Extended Hückel Calculation of the Electron Paramagnetic Resonance
Parameters of Copper(II) Bis(dithiocarbamate)

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The $g$ tensor and $^{64}$Cu hyperfine coupling tensor in bis(N,N-diethyldithiocarbamato)copper(II) have been calculated with the aid of the iterative extended Hückel LCAO-MO method. Two empirical parameters which were varied, the Wolfsberg-Helmholz parameter and the charge dependency of the Hamiltonian matrix elements, could be chosen such that fair agreement with the observed values was obtained. The molecular orbitals, calculated with this parameter set, illustrate that strong covalency occurs in this complex. With these parameters other experimental quantities (e.g., the electric field gradient) can also be calculated for similar complexes.

Introduction

For some time we have been studying the electronic properties of the dithiocarbamate and diselenocarbamate complexes of certain transition metals. Using epr we have investigated the Cu(II), Ag(II), and Au(II) complexes, and with Mössbauer spectroscopy, Fe(II) and Fe(III) complexes. In this article we will give a molecular orbital explanation for the measured $g$ and hyperfine coupling (hfc) parameters of bis(diethyl-dithiocarbamato)copper(II), Cu(dtc)$_2$.

In order to obtain information from epr experiments about the bonding properties of a transition metal complex, one often attempts to estimate the contribution of the metal and the ligand orbitals to the molecular orbitals (MO's) from the measured $g$ tensor and hfc tensor. This procedure necessitates a simplification of the MO picture. For complexes of low symmetry even then too many MO coefficients are left to be determined from the experimental data, so that an artificial addition of symmetry is usually needed.

In this paper we avoid these simplifications by directly comparing the measured epr quantities of Cu(dtc)$_2$ with those calculated by means of the iterative extended Hückel method. Since this method is semiempirical and some uncertainty exists about the best choice of the empirical constants, we have varied two important parameters in order to check their effect on the calculated $g$ and hfc tensors of Cu(dtc)$_2$.

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The Molecular Orbital Calculation

The MO's of Cu(dtc)$_2$ were calculated by means of the LCAO-MO extended Hückel method. The computer program used was based on the self-consistent charge method. In this method a set of secular equations

$$\sum_j (\epsilon_{ij} - E_S)C_i = 0 \quad (1)$$

is constructed in a semiempirical way. In these equations $\epsilon_{ij}$ and $S_{ij}$ are elements of the Hamiltonian and overlap matrix, respectively

$$\epsilon_{ij} = \langle \phi_i | \epsilon_{ij} | \phi_j \rangle \quad (2)$$

$$S_{ij} = \langle \phi_i | \phi_j \rangle \quad (3)$$

where $\phi_i$ are atomic orbitals and $\epsilon_{ij}$ is an effective one-electron Hamiltonian. By solving these secular equations, the orbital energies $E_S$ and LCAO coefficients $C_{ij}$ are obtained. After occupying the lowest MO's in agreement with the spin multiplicity of the ground state, the Mulliken charges for all atoms are calculated. The Hamiltonian matrix, which is chosen to be charge dependent, is recalculated with these charges. This procedure is repeated until self-consistency is reached, i.e., until the differences between the atomic charges in two successive cycles are less than 0.001 charge unit.

1. Structure.—Because the epr results have been obtained from single-crystal studies of Cu(dtc)$_2$ doped into single crystals of the diamagnetic Ni$^{II}$(dtt)$_2$ complex, we used for our calculations the crystal structur...
Copper(II) bis(dithiocarbamate)

2. Atomic Wave Functions.—To limit the number of atomic wave functions, we replaced the ethyl groups by hydrogen atoms and took the N-H distance to be 1.01 Å. This substitution is justified by the fact that experimental epr parameters of dithiocarbamates with other alkyl groups do not differ significantly. Moreover, a 40% decrease of the N-H distance did not measurably affect the calculated charge distributions except those on nitrogen and hydrogen.7 We have taken into account all 45 valence orbitals, in which 57 electrons were placed.

For the radial part of the atomic wave functions, we used Slater-type orbitals.8–10 Except for the 3d orbitals, which were represented by double-exponent orbitals, we have used single-exponent orbitals retaining only the term with the highest power of r from the functions given in the literature. These atomic orbitals were used to calculate the overlap matrix elements $S_{ij}$.

For calculating the expectation values required for the epr parameters, the complete multiple-exponent Slater-type orbitals were kept.

3. X Matrix. a. Diagonal Elements, $X_C$:—The off-diagonal elements are approximated by the Wolfsberg-Helmholz relation12

$$X_C = \frac{1}{2}KS_{ij}(X_C + X_{ij})$$  

(7)

where $K$ is an empirical constant, which is usually taken between 1.5 and 3.0. Cusachs13 and Jug14 proposed overlap-dependent formulas for $K$: $K = 2 - |S_{ij}|$ and $K = 2/(1 + S_{ij})$, respectively. These approximations appeared to be not very satisfactory for the calculation of the epr parameters of dithiocarbamates. Therefore, we have used the original relation and searched for the best value of $K$.

Values for the VSIE's and their charge dependencies ($\beta$) have been obtained from ref 15 and 16.

Calculation of Epr Parameters

The electronic configuration of Cu(II) is $3d^9$, so one unpaired electron is present. The interaction of this unpaired electron with an external magnetic field $\vec{H}$ and the copper nuclear spin $I$ may be represented by the following spin Hamiltonian

$$X_C = \beta g \cdot \vec{H} \cdot \vec{S} + S \cdot \vec{T} \cdot I$$

(8)

where $\beta$ is the Bohr magneton, $S$ is the electronic spin vector, and $\vec{T}$ is the anisotropic hfc tensor.

1. $g$ Tensor.—The elements $g_{ij}$ of $g$ can be computed, taking into account the electron spin Zeeman energy, the coupling of the electronic orbital motion to the external magnetic field, and the electronic spin–orbit interaction. With the aid of second-order perturbation theory and neglecting interatomic overlap, the following (gauge-invariant) formula has been derived17

$$g_{ij} = 2.00233g_{ij} + 2 \sum_{n \neq i} \sum_{j} \langle A^N | A^B \rangle \langle B^N | B^B \rangle | E_0 - E_n |$$

(9)

where the summation over $n$ is taken over all MO's, except the one of the unpaired electron ($\Phi_0$).

The summations over A and B run over all atoms, with $\lambda^N(r)$ being the radial part of the spin–orbit coupling operator and $\lambda^A$ the linear combination of those atomic orbitals in the nth MO ($\Phi_n$), which are centered on the atom A. $L^A$ is the angular momentum operator for the unpaired electron is present. The interaction of this unpaired electron with an external magnetic field $\vec{H}$ and the copper nuclear spin $I$ may be represented by the following spin Hamiltonian

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a. Isotropic Hyperfine Coupling.—The magnitude of the Fermi-contact interaction depends on the spin density at the copper nucleus. This spin density is caused by (1) the density of the unpaired electron at the nucleus and (2) spin polarization of the inner-core s orbitals.

The second contribution—which is negative for ions of the first transition series—cannot be calculated by means of the extended Hückel method.

A calculation of the first contribution

$$a_{iso} = \frac{8\pi}{3} g_\epsilon g_N |\phi_i(0)|^2 (C_{e4s})^2$$

yields $a_{iso} = 5.4(C_{e4s})^2$ cm$^{-1}$, where $C_{e4s}$ is the coefficient of the $4s$ atomic orbital in the MO of the unpaired electron, $g_\epsilon$ is the free-electron $g$ value, $g_N$ is the $g$ value of the copper nucleus, and $\beta_N$ is the nuclear magneton.

b. Anisotropic Hyperfine Coupling.—The elements of the anisotropic hyperfine coupling tensor $A$ have been calculated in first order, that is, taking into account the interaction of the nuclear spin $I$ with the electronic spin and neglecting spin–orbit coupling.

Because of the $r^{-3}$ dependency of this tensor, contributions from ligand atoms are neglected. The following expression results

$$A_{ij} = g_\epsilon g_N \beta_N \left\langle \frac{X_{Cu}^3}{r_{Cu}} X_j - \frac{\delta_{ij}}{r_{Cu}} X_{Cu} \right\rangle$$

where $X_{Cu}$ has the same meaning as in eq 9, $r_{Cu}$ is the length of the radius vector relative to the copper atom, and $X_j$ is its $i$th component. These integrals are calculated by rewriting the operator in real combinations of spherical harmonics, using the complete, core-orthogonalized, Slater-type atomic orbitals.

After diagonalizing the $g$ and $A$ tensors, the principal values and axes may be compared with those measured by Weeks and Fackler and by van Rens. All calculations were performed at the University Computing Center on the IBM 360/50 computer.

The experimentally determined values of $A_{ij}$, $a_{iso}$, and the deviations $\Delta g_{ii}$ from the free-electron $g$ value of the principal values $g_i$ of $\vec{g}$ ($\Delta g_{ll} = g_{ll} - 2.0023$) are listed in Table I and are shown in Figures 1 and 2.

<table>
<thead>
<tr>
<th>Table I</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimentally Determined Values for $\Delta g_{ll}$, $A_{ll}$, and $a_{iso}$</strong></td>
</tr>
<tr>
<td>$A_{xx}$</td>
</tr>
<tr>
<td>$A_{yy}$</td>
</tr>
<tr>
<td>$A_{zz}$</td>
</tr>
<tr>
<td>$a_{iso}$</td>
</tr>
</tbody>
</table>

Results and Discussion

1. Molecular Orbitals.—Table II lists the computed MO energies, the occupation numbers, and the atomic orbitals which have a coefficient larger than 0.3, using $K = 2.5$ (eq 7) and $k = 0.1$ (eq 5). As expected, the five highest occupied MO’s (which correspond with the “antibonding” 3d orbitals) and some of the lower occupied ones have mainly copper 3d character, whereas none of the unoccupied MO’s has a 3d coefficient larger than 0.13. From the calculations with $3c_{6}$ approximated by eq 5 it turned out that the MO of the unpaired electron has at most 50% 3d$_{xy}$ character, while calculations with a point charge approximation for the charge dependency

of 3C\textsubscript{4t} (eq 6) yield more than 50\% 3d\textsubscript{xy} character. For lower values of the Wolfsberg-Helmholz constant \( K \), the difference between the results from various charge-dependent 3C\textsubscript{4t} is considerable, but for increasing \( K \) this difference is diminished. This is clearly demonstrated in Figure 3 where the LCAO coefficient \( C_3^{3d_{xy}} \) is shown as a function of \( K \).

The computed Mulliken charges on the copper atom are shown in Figure 4. It appears that the ionicity decreases with increasing values for \( K \) and \( k \). For the same values of \( K \), calculations with the point charge correction yield a still higher ionicity. A calculation of the overlap population between the copper and sulfur atoms \( (O_{Cu-S}) \) indicates that the covalent bonding (for which the overlap population is a measure) between the copper and sulfur atoms increases when the ionicity decreases. An example of a nearly complete ionic bonding is the calculation with the point charge correction for 3C\textsubscript{4t} and \( K = 1.8 \) \( (q_{Cu} = 1.41; g_{8(1)} = -1.11; q_{8(2)} = -1.12; O_{Cu-S(1)} = 0.03; O_{Cu-S(2)} = 0.03 \text{ electron unit}) \); an example of a nearly complete covalent bonding is the calculation with \( k = 0.1 \) and \( K = 2.8 \) \( (q_{Cu} = -0.16; g_{8(1)} = -0.24; q_{8(2)} = -0.22; O_{Cu-S(1)} = 0.23; O_{Cu-S(2)} = 0.24 \text{ electron unit}) \). The calculation with \( k = 0.1 \) and \( K = 2.5 \) (for which the MO scheme has been given in Table II) yields a relatively strong covalent bonding with \( q_{Cu} = 0.04, g_{8(1)} = -0.28, g_{8(2)} = -0.26, O_{Cu-S(1)} = 0.22, \) and \( O_{Cu-S(2)} = 0.22 \text{ electron unit} \).

The results from calculations with \( k = 0 \) (that is, from the noniterative extended Hückel method) follow the trend of the other \( k \) values.

2. \( q \) Tensor.—The computed \( \Delta q_{4t} \) values are plotted in Figure 1 as a function of \( K \). The plots show that

**Table II**

Energies, Occupation Numbers, and Symmetries of MO's, Computed with \( K = 2.5 \) and \( k = 0.1 \), and the Most Important Coefficients of Copper and Sulfur Atomic Orbitals

<table>
<thead>
<tr>
<th>MO no.</th>
<th>No. of electrons</th>
<th>Energy, eV</th>
<th>Symmetry</th>
<th>Orbitals of Cu</th>
<th>Orbitals of S(1)</th>
<th>Orbitals of S(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0</td>
<td>62.8</td>
<td>u</td>
<td>-0.92 x</td>
<td>+0.48 s - 0.48 y</td>
<td>+0.54 s + 0.51 y</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>58.8</td>
<td>g</td>
<td>0.89 s</td>
<td>-0.52 s + 0.43 y</td>
<td>-0.55 s - 0.45 y</td>
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<tr>
<td>5</td>
<td>0</td>
<td>37.8</td>
<td>g</td>
<td>0.75 s</td>
<td>-0.32 y</td>
<td>-0.35 s</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>36.6</td>
<td>u</td>
<td>0.64 y</td>
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</tr>
<tr>
<td>9</td>
<td>0</td>
<td>28.6</td>
<td>u</td>
<td>0.86 y</td>
<td>-0.32 y</td>
<td>-0.35 s</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>23.7</td>
<td>g</td>
<td>0.83 s</td>
<td>0.33 z</td>
<td>+0.33 z</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>22.6</td>
<td>g</td>
<td>0.41 s</td>
<td>+0.36 x - 0.32 y</td>
<td>+0.43 x</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>20.5</td>
<td>u</td>
<td>1.03 x</td>
<td>+0.30 x</td>
<td>+0.46 x</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>17.6</td>
<td>u</td>
<td>0.81 y</td>
<td>-0.35 z</td>
<td>-0.36 z</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>17.3</td>
<td>u</td>
<td>0.86 s</td>
<td>+0.36 x</td>
<td>+0.43 x</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>-2.6</td>
<td>g</td>
<td>-0.58 z</td>
<td>-0.32 s</td>
<td>-0.35 s</td>
</tr>
<tr>
<td>16</td>
<td>0</td>
<td>-4.4</td>
<td>u</td>
<td>-0.58 z</td>
<td>-0.32 s</td>
<td>-0.35 s</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>-5.0</td>
<td>g</td>
<td>0.73 xy</td>
<td>+0.38 x</td>
<td>+0.37 x</td>
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<tr>
<td>18</td>
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<td>g</td>
<td>0.82 yz</td>
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<td>-0.39 y</td>
</tr>
<tr>
<td>19</td>
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<td>g</td>
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<td>-0.40 y</td>
<td>-0.40 y</td>
</tr>
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<td>20</td>
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<td>-10.3</td>
<td>g</td>
<td>0.98 x^2 - y^2</td>
<td>+0.36 x</td>
<td>+0.37 x</td>
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<tr>
<td>21</td>
<td>2</td>
<td>-10.5</td>
<td>g</td>
<td>0.90 z^2</td>
<td>+0.36 x</td>
<td>+0.37 x</td>
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<tr>
<td>22</td>
<td>2</td>
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<td>u</td>
<td>0.47 xy</td>
<td>0.44 y</td>
<td>+0.45 y</td>
</tr>
<tr>
<td>23</td>
<td>2</td>
<td>-11.7</td>
<td>g</td>
<td>0.47 xy</td>
<td>-0.39 y</td>
<td>-0.39 y</td>
</tr>
<tr>
<td>24</td>
<td>2</td>
<td>-11.8</td>
<td>u</td>
<td>-0.56 yz</td>
<td>0.41 x</td>
<td>+0.39 x</td>
</tr>
<tr>
<td>25</td>
<td>2</td>
<td>-12.0</td>
<td>g</td>
<td>0.35 yz</td>
<td>-0.31 y</td>
<td>-0.33 y</td>
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<td>26</td>
<td>2</td>
<td>-13.5</td>
<td>u</td>
<td>-0.35 yz</td>
<td>0.33 s</td>
<td>+0.34 s</td>
</tr>
<tr>
<td>27</td>
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<td>28</td>
<td>2</td>
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<td>u</td>
<td>0.45 xy</td>
<td>-0.39 y</td>
<td>-0.39 y</td>
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<td>29</td>
<td>2</td>
<td>-15.4</td>
<td>u</td>
<td>-0.34 y</td>
<td>-0.39 y</td>
<td>-0.39 y</td>
</tr>
<tr>
<td>30</td>
<td>2</td>
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<td>g</td>
<td>-0.36 s</td>
<td>-0.35 s</td>
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<td>31</td>
<td>2</td>
<td>-25.5</td>
<td>u</td>
<td>-0.36 s</td>
<td>-0.35 s</td>
<td>-0.35 s</td>
</tr>
</tbody>
</table>

* A complete table may be obtained on request from the authors.
\(\Delta g_{ii}\) increases as \(k\) is lowered from 1.0 to 0.1. Further it is clear that this dependency on \(k\) decreases when \(K\) increases and almost vanishes for \(K = 2.8\). The same trend is observed in Figures 3 and 4, which show that the dependency of \(C_{ii}\) and \(g_{Cu}\) on \(k\) also vanishes for \(K = 2.8\).

Figure 4.—Mulliken charges (in electron units) on the copper atom vs. the Wolfsberg-Helmholz parameter \(K\). Details are given in the caption of Figure 3.

A comparison with the observed values indicates that the best results for \(\Delta g_{ii}\) are obtained for \(K = 2.5\) and \(k = 0.1\). The MO scheme, that was given in Table II, refers also to these values. The value \(k = 0.1\) means that the charge dependency of \(3\) between 0.75 and 1.5.

For low values of \(K\) the point charge approximation for \(3\) yields much too large \(\Delta g_{ii}\) values. When \(K\) is raised from 1.8 to 3.0, these values are lowered and for \(K \approx 2.9\) they are in rather good agreement with the observed values. Surprisingly, the MO energies, the LCAO coefficients, and the atomic charges are very much the same as was found before, using eq 5 and \(K = 2.5\) and \(k = 0.1\).

The main contributions to \(\Delta g_{xx}\) and \(\Delta g_{yy}\) arise from excitations from MO's 19 and 20, respectively. This is due to the fact that these MO's have mainly 3d_{3z^2} or 3d_{x^2-y^2} character. The main contributions to \(\Delta g_{yy}\) arise from excitations from MO's 18 and 26 which have mainly 3d_{xz} character. The largest contribution is due to MO 26, although the 3d_{yz} coefficient in this MO is smaller and the excitation energy is higher than the corresponding values in MO 18. This is caused by the fact that the metal and sulfur contributions to \(\Delta g_{yy}\) partly cancel for the excitation arising from MO 18, whereas they reinforce each other for the excitation from MO 26.

As may be expected for a nearly D_{2h} symmetry, the directions of the principal axes are calculated to be (within 2°) along the chosen \(x\), \(y\), and \(z\) axes (see formula 1), which is in agreement with the experimentally observed directions.\(^{2,6}\)

3. Isotropic Hyperfine Coupling, \(a_{iso}\)—Because \(C_{0}^2\) (eq 10) has been computed to vary between 0.002 and 0.0050, \(a_{iso}\) varies between 0.24 \(\times 10^{-4}\) and 1.35 \(\times 10^{-4}\) cm\(^{-1}\). A comparison with the observed value of \((-79.0 \pm 1.2) \times 10^{-4}\) cm\(^{-1}\) shows that this contribution is negligibly small and has the wrong sign. Therefore the main contribution to \(a_{iso}\) must be the spin polarization of the inner-core \(s\) orbitals, which is indeed negative\(^{20}\) but cannot be calculated with the extended Hückel method.

Just a small amount of core polarization is needed to bring about an isotropic hfc of 79 \(\times 10^{-4}\) cm\(^{-1}\). For instance, a surplus of 4 \(\times 10^{-6}\) \(\beta\) spin in the copper 2s orbital would be enough to explain this hfc.

4. Anisotropic Hyperfine Coupling Tensor, \(\vec{A}\)—Figure 2 shows the principal values \(A_{ii}\) of \(\vec{A}\) as a function of \(K\). Because spin-orbit coupling has been neglected, the calculated differences between \(A_{xx}\) and \(A_{yy}\) are less than 1\%; so \(A_{yv}\) is not plotted in Figure 2.

As may be deduced from eq 11, \(A_{ii}\) is proportional to \((C_{ii})^2\), which is clearly demonstrated by comparing Figures 2 and 3. However the calculated couplings with parameters \(K = 2.5\) and \(k = 0.1\) (which give the best \(g\) values) are in absolute value too large by about 20\%. This result is improved when spin-orbit coupling is taken into account by the following approximate formulas\(^{21}\)

\[
A_{xx}(SO) = P \left( \frac{2}{3} \Delta g_{xx} - \frac{23}{42} \Delta g_{yy} - \frac{1}{3} \Delta g_{zz} \right) = -8.8 \times 10^{-4} \text{ cm}^{-1}
\]
\[
A_{yy}(SO) = P \left( \frac{23}{42} \Delta g_{xx} + \frac{2}{3} \Delta g_{yy} - \frac{1}{3} \Delta g_{zz} \right) = -6.9 \times 10^{-4} \text{ cm}^{-1}
\]
\[
A_{zz}(SO) = P \left( \frac{5}{42} \Delta g_{xx} - \frac{5}{42} \Delta g_{yy} + \frac{2}{3} \Delta g_{zz} \right) = +15.7 \times 10^{-4} \text{ cm}^{-1}
\]

where \(A_{ii}(SO)\) is the contribution to \(A_{ii}\) from the spin-orbit coupling and \(P = e_{\beta}^{3} \beta_{\alpha}^{12} D_{\alpha}^{12}(Cu\ 3d)/[rcu^{12}Cu\ 3d] = 315.98 \times 10^{-4} \text{ cm}^{-1}\). Adding these corrections to the first-order values of \(A_{ii}\), we obtained, for \(K = 2.5\) and \(k = 0.1\), \(A_{xx} = 39.7 \times 10^{-4} \text{ cm}^{-1}, A_{yy} = 41.6 \times 10^{-4} \text{ cm}^{-1}, \) and \(A_{zz} = -81.3 \times 10^{-4} \text{ cm}^{-1}\). This agrees very well with the observed hfc's.

This correction shifts the hfc's, calculated with the point charge approximation and \(K = 2.9\), to \(A_{xx} = 44.8 \times 10^{-4} \text{ cm}^{-1}, A_{yy} = 47.1 \times 10^{-4} \text{ cm}^{-1}, \) and \(A_{zz} = -91.8 \times 10^{-4} \text{ cm}^{-1}\). These couplings are in absolute value about 10\% greater than the experimental results. Therefore we conclude that the results, obtained with the point charge approximation for the charge dependency of the Hamiltonian matrix, are not as good as those obtained by employing eq 5 and \(K = 2.5\) and \(k = 0.1\).

Conclusions

Our calculations show that it is possible to calculate epr parameters for Cu(dtc)\(_2\) with the aid of the extended Hückel MO method, in agreement with the experimental values, employing values for the empirical parameters which are accepted as reasonable in the literature.

Alternatively one may conclude that the MO's, calculated with these parameter values, give a fair description for the ground state of this complex. The bonding is largely covalent, with overlap populations between the copper and sulfur atoms of 0.22 electron unit. The Mulliken charges on the atoms are rather low: for instance, 0.04 on the copper atom and —0.26 and —0.28 on the sulfur atoms.

The unpaired electron is strongly delocalized; the density on the copper atom (obtained by summing squares of LCAO coefficients) is just 0.54, while the density on each sulfur atom is 0.21 electron unit. The relatively high position of the MO of this single electron corresponds well with the experimentally observed reduced behavior of Cu(dtc)$_2$: oxidation to Cu(dtc)$_2^+$ is easy (half-wave potential 0.47 V with respect to a saturated calomel electrode in CH$_2$Cl$_2$), and reduction to Cu(dtc)$_2^-$ appeared impossible so far.22

Acknowledgment.—The authors want to thank Professor E. de Boer and Dr. J. G. M. van Rens for valuable discussions. The present investigations have been carried out under the auspices of The Netherlands Foundation of Chemical Research (S.O.N.) and with the aid of The Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

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Extended Hückel Calculation of the Quadrupole Splitting in Iron Dithiocarbamate Complexes

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The electric field gradient at the metal nucleus in some iron dithiocarbamate complexes has been calculated with the aid of the extended Hückel LCAO-MO method. The empirical constants, used in this method, were taken from the preceding article. It is shown that the abnormally large electric field gradient in two five-coordinated iron complexes, bis(N,N-diethyl-dithiocarbamato)iron(III) chloride and bis(N,N-diethyl-dithiocarbamato)iron(II), is mainly caused by covalency effects. Some other contributions to the electric field gradient are also discussed.

Introduction

Bis(N,N-diethyl-dithiocarbamato)iron(III) chloride, Fe(dtc)$_2$Cl, has been extensively investigated with the aid of Mössbauer spectroscopy.1-4 The quadrupole splitting (QS) of this five-coordinated complex is abnormally large for an iron(III) compound. From a crystal field approach one expects the electric field gradient arising from the 3d valence electrons on the copper atom (obtained by summing squares of LCAO coefficients) is just 0.54, while the density on each sulfur atom is 0.21 electron unit. The relatively high position of the MO of this single electron corresponds well with the experimentally observed reduced behavior of Cu(dtc)$_2$: oxidation to Cu(dtc)$_2^+$ is easy (half-wave potential 0.47 V with respect to a saturated calomel electrode in CH$_2$Cl$_2$), and reduction to Cu(dtc)$_2^-$ appeared impossible so far.22

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Experimental Section

The Mössbauer spectra of iron(III) dithiocarbamates have been reported.4-8 Among the iron(III) complexes the spectrum of Fe(dtc)$_2^+$ has not been measured before. This compound was prepared from iron(II) sulfate and Na(dtc) in aqueous solution by using the vacuum technique we described elsewhere.11 The light brown compound precipitated immediately after the solutions were mixed and the precipitate was dried under vacuum conditions. All these operations were carried out under vacuum conditions, since the compound proved to be very air sensitive. All these operations were carried out under vacuum conditions, since the compound proved to be very air sensitive. The compound was dried under vacuum conditions. All these operations were carried out under vacuum conditions, since the compound proved to be very air sensitive. All these operations were carried out under vacuum conditions, since the compound proved to be very air sensitive.

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In such a low-symmetry complex, however, it is not allowed to neglect the differences of covalency occurring in the various iron atomic orbitals. In this paper we show that these covalency effects can give rise to a considerable EFG. To this end we have computed the Fe(dtc)$_2$Cl molecular orbitals (MO) taking into account all the valence electrons. For this calculation we used the semiempirical iterative extended Hückel method, using those parameters which were shown in the preceding article (further denoted by I) to give the best agreement between the calculated and experimental g values and hyperfine couplings of Cu(dtc)$_2$.