Solid-State NMR Fermi Contact and Dipolar Shifts in Organometallic Complexes and Metalloporphyrins

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The NMR spectral shifts of paramagnetic metal complexes can provide valuable information about structure and bonding.¹ These shifts are made up of both isotropic Fermi contact and anisotropic dipolar hyperfine interactions, which, especially at low temperatures, can be very large, on the order of 1 MHz. In early work, Kreilick et al. investigated Cu⁴⁺(Dαl-alanine)₂·H₂O (I) single crystals using ¹H NMR and reported both isotropic and anisotropic hyperfine interactions and used these to determine the relative positions of nuclei in the ligands with respect to the central metal.²,³ This approach also enabled assignments for AgTPP (2, TPP = mesotetraphenylporphyrin), which were found to be in close agreement with single-crystal ENDOR results.⁴ The ENDOR hyperfine parameters for CuTPP (3) were also reported⁵ and confirmed in later studies.⁶ More recently, another approach, “magic-angle” sample spinning (MAS) NMR, has been used to investigate a variety of paramagnetic solids, including Cu(Dαl-alanine)₂·H₂O and V(acac)₃ (4, acac = CH₃COCHCOCH₃), and both ¹³C and ¹H/H shifts have been reported.⁶,⁷ Surprisingly, however, there have been no reports of the calculation of these NMR Fermi contact and dipolar interactions using quantum chemical methods, although there have been reports of the successful evaluation of large (up to ~6000 ppm) hyperfine shifts in solution NMR spectra of proteins and model systems.⁸,⁹

In this communication, we present the results of the first quantum chemical investigations of the solid-state MAS NMR and single-crystal NMR of a variety of paramagnetic solids, together with an investigation of several ENDOR spectra.

We used the hybrid Hartree–Fock density functional theory (HF-DFT) method B3LYP¹⁰ in our calculations, together with a large basis set,¹¹ used previously to evaluate solution NMR hyperfine shifts as well as ESR properties.⁹,¹² X-ray crystal structures¹³ of 2–4 were used with the TPP phenyl groups being replaced by H.⁹ Since there was no X-ray crystal structure of I, we synthesized it,⁶ obtained crystals by slow evaporation, and used the SHELXTL program¹⁴ to solve its structure (see Supporting Information for structural details). We also verified that our crystals gave identical NMR spectra to those reported.⁶,⁷

Cu(Dαl-alanine)₂·H₂O is not the five-coordinate complex anticipated. Instead, it is a 1D polymer with water-Cu centres (dCu–O = 2.653 Å) zigzagging along the crystallographic c-axis (Figure 1A), and these chains are further connected by a large 3D hydrogen bond network (Figure 1B). The central unit (H₂O–Cu–H₂O) has 14 hydrogen bonds with eight neighboring Cu(Dαl-alanine)₂ and two water molecules. These structural features have dramatic effects on the hyperfine interactions, as discussed later.

The total observed chemical shift (δtot) in MAS NMR includes both a diamagnetic or orbital contribution (δδδδm) from paired electrons and a hyperfine contribution (δδδδh) from unpaired electrons.⁸,⁹ The hyperfine shift can be further broken down into Fermi contact (δFC) and pseudocontact (δPC) terms. δFC of a given nucleus

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**Figure 1.** Unit cell of I viewed along (A) the a-axis, (water-red, Cu-green, others-gray, H omitted for clarity) and (B) the c-axis.

**Table 1.** Solid-State MAS NMR Chemical Shifts

<table>
<thead>
<tr>
<th>nucleus²</th>
<th>δFCcalcd (ppm)</th>
<th>δFCmexp (ppm)</th>
<th>δPCcalcd (ppm)</th>
<th>δPCmexp (ppm)</th>
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<tr>
<td>¹⁷OCH⁴⁺</td>
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<td>0.00034</td>
<td>36</td>
</tr>
</tbody>
</table>

² The nucleus of interest is in bold. ³ Reference 7. T = 331 K. ⁴ Reference 6. T = 298 K.

depends on the spin state (S) of the system, the spin density at the nucleus (ρₙ), and the temperature (T):¹⁰

\[
\delta_{FC} = m(S + 1)\rho_n/T
\]

where \(m\) is a collection of physical constants and is equal to 2.35 x 10⁻⁶ ppm K au⁻¹.¹⁰ Usually, \(\delta_{FC}\) dominates the hyperfine shift (e.g., for I, \(\delta_{PC}\) data for ¹³C and ¹H have been estimated to be from −6 to 0 ppm), and thus \(\delta_{PC}\) is neglected.⁸,⁹ Our initial DFT results for I using a five-coordinate Cu₁ complex resulted in large deviations from experiment (Figure 2A), but these progressively decreased with six-coordinate complexes containing 1, 3, and 9 Cu atoms (Figure 2A).¹⁵

As shown in Table 1 and Figure 2B, there is an excellent correlation (\(R² = 0.967\)) between the calculated and experimental total (chemical) shifts for I and 4, with a slope of 1.007, an intercept of −21.6 ppm, and an rms error of 28 ppm or 6.3% of the whole experimental range, of 442 ppm. This almost ideal slope indicates that this functional/basis set can accurately reproduce the principal electronic interactions in the solid-state MAS NMR shifts of these paramagnetic complexes. The correlation between \(\delta_{FC}\)calcd and \(\delta_{FC}\)mexp (= \(\delta_{FC}\)exp − \(\delta_{FC}\)calcd) is even better (\(R² = 0.980\)), again with an excellent slope (1.046).

In contrast to solid-state MAS NMR, single-crystal NMR/ENDOR experiments can provide accurate information on dipolar interactions, although there have been reports of the successful evaluation of large (up to ~6000 ppm) hyperfine shifts in solution NMR spectra of proteins and model systems.⁸,⁹

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Overall, the results presented above show that both NMR and ENDOR hyperfine properties can now be quite accurately predicted by use of DFT methods, opening up their further use in investigating paramagnetic solids, such as proteins.

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Supporting Information Available: Crystal structure information for 1 and more computational details (CIF, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(14) SHELXL, version 5.1; Bruker AXS: Madison, WI, 1998.
(15) The five-coordinate Cu(1) (Cu–H2O), six-coordinate Cu(1) (H2O–Cu–Cu–Cu), six-coordinate Cu(3) (H2O–Cu–H2O–Cu–Cu), and the central unit (H2O–Cu–H2O–Cu) of the Cu(9) cluster were treated with the large basis set (see ref 11). The Cu–Cu bond is 14 hydrogen bond partners to the central unit: a 3-21G* basis was used for the non-central unit atoms due to limited computational resources. This Cu9 cluster has 1628 basis functions. For more details, see the Supporting Information.