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Hyperfine Tensors of [Bis(maleonitriledithioleato)nickel]$^-$

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Introduction

[Bis(maleonitriledithioleato)nickel]$^-$ [abbreviated Ni(mnt)$_2^-$] is a member of a group of 1,2-dithiolene complexes which were studied extensively some years ago because of their interesting electronic ground states, which gave them unusual redox properties.[1−7] Interest in the compounds has continued because a number of enzymes that catalyze redox processes contain Ni atoms coordinated by S atoms.[8−10] A careful study of the hyperfine coupling constants to the various ligand nuclei of Ni-(mnt) $_2^-$ has been published.[11]

Recently, it has been shown that hybrid density functional methods can be used successfully to calculate the hyperfine coupling in organic free radicals that contain carbon, nitrogen, oxygen, and fluorine atoms and, most recently, in a free radical (1,3,2-dithiazol-2-yl) that contains sulfur atoms.[12] In particular, the isotropic coupling constants of the radicals were computed accurately. It has been difficult to compute isotropic hyperfine coupling constants well.[13,14]

In this work, we examine the extension of density functional methods to computation of the hyperfine tensors in transition metal species. Because complete hyperfine tensors of the various nuclei in Ni(mnt)$_2^-$ are available,[11] and because the electronic structure of the ion may be described with a single predominant determinant, this ion is appropriate for a test of the methods.

Methods

We have calculated the various hyperfine tensors of Ni(mnt)$_2^-$, and have found their principal values and the orientations of their principal axes. Most computations used the Gaussian 94 suite of programs.[15a] A few of the calculations used the Gaussian 98 suite of programs.[15b] Computations were performed at the UHF level, with pure density functionals (UBLYP, UMPWPW91), and at the hybrid level (UB3LYP, UB3PW91, UMPW1PW91). We tested an effective core potential basis set (LanL2DZ), a double-ζ basis set with polarization functions (3-21G*), and a triple-ζ basis set with and without polarization and diffuse functions (6-311G and 6-311+G*).

Spin densities at the nuclei of the molecule are routinely available from the Gaussian 94 code, and were used to calculate isotropic hyperfine interactions. The electronic spin contribution to the electric field gradient tensor at each nucleus may also be obtained from the Gaussian 94 code. The Gaussian codes use the PRISM algorithm for the calculation.[16] The results were used to obtain calculated anisotropic coupling tensors. In Gaussian 98, the calculation of the hyperfine coupling constants has been included in the code.

We have assumed that only the spin dipolar interaction in the unrestricted ground state need be considered in computing the anisotropic hyperfine coupling constants. This assumption is consistent with the small deviations of the spectroscopic splitting factors from the free-spin values.[11]

Previous hybrid DF calculations that used the LanL2DZ basis set produced spin densities at the various atoms of Ni(mnt)$_2^-$ that agreed well with spin densities that were derived from experiment.[11] The calculations that we report produced spin densities that were close to those from the LanL2DZ calculation.

Results

We have calculated the hyperfine parameters of Ni(mnt)$_2^-$ with two sets of coordinates. One set of coordinates we used is the set that is given in ref 11, citation 39. These are coordinates that were taken from the crystal structure and symmetrized. The other set of coordinates that we used come from an optimization of the geometry of the ion at the UB3LYP/6-311+G* level.

There was little dependence of the calculated hyperfine parameters on geometry. In the rest of this paper, we use only the geometry that was optimized at the UB3LYP/6-311+G* level. The bond lengths and angles are $r(\text{Ni}-\text{S}) = 2.194$ Å, $r(\text{S}-\text{C}_1) = 1.738$ Å, $r(\text{C}_1-\text{C}_1) = 1.379$ Å, $r(\text{C}_1-\text{C}_2) = 1.423$ Å, $r(\text{C}_2-\text{N}) = 1.158$ Å, $\angle\text{S}-\text{Ni}-\text{S} = 91.57°$, $\angle\text{Ni}-\text{S}-\text{C}_1 = 103.67°$, $\angle\text{S}-\text{C}_1-\text{C}_1 = 120.55°$, $\angle\text{C}_1-\text{C}_1-\text{C}_2 = 122.25°$, and $\angle\text{C}_1-\text{C}_2-\text{N} = 178.62°$. C$_1$ is the ethylenic carbon atom, and C$_2$ is the cyanide carbon atom.

It is much harder to calculate accurate isotropic coupling constants than to calculate anisotropic coupling constants.[18]

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Table 1. Observed and Calculated Isotropic Hyperfine Coupling Constants of $Ni(mnt)_2^-$ (MHz)

atom	^{61}Ni	^{33}S	$^{13}C_1$	$^{13}C_2$	^{14}N
exptl[1,11,17]	+17.9, +12.1[a,b]	+22.2, +4.4[a,b]	−2.1	−2.9	+0.55
ublyp/6-311+G*	+22.67	+2.41	−2.50	−2.37	+0.114
ub3lyp/6-311+G*	+27.80	+5.62	−2.88	−2.26	+0.103
ub3pw91/6-311+G*	+32.03	+5.00	−3.43	−2.21	+0.030
umpwpw91/6-311+G*	+25.68	+1.41	−3.26	−2.39	−0.005
umpw1pw91/6-311+G*	+33.39	+5.81	−3.43	−2.18	+0.034

[a] The first number assumes that the experimentally observed parallel and perpendicular coupling constants have the same sign. The second number assumes they have opposite signs. [b] The probable experimental uncertainties, estimated from the uncertainties in the cited papers, are (Ni) ±2.5 MHz and (S) ±1.0 MHz.

Table 2. Observed and Calculated Anisotropic Hyperfine Coupling Constants of $Ni(mnt)_2^-$ (MHz)

	^{61}Ni			^{33}S				$^{13}C_1$				$^{13}C_2$				^{14}N			
	T_{xx}	T_{yy}	T_{zz}	$T_{x'x'}$	$T_{y'y'}$	T_{zz}	θ^a (deg)	$T_{x'x'}$	$T_{y'y'}$	T_{zz}	θ (deg)	$T_{x'x'}$	$T_{y'y'}$	T_{zz}	θ (deg)	$T_{x'x'}$	$T_{y'y'}$	T_{zz}	θ (deg)
exptl[1,11,17]	+27.1, +32.9[b]	−9.2, −20.8	−17.9, −12.1	−8.8, −17.8	−8.8, −17.8	+17.7, +35.6	*c*	−2.5	−2.5	+5.0	*c*	+0.17	+0.27	−0.43	*c*	−0.35	−0.39	+0.75	*c*
ub3lyp/6-311G	+61.08	−34.56	−26.52	−18.41	−15.64	+34.05	+31.01	−2.85	−2.28	+5.13	−16.10	−0.11	+0.86	−0.75	−26.12	−0.49	−0.36	+0.85	−15.24
ublyp/6-311+G*	+52.96	−28.51	−24.45	−16.38	−14.95	+31.33	+23.0	−3.00	−2.69	+5.69	+0.81	−0.26	+0.79	−0.53	−29.82	−0.57	−0.45	+1.02	−20.18
rob3lyp/6-311+G*	+53.05	−26.69	−26.36	−13.74	−14.11	+27.85	+33.72	−3.35	−2.95	+6.30	+33.72	−0.45	+0.75	−0.30	−30.21	−0.51	−0.39	+0.90	−26.34
ub3lyp/LanL2DZ	+40.43	−21.93	−18.49	−1.2	−0.9	+2.1	+43.99	−3.09	−2.80	+5.89	−32.61	−0.10	+0.91	−0.81	−26.32	−0.51	−0.41	+0.92	−12.55
ub3lyp/6-311+G*	+54.82	−31.91	−22.91	−19.65	−16.93	+36.59	+27.01	−2.43	−2.05	+4.49	−0.60	−0.11	+0.71	−0.60	−28.69	−0.43	−0.29	+0.70	−21.75
ub3pw91/6-311+G*	+57.13	−33.47	−23.66	−19.34	−16.38	+35.72	+26.92	−2.29	−1.86	+4.15	−3.35	−0.10	+0.68	−0.58	−28.31	−0.42	−0.25	+0.67	−21.72
umpwpw91/6-311+G*	+53.76	−29.02	−24.74	−16.10	−14.60	+30.70	+22.10	−2.88	−2.56	+5.44	−1.14	−0.25	+0.78	−0.53	−29.69	−0.56	−0.44	+1.00	−19.20
umpw1pw91/6-311+G*	+55.10	−33.28	−21.82	−19.86	−16.40	+36.26	+27.88	−2.10	−1.67	+3.77	−3.53	−0.06	+0.63	−0.57	−27.94	−0.39	−0.21	+0.60	−22.38

[a] θ is the angle between the *xyz* (molecular) coordinate system and the $x'y'z$ (principal hyperfine axes) coordinate system. It is taken to be positive if the x' axis of an atom that lies in the $+x$, $+y$ quadrant lies between $+x$ and $+y$. [b] The meaning of the two values, and an estimate of the uncertainties, is as in Table 2. [c] The experimental values refer to the principal axis system of **g**. That is, to within experimental uncertainty, $\theta = 0$.

Also, effective core potential basis sets, such as the LanL2DZ set, which are often used for calculations on transition metal species, may give good anisotropic coupling constants, but are useless for isotropic coupling constants. Thus, we report the results on isotropic and anisotropic coupling constants separately. Table 1 reports our results on isotropic coupling constants.

A UHF calculation gave the wrong ground state for the ion, and a MO level scheme that was not close to expectations, so no attempt was made to seek the correct ground state and to obtain hyperfine constants at the UHF level.

All the DF calculations with the triple-ζ basis sets and hybrid exchange functionals fare about equally well, overall, in predicting isotropic hyperfine constants. The pure DF calculations, however, predict the ^{33}S isotropic coupling constant poorly. A hybrid DF calculation that used the 3-21G* basis put far more spin density on the Ni atom than the other calculations do. This made the ligand isotropic coupling constants too small. It also made the calculated Ni atom anisotropic coupling constants far too large, and the ligand anisotropic coupling constants far too small. Thus, we did not pursue calculations with the 3-21G* basis set further.

The calculated anisotropic coupling constants are reported, and are compared with the experimental results, in Table 2. In Table 2, the z axis is normal to the molecular plane, and the x axis bisects the S−Ni−S angle in the direction of one of the mnt^{2-} ions. The y axis forms a right-handed system with x and z. The primed directions are defined in a footnote to Table 2. We have included the results that we obtained with the LanL2DZ basis set, although they fare very badly in predicting the S atom coupling constants. (They agree well with the other calculations in the values of the other ligand anisotropic hyperfine tensor components, though.) This basis uses an effective core potential, and smooth valence pseudoorbitals, for atoms of the elements beyond Ne. Apparently, replacement of the inner loops of the S 3p orbital by a smooth function that is very small in the inner loop region makes $\langle r^{-3}\rangle$ far too small.

It is difficult to choose among the all-electron calculations. Even the restricted calculation does fairly well, although the unrestricted calculations are better. No calculation does well on the ^{61}Ni anisotropic hyperfine tensor, and all do about equally well on the rest, regardless of basis set details and details of the exchange and correlation functionals. No calculation does well enough to lend credence to one or the other set of values of the ^{61}Ni anisotropic hyperfine tensor. All, except the calculation with the LanL2DZ basis, do well enough to support the ^{33}S anisotropic hyperfine tensor that is obtained if one assumes that the experimental hyperfine coupling constant perpendicular to the molecular plane has the sign opposite that of the other two hyperfine coupling constants.

Discussion

The pure density functional calculations (BLYP and MPWPW91) produce significantly poorer ^{33}S isotropic hyperfine coupling constants than the hybrid calculations do. Similar effects have been noted previously, and have been regarded as evidence that the pure DF methods underestimate the exchange interaction and produce too little spin polarization.[17] Aside from this, no exchange/correlation functional, of the ones we tested, is clearly better or worse than another is. Expansion of the basis set with diffuse functions and polarization functions has comparatively little effect on predictions of either the isotropic or the anisotropic hyperfine coupling constants, and yields no improvement in the predictions.

The calculations support the assignment of the sign of the ^{33}S hyperfine couplings that makes the isotropic ^{33}S coupling constant equal to +4.4 MHz, and the out-of plane principal value of the anisotropic ^{33}S hyperfine tensor equal to +35.6 MHz. They are not very helpful for analysis of the ^{61}Ni hyperfine couplings, though.

Previous hybrid density functional calculations on the anisotropic hyperfine coupling constants of species that contain transition metals have included calculations on $CpCo(CO)_2^-$ [20] and on $Mn(CO)_5Cl^-$.[17] Only the ^{59}Co anisotropic hyperfine coupling tensor of $CpCo(CO)_2^-$ was calculated. Agreement with experiment was good. The calculated tensor components depended little on the basis sets that the authors used. One of the basis sets was similar to the 6-311+G* basis set we used. The ^{55}Mn and ^{35,37}Cl anisotropic hyperfine tensors of $Mn(CO)_5Cl^-$ were calculated. The calculated ^{55}Mn tensor agreed well with experiment, but the calculated ^{35,37}Cl tensor components were mostly 60% too large. These calculations used bases that were larger than the ones we used.

It is difficult to find a pattern in these data and our data. Apparently, our difficulty in reproducing the observed ^{61}Ni hyperfine coupling constants is not due to deficiencies in the bases we used.

On the whole, the calculations are not as useful for isotropic coupling constants as they are for anisotropic coupling tensors, as has been noted in other work.[12,13,14,18] The calculated ^{13}C isotropic coupling constants to the two types of carbon atoms in the molecule are not far from the experimental values, but the calculation puts the magnitudes of the coupling constants in reverse order. No calculation does well on the ^{14}N isotropic coupling constant.

The calculated anisotropic coupling tensor at the cyanide carbon atom (C_2) disagrees qualitatively with experimental data. The calculations predict that $T_{y'y'}$ is the largest principal value of the tensor in magnitude, and that it is positive. The analysis of the experimental data has yielded T_{zz} as the principal value of largest magnitude, and that T_{zz} is negative.[11] The anisotropic coupling to C_2 is very small, however, so it is especially susceptible to small errors in the various contributions to it.

Conclusions

Hybrid density functional calculations are of use in the analysis of the hyperfine coupling constants of compounds and ions that contain transition metals, judging from our experience with $Ni(mnt)_2^-$. The results are not as satisfactory as those that have been obtained from hybrid density functional calculations on radical species that contain only atoms of main-group elements, though.

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