

## Predicting $^9\text{Be}$ Nuclear Magnetic Resonance Chemical Shielding Tensors Utilizing Density Functional Theory

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**Abstract:** The structures of a series of beryllium containing complexes have been optimized at the B3LYP/6-31G(d) level and their  $^9\text{Be}$  magnetic shielding values have been determined using B3LYP/6-311G+g-(2d,p) and the gauge-including atomic orbital (GIAO) method. The calculated chemical shifts are in excellent agreement with experimental values. The performance of a variety of NMR methods (SGO, IGAIM, CSGT) were also examined but were found to be inferior to the GIAO method at the chosen level of theory employed. The theoretical method has been utilized to predict the beryllium chemical shifts of structurally characterized complexes for which no measured  $^9\text{Be}$  NMR spectrum exists, and to investigate a literature complex with an unusual  $^9\text{Be}$  NMR chemical shift. A new standard for beryllium NMR in nonaqueous solvents has been suggested.

### Introduction

The investigation of beryllium containing coordination complexes remains relatively unexplored. This is due to the well-documented extreme toxicity of beryllium.<sup>1</sup> Although less of a concern for the theoretician, relatively few computational studies (~20) have been reported involving the modeling of beryllium complexes. One of the first groups to examine beryllium complexes using computational methods was that of Marynick and co-workers in the mid seventies.<sup>2</sup> They examined beryllium phosphate interactions using self-consistent field methods and have more recently investigated the structure and calculated energies of beryllium hydrides<sup>3–5</sup> using density functional theory.<sup>6,7</sup> Since these early studies, a number of other groups have used theoretical methods to examine various aspects of beryllium coordination chemistry including structure prediction and ligand deprotonation trends,<sup>8</sup> ligand bond rotations,<sup>9</sup> stereoisomerization,<sup>10</sup> monosaccharide binding sites,<sup>11</sup> and beryllium peroxides.<sup>12</sup> A number of computational investigations into

the structure and energies of various hydrated beryllium(II) ions have been undertaken,<sup>13–17</sup> as has a theoretical study into the hydrolysis of the beryllium metal,<sup>18</sup> both due in part to the desire to understand biologically relevant interactions of this metal.

To date only a limited number of beryllium NMR theoretical studies have been attempted.<sup>15,19–21</sup> Tossell has examined various aqueous forms of beryllium at the 6-31G\* level with the gauge-including atomic orbital (GIAO) method and concluded that an increase in hydrolysis (i.e., sequential replacement of  $-\text{OH}_2$  with  $-\text{OH}$ ) deshielded the Be(II) nuclei in monoberyllium containing complexes, whereas oligomerization (increasing the beryllium cluster size from 1 to 3 beryllium atoms) had the opposite effect. A comparable result was also found for aqueous Al(III) species.<sup>15</sup> Further attempts by Tossell to correlate various factors such as  $^9\text{Be}$  NMR shifts with calculated nuclear quadrupole coupling constants (NQCC) values, calculated shielding anisotropies, and distortions from tetrahedral geometry met with limited success.<sup>19</sup> Bryce and Wasylishen examined the beryllium chemical shielding and electric field gradient of beryllium 2,4-pentanedionate in the solid state and via ab initio calculations.<sup>20</sup> Their methods demonstrated for the first time anisotropy in the chemical shielding tensor of beryllium.

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The present report seeks to establish conditions for the prediction of accurate  $^9\text{Be}$  NMR shifts using theoretical calculations and to then use these conditions to predict beryllium chemical shift values for beryllium complexes with known structures. Ultimately, the method will be employed for the structure elucidation of beryllium complexes for which the solution  $^9\text{Be}$  NMR spectrum can be safely measured. To aid in this predictive method known  $^9\text{Be}$  NMR chemical shifts have been compiled and various trends have been identified.

## Experimental

Basic beryllium acetate was prepared via the synthesis of Moeller et al.<sup>22</sup> Beryllium bis(2,4-pentanedionate) 99% was purchased from Alfa Aesar and used without further purification. CAUTION! BERYLLIUM SALTS ARE EXTREMELY TOXIC AND SHOULD BE HANDLED WITH APPROPRIATE CARE. All beryllium solid manipulations were handled in a Plas-Labs 818 Series, HEPA filtered (0.4 micron prefilter), reversed-pressure glovebox. All beryllium solution work was performed in a dedicated HEPA filtered chemical hood.  $^9\text{Be}$  NMR spectra were recorded on a Bruker Avance 300 at 42.17 MHz and referenced to an internal standard of  $\text{Be}(\text{H}_2\text{O})_4^{2+}$  (as the sulfate salt). All NMR samples containing beryllium were contained within Teflon sleeves in addition to the standard NMR glass tube.

## Computational

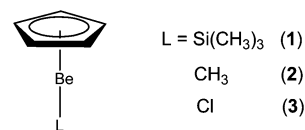
The following calculations were performed using the program GAUSSIAN03 for Windows,<sup>23</sup> running on a Dell OPTIPLEX GX270 personal computer equipped with an Intel Pentium 4 3.2GHz processor and 2.0 GB of RAM. We found that Becke's three-parameter hybrid exchange correlation functional<sup>24</sup> containing the nonlocal gradient correction of Lee, Yang, and Parr (B3LYP),<sup>25</sup> in conjunction with the 6-31(d) basis set, was satisfactory for geometries for the most part. In two cases [ $\text{Be}(\text{sal})(\text{H}_2\text{O})_2$  (**8**) and  $\text{Et}_2\text{OBeCl}_2\text{pyz}$  (**9**)] it was necessary to constrain bond lengths to more closely correlate with structural information ( $\text{Be}-\text{O}_{\text{H}_2\text{O}}$  for **8** and  $\text{Be}-\text{O}_{\text{ether}}$  and  $\text{Be}-\text{N}_{\text{pyrazole}}$  for **9**), which further enhanced accuracy of the computed NMR chemical shifts. All modeled structures are complete representations of the literature examples with the exception of complex **12** and are presented in Table 3. Due to the large number of methyl groups present in complex **12**, the complex was modeled in a simplified form (all methyl groups were replaced by hydrogen atoms). All optimized structures were confirmed as minima by calculation of the vibration frequencies. NMR shieldings for beryllium were evaluated at the minima using B3LYP or HF with 6-311+G(2d,p) as the basis set and the GIAO (gauge-including atomic orbital) NMR method<sup>26,27</sup> as implemented by Cheeseman, et al.<sup>28</sup> in the Gaussian03 package. The complex  $\text{Be}(\text{H}_2\text{O})_4^{2+}$  (**4**) is the standard reference for  $^9\text{Be}$  NMR spectroscopy and is defined as 0.00 ppm.

Structure optimization for this complex (B3LYP/6-31(d)) followed by calculation of the magnetic shielding (B3LYP/6-311G+(2d,p) gave a value of 108.96 ppm. All chemical shifts reported in this study are in relation to  $\text{Be}(\text{H}_2\text{O})_4^{2+}$ , using the expression  $\delta_{\text{complex}} = \sigma_{\text{reference}} - \sigma_{\text{complex}}$ . Beryllium speciation is strongly pH dependent in aqueous solutions. If a formula has been established for a new chemical species from the pH dependent behavior of a beryllium complex, then these have been included (Table 1) along with their  $^9\text{Be}$  chemical shift value.

## Results and Discussion

**Table of Beryllium NMR Shifts.** To aid in interpretation of beryllium complexes with unknown structure, an extensive tabulation of published  $^9\text{Be}$  NMR chemical shifts was undertaken (Table 1). The table can be broadly separated into 3 regions, cyclopentadienyl complexes ( $-28$  to  $-18$  ppm), tetrahedral beryllium coordination complexes ( $-2$  to 8 ppm) and finally those beryllium complexes with lower coordination numbers (8+ ppm). The records for the most extreme chemical shift values are currently held by Saulys and Powell for their beryllium trimethylsilane complex ( $-27.7$  ppm)<sup>29</sup> and Kovar and Morgan for their three-coordinate dimethyl beryllium diethyl ether adduct (20.8 ppm).<sup>30</sup> Interestingly there are no complexes with reported beryllium shifts between  $-18.3$  and  $-1.2$  ppm.

Beryllium coordinates to one cyclopentadienyl ring  $\eta^5$  with a second ligand bound sigma to the beryllium, whether it is a halide or a second cyclopentadienyl bound in a slipped fashion (Figure 1).



**Figure 1.** Cyclopentadienyl beryllium complexes modeled in the present study.

Chemical shifts for these cyclopentadienyl beryllium complexes constitute the upfield extreme of the chemical shift range for beryllium. High-field chemical shifts of Be nuclei in cyclopentadienide derivatives are ascribed to ring current effects. An examination of Mulliken charges for the Cp-Be complexes gives evidence that this upfield shift is also, in part, due to a higher electron density at the Cp ring, resulting in stronger ring-current effects.<sup>29</sup> Similar high field effects are mirrored in other metals bound  $\eta^5$  to Cp.<sup>31</sup>

The four coordinate complexes span the chemical shift range between  $-2$  and 8 ppm. The most striking trend is the relationship between the number and size of chelate rings vs chemical shift (Figure 2). This has been noted before but in less detail.<sup>32</sup> On reducing the chelate ring size, the beryllium chemical shift is shifted downfield. In addition, the number of chelate rings present incorporating beryllium (1 or 2) also affects the chemical shift. For example, on going from a beryllium atom that is incorporated into one five-membered chelate ring to a beryllium atom shared by two five-membered chelate rings, the beryllium chemical shift is moved further downfield. This latter effect is potentially very useful for identifying new BeL and

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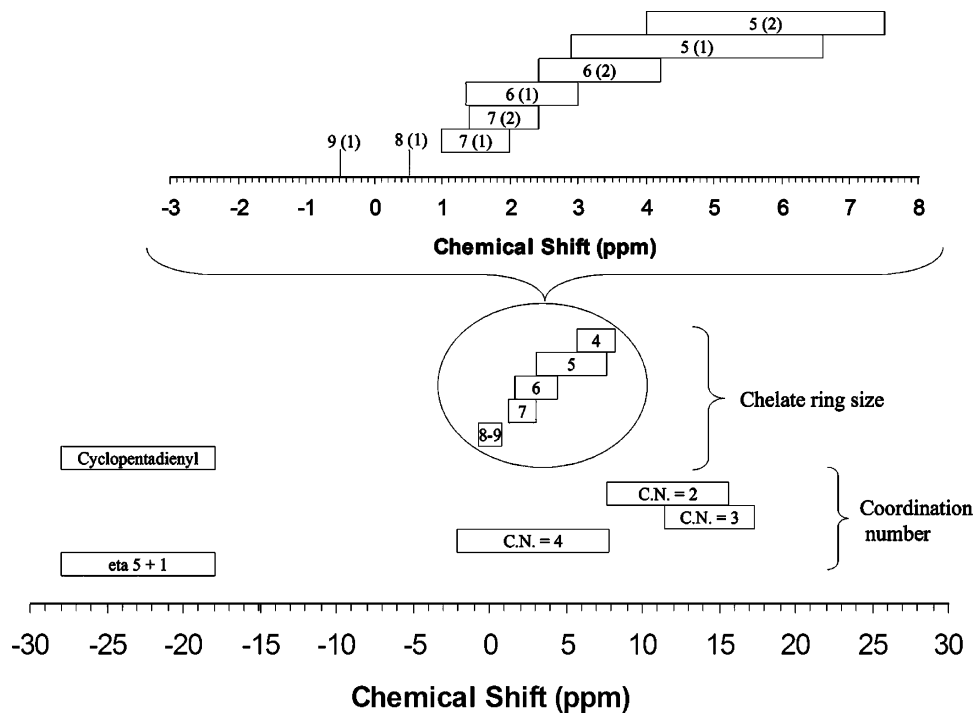
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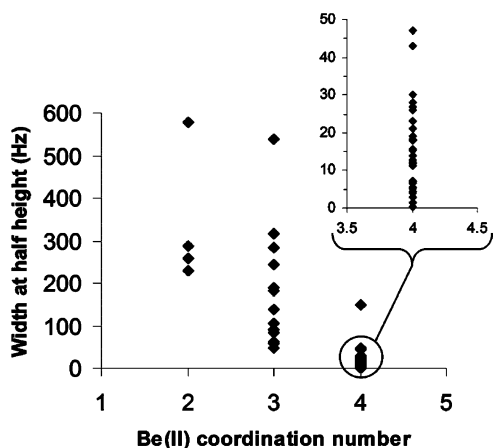
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**Figure 2.** Chemical shifts of known beryllium complexes sub-divided into coordination number and chelate ring size. The lower part of the figure shows the relationship between coordination number of the beryllium atom in the complexes and chemical shift. The middle part of the diagram shows the effect that chelate ring size has on the chemical shift for four coordinated beryllium complexes. This is further sub-divided (upper part of figure) into the number of chelate rings (1) or (2) per beryllium atom.



**Figure 3.** Relationship between width at half-height of beryllium NMR signal and coordination number of the beryllium cation.

groups such as trigonal. Similar affects are noticed with aluminum and boron nuclei.<sup>33</sup> From an analysis of the beryllium species (Figure 3), there is a correlation between narrow half-height widths of the NMR signal and highly symmetrical species, essentially the 4-coordinate beryllium species are symmetrical and hence have narrow peak widths. The exception to this is the unsymmetrical 4-coordinate species characterized by Niemeyer and Power,<sup>34</sup> with a peak width at half-height of 150 Hz, there is a tendency to suggest that in solution an alternative lower coordinate species may exist, however with a solution chemical shift of 2.7 ppm, a value typical of standard four coordinate beryllium species, and solid state evidence for a four coordinate species, the reason for the large peak width has to be due to the unsymmetrical nature of the coordination

**Table 2.** (A–C) Be–X Bond Comparison of Geometric Optimized Structures with Those of Known X-ray Data

(A)		CpBeSi(CH <sub>3</sub> ) <sub>3</sub>	CpBeCH <sub>3</sub>	CpBeCl	
Be–Cp	calcd.	1.497	1.512	1.484	
	exptl.	1.487		1.451(5)	
Be–C	calcd.		1.713		
	exptl.				
Be–X	calcd.	2.195 (Si)		1.871 (Cl)	
	exptl.	2.185(2)		1.869(3)	
(B)		Be(sal)(H <sub>2</sub> O) <sub>2</sub>	Be(Hima) <sub>2</sub>	Be(cat) <sub>2</sub>	Be(ima) <sub>2</sub>
Be–O (ligand)	calcd.	1.537 (phenol)	1.627 (phenol)	1.643	1.633
	exptl.	1.572(2)	1.599(6)	1.640(6) avg.	1.617(4)
Be–O (H <sub>2</sub> O)	calcd.	1.546 (carbox)	1.652 (carbox)		1.670
	exptl.	1.612(2)	1.642(5)		1.646(4)
Be–O (H <sub>2</sub> O)	calcd.	1.620			
	exptl.	1.623(2)			
Be–O (H <sub>2</sub> O)	calcd.	1.650			
	exptl.	1.658(2)			
(C)		Et <sub>2</sub> OBeCl <sub>2</sub> pyz	Be(NH <sub>3</sub> ) <sub>4</sub> <sup>2+</sup>	(PhCN) <sub>2</sub> BeCl <sub>2</sub>	
Be–O (ligand)	calcd.	1.749			
	exptl.	1.677(4)			
Be–N	calcd.	1.765	1.771	1.768	
	exptl.	1.717(4)		1.740(3)	
Be–Cl	calcd.	2.001		1.958	
	exptl.	1.997(4)		1.969(2)	
	calcd.	1.954			
	exptl.	1.979(3)			

sphere. This example serves as a warning that such comparisons need to be carefully examined. With the exception of the above example, a general trend useful to experimentalists can be stated that if the width at half-height is less than 47 Hz then the complex contains highly symmetric 4-coordinate beryllium. The trend between 2 and 3 coordinate species is less well defined (Figure 3), this is in part due to the difficulty in determining the coordination number for these low coordinate species.

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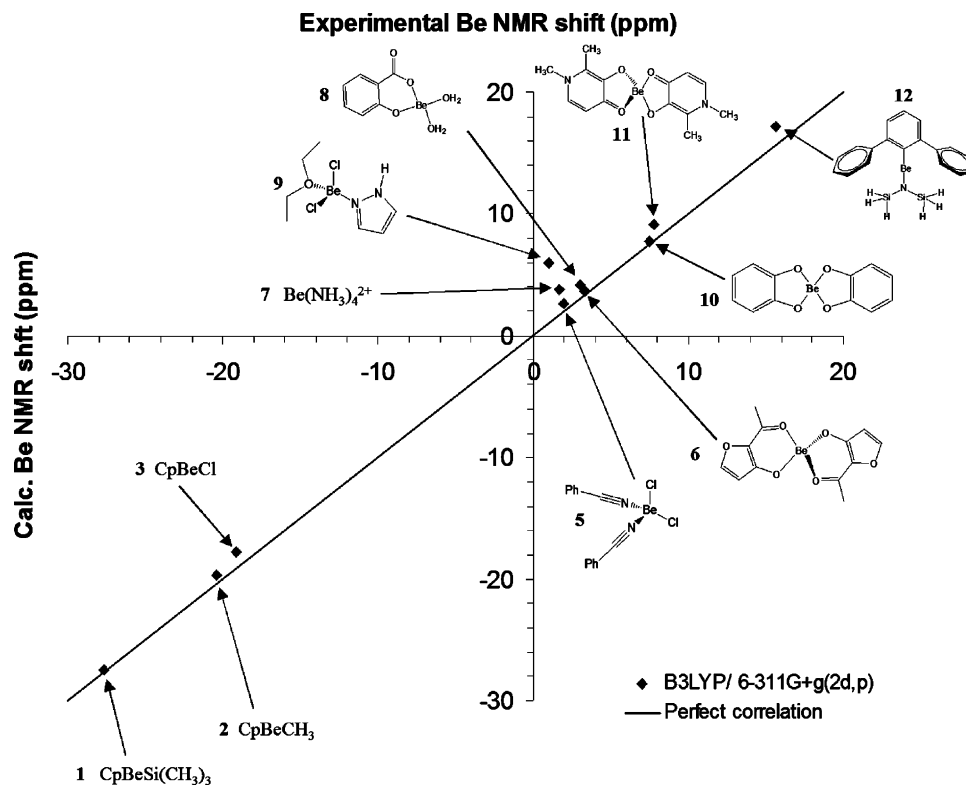


Figure 4. Graph of experimental beryllium NMR shifts vs calculated NMR shifts.

Table 3. Complexes Studied with Calculated Magnetic Shifts B3LYP/6-311G+G(2d,p)

complex	model complex <sup>a</sup>	$\sigma_{\text{ref}}$ / ppm	$\sigma_{\text{model}}$ / ppm	$\delta_{\text{model}}$ / ppm	exptl.	$ \Delta_{\text{exptl-calc}} $
1	CpBeSi(CH <sub>3</sub> ) <sub>3</sub>		136.44	-27.5	-27.7	0.2
2	CpBeCH <sub>3</sub>		128.59	-20.4	-20.4 av. <sup>b</sup>	0.0
3	CpBeCl		126.68	-19.1	-19.5	0.4
4	Be(H <sub>2</sub> O) <sub>4</sub> <sup>4+</sup>	108.96	108.96	0.0	0.0	0.0
5	(PhCN) <sub>2</sub> BeCl <sub>2</sub>		106.31	2.6	2.0	0.6
6	Be(ima) <sub>2</sub>		105.23	3.7	3.4	0.3
7	Be(NH <sub>3</sub> ) <sub>4</sub> <sup>2+</sup>		105.14	3.8	1.7	2.1
8	Be(sal)(H <sub>2</sub> O) <sub>2</sub>		104.74	4.2	3.0	1.2
9	Et <sub>2</sub> OBeCl <sub>2</sub> pyz		102.62	6.3	1.0	5.3
10	Be(cat) <sub>2</sub>		101.23	7.7	7.5	0.2
11	Be(dpp) <sub>2</sub>		99.98	9.0	7.8	1.2
12	Be(dipb)N(SiH <sub>3</sub> ) <sub>2</sub>		91.73	17.2	15.6	1.6

<sup>a</sup> Cp = cyclopentadienide, ima = 1-[2-(hydroxy)-3-furanyl]ethanolate, sal = 2-hydroxybenzoate, pyz = pyrazole, cat = 1,2-benzenediolate, dpp = 3-(hydroxy)-1,2-dimethyl-4(1H)-pyridinolate, dipb = 2,2'',4,4'',6,6''-hexamethyl[1,1':3',1''-terphenyl]-2'-yl. <sup>b</sup> Average chemical shift from four different solvents.

**Accuracy of Optimized Models.** Accurate geometries for complexes for which crystal structure data were available were obtained using B3LYP/6-31 g(d) as the level of theory (Table 2a–c). The models are loosely grouped according to coordinating groups with cyclopentadienyl (a), chelates (b) and nitrogen donors (c) being the broad categories. Typically, gas-phase calculated Be–X bond lengths were within 2.3% (excluding constrained structures) of those from the solid-state structures. Two of the complexes Be(sal)(H<sub>2</sub>O)<sub>2</sub> (8) and Et<sub>2</sub>OBeCl<sub>2</sub>pyz (9) required the Be–X bond lengths to be constrained to get within 5% of the solid-state structure values. We found that the level of theory employed tended to overestimate the Be–OH<sub>2</sub> bond lengths by a significant amount for any complex that had this type of bond present. Extensive hydrogen bonding in the crystal lattice of 9 may account for the poor performance in that case.

An attempt was made to describe 9 as a hydrogen bonded dimer, which did improve the beryllium coordination bond lengths (average improvement of 0.5%) but constraints were still required to get these bond lengths within close agreement with the solid-state structures.

A structure comparison of our <sup>9</sup>Be NMR reference [Be(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> was made to suitable literature examples. There are two crystallographic reports for Be(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> in the literature, both of which are extensively hydrogen bonded.<sup>35,36</sup> The average Be–O distance for these examples is 1.612(2). The calculated Be–O distance for our standard is 1.659, an overestimation of 2.9%. The discrepancy in lengths is due in part to the hydrogen bonding of the literature examples, which are noted to be shorter than typical Be–O distances,<sup>35</sup> the level of theory (B3LYP) and solid-state structures vs gas-phase models are also factors.

**Calculated NMR Chemical Shifts.** A comparison of calculated <sup>9</sup>Be NMR chemical shifts with published experimental values is shown in Figure 4 and data are presented in Table 3. Representative complexes to be studied were chosen to cover the currently known <sup>9</sup>Be chemical shift range for beryllium complexes. Experimental samples are in a variety of solvents (D<sub>2</sub>O, CDCl<sub>3</sub> etc). Changing NMR solvent has relatively little effect on beryllium chemical shifts as evidenced by the beryllium cyclopentadienyl complexes (1–3) and Be(ima)<sub>2</sub> (6) of Cecconi and co-workers<sup>8</sup> in Table 3. Likewise variations in counterions and anions have negligible effect on the chemical shift of <sup>9</sup>Be. Our reference complex Be(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> has a shielding value of 108.96 using the density functional B3LYP and 6-311G+(2d,p) optimized at 6–31 g(d) which compares well with other reported values, for example, Tossell has reported Be(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>

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shielding values of 119.98, 115.33, and 112.66 ppm using HF/6-31(d), HF/6-311G(2d,p) and BLYP/6-31(d), respectively.<sup>15</sup>

In preliminary investigations, a small number of chemical shifts were obtained using the GIAO, SGO, IGAIM, and CSGT NMR methods as implemented in Gaussian 03W. The GIAO method was found to give the most satisfactory (closest to experimental) values with HF and the 6-311G+(2d,p) basis set. A similar investigation with DFT and the 6-311G+(2d,p) basis set, showed little difference between the CGST and GIAO methods (the GIAO method tended to slightly overestimate the beryllium chemical shift values, an effect which has been noted previously<sup>15</sup>), but were superior to SGO and IGAIM (see Supporting Information). On the basis of these results the GIAO method was utilized for this study.

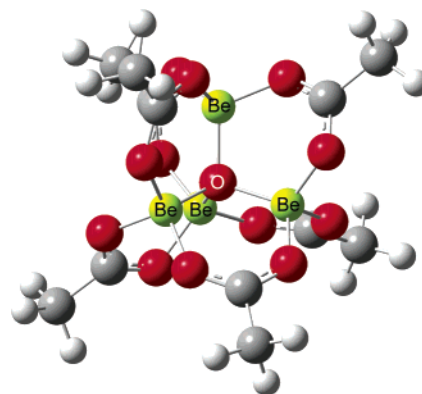
Predicted NMR values are in very close agreement with experimental values for most compounds. Compound **9** has the largest error ( $\delta_{\text{model}} = 6.3$  ppm vs  $\delta_{\text{exptl.}} = 1.0$  ppm), mirroring the error in the optimized bond lengths. An attempt was made to model **9** as a dimer, which did not have a significant effect on the chemical shift ( $\delta_{\text{dimer}} = 6.2$  ppm). Restraining the bond lengths in the monomer to bring them more in line with the solid state structure also improved the calculated NMR shift results slightly ( $\delta_{\text{restrained}} = 6.0$  ppm). The extreme difference between the model and experimental values for complex **9** implies that an alternative species may exist in solution. The Be–OEt<sub>2</sub> bond is notoriously labile and it is reasonable to expect that the ether molecule may be lost in solution (CDCl<sub>3</sub>). Unfortunately, no speciation studies were carried out for this complex.

Excluding the complexes that can hydrogen bond (**7–9**), the calculated chemical shift values are in excellent agreement with the reported experimental chemical shift values with an average error of only 0.5 ppm (range 0.0–1.6).

#### Application of the Method to Three Examples.

**Beryllium bis(2,4-pentanedionate).** Numerous NMR parameters (such as the nuclear quadrupole coupling constant, asymmetry parameter and solid-state isotropic chemical shift) have been reported for this compound,<sup>20,37</sup> yet surprisingly, the solution experimental  $^9\text{Be}$  NMR chemical shift has not been reported. Bryce and Wasylishen, when determining evidence for anisotropic shielding, determined the experimental solid-state chemical shift of 0.50 and 0.72 for this compound (for the unique beryllium centers in the solid state). Calculated  $^9\text{Be}$  nuclear magnetic shielding tensor components using restricted Hartree–Fock and the 6-311++G(3df,3pd) basis set gave a value of 3.3 ppm (referenced to calculated Be(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>).<sup>20</sup> Optimization of the complex (B3LYP/6-31(d)) gave bond coordinates in close agreement with the reported X-ray structural analysis (calc. vs exptl. is 1.623, 1.280 vs 1.618, 1.282 for Be–O and C=O bonds, respectively).<sup>38</sup> Calculation of the NMR chemical shift using GIAO (B3LYP/6-311G+g(2d,p)) resulted in a computed value of 3.95 ppm. We have determined the experimental value for beryllium 2,4-pentanedionate in deuterated chloroform to be 3.74 ppm (referenced to an internal standard of Be(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>), which compares favorably to our calculated value.

**Basic Beryllium Acetate.** Basic beryllium acetate has the formula Be<sub>4</sub>O(CH<sub>3</sub>COO)<sub>6</sub> and exists in the solid state as a cluster (Figure 5).<sup>39</sup> Studied since the turn of the century, it is another simple beryllium complex for which the  $^9\text{Be}$  NMR in solution



**Figure 5.** Optimized structure of basic beryllium acetate. Each beryllium atom is surrounded by a tetrahedral arrangement of oxygen atoms.

has not been reported. Geometric optimization of the complex (B3LYP/6-31(d)) and subsequent analysis revealed that the bond lengths were in good agreement with those of the solid-state structure (calcd. vs exptl. is 1.676, 1.633, 1.268 vs 1.673, 1.638, 1.263 for Be–O<sub>center</sub>, Be–O, and C=O bonds respectively).<sup>40</sup> We have determined the experimental value for beryllium acetate in deuterated chloroform to be 0.90 ppm (referenced to an internal standard of Be(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>), which compares favorably to our calculated value of 1.31 ppm (B3LYP/6-311G+g(2d,p)). As an aside, we believe that basic beryllium acetate would make an ideal internal standard for NMR studies in organic solvents. The thermal and chemical stability of the cluster is good, and it is free from the problems (e.g., changes in solution speciation) associated with variations in pH. It also has good solubility in deuterated chloroform.

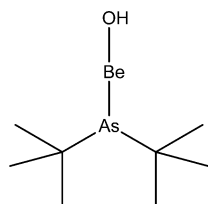
**$\eta^5\text{-(C}_5\text{Me}_5\text{)BeAs}(t\text{-Bu)}_2$ .** In 1999, Jones et al. reported the synthesis and characterization of  $\eta^5\text{-(C}_5\text{Me}_5\text{)BeAs}(t\text{-Bu)}_2$ , an  $\eta^5$  pentamethylcyclopentadienyl beryllium arsenide complex.<sup>41</sup> What struck us as surprising was the reported  $^9\text{Be}$  chemical shift value of 14.16 ppm. The cyclopentadienyl ring dominates the chemical shift of beryllium as evidenced from numerous examples of Cp–Be–X, where X has a fairly minimal effect on the  $^9\text{Be}$  NMR chemical shift of the complex. Generally these complexes exhibit significant upfield  $^9\text{Be}$  NMR chemical shifts (typical values are –27 to –18 ppm). From our earlier analysis a beryllium chemical shift at ~14 ppm is indicative of a low coordinate beryllium species, these are usually accompanied with a broad signal. These discrepancies led us to investigate this result of Jones et al. more thoroughly. Once again, two different basis sets were used for the optimizations and NMR calculations. For the geometry optimization C, H and Be were described with the standard 6-31G(d) basis set while 6-311G+g(2df) was used for Arsenic. Likewise the NMR calculation used the standard 6-311G+(2d,p) for C, H and Be and 6-311+g(3df) for arsenic. Optimization and calculation of the beryllium chemical shift of  $\eta^5\text{-CpBeAs}(t\text{-Bu)}_2$  gave a value of –25.4 ppm, whereas the full complex  $\eta^5\text{-(C}_5\text{Me}_5\text{)-BeAs}(t\text{-Bu)}_2$  gave a value of –22.30 ppm, both values are in keeping with beryllium chemical shifts of known cyclopentadienyl literature complexes implying that the solution complex

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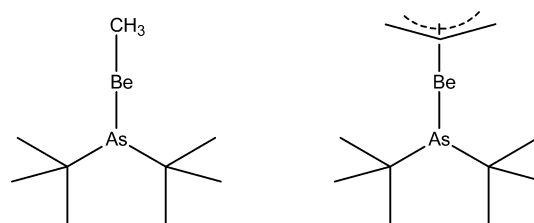
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**Figure 6.** Possible solution hydrolysis product for the title complex  $\eta^5\text{-(C}_5\text{Me}_5\text{)BeAs(t-Bu)}_2$ .

is indeed different from the solid-state complex as determined by Jones et al. The discrepancy between our calculated results and the experimental data as reported may result from the fact that the coordination sphere of  $\eta^5\text{-(C}_5\text{Me}_5\text{)BeAs(t-Bu)}_2$  is significantly altered in solution. A test was carried out for a possible hydrolysis product  $\text{HOBAs(t-Bu)}_2$  (Figure 6), the calculated NMR value for this complex was 4.89 ppm, which is closer to the reported value of 14.16 but was not close enough for us to be confident that this was the correct answer.

A more plausible reason for this positive chemical shift lies in the fluxional nature of the pentamethylcyclopentadienyl ring in solution. Shapiro has reported that the  $^{27}\text{Al}$  chemical shift is useful in diagnosing changes in the cyclopentadienyl coordination environment for complexes containing this motif. For  $^{27}\text{Al}$  a shift to higher frequency is indicative of a change to  $\eta^1$  ring geometries.<sup>31</sup> To test this idea, the  $\eta^1$  cyclopentadienyl complex was constructed and optimized. Unfortunately, the geometric optimization of the  $\eta^1$  starting model optimized to the  $\eta^5$  complex and so two new models, namely, methyl coordinated and allyl coordinated beryllium arsenic derivatives were chosen as  $\eta^1$  and  $\eta^3$  models respectively (Figure 7).



**Figure 7.** Two models optimized as mimics for  $\eta^1$  and  $\eta^3$  bound pentamethylcyclopentadienyl, respectively.

Optimization and  $^9\text{Be}$  NMR chemical shift calculations were performed on each model resulting in chemical shift values of 41.6 and 15.59 ppm for the methyl and allyl complexes, respectively, providing evidence that the solution structure is highly likely to exist with a lower coordination configuration. Whether it is a time-averaged signal between  $\eta^1$  and  $\eta^5$  (an average of these two chemical shifts is 16.2 ppm) or  $\eta^3$  coordination is difficult to say, however Jones reported that a sharp signal was observed which implies  $\eta^3$  coordination is the more likely option (given that a time averaged signal would be expected to be broad). It would be interesting to conduct a variable temperature  $^9\text{Be}$  NMR experiment on this complex to determine whether the observed signal is a result of a fluxional process.

## Conclusions

DFT calculations using B3LYP and the standard 6-31G(d) basis provide good structural representations of most beryllium complexes. NMR calculations performed on minimized structures, using the GIAO method with the expanded basis set 6-311G+g(2d,p) provides accurate results as compared to experimental values in the majority of cases. This level of theory performed less well when the molecule possessed hydrogen donors and acceptors. Correct structure is important for accurate prediction of NMR data. Overall structural errors of  $\sim 2\%$  were compounded to errors as large as 11% in the  $^9\text{Be}$  NMR chemical shifts. From Table 1 lower coordination numbers are characterized by broad upfield beryllium shifts. Four-coordinate beryllium complexes are affected by multiple factors including chelate ring size, number of chelate rings, symmetrical nature of the beryllium environment and nature of the donor atoms. As a tool for prediction, the resulting models are robust and should provide a powerful tool to aid in the interpretation of complex NMR data for beryllium containing solutions of unknown structural composition.

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**Supporting Information Available:** Graph and table comparing the various NMR methods as implemented in Gaussian03 (Figure S1 and Table S1) and list of  $^9\text{Be}$  NMR output from Gaussian for all complexes studied in this manuscript (Table S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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