered off, and ethylchloroacetate (3.8 g, 31 mmol) in diethyl ether (5 mL) was added dropwise to the solution (ca. 0.5 h) at 273 K. The resulting mixture was refluxed for 1 h, then the precipitated NaCl was filtered off, and the solvent was evaporated to give a thick oil. This was distilled at 419−424 K (0.5 mmHg) to afford 4.1 g (yield 52%) of EtO(O)CCH$_2$P(Ph)(O)OEt. $^{31}P\{^1H\}(D_2O)$: δ 33.8 (s) ppm. ^1H NMR(D_2O): δ 7.9−7.4 (m, 5H, C_6H_5), 4.25−3.9 (m, 4H, CH_2O), 3.08 (d, 2H, $^2J_{PH} = 16$ Hz, CH_2P), 1.31 (t, 3H, CH_3), 1.11 (t, 3H, CH_3) ppm.

Preparation of HO(O)CCH$_2$P(Ph)(O)OH, H$_2$ccp. HCl (37%, 50 mL) was added to 4 g (15.6) of EtO(O)CCH$_2$P(Ph)(O)OEt, and the resulting solution was refluxed for 1.5 h. The solvent was evaporated, and the resulting thick oil of (HO(O)C)CH$_2$(P(Ph)(O)OH) was dried in vacuo. Yield 3.02 g, (97%). $^{31}P\{^1H\}(D_2O)$: δ 24.74 ppm.

Preparation of K$_2$(ccp). H$_2$ccp (1 g, 5.3 mmol) was dissolved in 10 mL of H_2O, and the solution was adjusted at pH 8.0 with 2 N KOH. Addition of ethanol allowed the precipitation of colorless microcrystals, which were recrystallized from water/ethanol. Yield 1.29 g (88%). Anal. Found: C, 34.55; H, 2.55. Calcd for $C_8H_7K_2O_4P$: C, 34.77; H, 2.55. $^{31}P\{^1H\}$ NMR(D_2O): δ 27.74 (s) ppm. ^1H NMR(D_2O): δ 7.68−7.33 (m, 5H, C_6H_5), 2.69 (d,2H, $^2J_{PH} = 18$ Hz, CH_2) ppm.

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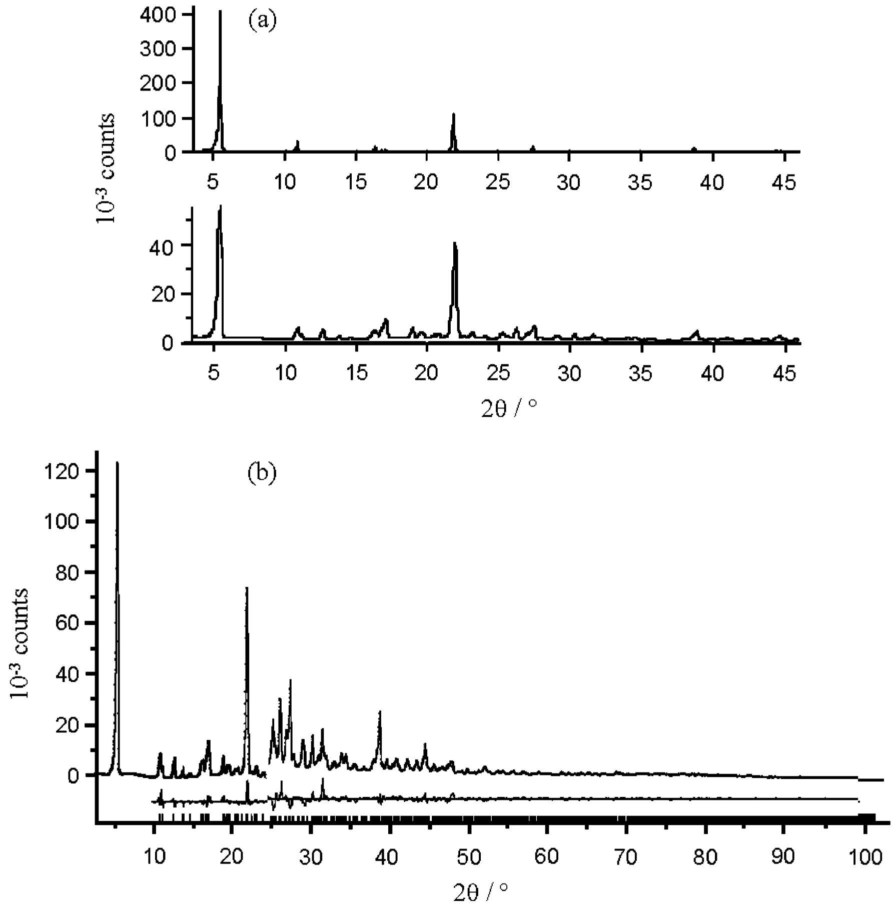


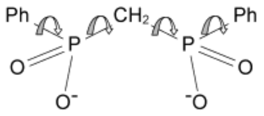
Figure 1. (a) Comparison of raw XRPD data ($5° < 2\theta < 45°$) for a conventional sample preparation (as thin layer on a zero-background plate, top) and a thick, but carefully side-loaded, specimen (bottom). (b) Rietveld refinement plot for Be(pcp)(H_2O)$_2$, with difference plots and peak markers at the bottom. The section above 25° has been enlarged five times.

Preparation of Be(pcp)(H_2O)$_2$. A solution of $BeSO_4 \cdot 4H_2O$ (0.088 g, 0.5 mmol) in H_2O (10 mL) was rapidly added to 60 mL of an aqueous solution of H_2pcp (0.148 g, 0.5 mmol) at 353 K. The mixture was cooled slowly to room temperature and afforded colorless microcrystals which were filtered, washed with H_2O, and dried in air. Yield 0.292 g, 86%. Anal. Found: C, 45.85; H, 4.80. Calcd for $C_{13}H_{16}BeO_6P_2$: C, 46.03; H, 4.75%. IR (KBr): 2997 (vs, b), 1627 (w, b), 1437 (m), 1357 (w), 1182 (vs), 1141 (vs), 1083 (s), 1072 (s), 1022 (m), 999 (w), 922 (w), 801 (vs), 741 (s), 693 (vs), 590 (m), 522 (s), 488 (w), 466 (w).

X-ray Powder Diffraction Analysis. The solid Be(pcp)(H_2O)$_2$ containing very thin platelets typically resulted in highly textured samples, rather unsuitable for structural analysis by X-ray powder diffraction methods. Therefore, we resorted to a side-loaded mounting, which gave a much better diffraction pattern, as shown in Figure 1a. Diffraction data (Cu Kα, $\lambda = 1.5418$ Å) were collected on a vertical scan PW1820 diffractometer, equipped with parallel (Soller) slits, a secondary beam curved graphite monochromator, a Na(Tl)I scintillation detector, and pulse height amplifier discrimination. The generator was operated at 40 kV and 40 mA. Slits: divergence 1.0°, antiscatter 1.0°, receiving 0.2 mm. Nominal resolution for the present setup is 0.14° 2θ (fwhm) for the Si(111) peak at 28.44° (2θ). A long overnight scan on a carefully side-loaded sample was performed with $5° < 2\theta < 105°$, with $t = 10$ s and $\Delta 2\theta = 0.02°$, and used for structure solution and refinement.

Indexing, using TREOR,[13] of the low angle diffraction peaks of a sample prepared as thin layer on a zero-background quartz monocrystal plate, suggested a primitive monoclinic (but nearly orthorhombic) cell of approximate dimensions $a = 16.22$ Å, $b = 8.97$ Å, $c = 10.92$ Å, $\beta = 90.39°$ [$M(20)^{14} = 20$; $F(20)^{15} = 45$ (0.009, 47)]. Careful visual inspection of the diffraction pattern indicated that splitting (or broadening) of a few $h0l$ reflections (like 302 and $30\bar{2}$) was consistent with a monoclinic, rather than orthorhombic, system. Systematic absences indicated $P2_1/c$ as the probable space group, later confirmed by successful solution and refinement.

Chart 2



Structure determination was initiated on the data collected on the side-loaded specimen by the simulated annealing technique implemented in TOPAS-R,[16] using a flexible $PhPO_2CH_2O_2PPh$ fragment (with freed rotation about the four independent P−C bonds, Chart 2). Difference Fourier syntheses (using GSAS[17]) and geometrical modeling later afforded approximate coordinates for the remaining three non-hydrogen atoms. The final refinements were

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performed by the Rietveld method with the aid of TOPAS-R, using a flexible $PhPO_2CH_2O_2PPh$ fragment hinged about a $Be(H_2O)_2$ fragment, whose coordination was imposed as tetrahedral by adding geometric constraints to Be−O contacts. The peak shapes were best described by the fundamental parameter approach and an isotropic crystal size broadening factor of Lorentzian contribution. The background function was modeled by a polynomial function, while further systematic errors were corrected with the aid of a sample-displacement angular shift and a preferred orientation model (100 pole, in the March−Dollase[18] formulation); a single isotropic displacement parameter was also refined. The contribution of the water (and methylene) hydrogen atoms to the scattered intensity was neglected. The low angle section of the XRPD pattern ($2\theta < 10°$, with one reflection only) was excluded from the final refinement, being affected by beam overflow and a structured background, due to contaminating glassy material. Scattering factors, corrected for real and imaginary anomalous dispersion terms, were taken from the internal library of TOPAS. Final fractional coordinates and a full list of bond distances and angles are supplied as Supporting Information. Crystal data: $C_{13}H_{16}BeO_6P_2$, fw 339.21, monoclinic $P2_1/c$, $a = 16.174(1)$ Å, $b = 8.979(1)$ Å, $c = 10.929(1)$ Å, $\beta = 90.398(9)°$, $V = 1587.2(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.419$ g cm^{-3}. Final agreement factors R_{wp}, R_p, and $R_{Bragg} = 0.109$, 0.077, 0.083, respectively, for 4500 data points collected in the $10° < 2\theta < 100°$ range. The final Rietveld refinement plot is shown in Figure 1b.

Potentiometric Measurements. Potentiometric determinations of the equilibrium constants were carried out at 298 K at an ionic strength of 0.5 mol dm^{-3} in $[Me_4N]Cl$ and with the use of the HYPERQUAD program.[19] The potentiometric apparatus and the experimental technique have been described previously.[7] The potentiometric titrations were performed by adding a 0.1 mol dm^{-3} $[Me_4N]OH$ solution to acid solutions containing either ligand (in the deprotonation experiments) or beryllium sulfate and the ligand (in the complex formation experiments). Concentrations of metal and ligand were in the ranges 3−6 and 3−4 mmol dm^{-3}, respectively. The ligand-to-metal ratios were 1:1, 2:1, and 1:1.5 (four titrations, 134 data points in the pH range 2.1−6.4). The electrode system was calibrated in terms of hydrogen ion concentration $[H_3O^+]$, using the Gran procedure,[20] and the log value of K_w ($=[H_3O^+][OH^-]$) determined for this system is −13.70.

NMR Measurements. The ^1H, $^{31}P\{^1H\}$, and ^9Be NMR spectra were recorded by a Bruker AC-200 spectrometer operating at 200.130, 81.018, and 28.18 MHz and were referred to internal TMS and external 85% H_3PO_4 and aqueous 0.1 mol dm^{-3} $BeSO_4$, respectively. Downfield values of the chemical shifts are reported as positive. If not otherwise specified, the NMR measurements were carried out in H_2O, 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).

Results and Discussion

Solution Studies. The stepwise basicity constants of ccp^{2-} and pcp^{2-} are shown in Table 1. The values obtained for ccp^{2-} can be compared with the corresponding values obtained in previous investigations[7,9] for malonate, mal^{2-}, phosphonoacetate, pa^{3-}, and methylenediphosphonate, mdp^{4-}, which are included in the table. The logarithm of the first basicity constant for ccp^{2-} is close to the log K_1 for mal^{2-} and to log K_2 for pa^{3-}, which were assigned to the protonation of the carboxylate group.[7] Therefore, it is reasonable to assume that the carboxylate group is protonated first in ccp^{2-} and the second protonation step is to be ascribed to the phosphinate group. The ligand pcp^{2-} is significantly less basic than ccp^{2-} in the first step of protonation because in pcp^{2-} the protonation takes place at the phenylphosphinate group. Previous determinations of log K for phenylphosphinates are in the range 2.75−1.85,[21] in satisfactory agreement with the value of log K_2 for ccp^{2-}, and both log K_1 and log K_2 for pcp^{2-}. On the other hand, the two phosphinate ligands are much less basic than mdp^{4-}, where protonation occurs on phosphonate groups, in line with the basicity order proposed previously,[22] phosphonate (first stage) > carboxylate > phenylphosphinate. Species distribution diagrams for ccp^{2-} and pcp^{2-} as a function of pH were obtained using the HYSS program[23] and are given in the Supporting Information.

Table 1. Decimal Logarithm (log *K*) Values of the Stepwise Basicity Constants[a]

	L				
reaction[b]	mal[c]	pa[c]	mdp[c]	ccp	pcp
$L + H \rightarrow HL$	5.054(2)	8.08(1)	10.41(1)	4.95(1)	3.34(9)
$HL + H \rightarrow H_2L$	2.51(2)	4.80(1)	6.90(1)	1.38(3)	1.3(2)
$H_2L + H \rightarrow H_3L$		0.9(1)	2.75(1)		
$H_3L + H \rightarrow H_4L$			0.7(2)		

[a] $T = 298$ K and $I = 0.5$ mol dm^{-3} (Me_4NCl). Values in parentheses are standard deviations on the last significant figure. [b] Charges are omitted for sake of simplicity. [c] Data from Alderighi et al.[7]

A model for the equilibria present in the system beryllium(II)−H_2ccp under the present experimental conditions was determined with the aid of the HYPERQUAD program.[19] The model includes both the ligand protonation constants (Table 1) and the equilibrium constants for the hydrolysis of the beryllium ion.[24] The formation constant of each complex species present is shown in Table 2, together with values for related complexes involving malonate (mal),[9] phosphonoacetate (pa),[7] and methylenediphosphonate (mdp).[7] The model for ccp^{2-} is similar to that proposed for the beryllium(II) phosphonoacetate system[7] with the main difference being the formation of $[BeHL_2]^-$, rather than $[Be(HL)_2]^{2-}$. However, the trimeric hydroxo species $[Be_3(OH)_3L_3]^{6-}$ and $Be_3(OH)_3L$ were found for L = pa and were not found for L = ccp, presumably because of differences in the ligands' basicity.

The formation constants of the beryllium (II) complexes with ccp^{2-} are lower than those of the corresponding

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Table 2. Decimal Logarithm (log *K*) Values of the Beryllium(II) Complex Formation Constants[a]

	L			
reaction[b]	mal[c]	pa[d]	mdp[d]	ccp[e]
$Be + L \rightarrow BeL$	5.36(2)	9.24(1)	13.7(1)	4.70(1)
$BeL + L \rightarrow BeL_2$	3.85(3)	5.74(2)	7.66(7)	2.52(3)
$Be + HL \rightarrow BeHL$		4.53(1)	8.3(1)	2.09(5)
$BeL + HL \rightarrow BeHL_2$			3.6(1)	1.5 (1)
$BeHL + HL \rightarrow Be(HL)_2$		≈2	5.0(1)	
$Be + H_2L \rightarrow BeH_2L$			4.0(2)	
$Be + 2\,H_2L \rightarrow Be(H_2L)_2$			7.6(2)	
$Be_3(OH)_3 + L \rightarrow Be_3(OH)_3L$	5.26(7)	7.2(3)		
$Be_3(OH)_3 + 3L \rightarrow Be_3(OH)_3L_3$	12.84(6)	20.86(3)		

[a] $T = 298$ K and $I = 0.5$ mol dm^{-3} (Me_4NCl). Values in parentheses are standard deviations on the last significant figure. [b] The charges of the species have been omitted for simplicity. [c] Data from Barbaro et al.[9] [d] Data from Alderighi et al.[7] [e] This work.

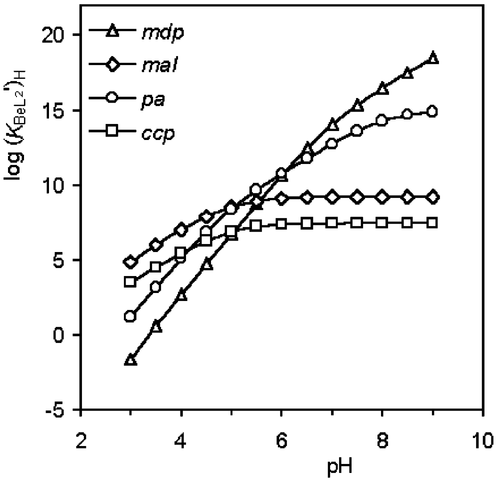

Figure 2. Plot of the pH dependence of the effective stability constant of $[BeL_2]^{2-}$ (L = mdp^{4-}, mal^{2-}, pa^{2-}, and ccp^{2-}).

complexes with other ligands shown in Table 2. This is also a reflection of the ligands' different basicity. In a recent paper,[5] we showed that, because of the competition of metal and proton for the ligand, it is preferable to compare coordinating ability in terms of "effective stability constants", K_{eff}, as defined by Schwarzenbach.[25] The dependence of log K_{eff} for the $[BeL_2]^{2+}$ complexes is illustrated in Figure 2. It can be seen that at high pH, where the ligands are completely deprotonated, the trend in effective constants is the same as the trend in stability constants. At lower pH values, where the ligand is partially protonated, the order changes, and it is particularly noteworthy that at pH < 4 the ligand ccp^{2-} exhibits a high coordination ability, second only to malonate.

The species distribution diagrams shown in Figure 3 were constructed using the HySS program.[23] The percentages of the various species were calculated using the equilibrium constants shown in Tables 1 and 2, the solubility product of beryllium hydroxide ($K_{sp} = [Be^{2+}][H^+]^{-2} = 10^{6.87}$) reported by Bruno,[26] and a metal-to-ligand ratio of 1:2. Beryllium hydroxide precipitates at pH values above ca. 6. The two concentrations that were used correspond to some experimental conditions. Note that there is considerable difference between the upper and lower plots resulting from the difference in total metal and ligand concentrations.

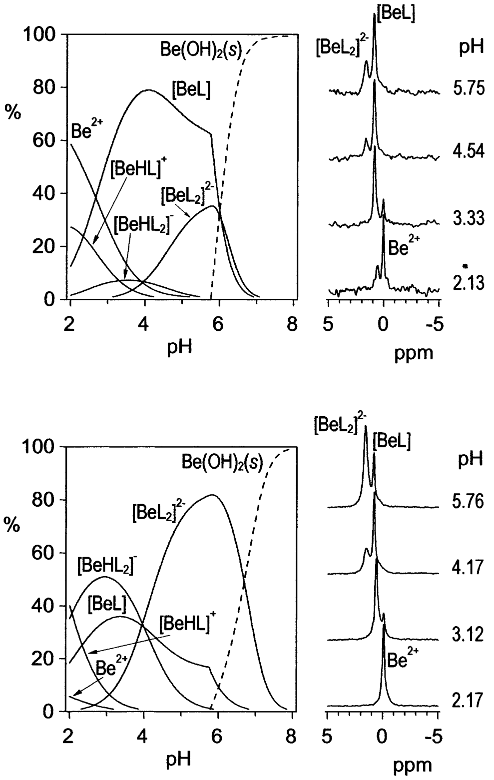

Figure 3. Distribution diagrams and ^{9}Be NMR spectra at variable pH for the system $BeSO_4-H_2ccp$ 1:2, with $C_{Be} = 0.003$ mol dm^{-3} (top) and $C_{Be} = 0.1$ mol dm^{-3} (bottom). The percentages are calculated relative to the total beryllium concentration. For the sake of clarity, the water molecules that complete the coordination sphere of the metal ion have been omitted in the formulas.

The experimental ^{9}Be NMR spectra, obtained under the same conditions of concentration, are shown at the right of Figure 3. The sharp resonance at ca. 0.0 ppm is due to the $[Be(H_2O)_4]^{2+}$ complex. The other broader peaks can be assigned with the aid of the speciation diagrams, as follows. The two signals at 0.9 and 1.65 ppm are assigned to the species $BeL(H_2O)_2$ and $[BeL_2]^{2-}$. The downfield shift of the resonance of the bis-chelate complex is in line with previously reported spectra.[8a] The resonance centered at ca. 0.6 ppm (pH = 2.13) may be due to the two rapidly exchanging species $[BeHL\ (H_2O)_3]^+$ and $BeL(H_2O)_2$, eq 1.

$$[BeHL(H_2O)_3]^+ \leftrightharpoons BeL(H_2O)_2 + H_3O^+ \qquad (1)$$

The corresponding $^{31}P\{^1H\}$ NMR spectra have been found to be consistent. They show two resonances at δ 31.5 and 31.2 ppm attributable to $BeL(H_2O)_2$ and $[BeL_2]^{2-}$, respectively, together with a high field signal due to the rapidly exchanging, uncoordinated, species H_2L, HL^-, and L^{2-}.

The clearest difference between the speciation at the two concentrations occurs at high pH values. In both cases, the two species $BeL(H_2O)_2$ and $[BeL_2]^-$ are present together, but $[BeL_2]^-$ predominates when the concentration is high, whereas $BeL(H_2O)_2$ predominates when the concentration is low. This behavior is expected as dilution strongly favors dissociation.

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(25) Schwarzenbach, G. *Die komplexometrische Titration*; Ferdinand Enke Verlag: Stuttgart, 1955; p 9.
(26) Bruno, J. *J. Chem. Soc., Dalton Trans.* **1987**, 2431−2437.

Solid State Studies. H_2ccp reacts with $Be(OH)_2$ (molar ratios 1:1 or 2:1) under continuous stirring, to yield colorless solutions. Evaporation of the solvent, after adjusting the pH with ammonia or KOH, always produced amorphous solids whose elemental analyses and NMR spectra were not consistent with any pure beryllium compound.

H_2pcp reacts with $BeSO_4$ in aqueous solution at 353 K to give a metastable solution[27] from which irregularly shaped microcrystals of formula Be(pcp)$(H_2O)_2$ slowly separate. This compound is insoluble in water and common organic solvents, so that single crystals suitable for a conventional structural analysis could not be prepared. It decomposes without melting upon heating. It was characterized by X-ray powder diffraction and solid-state IR spectroscopy. The IR spectrum shows a very strong, broad band centered at 3000 cm^{-1}, due to the OH stretching of H_2O. Both the broadness and the shift of the band toward lower energies are consistent with the presence of an extended hydrogen bond network.

Crystals of Be(pcp)$(H_2O)_2$ contain discrete monomeric molecules, with the Be(II) ion tetrahedrally coordinated by two water molecules and one chelating pcp ligand (see Figure 4a). The six-membered ring formed by chelation is slightly puckered toward a boat conformation, with torsional angles defined by the two $C_{ipso}-P-CH_2-P$ sequences of 70.2° and 87.3°. The two phenyls attached to the phosphorus atoms possess slightly different conformations about the $P-C_{ipso}$ vectors ($O_{Be}-P-C_{ipso}-C$ 6.3° vs 10.2°) and lie on the same side of the molecule, opposite to the $Be(H_2O)_2$ fragment; therefore, each molecule possess two distinct contact surfaces, of lipophilic and hydrophilic character, respectively. Accordingly, in the crystal, aryls of different molecules face each other, while water molecules and oxygen atoms of the phosphinic residue extensively interact through a complex, two-dimensional, hydrogen bond network (O1w··O3 2.44 Å; O1w···O2 2.71 Å, O2w···O2 2.47 Å; O2w···O3 2.86 Å; note that only the terminal O(P) atoms act as hydrogen bond acceptors, thus uniquely determining the H-atom locations). The resulting crystal structure is therefore built up from two-dimensional *double* layers, stacked along the crystallographic *a* axis, where the polar residues are deeply buried in the bilayer core (see Figure 4b). The very poor solubility of this species in water and organic solvents initially suggested a polymeric structure,[28] possibly built around the same structural motifs, but with O−P(O)Ph−CH_2−Ph(O)P−O ligands linking $Be(H_2O)_2$ fragments in the *exo*-, rather than *endo*-bidentate mode. The present structure determination clearly ruled out the presence of fully stretched phosphinates and revealed the stereochemistry of a monomeric compound, similar to the Be[salycilate]$(H_2O)_2$ species reported by Schmidbaur et al. in 1991.[29] Interestingly, also the latter species contains several H-bonded interactions, and a double layer structure very similar to ours (although the lipophilic part is somewhat smaller), but is slightly more soluble, allowing ^1H and ^9Be NMR characterization in solution.

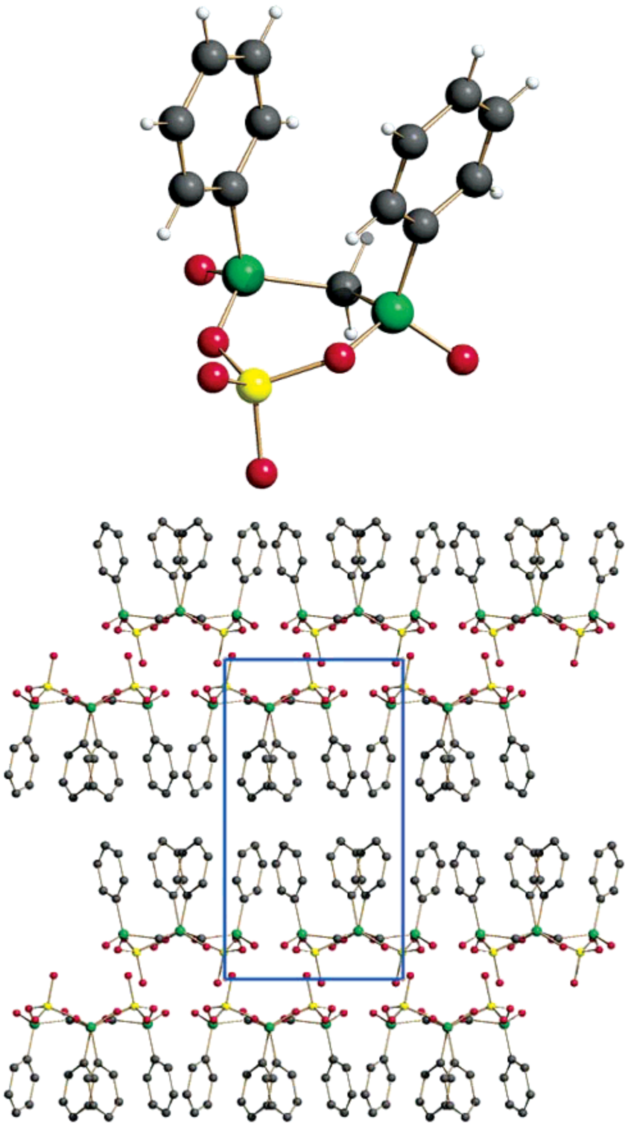

Figure 4. (a) Drawing of the molecular structure of Be(pcp)$(H_2O)_2$. (b) Crystal packing viewed down [001], highlighting the bilayer structure, stacking along *a* (vertical axis); for sake of simplicity, hydrogen atoms have been omitted.

When Be(pcp)$(H_2O)_2$ is heated in a nitrogen gas stream, it loses water in the range 110−150 °C, and the dehydrated species Be(pcp) is produced. A complete structural characterization of this material was not possible, since its XRPD pattern showed only one very strong peak at $2\theta = 6.21°$, two diffuse halos centered at ca. 17 and 24°, and two weak (second and third) harmonics of the major peak. The corresponding *d*-value, of ca. 14.2 Å, needs to be compared to the 16.2 Å value of the parent species and suggests that loss of water preserves the bilayer structure (even if shrunk by ca. 2 Å along the **a** direction), accompanied by amorphization in the *bc* plane. Moreover, we have found that the powders of the anhydrous material are stable as such if left in contact with humid atmosphere and do not restore the original hydrated crystalline phase.

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(27) A ^9Be NMR spectrum of this solution showed a singlet ($w_{1/2} = 7$ Hz) at δ 0.344 ppm, indicating the presence of only one beryllium(II) species.

(28) Polymeric complexes prepared by direct reaction of beryllium acetylacetonate and monophosphinic acids had been characterized about 30 years ago. See: Block, B. P. *Inorg. Macromol. Rev.* **1970**, *1*, 115−125.

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Conclusions

The bifunctional ligands ccp^{2-} and pcp^{2-} have been found to be capable of coordination to the beryllium(II) ion. In the case of ccp^{2-}, both mono-chelated and bis-chelated complexes have been characterized in aqueous solution. Because of the low basicity of the $-PO_2Ph$ donor group, the formation constants of the complexes are lower than those reported for the complexes of the related phosphonate ligands pa^{3-} and mdp^{4-} (Chart 1). However, it is noteworthy that at pH < 4 the effective stability constant of the complex $[Be(ccp)_2]^{2-}$ is greater than those of the corresponding phosphonoacetate and methylenediphosphonate derivatives. Accordingly, despite its low basicity, the $-PO_2Ph$ group can form the monodentate complex $[Be(Hccp)(H_2O)_3]^+$ at low pH values even without the assistance of a chelate.

In the case of the ligand pcp^{2-}, the insolubility of the complex $Be(pcp)(H_2O)_2$ prevents the formation of other derivatives. The structure determination of $Be(pcp)(H_2O)_2$ performed on a highly textured polycrystalline material shows that conventional laboratory techniques can provide useful stereochemical information even on moderately complex species (22 crystallographically independent non-hydrogen atoms). A distinctive feature of this study is that, despite the obvious lack of resolution, analysis of the intermolecular contacts has allowed the unambiguous assignment of elusive (water) H-atoms. It is well-known that such low-resolution XRPD structure analyses cannot provide detailed molecular information without the use of rigid body approximations or other geometrical constraints. Accordingly, several problematic structures of polycrystalline substances have been recently determined by the joint use of XRPD methods and ancillary (geometric and/or energetic) information, including cases of unknown stoichiometry[30] and of wrong stereochemistry,[31]connectivity,[32] and geometry.[33]

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Supporting Information Available: Speciation diagrams for pcp^{2-} and ccp^{2-} protonation. Final fractional coordinates and full list of bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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