



Beryllium (II) Chloride Complexes with Phosphoryl Ligands: A DFT Study

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Authors' contributions

This work was carried out in collaboration among all authors. Author KE designed the study, performed the theoretical statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author MAK performed the experimental work, managed the analyses of the study and wrote the final version of the manuscript. Authors MTBD and MRK managed the literature searches and general remarks. All authors read and approved the final manuscript.

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ABSTRACT

Beryllium complexes of the types $[\text{BeCl}_2\text{L}_2]$ (L = $(\text{Me}_2\text{N})_3\text{P}(\text{O})$ (1), $(\text{Me}_2\text{N})_2\text{P}(\text{O})\text{F}$ (2), $\text{Me}_2\text{NP}(\text{O})\text{F}_2$ (3) and $\text{P}(\text{O})\text{F}_3$ (4)) have been theoretically studied by means of DFT geometry optimization and NMR chemical shift calculations (B3LYP/6-31G(d)). A good correlation was found between calculated and experimental data for complex 2. On going from complex 1 to 4, the Be-L bond underwent considerable lengthening, while that of Be-Cl was shortened (Be-O: 1.646 in 1 vs. 1.740 Å in 4; Be-Cl: 2.043 in 1 vs. 1.953 Å in 4). In the same way, the Be-O-P bond angle was found to decrease from 135° for 1 to 124° for 4. The trends are in good agreement with the calculated metal-ligand binding energies of complexes 1-4. Interestingly, the structural changes are

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accompanied by increased ^9Be chemical shifts towards higher frequencies as the Me_2N groups in the ligand are substituted by fluorine atoms. The results were compared to corresponding complexes with tin (IV) chloride, $[\text{SnCl}_4\text{L}_2]$. The theoretical data showed that the use of the 6-31G* basis set could efficiently predict the ^9Be NMR chemical shifts in the complexes $[\text{BeCl}_2\text{L}_2]$.

Keywords: Phosphoryl ligand; beryllium (II) chloride; HMPA; shielding constant; ^9Be NMR; DFT/B3LYP.

1. INTRODUCTION

Beryllium is finding increasing use as a vital component in modern industry due to its unique physical properties [1-3]. However, beryllium is extremely toxic and can cause beryllium chronic disease (CBD), for which there is no current cure [4]. This has acted as a deterrent to the experimentalist if not to the theorician and limited the exploration of its chemistry, which is underdeveloped compared to its neighbouring elements [5]. Previous studies on beryllium showed that coordination of this small and hard cation with fluoride and oxygen donor compounds dominates the chemistry, with more interest being focussed on the oxygen functional ligands in terms of the toxicity of the metal [6-11]. It was also shown that in systems with multifunctional O/N/S-ligands, such as amino acids or peptides, beryllium appears to be coordinated only to the oxygen centres [12-21]. More recently, Buchner and Muller reported on beryllium chloride complexes with oxygen-containing bio-relevant functional groups as a model to evaluate the potential beryllium binding sites inside proteins, which is important to understand the mechanism of metal-triggered immune responses [22].

Phosphine oxides are potential oxygen donor ligands and can represent another path for mimicking nucleic acid sites in the body. The magnitude of their interaction with metal cations can be easily tuned through substitution of the groups bound to the phosphorus atom. The nature of these substituents could therefore play an important role in the stability of corresponding metal complexes [23-25]. Thus, understanding the coordination environment of these ligand-metal centre complexes is crucial for investigating both the coordination geometries and the binding affinities. Often the most informative studies result from examining how the ligand structure influences the donor-acceptor interaction in the complex whilst the metal is kept constant.

On the other hand, theoretical methods represent an attractive tool for investigation of metal ligand

complexes providing information on the geometries and metal-ligand interactions. In particular, DFT constitutes an attractive approach in this context and is also suitable for NMR chemical shift calculations in metal complexes due to its relatively good accuracy and favourable scaling with system size [26].

In a previous work [27], we have used DFT calculations to study the effect of subsequent substitution in a series of phosphoryl ligands of the type $(\text{R}_2\text{N})_n\text{P}(\text{O})\text{F}_{3-n}$ ($n = 1, 2$ or 3) on their magnitude of interaction with tin(IV) chloride. Herein, we report on the theoretical study of coordination geometries and binding affinities of beryllium chloride complexes with the same oxygen donor ligands by means of DFT geometry optimisation (B3LYP/6-31G(d) and NMR chemical shift calculations (B3LYP/6-31G(d)).

2. COMPUTATIONAL METHODS

Density functional theory (DFT) calculations were carried out on complexes 1-4 and their ligands using the Gaussian 98 suite of programs [28], with the hybrid functional B3LYP [29]. Basis set used was 6-31G* [30] for all the atoms. The geometries of complex 1-4 and their ligands were optimised using analytical gradient. The harmonic vibrational frequencies of the different stationary points of the potential energy surfaces (PES) have been calculated at the same level of theory in order to identify the local minima. The calculations of the shielding constants were performed on the optimised geometries in conjunction with the Gauge Independent Atomic Orbital (GIAO) formalism using the 6-31G* for all atoms. The use of larger basis sets for the ligand and chlorine atoms has been intentionally avoided in order to keep the computational cost at a reasonable level.

The theoretical ^{31}P , ^{19}F and ^9Be chemical shifts were obtained by difference between the calculated shielding constant for the complex, σ_{comp} and the corresponding value for the reference compounds H_3PO_4 , CFCl_3 and

$[\text{Be}(\text{H}_2\text{O})_4]^{+2}$, σ_{ref} according to: $\bar{\delta}_{\text{comp}} = \sigma_{\text{ref}} - \sigma_{\text{comp}}$, with $\sigma_{\text{ref}} = 370.0977$, 179.417 and 112.9495 ppm for H_3PO_4 , CFCl_3 and $[\text{Be}(\text{H}_2\text{O})_4]^{+2}$, respectively.

3. RESULTS AND DISCUSSION

3.1 Geometry Optimisations

Geometry optimizations of the complexes $[\text{BeCl}_2\text{L}_2]$ (1-4) were all carried out by means of the DFT/B3LYP method using the 6-31G(d) basis set (Table 1). All optimized geometries present nearly distorted C_2 symmetries. Two ligand molecules and two chlorine atoms are coordinated to the Be^{2+} ion providing a fairly distorted tetrahedral coordination environment (Fig. 1). Unfortunately, there is no experimental X-ray structural analysis of beryllium chloride complexes with phosphine oxide ligands available in the literature. However, the calculated Be-O and Be-Cl bond distances as well as angles at Be are in good agreement with those determined in the solid state using X-diffraction measurements for beryllium nitrate complexes with some phosphine oxides [31,32] and BeCl_2 complexes with other N and O-donor ligands [33]. For example, a search in the Cambridge Structural Database (CSD version 5.36, 2015 release) provides seven entries containing $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ entities that show tetrahedral coordination geometries with Be-O distances in the range 1.593–1.636 Å [34–39] and O-Be-O bond angles (104.9–117.98) that present relatively small deviations from the ideal

tetrahedral angle. Overall, the data reported in Table 1 show that the title complexes explored in this work have a relatively different geometries depending upon the ligand. The considerably shorter (stronger) Be-O distance in 1 compared to that in 4 is reflected by their Be-Cl distances. This is probably due to the difference in basicity between HMPA and $\text{P}(\text{O})\text{F}_3$, in fair agreement with our previous calculations of the Sn-O distance in *cis*- $[\text{SnCl}_4(\text{HMPA})_2]$ compared to that of *cis*- $[\text{SnCl}_4(\text{P}(\text{O})\text{F}_3)_2]$ and the effect on corresponding Sn-Cl distances [27].

Table 1 shows also that the increase in the electronegativity of the substituents on the phosphorus atom of the ligand in complexes 2-4 as compared to that of HMPA resulted in smaller Be-O-P bond angles, in view of the more bent structures observed in the optimised geometries (124° in 4 vs. 135° in 1). This is consistent with previous data reported for related systems [27, 40,41].

3.2 Binding Energies

The binding energy of metal-ligand interaction is generally related to the stability of the corresponding complex. A stable complex always gives a negative binding energy. Hence the stability of complexes will improve with the increase in negative value of binding energy. In other words, the stronger the binding capacity the more stable the resulting complex.

Table 1. Geometric parameters^a calculated at B3LYP/6-31G(d) level of theory for $[\text{BeCl}_2\text{L}_2]$

	L	$(\text{Me}_2\text{N})_3\text{P}(\text{O})$	$(\text{Me}_2\text{N})_2\text{P}(\text{O})\text{F}$	$\text{Me}_2\text{NP}(\text{O})\text{F}_2$	$\text{P}(\text{O})\text{F}_3$
L	P-O	1.494	1.482	1.470	1.456
	P-N	1.694	1.671	1.662	-
	P-F	-	1.604	1.577	1.559
	N-P-O	115.1	117.0	122.5	-
	F-P-O	-	112.1	113.8	117.4
$[\text{BeCl}_2\text{L}_2]$	Be-O	1.646	1.656	1.713	1.740
	Be-Cl ^b	2.043	2.025	1.977	1.953
	P-O	1.524	1.509	1.491	1.478
	P-N	1.668	1.643	1619	-
	P-F	-	1.594	1.568	1.544
	Be-O-P	135.0	133.4	127.8	124.1
	Cl-Be-Cl	114.5	113.8	119.2	122.7
	O-Be-O	104.4	103.7	99.4	100.2
	N-P-O	119.3	122.0	116.9	-
	F-P-O	-	106.1	113.1	117.9

^aDistances are in Å. Angles are in degree; ^bBe-Cl in BeCl_2 1.803 Å at B3LYP/6-31G (d).

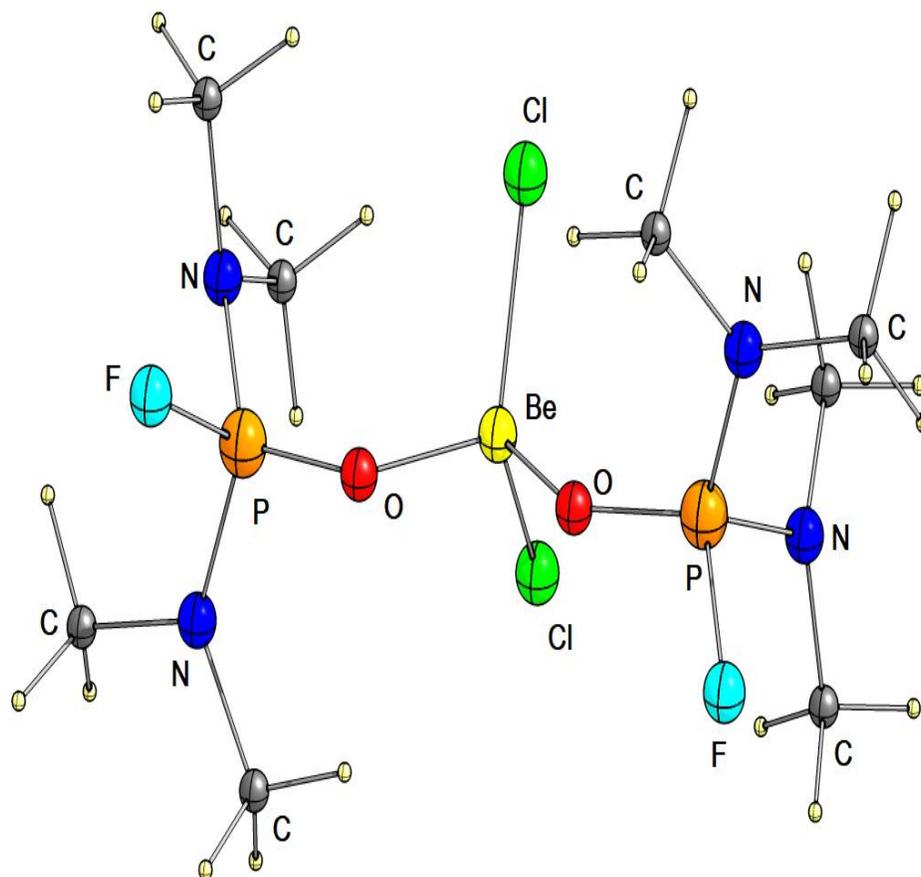


Fig. 1. DFT/B3LYP optimized structure of the complex $[\text{BeCl}_2((\text{Me}_2\text{N})_2\text{P}(\text{O})\text{F})_2]$ (2)

Table 2. The calculated binding energies (ΔE) and those corrected by ZPE ($\Delta(E + \text{ZPE})$) for the reaction of BeCl_2 with each ligand at B3LYP/6-31G(d) level (kcal.mol^{-1})

	$\text{BeCl}_2 + 2 \text{L} \rightleftharpoons \text{L}_2\text{BeCl}_2$			
	$(\text{Me}_2\text{N})_3\text{P}(\text{O})$	$(\text{Me}_2\text{N})_2\text{P}(\text{O})\text{F}$	$\text{Me}_2\text{NP}(\text{O})\text{F}_2$	$\text{P}(\text{O})\text{F}_3$
ΔE	-60.16	-57.02	-47.45	-29.48
$\Delta(E+\text{ZPE})$	-57.44	-54.10	-45.26	-27.45

Table 2 lists the binding energies (ΔE) of BeCl_2 complexes with the four ligands used in this study, calculated as the difference between the energy of complex with optimised geometry (E_{comp}) and the sum of energies of optimised ligands (E_{L}) and BeCl_2 (E_{BeCl_2}) (Eq.(1)).

$$\Delta E = E_{\text{comp}} - (E_{\text{L}} + E_{\text{BeCl}_2}) \quad (1)$$

As can be seen from Table 2, the calculated binding energies indicated that the presence of dimethylamino groups in the ligand played an important role in determining the stability of

complexes 1-4. The results suggested, therefore, that HMPA represents the highest binding capacity among the four ligands used. With increased number of fluorine atoms in the ligand, the order of calculated binding energies of corresponding complexes is $1 > 2 > 3 > 4$. This order is, as expected, in agreement with both the decreasing order of the basicity of the ligand and our structural data discussed above, demonstrating the weak donating ability of the ligand $\text{P}(\text{O})\text{F}_3$. However, despite the weaker basicity of the latter ligand, it still binds beryllium with a considerable binding energy ($-29.47 \text{ kcal.mol}^{-1}$), suggesting the high affinity of

beryllium to even the weakest phosphoryl ligands.

Interestingly, we have calculated at the same level of theory the stepwise formation of complexes 1-4 following eq. 2-3 and results are shown in Table 3.

The results shown in Table 3 allow us to compare the binding energies of the first and second ligand within the title phosphine oxide ligands and with other non oxygen donor ligands. For example, the calculated dissociation energy of [BeCl₂HMPA] is two-fold that of the second ligand, whilst those of F₃PO are almost the same (Table 3). Such a difference was not observed towards SnCl₄, which adds the two ligands, in the stepwise reaction, with nearly the same binding energy [27]. Surprisingly, the energy of addition of the second ligand for (Me₂N)₂P(O)F is more favourable than that of HMPA (-23.32 vs. -19.6, respectively) and even the second ligand Me₂NP(O)F₂ adds with nearly the same energy as that of HMPA (-19.6) (Table 3). This may be explained in terms of importance of steric hindrance in this case. On the other hand, the energy of the addition of the first ligand HMPA of 40.55 is comparable to the calculated bond dissociation energy (BDE) of the Cl₂Be-C(PPh₃)₂ bond at BP86/TZVPP//BP86/SVP (42.9 kcal·mol⁻¹) [42]. This is significantly higher than the calculated BDE of Cl₂Be-NH₃ which is only 27.4 kcal·mol⁻¹ [43] and also much higher than the calculated value for the complex Cl₂Be-PPh₂(CH₂PPh₂) (24.3 kcal·mol⁻¹) [44], indicating the large donor strength of HMPA.

3.3 NMR Chemical Shift Calculations

Our results, collected in Table 4 together with the experimentally observed data, do not take account of relativity. This is mainly because our major interest lies in correlating computed chemical shifts with experimental values for

closely-related series of molecules, rather than in obtaining absolute shielding values.

Examination of Table 4 shows that correlation between computed and experimentally obtained (³¹P, ¹⁹F and ⁹Be) chemical shift and (¹J_{P-F} and ²J_{P-Be}) coupling constant values for title ligands and complex 2 is good. The results show that the magnitudes of the chemical shifts and coupling constants seem to depend on the electronegativity of the substituents on the phosphorus atom of the ligand. Thus, the two-bond phosphorus-beryllium coupling constant is weakened and the ⁹Be chemical resonances shift towards higher frequency when passing from HMPA complex to that of P(O)F₃, in good agreement with the experimental results and also with the calculated Mulliken charges transferred to the Be atom upon complex formation (Table 5).

As can be seen from Tables 1 and 4, an observed increase to higher frequency in ⁹Be chemical shifts as a function of the ligand present is accompanied by an increase in Be-O bond distances and a decrease in the Be-O-P bond angles as dimethylamino groups are successively substituted by fluorine atoms, consistent with decreased donor power along the series (Me₂N)₃P(O) > (Me₂N)₂P(O)F > Me₂NP(O)F₂ > P(O)F₃. This is also in good agreement with the calculated binding energies of complexes 1-4. The same dichotomy was observed for tin(IV) chloride complexes with the same ligands in our previous work [27]. The influence of the substitution on the strength of the Be-O coordination has already been observed for some related compounds [45,46]. In our case, the shift towards higher frequency is nicely explained by the decrease in the charge on the Be and Cl atoms as the ligand becomes weaker donor (see Table 5).

Table 3. The calculated binding energies (ΔE) and those corrected by ZPE (Δ(E + ZPE)) for the reaction of BeCl₂ with each ligand at B3LYP/6-31G(d) level (kcal mol⁻¹)

Reaction	BeCl ₂ + L ⇌ L-BeCl ₂			
L	(Me ₂ N) ₃ P(O)	(Me ₂ N) ₂ P(O)F	Me ₂ NP(O)F ₂	P(O)F ₃
ΔE	-40.55	-33.70	-29.01	-17.08
Δ(E+ZPE)	-38.63	-32.24	-27.75	-15.93
Reaction	LBeCl ₂ + L ⇌ L ₂ BeCl ₂			
L	(Me ₂ N) ₃ P(O)	(Me ₂ N) ₂ P(O)F	Me ₂ NP(O)F ₂	P(O)F ₃
ΔE	-19.60	-23.32	-18.43	-12.40
Δ(E+ZPE)	-18.81	-21.86	-17.50	-11.52

Table 4. NMR data (δ /ppm and J/Hz) calculated at B3LYP level of theory for different ligands (L) and [BeCl₂L₂]

		(Me ₂ N) ₃ P(O)	(Me ₂ N) ₂ P(O)F	Me ₂ NP(O)F ₂	P(O)F ₃
L	δ (³¹ P) (exp)	18.02 (24)	16.2 (17.3)	-1.52 (-3.9)	-32.0
	δ (¹⁹ F) (exp)	-	-94.4 (-79.1)	-90.8 (-81.0)	-87.8
	¹ J _{P-F} (exp)	-	900 (948)	972 (1000)	1101
[BeCl ₂ L ₂]	⁹ Be (exp.)	2.64	2.94 (3.0)	3.92	4.46
	³¹ P (exp.)	25.22	22.50 (15.0)	3.44	-24.85
	¹⁹ F (exp.)	-	-94.90 (-78.8)	-82.20	-80.70
	² J _{Be-P} (exp.)	4.3	6.3 (4.0)	5.6	0.1
	¹ J _{P-F} (exp.)	-	854 (945)	929	1077

Table 5. The calculated Mulliken charges for complexes 1-4 and their ligands

		Be	Cl	O	P	F	N
L	BeCl ₂	0.359	-0.180	-	-	-	-
	(Me ₂ N) ₃ P(O)	-	-	-0.58	1.20	-	-0.53
	(Me ₂ N) ₂ P(O)F	-	-	-0.54	1.17	-0.33	-0.51
	Me ₂ NP(O)F ₂	-	-	-0.52	1.21	-0.31	-0.48
	P(O)F ₃	-	-	-0.47	1.30	-0.28	-
[BeCl ₂ L ₂]	(Me ₂ N) ₃ P(O)	0.507	-0.557	-0.548	1.276	-	-0.512
	(Me ₂ N) ₂ P(O)F	0.466	-0.534	-0.498	1.255	-0.33	-0.506
	Me ₂ NP(O)F ₂	0.448	-0.462	-0.511	1.291	-0.30	-0.477
	P(O)F ₃	0.392	-0.410	-0.453	1.392	-0.26	-

It can also be seen from Table 5 that the charge on the donor (oxygen) atom does decrease in the complex as compared to the free ligand. This is in sharp contrast with ligands behaviour towards tin(IV) chloride [27] and to conclusions reported for the interpretation of the redistribution of charges and the strength of the metal-ligand interaction on the basis of Mossbauer isomer shift values in [SnCl₄(P(O)Cl₃)₂] [47]. Since the source of electrons from phosphorus substituents is the same (charge on nitrogen atoms are nearly the same in both Be and tin complexes), such a behaviour could be explained by a more significant charge transfer from the ligand to beryllium than from ligand to tin centres, presumably due to the difference in the Lewis acidity between Be²⁺ and Sn⁴⁺.

4. CONCLUSIONS

Complexes of beryllium(II) chloride with phosphoryl ligands of different basicity of the types [BeCl₂L₂] (L = (R₂N)_nP(O)F_{3-n}; n = 1, 2 or 3) were theoretically studied using DFT/B3LYP calculations. The correlation of theoretical and experimental results on the moderate ligand complex, [BeCl₂((Me₂N)₂P(O)F₂)], showed that it is possible to reproduce the general trends observed in the experimental

results for the complexes [BeCl₂L₂]. The theoretical calculations indicate that, for such compounds, ⁹Be NMR chemical resonances are shifted to higher fields as the donor ability of the ligand increases. Importantly, the results were applied for the geometry optimisation and NMR chemical shift calculations on the unreported complexes [BeCl₂(Me₂NP(O)F₂)₂] and [BeCl₂(P(O)F₃)₂]. A more extended application of these calculations on different beryllium complexes using different basis sets is currently ongoing.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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