



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

K. Essalah¹, M. A. K. Sanhoury^{2,3*}, M. T. Ben Dhia² and M. R. Khaddar²

¹Université Tunis El Manar, Unité de Recherche Modélisation en Sciences Fondamentales et en Didactique, Equipe de Chimie Théorique et Réactivité (UR14ES10), Institut Préparatoire aux Etudes d'Ingénieur d'El Manar B.P 244, Tunis 2092, Tunisia.

²Laboratory of Coordination Chemistry, Department of Chemistry, Faculty of Sciences of Tunis, University of Tunis El Manar, 1060 Tunis, Tunisia.

³Research Unit of Materials Chemistry, Faculty of Sciences and Techniques, UNA, Nouakchott, Mauritania.

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 MAKS 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.

Article Information

DOI: 10.9734/IRJPAC/2021/v22i130366

Editor(s):

(1) Dr. Richard Sawadogo, Research Institute for Health Sciences, Burkina Faso.

Reviewers:

(1) Pratishtha Sharma, College of Veterinary Science and Animal Husbandary, India.

(2) Shaymaa Riyadh Mohammed Ali, Al-Nahrain University, Iraq.

Complete Peer review History: <http://www.sdiarticle4.com/review-history/64877>

Original Research Article

Received 24 November 2020

Accepted 29 January 2021

Published 26 February 2021

ABSTRACT

Beryllium complexes of the types $[\text{BeCl}_2\text{L}_2]$ ($\text{L} = (\text{Me}_2\text{N})_3\text{P}(\text{O})$ (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

*Corresponding author: E-mail: senhoury@yahoo.com;

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 $\text{H}_3\text{PO}_4, \text{CFCl}_3$ 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).

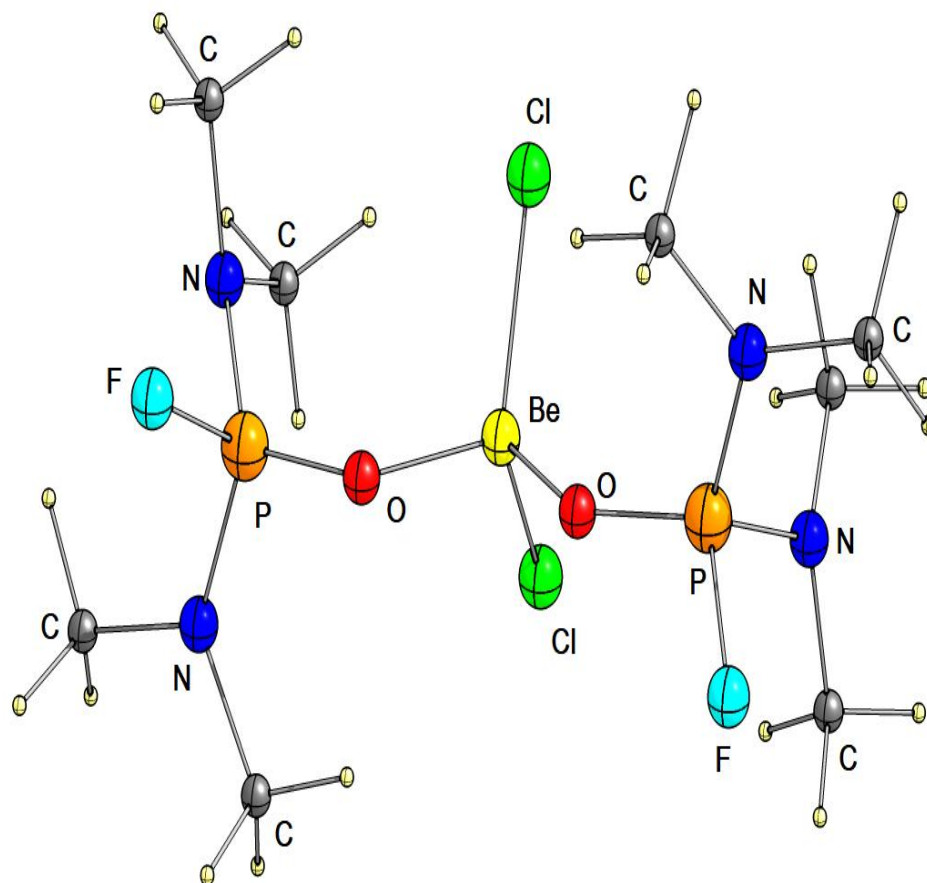


Fig. 1. DFT/B3LYP optimized structure of the complex $[\text{BeCl}_2((\text{Me}_2\text{N})_2\text{P}(\text{O})\text{F})_2]$ (2)

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.

ACKNOWLEDGEMENT

We are grateful to the Tunisian Ministry of High Education and Scientific Research and Technology for financial support (LR99ES14) of this research.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Davies AG. In Comprehensive organo metallic chemistry II; Abel EW, Stone FGA, Wilkinson G, Eds.; Elsevier Science Inc.; Tarrytown, NY. 1995;2.

2. (a) Harrison PG. Compounds of tin: General trends. In chemistry of tin; Harrison PG Ed.; Champan and Hall; New York; 1989.
(b) Munguia T, Lopez-Cardoso M, Cervantes-Lee F, Pannell KH. Intramolecular Chalcogen-Tin Interactions in $(\sigma\text{-MeE-C}_6\text{H}_4)\text{CH}_2\text{SnPh}_{3-n}\text{Cl}_n$ (E = S, O; $n = 0, 1, 2$), Characterized by X-ray Diffraction and ^{119}Sn Solution and Solid-State NMR, *Inorg Chem.* 2007;46: 1305.
3. Denmark SE, Fu J. Understanding the Correlation of Structure and Selectivity in the Chiral-Phosphoramidate-Catalyzed Enantioselective Allylation Reactions: Solution and Solid-State Structural Studies of Bisphosphoramidate-SnCl₄ Complexes, *J Am Chem Soc.* 2003;125:2208.
4. Dann SE, Genge ARJ, Levason W, Reid G. Synthesis, multinuclear magnetic resonance spectroscopic studies and crystal structures of mono- and di-selenoether complexes of tin(IV) halides. *J Chem Soc Dalton Trans.* 1997;2207.
5. Fàrsaiu D, Leu R, Ream PJ. The 1 : 1 and 2 : 1 complexes of diethyl ether with tin tetrachloride and their stability, studied by ^{119}Sn NMR spectroscopy. *J Chem Soc Perkin Trans.* 2001;2:427-431.
6. Scott BL, Wang Z, Marrone BL, Sauer NN. Potential binding modes of beryllium with the class II major histocompatibility complex HLA-DP: A combined theoretical and structural database study. *J Inorg Biochem.* 2003;94:5-13.
7. Rossman MD, Preuss OP, Powers MB. "Beryllium: Biomedical and Environmental Aspects", Williams, Wilkens, Baltimore; 1991.
8. Eisenbud M. *Appl Occup Environ Hyg.* 1998;13:25.
9. Guy RH, Hostynek JJ, Hinz RS, Lorence CR. *Metal and the Skin: Topical Effects and Systematic Absorption.* Marcel Dekker, New York; 1999.
10. Griffitt WR, Skilleter DN. In Merrian E (ed.): "Metals and their compounds in the environment, Beryllium", VCH, Weinheim, Germany. 1991;775.
11. Saltini C, Amicosante M, Franchi A, Lombardi G, Richeldi L. Immunogenetic basis of environmental lung disease: lessons from the berylliosis model, *Eur Resp J.* 1998;12:1463.
12. Skilleter DN. *Chem Ber.* 1990;26:26.
13. Rich V. Officials "held back data" on Soviet blast *New Sci.* 1990;1737:19 and 1990; 1743:15.
14. Kumberger O, Schmidbaur H. Warum ist Beryllium so toxisch? *Chem Unserer Zeit.* 1993;27:310.
15. Schmidbaur H, Kumberger O, Riede J. Beryllium salicylate dehydrate. *Inorg Chem.* 1991;30:3101.
16. Kumberger O, Riede J, Schmidbaur H. Preparation and Crystal Structure of $\text{Na}_2[\text{Be}(\sigma\text{-C}_6\text{H}_4\text{O}_2)_2]\cdot 5\text{H}_2\text{O}$. *Chem Ber.* 1992;125:2701.
17. Kumberger O, Schmidbaur H. Beryllium coordination to bio-ligands: Isolation from aqueous solution and crystal structure of a hexanuclear complex of Be^{2+} with glycolic acid, $\text{Na}_4[\text{Be}_6(\text{OCH}_2\text{CO}_2)_6]$, *Z Natur Forsch.* 1992;47b:1717.
18. Schmidt M, Bauer A, Schmidbaur H. Beryllium Chelation by Dicarboxylic Acids in Aqueous Solutions, *Inorg Chem.* 1997;36:2040.
19. Schmidt M, Bauer A, Schier A, Schmidbaur H. Complexation of Beryllium(II) by Maleic and Succinic Acid, *Z Naturforsch.* 1998; 53b:727.
20. Schmidt M, Schmidbaur H. Ligand Redistribution Equilibria in Aqueous Fluoroberyllate Solutions, *Z Naturforsch.* 1998;53b:1294.
21. Mederos A, Dominguez S, Chinea E, Brito F, Cecconi F. New Advances in the coordination chemistry of the beryllium(II). *J Coord Chem.* 2001;53:191.
22. Muller M, Buchner MR. Beryllium Complexes with Bio-Relevant Functional Groups: Coordination Geometries and Binding Affinities. *Angew Chem Int Ed.* 2018;57:1-6.
23. Le Coz E, Guerchais JE. *Bull Soc Chim Fr* N°1. 1971;80.
24. Tudela D, Fernández V, Tornero JD. Mössbauer study of the *cis-trans* isomers of tin(IV) complexes. Some considerations about the sign of the electric-field gradient; *J Chem Soc Dalton Trans.* 1985;1281-1284.
25. Rupp-Bensadon J, Lucken EAC. Nuclear quadrupole resonance and stereochemistry. Part 8. *cis-trans* isomerism in octahedral SnCl_4L_2 complexes. *J Chem Soc Dalton Trans.* 1983;495-497.
26. Aslanov LA, Ionov VM, Attiya VM, Permin AB. Petrosyan vs Zhur *Strukt Khim.* 1977;18:1103.

27. Essalah K, Sanhoury MA, Ben Dhia MT, Abderrabba M, Khaddar MR. Tin tetrachloride adducts with phosphoryl ligands: A DFT study. *J Mol Struct: Theochem.* 2010;942:110–114.
28. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G. (2009) Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT; 2013.
29. (a) Becke AD. Density-functional thermochemistry. III. The role of exact exchange, *J Chem Phys.* 1993;98:5648.
(b) Lee C, Yang W, Parr RG. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B.* 1988;37:785.
30. (a) J. Hehre, Ditchfield, R., Pople, J. A.. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules, *J. Chem. Phys.* 1972;56:2257.
(b) Petersson GAW, Bennett A, Tensfeldt TG, Al-Laham MA, Shirley WA, Mantzaris J. A complete basis set model chemistry. I. The total energies of closed-shell atoms and hydrides of the first-row elements, *J Chem Phys.* 1988;89:2193.
(c) Petersson GA, Al-Laham MA. A complete basis set model chemistry. II. Open-shell systems and the total energies of the first-row atoms. *J Chem Phys.* 1991;94:6081.
(d) Hariharan PC, Pople JA. The influence of polarization functions on molecular orbital hydrogenation energies, *Theoret Chim. Acta.* 1973;28:213.
(e) Rassolov VA, Ratner MA, Pople JA, Redfern PC, Curtiss LA. 6-31G* basis set for third-row atoms, *J Comp Chem.* 2001; 22:976.
31. Cecconi F, Ghilardi CA, Midollini S, Orlandini A. Beryllium complexes with mono- and tripodal-phosphin oxide ligands. X-ray crystal structure of $[\{N(CH_2PPh_2O)_3\}Be(OH_2)](ClO_4)_2$, *Inorg Chem Commun.* 2000;3:350–353.
32. Davis MF, Levason W, Ratnani R, Reid G, Webster M. Synthesis, spectroscopic studies and structural systematics of phosphine oxide complexes with Group II metal (beryllium–barium) nitrates. *New J Chem.* 2006;30:782–790.
33. Perera LC, Raymond O, Henderson W, Brothers PJ, Plieger PG. Advances in beryllium coordination chemistry, *Coord Chem Rev.* 2017;352:264–290.
34. Fischer N, Klapötke TM, Peters K, Rusan M, Stierstorfer J. Alkaline Earth Metal Salts of 5,5'-Bistetrazole – from Academic Interest to Practical Application, *Z Anorg Allg Chem.* 2011;637:1693.
35. Yasodha V, Govindarajan S, Low JN, Glidewell C. Cationic, neutral and anionic metal(II) complexes derived from 4-oxo-4H-pyran-2,6-dicarboxylic acid (chelidonic acid), *Acta Crystallogr C.* 2007;63: 207.
36. Puchta R, Neumüller B, Dehnicke K. $[Be_3(\mu_3-O)_3(MeCN)_6\{Be(MeCN)_3\}_3](I)_6$ – ein Berylliumkomplex mit Cyclo- (Be_3O_3) -Kern und sein Hydrolyseprodukt $[Be(H_2O)_4](I)_2 \cdot 2MeCN$, *Z Anorg Allg Chem.* 2011;637:67.
37. Klepov VV, Vologzhanina AV, Serezhkina LB, Serezhkin VN. Synthesis, structure, and properties of $[Be(H_2O)_4][UO_2(CH_3COO)_3]_2$, *Radiochemistry.* 2013;55:36.
38. Robl C, Hentschel S, McIntyre GJ. Hydrogen bonding in $Be[C_2(COO)_2] \cdot 4H_2O$ —A neutron diffraction study at 15 K. *J Solid State Chem.* 1992;96:318.
39. Robl C, Hentschel S. Zur Kenntnis von $Be[C_2(COO)_2] \cdot 4 H_2O$ — Ein durch starke Wasserstoffbrückenbindungen stabilisiertes anorganisches Derivat der Acetylendicarbonsäure / On $Be[C_2(COO)_2] \cdot 4 H_2O$, *Z Naturforsch.* 1990;B45:1499.
40. Ben Dhia MT, Sanhoury MAMK, Owono LCO, Khaddar MR. Phosphine oxide adducts of tin(IV) chloride: Experimental NMR and DFT computational study. *J Mol Struct.* 2008;892:103-109.
41. Burford N, Royan BW, Spence REvH, Rogers RD. Nuclear magnetic resonance spectroscopic characterisation and the crystal and molecular structures of $Ph_3PSe \cdot AlCl_3$ and $Ph_3PSe \cdot AlCl_3$: a classification of the co-ordinative bonding modes of the phosphine chalcogenides, *J Chem Soc Dalton Trans* and refs. There in. 1990;2111-2117.
42. Petz W, Dehnicke K, Holzmann N, Frenking G, Neumüller B. The Reaction of $BeCl_2$ with Carbodiphosphorane $C(PPh_3)_2$; Experimental and Theoretical Studies. *Z Anorg Allg Chem.* 2011;637:1702–1710.

43. Metz S, Holthausen MC, Frenking G. Theoretical Studies of Inorganic Compounds. 36¹) Structures and Bonding Analyses of Beryllium Chloro Complexes with Nitrogen Donors, *Z Anorg Allg Chem.* 2006;632:814–818.
44. Frenking G, Holzmann N, Neumüller B, Dehnicke K. [BeCl₂(Ph₂PCH₂PPh₂)₂] – ein Donor-Akzeptorkomplex des Berylliums mit dem Bis(diphenylphosphanyl)methan-Liganden [BeCl₂(Ph₂PCH₂PPh₂)₂], *Z Anorg Allg Chem.* 2010;636:1772-1775.
45. Jambor R, Dostal L, Ruzicka A, Sisarova I, Brus J, Holcapek M, Holecek Organotin(IV) Derivatives of Some O,C,O-Chelating Ligands, *J. Organo Metallica.* 2002;21: 3996.
46. Kasna B, Jambor R, Schurman M, Jurkschat K. Synthesis and characterization of novel intramolecularly O,C,O-coordinated heteroleptic organostannylenes and their tungstenpentacarbonyl complexes. *J Organomet Chem.* 2008;693:3446-3450.
47. Varnek VA, Varnek AA. On the nature of the isomer shift in tin(IV) tetrachloride complexes with organic ligands from quantum chemical data. *J Struct Chem.* 1997;38:970-973.

© 2021 Essalah et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

The peer review history for this paper can be accessed here:
<http://www.sdiarticle4.com/review-history/64877>