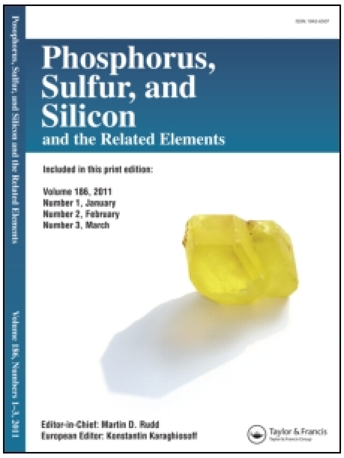

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BERYLLIUM(II) COMPLEXES WITH BIS(DIMETHYLAMINO)PHOSPHORYLFLUORIDE: A MULTINUCLEAR NMR (^{31}P, ^{19}F, AND ^{9}Be) CHARACTERIZATION IN SOLUTION

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Complexes of beryllium chloride and nitrate with $(Me_2N)_2P(O)F$ were characterized in solution by multinuclear NMR spectroscopy and in some cases by IR spectroscopy and conductimetry. ^{31}P and ^{19}F NMR spectra were informative of changes associated with complex formation revealing resonances consistent with different species in solution and suggest an equilibrium between these species in both beryllium derivatives. These compounds show narrow lines in the solution ^{9}Be NMR spectra, indicative of a highly symmetric environment for beryllium. The presence of the different species was more pronounced in beryllium chloride complexes. The results are compared to those reported in the literature for hexamethylphosphoramide (HMPA).

Keywords: ^{9}Be NMR spectroscopy; ^{31}P NMR spectroscopy; Beryllium complexes; phosphoryl ligands

The chemistry of beryllium is relatively unexplored compared to that of its neighboring elements.[1] This is due to its high toxicity,[2] which acts as a deterrent to the experimentalist. Phosphorylated compounds have been used widely as extractants for separating various metal ions by liquid-liquid extraction and hence the coordination chemistry of these ligands has attracted the attention of several workers.[3–5a] We recently have characterized in solution a mixture of new beryllium complexes[5b] with $(Me_2N)_2P(O)F$, the fluorinated derivative of hexamethylphosphoramide (HMPA) using multinuclear NMR spectroscopy. The choice of

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this type of ligand was inspired by the possibility of using ^{19}F NMR spectroscopy and thus obtaining complementary information to that obtained from ^{31}P NMR data about changes related to complex formation. Moreover, the introduction of the fluorine atom has little effect on the extracting ability of the ligand on account of the remaining two dimethylamino groups which maintain its complexing properties. The complexes were characterized by multinuclear NMR spectroscopy and compared to those reported for HMPA.[6,7] The results, in agreement with our previously reported works[7–9] and with IR data,[10] suggest that the ligand is coordinated to the beryllium atom via the phosphoryl oxygen.

RESULTS AND DISCUSSION

A mixture of the complexes $LBeCl_2$ **1**, $(L)_2BeCl_2$ **2**, $(L)_3BeCl_2$ **3**, and $(L)_4BeCl_2$ **4** were obtained by treating $BeCl_2$ with bis(dimethylamino)phosphoryl fluoride (L) in dichloromethane as solvent, whereas the complexes $(L)_2Be(NO_3)_2$ **5** and $(L)_3Be(NO_3)_2$ **6** were obtained following a method[11] well-known in the literature.

The products are oils soluble in dichloromethane, acetonitrile and nitromethane. The characterization of the compounds was based on their ^{31}P, ^{19}F, and ^{9}Be NMR data and comparison with the corresponding data for the free ligand (see Table I).

The ^{31}P{H} NMR spectrum for the free ligand, $(Me_2N)_2P(O)F$ showed a doublet due to coupling with ^{19}F atom; a similar doublet shifted to higher field was observed for all the complexes prepared. In the latter, each signal of the doublet appears as a quartet owing to coupling with ^{9}Be atom ($I = 3/2$) (Figure 1). The upfield shift of the doublet related to the bound ligand compared to that of the free ligand is indicative of disruption of the PO π interaction as a result of adduct bond formation, in agreement with IR data.[10] This relatively small upfield shift

TABLE I ^{31}P, ^{19}F, and ^{9}Be NMR Data of the Ligand and Compounds **1–6**

Compound	δ^{31}_{P}	δ^{19}_{F}	δ^{9}_{Be}	$^{1}J_{P-F}$	$^{2}J_{P-Be}$
L	17.3	79.2	—	948	—
1	16.5	79.0	4.2	931	4.0
2	15.0	78.8	3.0	945	4.0
3	14.7	78.4	1.2	941	4.5
4	14.4	78.2	−0.5	938	5.0
5	14.6	78.0	1.8	937	5.0
6	14.4	78.2	1.0	939	5.0

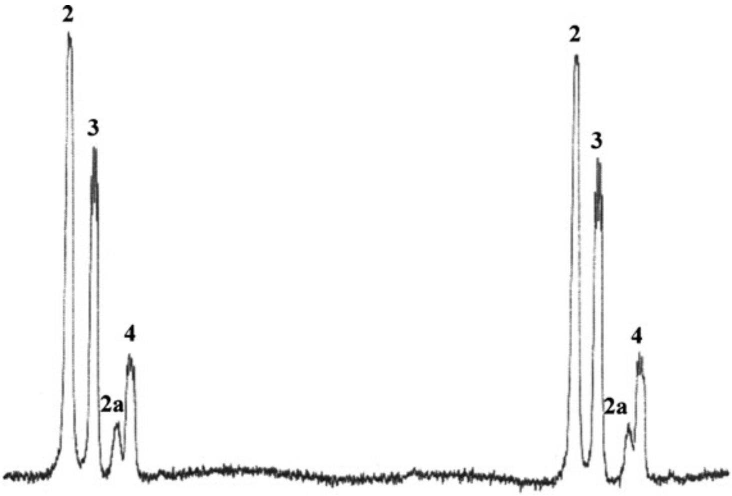


FIGURE 1 ^{31}P proton decoupled NMR spectrum of the solution (1:3; $BeCl_2/L$) in CD_2Cl_2 at $-33^{\circ}C$ showing the presence of species **2**, **3**, **2a**, and **4** in equilibrium.

(approximately 3 ppm) is perhaps demonstrative of a sizeable $N \rightarrow P$ inductive effect (electronic buffering of the phosphorus center) by means of π donation from the nitrogen centers of NMe_2 to compensate the loss of electron density around phosphorus following complexation. The same dichotomy has been observed with HMPA as ligand.[12]

The electronic adjustments associated with complex formation also are transmitted to the fluorine centers and the same behavior, as for ^{31}P NMR, was observed for ^{19}F chemical shifts. The ^{31}P NMR spectra of the solution (1:3) showed the coexistence of various species in equilibrium (Figure 1) to each species corresponds a doublet of quartets owing to coupling with both ^{19}F and ^{9}Be nuclei respectively. The almost constant frequency interval (approximately of 0.4 ppm) between two consecutive species (doublets) suggests that consecutive doublets should be assigned to the complexes **2**, **3**, **2a**, and **4**, this assignment is based on a comparison of their ^{31}P NMR data and the corresponding ^{9}Be NMR spectrum. We observed that the larger the amount of the ligand added the higher the ^{31}P chemical shifts were observed. In order to identify better these species, ^{9}Be NMR spectroscopy was used.

Beryllium Chloride Complexes

^{9}Be NMR spectra confirm the presence of the different species observed in ^{31}P NMR spectra. These spectra show the coexistence for the solution

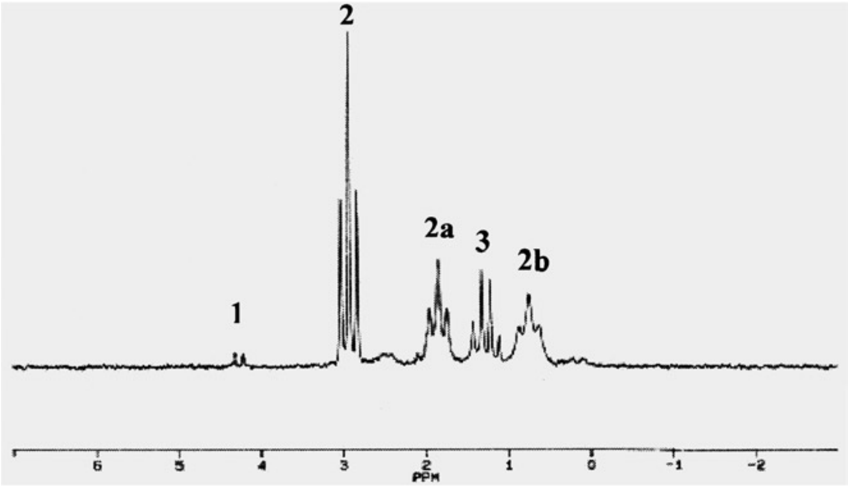
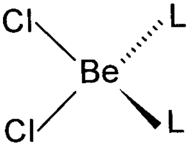


FIGURE 2 ^{9}Be NMR spectrum of the solution (1:2; $BeCl_2$/L) in CD_2Cl_2 at 0°C showing the presence of compounds **1**, **2**, **3**, **2a**, and **2b**.

(1:2) of a doublet for compound **1**, a triplet for compound **2**, and a quadruplet for compound **3** as a result of coupling with one, two, and three phosphorus atoms respectively (Figure 2). All these compounds possess relatively sharp resonances, with the exception of the two species **2a** and **2b**, which exhibited broad triplets (Figure 2) at 1.8 ppm for **2a** and at 0.7 ppm for **2b** with $^2J_{P-Be} = 4.5$ Hz and $^2J_{P-Be} = 4.8$ Hz respectively. The beryllium center in these two species may have an environment different from that observed for the beryllium center in compound **2**. As for the solution (1:4), a predominant quintet was observed for compound **4** due to coupling with four phosphorus atoms, which is consistent with a tetrahedral arrangement for 4 equivalent ligands around the beryllium cation.

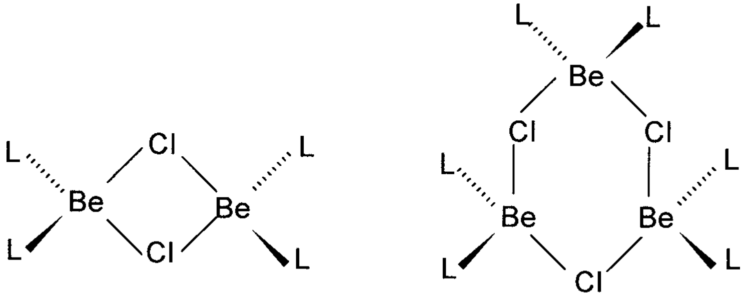
The predominant sharp triplet observed in ^{9}Be NMR spectrum for compound **2** (Figure 2) is indicative of a highly symmetric environment for the beryllium center in solution, composed of monomer entities (Scheme 1). Further evidence in support of this assignment is



SCHEME 1 Proposed structure for compound **2**.

obtained from conductivity measurements, which showed that this compound behaves as a non-electrolyte in nitromethane, and suggest that the complexes **1** and **2** are adducts containing coordinated chloride atoms whereas complexes **3** and **4** are electrolytes and may be represented as $(BeL_3Cl)^+$, Cl^- and $(BeL_4)^{2+}$, $2Cl^-$ respectively. The species **2a** and **2b** showed broad resonances (presumably due to bridge-terminal exchange).

This may be due to the fact that these species (**2a** and **2b**) are dimers or trimers similar to species observed in aqueous solutions of Be^{2+} cation,[13] and for which the following structures are proposed:



2a **2b**

SCHEME 2 Structures proposed for compounds **2a** and **2b**.

The assignement of these two structures is based on the fact that the more sterically encumbered species may have an upfield ^{9}Be chemical shift[14] (Figure 2).

Examination of the values of the chemical shifts in the Table I show an increase when we pass from compound **1** to **4**. This corresponds to a difference of approximately 1.7 ppm between two consecutive species (i.e., 1.7 ppm per ligand) showing an additive effect on the ^{9}Be chemical shifts when the number of ligands is increased. This upfield shift produced by the phosphoryl oxygen on the ^{9}Be NMR signals is consistent with the upfield shift observed for beryllium complexes with organic ligands containing the P=O group such as HMPA.[8]

These results are in agreement with previously reported data,[15,16] which showed that increasing the electronegativity of the substituent on the beryllium shifts the ^{9}Be resonance to lower field. The range of measured chemical shifts for the different complexes prepared (−0.5 to +4.2 ppm) fits into the range for four-coordinate ^{9}Be centers as previously established (ca. −2 to +6 ppm).[16,17] The coupling constants $^1J_{P-F}$ are smaller for bound ligands than for the free ligand. This was observed for AuCl complexes[18] with fluorophosphine(III) ligands. The coupling constant $^2J_{P\text{-}Be}$ for compound **2** is 4.0 Hz against 6 Hz for the complexes Be(HMPA)$_2$Cl$_2$ and Be(HMPA)$_4$(ClO$_4$)$_2$.[8] This may explain the shifts observed in ^{31}P NMR spectra (–2.4 ppm for the system BeCl$_2$-L against −4.4 ppm for BeCl$_2$-HMPA[7]). The difference may be explained by the fact that the movement of the nitrogen lone pair towards phosphorus upon complex formation is more important in the case of HMPA than that of (Me$_2$N)$_2$P(O)F due to a deficiency of Me$_2$N group in the latter. It is also worth noting that in Table I the coupling constants $^2J_{P\text{-}Be}$ show an increase of 1 Hz when passing from compound **2** to **4** (i.e. 0.5 Hz per ligand). The two bonds spin coupling of beryllium with phosphorus is consistent with a Be—OP bond, which is analogous to our previously reported results.[7–9]

Beryllium Nitrate Complexes

In order to investigate the behaviour of the ligand with a different beryllium salt, we have used beryllium nitrate. Similar results were obtained for these solutions, except for the number of species which was decreased and only compounds **5** and **6** were observed in the ^{9}Be NMR spectrum (Figure 3) even at higher concentrations of the ligand.

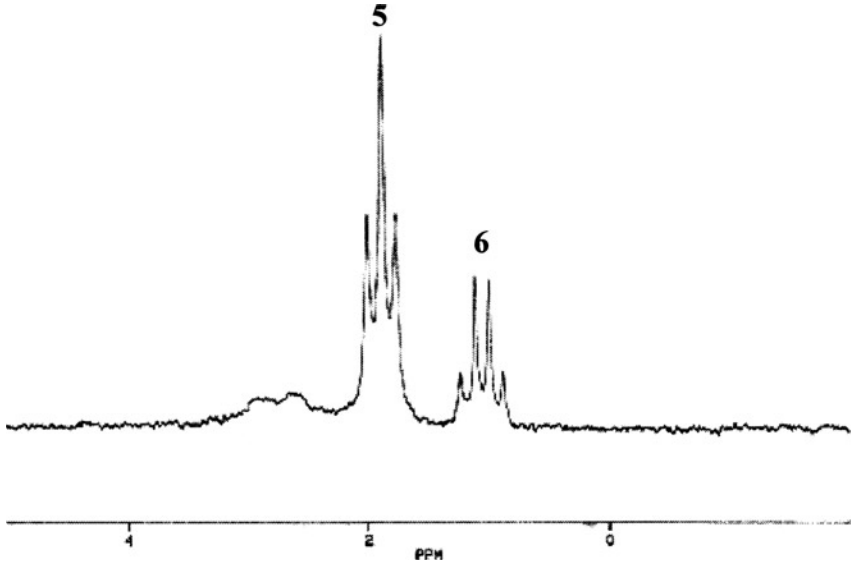


FIGURE 3 ^{9}Be NMR spectrum of the solution (1:2; Be(NO$_3$)$_2$/L) in CD$_3$CN at 25°C showing the presence of compounds **5** and **6**.

The predominant triplet observed for the species **5** in the ^{9}Be NMR spectrum (Figure 3) shows that beryllium is coordinated to two phosphorus atoms and the coordination number of this metal ion is invariably four. It may be then concluded that the structure of the species **5** is pseudotetrahedral containing two ligands and two monocoordinated nitrato groups similar to the complex obtained with HMPA $[Be(HMPA)_2(NO_3)_2]$.[6] The coupling constants $^2J_{P\text{-}Be}$ for the nitrate complexes are larger than for the chloride complexes (see Table I) showing that $^2J_{P\text{-}Be}$ depends also on the nature of the salt used[8] and suggests that the ligands are closer to Be^{2+} cation in beryllium nitrate compounds than that of beryllium chloride. This is due to the fact that beryllium nitrate is more solvated than beryllium chloride which was confirmed in the complexes by conductivity measurements that gave larger values for nitrate complexes than that of chloride complexes (75 $cm^2\ \Omega^{-1}\ M^{-1}$ and 15 $cm^2\ \Omega^{-1}\ M^{-1}$ respectively). These results are in good agreement with our previously reported work[19] for the solvate $Be(HMPA)_4(ClO_4)_2$ which contains tetrahedrally surrounded Be^{2+} ions with $^2J_{P\text{-}Be} = 6$ Hz showing an increase of this constant compared to the values obtained for the nitrate and chloride complexes. The bands observed at 637 cm^{-1} and 614 cm^{-1} in the IR spectrum of these complexes for the bond (O—Be) are also in good agreement with literature results.[6]

EXPERIMENTAL SECTION

Toxicity

Beryllium and its compounds are highly toxic[13,20] and should be handled with extreme care.[21] Experiments were conducted in a well-ventilated fumehood. Spillages and especially ones of particular nature were washed down well with water. Transportation of samples outside the fumehood were minimised and NMR measurements were carried out with extreme caution.

All preparations were carried out in a nitrogen atmosphere in solvents dried by standard techniques[22] and stored over molecular sieves. Beryllium chloride and beryllium nitrate were purchased from Alfa Inorganics and used without further purification. The ligand, $(Me_2N)_2P(O)F$ was prepared according to a method described in literature.[23] NMR spectra were recorded on a Bruker AC-300 instrument in $CDCl_3$ (for the ligand), CD_2Cl_2(for the chloride complexes) or CD_3CN (for the nitrate complexes) as solvents: ^{19}F at 282.39 MHz with CCl_3F as internal standard ^{31}P at 121.49 MHz with 85% H_3PO_4 as external standard and ^{9}Be at 42.17 MHz with $Be(H_2O)_4^{2+}$ as external standard. IR Spectra were recorded on Perkin Elmer Paragon 1000 PC instruments. The conductivity of the complexes was determined for 10^{-3} M solutions in nitromethane (dried on molecular sieves).

Preparation of the Mixture of Beryllium Chloride Complexes 1–4

To a solution of $BeCl_2$ (3 mmol, 0.24 g) in dichloromethane (20 mL) was added the stoichiometric amount of bis(dimethylamino)-phosphorylfluoride in 5 mL of CH_2Cl_2. The solution was stirred for 2 h in refluxing dichloromethane until dissolution of $BeCl_2$ was complete. The crude product was taken up in CH_2Cl_2 (5 mL) and the solution filtered through a sintered glass disk. The solvent was again removed in vacuo and the complexes were isolated as oils; these oils were washed several times with anhydrous ether and even on cooling for several days gave no precipitate. In addition, their distillation led to decomposition as shown by ^{9}Be and ^{31}P NMR spectra.

Preparation of the Mixture of Beryllium Nitrate Complexes 5 and 6

These complexes were prepared following a method described by Van Leeuwen et al.[11] The hydrated beryllium nitrate (3 mmol; 0.61 g) was dissolved in ethanol and an appropriate amount of triethylorthoformate was added. After 1 h the stoichiometric amount of the ligand was added, the solution was then concentrated by distilling off the solvent at reduced pressure. Addition of anhydrous ether led to the formation of the complexes in the form of oils.

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