^{15}N Shielding of the Nitrosyl Ligand in Co(NO)(TPP)

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Using the density functional theory-individual gauge for localized orbitals (DFT-IGLO) method, the ^{15}N shielding for a nitrosyl ligand bound to a cobalt in a tetraphenylporphyrin (TPP) complex is studied. The effects of changing the Co−N−O bond angle, N−O and Co−N bond lengths, and the displacement of the cobalt atom from the porphinato core on the nitrosyl ^{15}N shielding tensor have been investigated. Results indicate a great sensitivity of the nitrosyl ^{15}N shielding to local geometry. Using an experimental geometry, qualitative agreement between calculated and observed values is achieved. The presence of a swinging motion of the nitrosyl ligand is also discussed.

Introduction

There has been a renewed interest in understanding how small ligands bind to porphinato metal complexes.[1] In this recent work, a combination of various spectroscopic techniques and ab initio calculations was used to explain and deduce the geometry of a CO ligand bound to an iron porphyrin complex. Quantum mechanical computations were used to derive the shielding dependence on tilt and bent angles. The major conclusion from this recent work is that the Fe−C−O linkage is very close to linear and the trends seen in various nuclear magnetic resonance (NMR), infrared (IR), and Mössbauer spectroscopic parameters are due to one single factor, weak electrostatic interactions.[1,2]

The shielding tensor (focusing only on its symmetric part) provides six independent pieces of information, namely, the magnitude and the direction of its principal components. Both experimentalists and theoreticians are currently paying significantly increased attention to shielding as a tensor. Present computational methodologies are now claimed to be adequate not only in predicting isotropic shielding values for the first row nuclei but also in serving as an alternate route to extracting shielding tensor data. Extracting the full shielding tensor information experimentally is a difficult task since it requires single crystal NMR data. Assigning orientations of the principal axis system (PAS) of a shielding tensor solely from a powder pattern and symmetry arguments is very risky. Hence, being able to rely on ab initio methods for the determination of the shielding tensor orientation will be extremely complementary to experiments.

The ^{15}N shielding in nitrosyl($\alpha,\beta,\gamma,\delta$-tetraphenylporphinato)-cobalt(II), Co(NO)(TPP), offers a very interesting test for present theories of the NMR chemical shielding, to see if such methods can reproduce not just the isotropic value but also the tensor in the absence and presence of motion. A theoretical study of this system is warranted since it covers several interesting physical aspects of the shielding tensor. The X-ray structure revealed a bent and swinging nitrosyl ligand.[3] In addition, NMR spectroscopy[4] at room temperature showed a narrow axially symmetric ^{15}N shielding tensor with a span of only 240 ppm. At 200 K, the tensor loses axial symmetry and becomes suddenly wide, with a span of 1655 ppm. The observed decrease in the span of the tensor has been explained[4] using a rapid four-site exchange model. This work aims to reproduce the experimental values and trends observed for N shielding in Co(^{15}NO)(TPP) via present ab initio methods. The orientation of the PAS of the N shielding tensor in Co(^{15}NO)(TPP) has not been determined experimentally but Groombridge et al.[4] have predicted using symmetry arguments that the least shielded component will be lying parallel to the N−O bond. This predicted orientation is opposite to what is observed for the shielding tensor of the central nitrogen in NNO and linear nitrosyl ligands. With linear nitrosyl arrangements the unique component (the one that lies along the internuclear axis) is found to be most shielded. Thus, it is desirable to obtain additional information regarding the shielding tensor orientation of ^{15}N in a bent nitrosyl ligand.

As theories of nuclear magnetic shielding reach higher levels, it is important to be reminded of how sensitive shielding can be on local geometric parameters. One advantage of theory over experiment is its capability to deduce the effect of geometry, one parameter at a time, on the shielding property. A shielding surface, a mathematical construct that describes how shielding changes with geometry, can be derived in a straightforward manner. To obtain such information, variable temperature and isotope substitution studies are necessary and, oftentimes, more than one geometric parameter is changing from one system to another in these experiments. This present study explores the case where the small ligand is known to bind in a bent fashion to a metalloporphyrin. The ^{15}N shielding is studied in detail for the nitrosyl ligand in Co(NO)(TPP). Using currently available computational methodology, the dependence of the ^{15}N shielding on various local geometry factors is investigated. In particular, its sensitivity to the N−O and Co−N bond lengths, the Co−N−O bond angle, and displacement of the cobalt atom from the plane of the porphyrin nitrogen atoms is explored.

Computational Details

The molecular fragment used in the calculations (shown in Figure 1) consists of two amidinato ligands and a nitrosyl ligand bound to a cobalt atom. The use of this model to describe metalloporphyrins was first introduced by Strich and Veillard.[5] The *deMon-KS* program[6−8] was used for the density functional computations and geometry optimization, while the sum over states density functional perturbation theory (SOS-DFPT) shielding calculations were performed with the additional *deMon-NMR* code.[9−11] An all-electron basis set for Co is used

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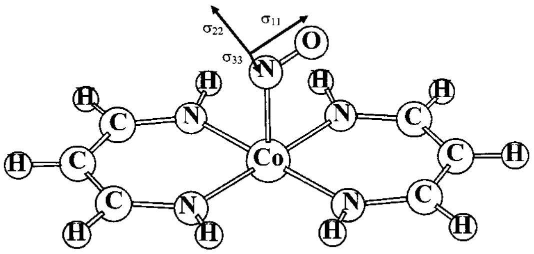

Figure 1. Molecular fragment used for the shielding computations.

(uncontracted 20s12p9d),[12] while the nitrosyl ligand and the rest of the nitrogen atoms were assigned a standard triple-ζ basis. The rest of the model is given double-ζ basis sets. The exchange correlation functional employed was taken from Perdew and Wang[13] (PW91), the one recommended by the authors of the *deMon-NMR* program.[11] Computations were carried out on an IBM RS/6000 model 390 computer. A single-point shielding calculation takes about 12 h.

The positions of the heavy atoms of the amidinato ligand match the positions of heavy atoms of the porphyrin ring, as suggested by the X-ray structure of Co(NO)(TPP).[3] The C−H and N−H bond were the optimized values obtained by Jewsbury et al. in their geometry optimization.[14] The Co−N vector is always placed normal to the plane of the amidinato ligands in all of the calculations. Several geometries were investigated to extract the dependence of the nitrosyl ^{15}N shielding tensor on the following local structural factors: Co−N and N−O bond lengths, Co−N−O bond angle, displacement of the Co atom from the porphyrin center. First, with fixed Co−N (1.927 Å) and N−O (1.833 Å) and the Co atom placed on the plane of the amidinato ligands, shielding computations were performed at various values of the Co−N−O angle (120°, 127°, 140°, 150°, 160°, 170°). Then, at a fixed Co−N−O angle (127°), additional shielding computations were performed at other values of the Co−N (1.83 Å, 1.93 Å, 1.96 Å) and N−O (1.01 Å, 1.10 Å, 1.15 Å) bond lengths. Partial optimizations of the molecular structure while varying the N−O and Co−N distances were not performed, so that the shielding trace obtained is a function purely of the coordinate that is being altered. Since the shielding traces, for example, with respect to the N−O distance, are obtained at three different Co−N bond lengths, the mixed derivative can be likewise extracted. In addition, the effect of displacing the Co atom from the plane of the amidinato ligands was also explored by lifting the Co atom 0.1 Å from the plane, bringing it closer to the nitrosyl N atom (Co−N bond length for this calculation is 1.83 Å). This additional geometry (as shown later in the Results section) shows that it leads to the same effect as changing the Co−N bond length. Last, the fragment shown in Figure 1 was also partially geometry optimized and the shielding was also calculated at this theoretical geometry. The partially optimized geometry fairly agrees with the X-ray structure. It places the cobalt atom 0.1 Å above the plane of the amidinato ligands and the nitrosyl N atom 1.83 Å from the cobalt atom. The Co−N−O angle is 124°. The major difference lies in the N−O bond length. Its optimized value is 1.19 Å.

Results and Discussion

Results of the calculations are given in Table 1 together with the experimental values.[4] At first glance, one will arrive at the conclusion that all of the calculations overestimate the shielding. Relativistic effects were not considered in any of these calculations and the overestimation may be due to this missing factor.

TABLE 1: Calculated ^{15}N Shieldings in Co(NO)(TPP)

∠Co−N−O (deg)	R (Å) Co−N	N−O	σ_{iso} (ppm)	σ_{11} (ppm)	σ_{22} (ppm)	σ_{33} (ppm)	Ω (ppm)
127	1.83	1.01	−440	−1194	−181	55	1249
127	1.83	1.10	−585	−1514	−264	22	1536
127	1.83	1.15	−662	−1667	−315	−5	1662
127	1.93	1.01	−486	−1324	−181	43	1367
127	1.93	1.10	−647	−1687	−267	14	1701
127	1.93	1.15	−731	−1860	−319	−13	1847
127	1.96	1.01	−506	−1377	−182	43	1420
127	1.96	1.10	−672	−1758	−268	10	1768
127	1.96	1.15	−759	−1939	−321	−17	1922
120	1.93	1.10	−648	−1638	−299	−8	1630
140	1.93	1.10	−631	−1821	−151	79	1900
150	1.93	1.10	−514	−1928	29	176	2104
160	1.93	1.10	−396	−1947	372	387	2334
170	1.93	1.10	171	−1482	843	1153	2635
127[a]	1.83	1.10	−580	−1505	−263	28	1533
124[b]	1.83	1.19	−704	−1737	−353	−24	1713
expt[c]			−893	−1853	−626	−198	1655

[a] In this geometry, the cobalt atom is placed 0.1 Å above the plane of the amidinato ligands. [b] Optimized geometry. [c] From ref 4.

However, one should not overlook the large dependence of the ^{15}N shielding on the Co−N and N−O bond lengths. The ^{15}N shielding tensor is extremely sensitive to the values of these two bond lengths. This large sensitivity should not come as a surprise since the shielding of a N nucleus in this type of environment is known to be influenced dramatically by changes in bond length. From variable temperature gas-phase NMR measurements[15] of the ^{15}N shielding of the central N in NNO, the shielding derivative (averaged between the N−N and the N−O bonds) is about −1030 ppm/Å. The shielding derivatives obtained in this work are similar in magnitude to this experimental number. The first derivative of the ^{15}N shielding in the nitrosyl ligand of Co(NO)(TPP) with respect to the N−O distance is very large and negative: −1760 ppm/Å, while with respect to the Co−N length, it is −660 ppm/Å. The two derivatives are not quite independent from each other. They become more negative as the other bond length increases. For example, when the Co−N distance is changed to 1.96 Å, the first derivative of the shielding with respect to the N−O distance becomes −1810 ppm/Å. The calculated derivative with respect to the Co−N distance is not as large compared to what is observed in a series of Co−NO complexes.[16] It is important to note, however, that the computations in this paper determine the dependence of the shielding with respect to the Co−N distance while the other parameters are held constant. The experiments, on the other hand, involve a change in the other parameters such as the identity of the other ligands.[16] The magnitude of each of the three principal components are also displayed in Table 1, while the principal axis system is shown in Figure 1. It can be seen that the least shielded component is most sensitive to changes in both bond lengths. This component lies parallel to the N−O bond, in agreement with the orientation predicted by Groombridge et al.[4] from symmetry arguments. The central component is not sensitive at all to changes in the Co−N bond length. This component lies on the plane defined by the Co−N−O atoms and is perpendicular to the N−O bond. The most shielded component lies normal to the Co−N−O plane and is shown to be only mildly influenced by changes in the Co−N and N−O bond lengths. In addition to the principal components, the span (Ω), defined as $\sigma_{33} - \sigma_{11}$, is also included in Table 1. Since the sensitivity to changes in bond length is mostly due to changes in σ_{11}, the span shows an even greater sensitivity to these bond lengths. Its first derivative, for example, with respect to changes in the N−O bond length is about 3500 ppm/Å.

The nitrosyl ^{15}N isotropic shielding is not sensitive to changes in the Co−N−O bond angle in the vicinity of the experimental value, 127°. It changes by only 1 ppm when the Co−N−O angle is varied from 120° to 127°. Outside this experimental bond angle, the shielding tensor becomes more sensitive to the Co−N−O angle. Likewise, the span of the tensor also increases with an increasing Co−N−O angle. From the localized molecular contributions to the shielding, it is seen that the majority of the deshielding comes from an orbital shared by the Co and the nitrosyl N atom. For the model where Co−N = 1.93 Å, N−O = 1.10 Å, and ∠Co−N−O = 127°, this orbital accounts for about −600 ppm and almost all of it is in σ_{11} (−1700 ppm of σ_{11} is attributable to the Co−N bond). Comparing the experimental values of the principal components with the calculated values at this geometry, one finds that the computed numbers are more positive (around 200 ppm for both σ_{11} and σ_{33}, an error well outside the experimental uncertainty of 60 ppm[4]). Since the errors in computing the most and the least shielded components are comparable in magnitude, the resulting span is very close to experiment ($\Omega_{\text{calculated}} = 1701$ ppm to be compared with $\Omega_{\text{experimental}} = 1655$ ppm). The geometry that gives a value for the span that is closest to experiment has Co−N = 1.83 Å, N−O = 1.15 Å, and ∠Co−N−O = 127°.

The influence of the atoms of the amidinato ligands is not yet significant compared to the present errors or inherent limitations of the computation. Upon moving the cobalt atom 0.1 Å above the plane of these ligands, it can be seen that the change in the shielding and in its principal components can be fully accounted for by the shortened Co−N bond. Calculations where N−O = 1.10 Å and Co−N = 1.83 Å give identical results in both cases: Co on the plane and Co 0.1 Å above the plane. Additional calculations were also performed where the O atom of the nitrosyl ligand is placed above one of the N atoms of the amidinato ligand. The magnitudes of the principal components are not sensitive to this factor, however, their orientation is attached to the direction of the N−O bond. As in the models where the O atom lies above the region between two N atoms of the amidinato ligand, the least shielded component is still parallel to the NO bond, σ_{22} lies on the Co−N−O plane and is perpendicular to the NO bond while the most shielded component is still normal to the plane of the Co−N−O atoms. These additional calculations clearly show that the ^{15}N shielding tensor and its components are strongly dependent only on the Co−N and N−O bond lengths and the Co−N−O bond angle. These are the structural parameters in the immediate vicinity of the nucleus under study, indicating the highly localized nature of the chemical shielding tensor. It is therefore possible to use the ^{15}N shielding tensor of nitrosyl ligands in deducing these local geometry parameters.

A tensor of axial symmetry usually can be taken as an indication of a linear metal−nitrosyl arrangement. Mason has compiled experimental ^{15}N shielding tensors from a variety of nitrosyl complexes, sampling both linear and bent geometries.[17] The ^{15}N nucleus in linear nitrosyls is usually more shielded by about 200−800 ppm compared to bent nitrosyls. Moreover, the shielding tensor components are also shown to be very sensitive to the geometry of the nitrosyl ligand and the manner it is attached to the metal atom. In general, bent nitrosyls usually show a larger span while linear nitrosyls display a tensor of axial symmetry and a smaller span. For this reason, the *meso*-tetraphenylporphinato complex, Co(NO)(TPP), is considered an extraordinary system. At room temperature, it exhibits a tensor characteristic of a linear nitrosyl ligand. It has axial symmetry and relatively low span, 242 ppm. Its isotropic shielding (−901 ppm[17]), however, is characteristic of a bent nitrosyl. It is only at 200 K that the full tensor manifests itself. At this temperature, the measured span is 1655 ppm and the tensor is no longer symmetric, indicative of a bent nitrosyl geometry. As mentioned earlier, this observation has already been explained by Groombridge et al.[4] using a rapid four-site exchange model. In this model, the oxygen of the nitrosyl ligand is believed to be swinging between four equivalent sites, each one lies above the region between two porphyrin N atoms. Simple averaging for a fast four-site exchange involves the following equations for the motion-averaged tensor components[4]:

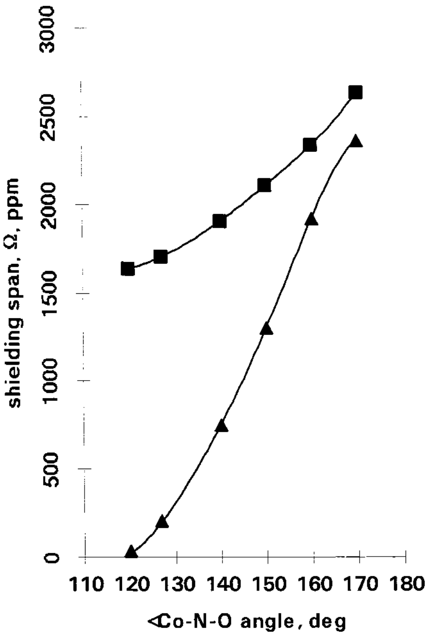

Figure 2. Dependence of the span (Ω) of the N shielding tensor in the model compound Co(^{15}NO)(amidinato)$_2$ on the Co−N−O angle in both static (■) and swinging (▲) cases.

$$\sigma_{\parallel} = \sigma_{11} \cos^2 \theta + \sigma_{22} \sin^2 \theta$$

$$\sigma_{\perp} = {}^{1}\!/_{2}(\sigma_{33} + \sigma_{22} \cos^2 \theta + \sigma_{11} \sin^2 \theta)$$

where θ = 180 − ∠Co−N−O. The above equations work because the orientation of the principal axis system of the ^{15}N shielding tensor of the nitrosyl ligand is intimately linked to the Co−N−O linkage; that is, σ_{11} lies parallel to the N−O vector, σ_{22} lies on the Co−N−O plane but is perpendicular to the N−O bond, and σ_{33} is normal to the Co−N−O plane. Using the experimentally observed magnitudes of the principal components at 200 K, Groombridge et al.[4] have arrived at a value of 127° for the Co−N−O angle.

The computational results will now be discussed in the presence of the swinging motion of the nitrosyl ligand. The calculated values agree with the previous experimental analysis and do not offer a novel interpretation. The knowledge, however, of the principal components, their magnitude and direction, and their dependence on local geometry, as obtained from the computations, offers a new horizon in analyzing the NMR data. Although σ_{11} contributes to both $\sigma_{\parallel}$ and $\sigma_{\perp}$, it has a more dominant effect on the behavior of $\sigma_{\parallel}$. Since σ_{11} is shown to be very sensitive to the N−O bond length, it is expected that the bond length dependence of $\sigma_{||}$ will be different from that of $\sigma_{\perp}$. The motion-averaged span will therefore still show some dependence on the bond length. At ∠Co−N−O = 127° and Co−N = 1.93 Å, the motion-averaged span for the following N−O bond lengths, 1.01, 1.10, and 1.15 Å are 160 ppm, 200 and 220 ppm, respectively. Thus, the motion averaged span shows a first derivative with respect to the N−O bond length of about 400 ppm/Å. The motion averaged span is not that sensitive to the Co−N bond, showing a first derivative of only 60 ppm/Å. Changes in the Co−N−O bond angle lead to dramatic changes in the value of the motion-averaged span. At <Co−N−O = 120°, the motion averaged tensor is almost spherical, giving a span of only 20 ppm. At Co−N−O = 140°, the motion averaged span has reached 750 ppm. This apparent strong sensitivity of the value of the motion-averaged span can serve as an excellent monitor of the Co−N−O bond angle. Figure 2 displays the span in the presence and absence of the swinging motion as a function of the Co−N−O bond angle.

Conclusion

Previous experimental work on cobalt nitrosyl complexes has provided excellent systems for testing present shielding computational methodologies.[16] Essentially, the conclusions derived from this present theoretical work are not different from those attained via an experimental analysis.[4] The present work has demonstrated that presently available computational methodologies can reasonably predict the isotropic shielding as well as the magnitude and direction of its principal components. Although the magnitude of the principal components can be readily obtained, their directions with respect to a molecular frame are difficult to obtain. A theoretical route that can provide such information with enough confidence can therefore become invaluable. More importantly, information regarding the dependence of the isotropic shielding and its components on various structural parameters can be readily obtained from theoretical methods. Such treatment can help explore which piece of the shielding tensor can provide information regarding the structure. Without such theoretical studies, it will be very difficult to find which structural parameter greatly influences the shielding property.

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References and Notes

(1) McMahon, M. T.; de Dios, A. C.; Godbout, N.; Salzmann, R.; Laws, D. D.; Le, H.; Havlin, R. H.; Oldfield, E. *J. Am. Chem. Soc.* **1998**, *120*, 4784.
(2) de Dios, A. C.; Earle, E. M. *J. Phys. Chem. A* **1997,** *101*, 8132.
(3) Scheidt, W. R.; Hoard, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 8281.
(4) Groombridge, C. J.; Larkworthy, L. F.; Mason, J. *Inorg. Chem.* **1993**, *32*, 2, 379.
(5) Strich, A.; Veillard, A. *Theor. Chim. Acta* **1981,** *60*, 379.
(6) Salahub, D. R.; Fournier, R.; Mlynarski, P.; Papai, I.; St-Amant, A.; Ushio, J. In *Density Functional Methods in Chemistry*; Labanowski, J., Anszelm, J., Eds.; Springer, New York, 1991.
(7) St-Amant, A.; Salahub, D. R. *Chem. Phys. Lett.* **1990,** *169*, 387.
(8) St-Amant, A. Thesis, Université de Montréal, 1992.
(9) Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *Chem. Phys. Lett.* **1993,** *204*, 87.
(10) Malkin, V. G.; Malkina, O. L.; Eriksson, L. A.; Salahub, D. R. In *Modern Density Functional Theory: A Tool for Chemistry; Theoretical and Computational Chemistry;* Seminario, J. M., Politzer, P., Eds.; Elsevier: Amsterdam, 1995; Vol. 2.
(11) Malkin, V. G.; Malkina, O. L.; Casida, M. E.; Salahub, D. R. *J. Am. Chem. Soc.* **1994,** *116*, 5898.
(12) Partridge, H. *NASA Technical Memo* **1987,** *89449.*
(13) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992,** 13244.
(14) Jewsbury, P.; Yamamoto, S.; Minato, T.; Saito, M.; Kitagawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 11586.
(15) Jameson, C. J.; Osten, H.-J. *J. Chem. Phys.* **1984,** *81*, 2556.
(16) Duffin, P. A.; Larkworthy, L. F.; Mason, J.; Stephens, A. N.; Thompson, R. M. *Inorg. Chem.* **1987**, *26*, 2034.
(17) Mason, J. In *Nuclear Magnetic Shieldings and Molecular Structure;* Tossell, J. A., Ed.; NATO ASI Series C.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993; Vol. 386; p 449.