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Relativistic DFT Calculations of Copper Hyperfine Coupling Constants: Effect of Spin−Orbit Coupling

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Relativistic density functional theory (DFT) calculations of transition metal hyperfine interaction (*A*) tensors have been completed for a series of Cu^{2+} complexes including $Cu(Quin)_2$, $Cu(Acac)_2$, $Cu(L\text{-}AlaO)_2$, and $[Cu(Ox)_2]^{2-}$. The *A* tensors were calculated with the zero order regular approximation (ZORA) for relativistic effects as implemented in the Amsterdam Density Functional (ADF) program. For the isotropic hyperfine coupling constant, the agreement between the calculated and experimental values was quite good, but the good agreement was determined to be a result of a cancellation of errors due to the neglect of spin−orbit coupling and an underestimation of core spin polarization. The anisotropic components of the hyperfine coupling constant calculated with the scalar-relativistic spin-restricted open-shell Kohn Sham (SO + SR ROKS) method provided the best agreement with experimental values.

Introduction

Electron paramagnetic resonance (EPR) spectroscopy is widely used to investigate the electronic environment of paramagnetic transition metals, such as Cu^{2+}, in biological systems[1−3] and in copper-exchanged zeolites.[4−11] Cu^{2+} has a d^9 electronic configuration with one unpaired electron and a nuclear spin of 3/2. It is well-known that the hyperfine coupling constants and *g* values depend on the ligand field surrounding the copper ion, and ligand field theory has been used to relate electronic structure to the measured EPR parameters.[12−15] It was also recognized very early on that the spin−orbit interaction contributed significantly to the hyperfine coupling constant for transition metals such as Cu^{2+}.[12−14] Ligand field theory (LFT) has been widely used to relate the spin−orbit coupling contribution to the hyperfine interaction and the *g* shifts.[12−14,16] Peisach and Blumberg developed empirical correlations between the parallel components of *A* and *g* for a series of tetragonal Cu^{2+} model compounds with varying ligands and well-defined structures.[1] Trends were found that enabled Cu^{2+} EPR parameters to be correlated to the copper ligands and to the overall charge of the model complexes in solution. These empirical relationships have been used very successfully to probe the ligand environment of Cu^{2+} in proteins.[17,18]

To advance the interpretation of EPR spectra of transition metal systems to a quantum chemical approach, density functional theory (DFT) based methods have been developed for calculating EPR parameters. In the DFT methods developed by van Lenthe and co-workers, spin−orbit coupling is included variationally using the zero-order regular approximation (ZORA)[19−23] to the Dirac equation. These DFT methods[21,22,24,25] have been incorporated into a commercial software package, ADF (Amsterdam Density Functional Theory 2002.01),[26] and are used to calculate EPR parameters, such as *A*- and *g*-tensors. Recently, these methods have been applied to the calculation of EPR parameters for transition metal complexes.[27−32]

Several other methods for *A* and *g* calculations have been developed by other groups.[16,33−39] A DFT method for calculating *A* tensors has been incorporated into Gaussian98 software.[40] This method does not include spin−orbit coupling effects and uses Gaussian-type orbitals (GTO's).[41] Barone and co-workers have calculated EPR hyperfine coupling constants using the nonrelativistic methods incorporated in Gaussian for organic π radicals.[42,43] Kaupp and co-workers have recently evaluated the use of Gaussian for nonrelativistic calculations of *A* tensors for transition metal systems.[44−46] Recently, Neese has reported a new method for calculating spin−orbit coupling contributions to hyperfine coupling constants for transition metals.[47] In his work, the spin−orbit coupling term is calculated as a second-order property using coupled-perturbed Kohn−Sham theory.[47]

In this study, *A*- and *g*-tensor calculations were completed for the series of Cu^{2+} complexes shown in Figure 1, including $Cu(Quin)_2$, $[Cu(ox)_2]^{2-}$, $Cu(acac)_2$, and $Cu(L\text{-}alaO)_2$. Complexes were chosen for which crystal structures and EPR experimental data were available, so that the accuracy of the computational methods could be assessed. The relativistic methods incorporated into the ADF program were used to calculate the *A* and *g* tensors for each of the complexes.

Computational Details

Crystallographic Information. Calculations of the *A* tensors were performed using the molecular structures from X-ray diffraction (XRD) data for $Cu(Quin)_2$,[48] $[Cu(ox)_2]^{2-}$,[49] $Cu(acac)_2$,[50] and $Cu(L\text{-}alaO)_2$,[51] where quin = 8-quinolinolato, ox = oxalate, acac = acetylacetonate, and L-alaO = alaninate.

Calculations with ADF. The ADF program package (ADF 2002.01)[26,52,53] was used to calculate the *A*- and *g*-tensors for each of the Cu^{2+} complexes. The methods for the calculations of the *A* and *g* tensors were developed by van Lenthe and co-workers[24,25,28] and are implemented in ADF software. Relativistic effects are included using the ZORA Hamiltonian which includes scalar relativistic (SR) and spin−orbit (SO) coupling. Three approaches can be used for *A*-tensor calculations with ADF: the scalar-relativistic spin-unrestricted open-shell Kohn Sham (SR UKS) calculation; the spin−orbit coupling and scalar-relativistic spin-restricted open-shell Kohn Sham (SO + SR ROKS) calculation; scalar-relativistic spin-restricted open-shell

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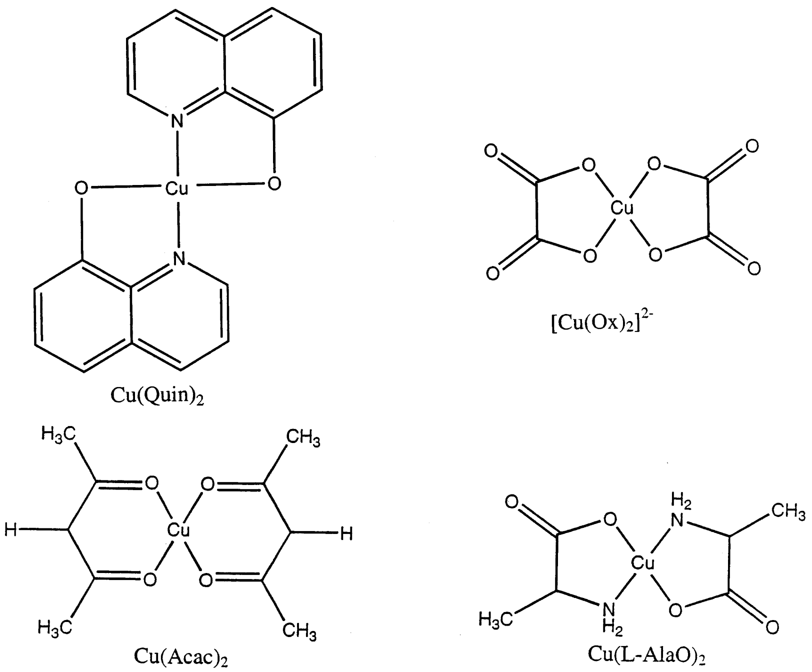

$Cu(Quin)_2$

$[Cu(Ox)_2]^{2-}$

$Cu(Acac)_2$

$Cu(L\text{-}AlaO)_2$

Figure 1. Copper complexes studied: $[Cu(Quin)_2]$; $[Cu(ox)_2]^{2-}$; $Cu(acac)_2$; $Cu(\text{L-alaO})_2$.

Kohn Sham (SR ROKS) calculation. In the SR UKS method, spin−orbit coupling is not included, but spin polarization effects are included making this the preferred method for calculating isotropic hyperfine coupling constants (A_{iso}). In the SO + SR ROKS method, spin−orbit coupling effects are included but not spin polarization effects. The SO + SR ROKS method is used for calculating the *g* tensor and the anisotropic contributions to the hyperfine coupling constants (A_D). In the SR ROKS method, neither spin−orbit coupling effects or spin polarization is included. The SR ROKS method is used for evaluating the relative magnitudes of the effects of spin polarization and spin−orbit coupling. A comparison can be made between SR UKS and SR ROKS so that the direct effects of spin polarization can be examined. A comparison of SO + SR ROKS and SR ROKS will yield the contribution of spin−orbit coupling to the calculated *A* values.

Three different combinations of exchange and correlation potentials were used in the *A*-tensor calculations: BLYP; BP86; BPW91. BLYP uses the pure-exchange electron gas formula as the local density approximation (LDA) with Becke gradient correction[54] for exchange and Lee, Yang, and Parr correction for correlation added.[55,56] Both BP86 and BPW91 use the parametrized electron gas data given by Vosko et al. for the LDA[57] with the Becke gradient correction for exchange. BP86 uses the correlation correction by Perdew[58] while BPW91 used the correlation correction by Perdew−Wang.[59−61] The basis set TZ2P was used for all calculations and all atoms.[52,62−64] The basis set TZ2P is a double ζ Slater-type orbital (STO) in the core and triple ζ in the valence shell with two polarization functions.

Comparison with Experimental EPR Parameters. Cu^{2+} complexes with readily available experimental EPR and crystallographic data were chosen for this study to facilitate a comparison of calculated and experimental EPR parameters. Despite the careful choice of model systems, there are some issues related to the direct comparison of calculated and experimental EPR parameters that should be addressed. The experimental EPR parameters for the Cu^{2+} complexes were obtained from solid-state EPR spectroscopy.[10,65−68] Therefore, only the absolute *A* values can be determined experimentally. To facilitate a comparison with the calculated *A* values, the signs of experimental *A* values were chosen such that agreement with the signs of the calculated *A* values was maintained. The effect of the molecular environment of the complex will influence the *A* values, and these effects have not been explored yet. Further research in which the effect of the environment is included in DFT calculations using a solvent model or other methods will be important in the future when the best computational methods for calculating *A* values for transition metals are better understood and more widely accepted. Currently, errors due to the exclusion of the effect of the molecular environment are probably small compared to errors inherent in the computational methods.

Results and Discussion

Calculations of *A*-Tensor for Cu^{2+} Complexes. Each of the square planar Cu^{2+} complexes studied here has a d^9 electronic configuration with one unpaired electron. The copper electron nuclear hyperfine interaction is characterized by an interaction between the unpaired electron ($S = 1/2$) and the copper nuclear spin (^{63}Cu, ^{65}Cu, 69.1% and 30.9% natural abundance, respectively, both $I = 3/2$). Two interactions contribute to the hyperfine coupling tensor: an isotropic or Fermi contact interaction, A_{iso}, and an anisotropic or dipolar hyperfine interaction, A_D.[15] A_{iso} and A_D can be calculated from the principal values of the *A* tensor using the following equations:

$$A_{iso} = (A_{11} + A_{22} + A_{33})/3$$

$$A_{D,x} = A_{11} - A_{iso}$$

$$A_{D,y} = A_{22} - A_{iso}$$

$$A_{D,z} = A_{33} - A_{iso}$$

The isotropic hyperfine interaction, A_{iso}, is related to the spin density at the magnetic nucleus, and therefore, inclusion of spin polarization effects is particularly important for accurate calculations of A_{iso}.[16,44,46,47] In some cases, spin polarization may also

TABLE 1: Relativistic (ADF) Calculated and Experimental Isotropic and Dipolar Hyperfine Coupling Constants for Copper Model Complexes[a]

		ADF									
		SR UKS			SO + SR ROKS				SR ROKS		
		BLYP	BP86	BPW91	B	BP86	BPW91		BP86	BPW91	expt[b]
[Cu(quin)]	A_{iso}	−194	−214	−209	110	111	112	13	14	14	−238[c]
	$A_{\mathrm{D},x}$	223	221	222	143	141	141	212	211	211	132
	$A_{\mathrm{D},y}$	166	164	165	125	124	124	160	160	160	132
	$A_{\mathrm{D},z}$	−390	−386	−388	−267	−265	−266	−372	−370	−371	−263
$[\mathrm{Cu(ox)_2}]^{2-}$	A_{iso}	−208	−228	−224	92	93	93	1	1	1	−180[d]
	$A_{\mathrm{D},x}$	191	189	190	130	129	129	182	181	182	156
	$A_{\mathrm{D},y}$	193	191	192	128	127	127	182	181	182	156
	$A_{\mathrm{D},z}$	−384	-380	−382	−258	−255	−256	−364	−362	−364	−312
$\mathrm{Cu(acac)_2}$	A_{iso}	−205	−225	−220	94	91	95	1	1	1	−231[e]
	$A_{\mathrm{D},x}$	194	192	192	126	127	124	178	185	185	146
	$A_{\mathrm{D},y}$	199	197	197	135	127	134	179	185	186	146
	$A_{\mathrm{D},z}$	−393	−388	−390	−261	−255	−258	−357	−370	−371	−292
Cu(L-alaO)$_2$	A_{iso}	−186	−206	-202	90	90	91	9	7	8	−222[f]
	$A_{\mathrm{D},x}$	164	162	163	118	118	118	156	163	164	132
	$A_{\mathrm{D},y}$	202	201	202	134	134	134	189	198	199	132
	$A_{\mathrm{D},z}$	−366	−363	−365	−253	−251	−252	−345	−361	−362	−264

[a] All A values are given in MHz. [b] A negative value for A_{iso} has been assumed for the experimental value for comparison with calculated values. [c] Reference 68. [d] Reference 67. [e] Reference 65. [f] Reference 66.

have a nonnegligible effect on A_{D}.[44−46,69] In this study, calculations of the EPR parameters for several Cu^{2+} complexes were conducted using different computational methods so that the performance of the different methods could be compared and the relative contributions of spin polarization and spin−orbit coupling to the hyperfine tensors could be evaluated. Three relativistic methods for calculating the A tensors for Cu^{2+} complexes were compared: the SR UKS; SR ROKS; SO + SR ROKS. For each method, the calculation was performed with three different functionals, BLYP, BP86, and BPW91. The results are presented in Table 1.

Calculations of A_{iso} for Cu^{2+} Complexes. The A_{iso} values calculated for Cu^{2+} complexes with the pure generalized gradient correction (GGA) functionals with the SR UKS method are in relatively good agreement with the experimental values, with an average deviation of 11%. However, the good agreement observed in this study for the A_{iso} for the copper complexes is most likely due to a cancellation of errors. This conclusion can be tested by comparing the A_{iso} values calculated by the SO + SR ROKS and the SR ROKS methods in which the calculations are identical except for the inclusion of spin−orbit coupling in the first method only. The overall accuracy of these two methods for calculating A_{iso} is very poor due to the exclusion of spin polarization effects, but the comparison is useful for evaluating the contribution of spin−orbit coupling to A_{iso}. The A_{iso} values in Table 1 calculated with the SR ROKS method range from 1 to 14 MHz for all of the complexes studied here. By comparison, the A_{iso} values in Table 1 calculated with the SO + SR ROKS method range from 90 to 112 MHz. The comparison of these results suggests that the spin−orbit coupling contribution to A_{iso} for these copper complexes is large (∼80−100 MHz) and positive and, therefore, will have a substantial impact on the calculated A_{iso} values. A similar analysis of spin−orbit coupling contributions to A_{iso} for nickel complexes has been previously utilized.[28] The exclusion of spin−orbit coupling effects (∼+80−100 MHz) in the SR UKS calculation offsets the underestimation of core shell spin polarization that has been observed previously[44,45,47] when using GGA functionals. This cancellation of errors in the A_{iso} calculations results in the fortuitous agreement of the calculated (SR UKS) and experimental copper A_{iso} values.

The conclusion is that better computational results would be obtained if spin−orbit coupling effects were included in the DFT calculations as well as a more accurate description of core shell spin polarization.[28,47] Recently, Neese has addressed this issue with a new method for calculating transition metal hyperfine coupling constants through the inclusion of spin−orbit coupling effects in a spin-unrestricted DFT calculation.[47] Although this new method signifcantly improved the A-tensor calculations, Neese concluded that more accurate functionals are still needed to further improve DFT calculations of spin-dependent properties.[47]

Calculations of A_{D} for Cu^{2+} Complexes. A comparison of the SR UKS and SO + SR ROKS results in Table 1 indicates that, for A_{D}, the best agreement with experimental data is obtained with the SO + SR ROKS method. This has been previously observed[28,31,32] and is a result of the decreased importance of spin polarization effects for the calculation of A_{D} relative to A_{iso}. However, analogous to A_{iso}, spin−orbit coupling contributions to A_{D} are very important for the copper complexes in this study. The spin−orbit coupling contribution to $A_{\mathrm{D},z}$ is estimated to be approximately 100 MHz by comparing the SO + SR ROKS and SR ROKS results in Table 1. This explains the good performance of the SO + SR ROKS method relative to poor performance of the other methods that do not include spin−orbit coupling and underscores the importance of including spin−orbit coupling for accurate calculations of A_{D}.

Comparison of DFT Methods and Ligand Field Theory for Calculating Spin−Orbit Coupling. Following the recent work of Neese,[47] the second-order spin−orbit contribution to the copper hyperfine coupling constant will be calculated using DFT methods and the data in Table 1 and using ligand field theory according to McGarvey.[12] Using ligand field theory, the spin−orbit coupling contribution to the largest copper hyperfine coupling constant principal value, A_{33}(SO-LFT), is given by the following expression:

$$A_{33}(\mathrm{SO-LFT}) = g_{\mathrm{e}}g_{\mathrm{N}}\beta_{\mathrm{e}}\beta_{\mathrm{N}}\langle \mathrm{r}^{-3}\rangle_{3\mathrm{d}}\left[\Delta g_{33} + \frac{3}{14}\Delta g_{22} + \frac{3}{14}\Delta g_{11}\right]$$

A constant value of 1134 MHz for $^{63}\mathrm{Cu}$ (assuming a value of 8.006 au^{-3} for $\langle r^{-3}\rangle_{3\mathrm{d}}$) was used in the calculation of A_{33}(SO-LFT).[47] The Δg values (where $\Delta g = g - g_{\mathrm{e}}$) calculated with the SO + SR ROKS method and the BP86 functional are listed

TABLE 2: Comparison of Ligand Field Theory and the ZORA DFT Method for Calculating the Spin−Orbit Coupling Contribution to the Copper Hyperfine Coupling Constant, A_{33}(Cu), Given in MHz

molecule	Δg_{11}[a]	Δg_{22}	Δg_{33}	A_{33}(SO-LFT)[b]	A_{33}(SO-DFT)[c]	ratio
Cu(quin)	0.034	0.024	0.113	142	202	1.42
$[Cu(ox)_2]^{2-}$	0.030	0.024	0.116	145	198	1.38
$Cu(acac)_2$	0.032	0.025	0.124	155	205	1.33
Cu(L-alaO)$_2$	0.028	0.019	0.101	126	193	1.53

[a] g values were calculated using the SO + SR ROKS method with the BP86 functional. [b] Calculated using the equation in ref 47. [c] Obtained by subtracting the A_{33}(SR ROKS) result from the A_{33}(SO + SR ROKS) result using the data in Table 1 (BP86 functional).

in Table 2. Using the Δg values and the ligand field theory expression above, the contributions of spin−orbit coupling to the copper hyperfine coupling constants, A_{33}(SO-LFT), were calculated and are listed in Table 2. For comparison, the spin−orbit coupling contributions to A_{33} calculated from the DFT calculations, A_{33}(SO-DFT) are also listed in Table 2. These values were calculated according to the following expression using the data in Table 1:

$$A_{33}(\text{SO-DFT}) = A_{33}(\text{SO} + \text{SR ROKS}) - A_{33}(\text{SR ROKS})$$

The results shown in Table 2 indicate that the ligand field theory treatment underestimates the contribution of spin−orbit coupling to the hyperfine coupling constant by a factor ranging from 1.3 to 1.5.

Neese found a similar trend using coupled perturbed Kohn Sham theory for the DFT calculations of the copper hyperfine coupling constants.[47] He observed a ratio of 1.1−1.5 for the ratio of A_{33}(SO-DFT)/A_{33}(SO-LFT) for the copper complexes in his study. Neese has explained this discrepancy between the DFT and LFT results in terms of the different integrals that are needed to calculate the g-tensor and the A-tensor, respectively, which are assumed to be proportional in the LFT treatment.[47] The results presented in this study exhibit the same trends observed by Neese and similarly suggest that the ligand field theory relationship between the hyperfine coupling constants and the g shift are not sufficient for predicting spin−orbit coupling effects in these systems. These results underscore the importance of DFT methods for calculating EPR parameters for transition metal complexes.

This study also demonstrates that the results of the DFT calculations of the EPR parameters of transitions metals must be examined carefully with respect to the different contributions (spin−orbit coupling, spin polarization) to the A-tensor. The different contributions to the hyperfine coupling constant should be considered individually when possible so that a fortuitous cancellation of errors will be recognized. Further improvements to the ADF method where spin−orbit coupling and spin polarization are both included are needed for more accurate calculations of copper hyperfine tensors. It has also been suggested that improved functionals are also needed to improve the accuracy of the calculations.[44,45,47]

Conclusions

DFT methods were utilized to calculate the hyperfine coupling constants of the following four Cu^{2+} complexes: $Cu(Quin)_2$; $[Cu(ox)_2]^{2-}$; $Cu(acac)_2$; Cu(L-alaO)$_2$. The A tensors were calculated using relativistic methods incorporated into the ADF program. The good agreement obtained with pure GGA functionals for SR UKS calculations was due to a cancellation of errors. The effects of spin−orbit coupling and core shell spin polarization offset each other leading to improved but fortuitous quantitative agreement when SR UKS and GGA functionals were used for the calculations. The agreement of A_D with experimental data was on average very good when the relativistic SO + SR ROKS method was used for the copper complex calculations. An estimate of the spin−orbit coupling contributions to the copper hyperfine coupling constant principal value, A_{33}, from DFT calculations and LFT calculations suggests that LFT calculations underestimate the spin−orbit coupling contributions to the hyperfine coupling constant.

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