ferromagnetic and to have intermolecular ferromagnetic contributions. An additional possibility for the observed variation of $2J_{12}$ could be a very slight contamination by excess free radical or copper complex or both. Our main interest, however, is the predominant intramolecular antiferromagnetic coupling which has been conclusively shown.

Acknowledgment.—The authors are grateful for the generous support of the Paint Research Institute and the National Science Foundation for support of this research. We also acknowledge a National Science Foundation grant to the University of Illinois for the purchase of the HR-220 nmr spectrometer. We are also thankful to Professor D. Hendrickson for the magnetic susceptibility measurements.

CONTRIBUTION FROM THE DEPARTMENTS OF THEORETICAL AND PHYSICAL CHEMISTRY,
UNIVERSITY OF NIJMEGEN, NIJMEGEN, THE NETHERLANDS

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

BY C. P. KEIJZERS, H. J. M. DE VRIES, AND A. VAN DER AVOIRD*

Received August 2, 1971

The g tensor and ^{63}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 dithiocarbamato and diselenocarbamato complexes of certain transition metals.[1] 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(diethyldithiocarbamato)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.[2]

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)$_2$.

The Molecular Orbital Calculation

The MO's of Cu(dtc)$_2$ were calculated by means of the LCAO–MO extended Hückel method.[3] The computer program[4] used was based on the self-consistent charge method. In this method a set of secular equations

$$\sum_j (\mathcal{H}_{ij} - ES_{ij})C_j = 0 \qquad (1)$$

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

$$\mathcal{H}_{ij} = \langle \phi_i | \mathcal{H}_{\text{eff}} | \phi_j \rangle \qquad (2)$$

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

where ϕ_i are atomic orbitals and $\mathcal{H}_{\text{eff}}$ is an effective one-electron Hamiltonian. By solving these secular equations, the orbital energies E_k and LCAO coefficients C_{jk} are obtained. After occupying the lowest MO's in agreement with the spin multiplicity of the ground state, the Mulliken charges[5] 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$^{\text{II}}$(dtc)$_2$ complex,[2,6] we used for our calculations the crystal struc-

---

* Address correspondence to this author, Department of Theoretical Chemistry, University of Nijmegen, Nijmegen, The Netherlands.

(1) H. van Willigen and J. G. M. van Rens, *Chem. Phys. Lett.*, **2**, 283 (1968); H. C. Brinkhoff, J. A. Cras, J. J. Steggerda, and J. Willemse, *Recl. Trav. Chim. Pays-Bas*, **88**, 633 (1969); J. G. M. van Rens, C. P. Keijzers, and H. van Willigen, *J. Chem. Phys.*, **52**, 2858 (1970); J. L. K. F. de Vries, J. M. Trooster, and E. de Boer, *Inorg. Chem.*, **10**, 81 (1971).

(2) M. J. Weeks and J. P. Fackler, *ibid.*, **7**, 2548 (1968).

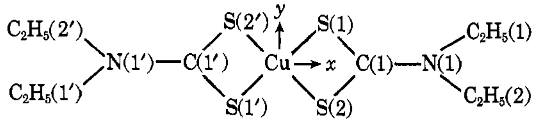
(3) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(4) The authors wish to thank Professor P. Ros and Dr. W. Th. A. M. van der Lugt for making the computer program available to them.

(5) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(6) J. G. M. van Rens, unpublished results.

ture of the latter compound.[7] The cartesian coordinates of the atoms were computed in a coordinate system with the x and y axes along the bisectors of the angles S–Cu–S and the z axis perpendicular to the plane of the copper and the four sulfur atoms



1

The local symmetry around the copper atom is nearly D_{2h}, but in our calculations we used the real symmetry of the molecule, which is just C_i.

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.[7a] 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 functions, 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. **$\mathcal{H}$ Matrix. a. Diagonal Elements, $\mathcal{H}_{ii}$.**—$\mathcal{H}_{ii}$, which is the energy of an electron in the atomic orbital ϕ_i, is approximated by

$$\mathcal{H}_{ii} = -\alpha_i - \beta_i q_{\mathrm{A}} \qquad (4)$$

where α_i is the valence state ionization energy (VSIE) of orbital ϕ_i, q_{A} is the Mulliken charge of the atom A to which the orbital ϕ_i belongs, and $\beta_i q_{\mathrm{A}}$ describes the charge dependence of the VSIE.

The influence of surrounding atoms on $\mathcal{H}_{ii}$ is generally to lower the charge dependency. This effect can be taken into account by introducing a parameter k

$$\mathcal{H}_{ii} = -\alpha_i - k\beta_i q_{\mathrm{A}} \quad (0 \leqslant k \leqslant 1) \qquad (5)$$

Alternatively a point charge approximation can be used[11]

$$\mathcal{H}_{ii} = -\alpha_i - \beta_i q_{\mathrm{A}} - \sum_{\mathrm{B}\neq\mathrm{A}} \frac{q_{\mathrm{B}}}{R_{\mathrm{AB}}} \qquad (6)$$

in which q_{B} is the Mulliken charge of the atom B and R_{AB} is the distance between the atoms A and B. The sum is taken over all atoms, except the atom A.

b. Off-Diagonal Elements, $\mathcal{H}_{ij}$.—The off-diagonal elements are approximated by the Wolfsberg–Helmholz relation[12]

$$\mathcal{H}_{ij} = {}^1\!/_2 K S_{ij}(\mathcal{H}_{ii} + \mathcal{H}_{jj}) \qquad (7)$$

where K is an empirical constant, which is usually taken between 1.5 and 3.0. Cusachs[13] and Jug[14] proposed overlap-dependent formulas for K: $K = 2 - |S_{ij}|$ and $K = 2/(1 + S_{ij}^2)$, 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 (β) 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 $\bar{H}$ and the copper nuclear spin $\bar{I}$ may be represented by the following spin Hamiltonian

$$\mathcal{H}_{\mathrm{s}} = \beta_{\mathrm{e}}\bar{H}\cdot\bar{\bar{g}}\cdot\bar{S} + \bar{S}\cdot\bar{\bar{T}}\cdot\bar{I} \qquad (8)$$

where β_{e} is the Bohr magneton, $\bar{S}$ is the electronic spin vector, $\bar{\bar{g}}$ is the anisotropic g tensor and $\bar{\bar{T}}$ is the anisotropic hfc tensor.

1. **g Tensor.**—The elements g_{ij} of $\bar{\bar{g}}$ 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 coupling. With the aid of second-order perturbation theory and neglecting interatomic overlap, the following (gauge-invariant) formula has been derived[17]

$$g_{ij} = 2.0023\delta_{ij} + 2\sum_{n\neq0}\sum_{\mathrm{A}}\sum_{\mathrm{B}} \frac{\langle \chi^{\mathrm{A}}{}_0|\lambda^{\mathrm{A}}(\mathrm{r})L^{\mathrm{A}}{}_i|\chi^{\mathrm{A}}{}_n\rangle\langle\chi^{\mathrm{B}}{}_n|L^{\mathrm{B}}{}_j|\chi^{\mathrm{B}}{}_0\rangle}{E_0 - E_n} \qquad (9)$$

where the summation over n is taken over all MO's, except the one of the unpaired electron (Φ_0).

The summations over A and B run over all atoms, with $\lambda^{\mathrm{A}}(\mathrm{r})$ being the radial part of the spin–orbit coupling operator and $\chi^{\mathrm{A}}{}_n$ the linear combination of those atomic orbitals in the nth MO (Φ_n), which are centered on the atom A. $\mathrm{L}^{\mathrm{A}}{}_i$ is the angular momentum operator L_i ($i = x, y, z$) with the origin on atom A. For the excitation energy ($E_0 - E_n$) we have used the difference in calculated MO energies.

The radial parts of the integrals occurring in this formula are not calculated but approximated by the atomic spin–orbit coupling constants[18,19] $\lambda(\mathrm{Cu\ 3d}) = 828\ \mathrm{cm}^{-1}$, $\lambda(\mathrm{S\ 3p}) = 382\ \mathrm{cm}^{-1}$, $\lambda(\mathrm{C\ 2p}) = 28\ \mathrm{cm}^{-1}$, and $\lambda(\mathrm{N\ 2p}) = 76\ \mathrm{cm}^{-1}$.

2. **T Tensor.**—The hyperfine term in eq 8 consists of an isotropic part $a_{\mathrm{iso}}\bar{S}\cdot\bar{I}$, arising from the Fermi-contact interaction, and an anisotropic part $\bar{S}\cdot\bar{\bar{A}}\cdot\bar{I}$.

---

(7) M. Bonamico, G. Dessy, C. Mariani, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, **19**, 619 (1965).

(7a) NOTE ADDED IN PROOF.—One sample calculation carried out with full ethyl groups demonstrated that there may be a negligible effect of these groups on the calculated epr parameters.

(8) J. Richardson, W. Nieuwpoort, R. Powell, and W. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

(9) J. Richardson, R. Powell, and W. Nieupoort, *ibid.*, **38**, 796 (1963).

(10) E. Clementi and D. Raimondi, *ibid.*, **38**, 2686 (1963).

(11) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 369 (1967).

(12) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

(13) L. C. Cusachs, *ibid.*, **43**, S157 (1965).

(14) K. Jug, *Theor. Chim. Acta*, **19**, 301 (1970).

(15) M. Zerner and M. Gouterman, *ibid.*, **4**, 44 (1966).

(16) L. Cusachs, J. Reynolds, and D. Barnard, *J. Chem. Phys.*, **44**, 835 (1966).

(17) C. P. Slichter, "Principles of Magnetic Resonance," 1st ed, Harper and Row, New York, N. Y., 1963, p 195.

(18) J. S. Griffith, "The Theory of Transition-Metal Ions," 2nd ed, Cambridge University Press, London, 1964, p 437.

(19) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," 1st ed, Harper and Row, New York, N. Y., 1967, p 138.

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[20]—cannot be calculated by means of the extended Hückel method.

A calculation of the first contribution

$$a_{\text{iso}} = \frac{8\pi}{3} g_e\beta_e g_N\beta_N|\phi_{4s}(0)|^2(C_0^{4s})^2 \qquad (10)$$

yields $a_{\text{iso}} = 5.4(C_0^{4s})^2$ cm^{-1}, where C_0^{4s} is the coefficient of the 4s atomic orbital in the MO of the unpaired electron, g_e is the free-electron g value, g_N is the g value of the copper nucleus, and β_N is the nuclear magneton.

b. Anisotropic Hyperfine Coupling.—The elements of the anisotropic hyperfine coupling tensor $\bar{\bar{A}}$ have been calculated in first order, that is, taking into account the interaction of the nuclear spin $\bar{I}$ 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

$$A_{ij} = g_e\beta_e g_N\beta_N\left\langle \chi^{\text{Cu}}_0 \left| \frac{3x_ix_j}{r_{\text{Cu}}^5} - \frac{\delta_{ij}}{r_{\text{Cu}}^3}\right| \chi^{\text{Cu}}_0\right\rangle \qquad (11)$$

where χ^{Cu}_0 has the same meaning as in eq 9, r_{Cu} is the length of the radius vector relative to the copper atom, and x_i its ith 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[2] and by van Rens.[6] All calculations were performed at the University Computing Center on the IBM 360/50 computer.

The experimentally determined[2,6] values of A_{ii}, a_{iso}, and the deviations Δg_{ii} from the free-electron g value of the principal values g_{ii} of $\bar{\bar{g}}$ ($\Delta g_{ii} = g_{ii} - 2.0023$) are listed in Table I and are shown in Figures 1 and 2.

TABLE I

EXPERIMENTALLY DETERMINED[a] VALUES FOR Δg_{ii}, A_{ii},[b] AND a_{iso}[b]

A_{xx} =	43.0 ± 2.8	Δg_{xx} =	0.0177 ± 0.0010
A_{yy} =	37.0 ± 2.8	Δg_{yy} =	0.0227 ± 0.0010
A_{zz} =	−80.0 ± 1.6	Δg_{zz} =	0.0817 ± 0.0005
a_{iso} =	−79.0 ± 1.2		

[a] Values obtained from ref 2 and 6. [b] Values for A_{ii} and a_{iso} in 10^{-4} cm^{-1}.

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.

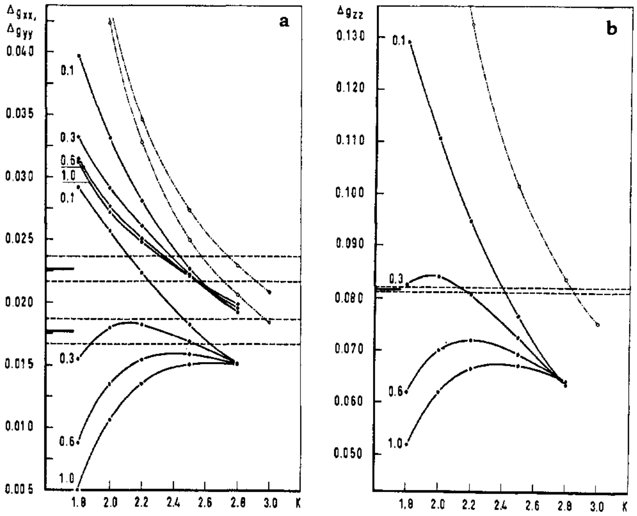


Figure 1.—Deviations from the free electron g value (Δg_{ii}) *vs.* the Wolfsberg–Helmholz parameter K. The solid bars and the dashed lines refer to the experimentally measured values of Δg_{ii} with their errors. The lowest one in part a is the Δg_{xx} value and the highest is Δg_{yy}. Part b shows Δg_{zz}. In the same order the groups of solid lines represent calculated values for Δg_{xx}, Δg_{yy}, and Δg_{zz} for different values of k. The dashed–dotted curves give the results for the calculations assuming a point charge approximation for the charge dependency of the Hamiltonian matrix.

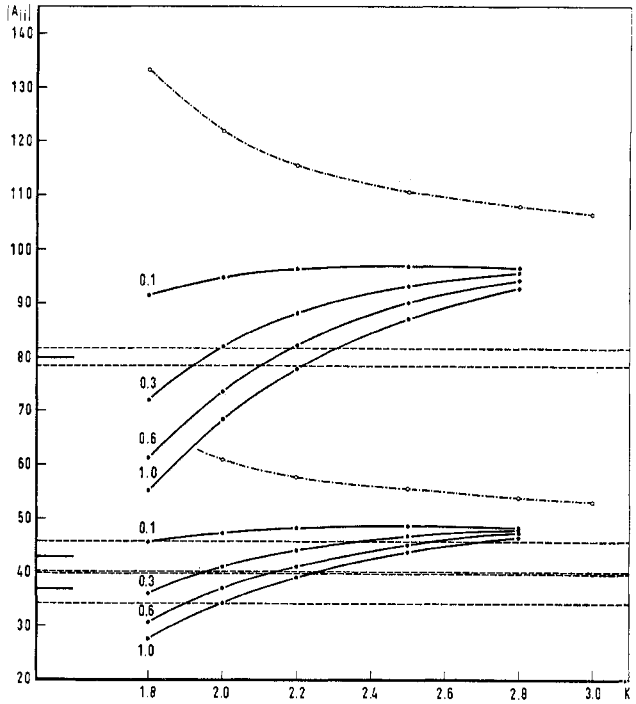


Figure 2.—Absolute values (in 10^{-4} cm^{-1}) of the anisotropic hyperfine couplings A_{xx} and A_{zz} *vs.* the Wolfsberg–Helmholz parameter K. The solid bars and the dashed lines refer to the absolute values of the experimentally measured values of A_{ii} with their errors. The lowest one is the A_{yy} value, the next is A_{xx}, and the highest is A_{zz}. In the same order the two groups of solid lines represent calculated absolute values for A_{xx} and A_{zz} for different values of k. The dashed–dotted curves give the results for the calculations assuming a point charge approximation for the charge dependency of the Hamiltonian matrix.

From the calculations with $\mathcal{H}_{ii}$ 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

---

(20) B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).

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[a]

MO no.	No. of electrons	Energy, eV	Symmetry	Orbitals of Cu	Orbitals of S(1)	Orbitals of S(2)
3	0	62.8	u	$-0.92\,x$	$+0.48\,\mathrm{s} - 0.48\,y$	$+0.54\,\mathrm{s} + 0.51\,y$
4	0	58.8	g	$0.89\,\mathrm{s}$	$-0.52\,\mathrm{s} + 0.43\,y$	$-0.55\,\mathrm{s} - 0.45\,y$
5	0	37.8	g	$0.75\,\mathrm{s}$		
6	0	36.6	u	$0.64\,y$	$-0.41\,\mathrm{s}$	$+0.48\,\mathrm{s}$
9	0	28.6	u	$0.86\,y$		
10	0	23.7	g	$0.83\,\mathrm{s}$		$+0.43\,x$
11	0	22.6	g	$0.41\,\mathrm{s}$	$+0.36\,x - 0.32\,y$	
12	0	20.5	u	$1.03\,x$	$+0.30\,x$	$+0.46\,x$
13	0	17.6	u	$0.81\,y$	$+0.54\,x$	$-0.41\,x$
14	0	0.3	u	$0.86\,z$	$-0.35\,z$	$-0.36\,z$
15	0	−2.6	g		$0.33\,z$	$+0.33\,z$
16	0	−4.4	u	$-0.58\,z$		
17	1	−5.0	g	$0.73\,xy$	$+0.38\,x$	$-0.37\,x$
18	2	−9.8	g	$0.82\,yz$	$-0.32\,z$	$+0.31\,z$
19	2	−10.2	g	$0.93\,xz$		
20	2	−10.3	g	$0.98\,x^2-y^2$		
21	2	−10.5	g	$0.96\,z^2$		
22	2	−10.5	u		$0.44\,y$	$+0.45\,y$
23	2	−11.0	u		$0.51\,z$	$-0.50\,z$
24	2	−11.7	g	$0.47\,xy$	$-0.39\,y$	$-0.39\,y$
25	2	−11.8	u		$0.41\,x$	$+0.39\,x$
26	2	−12.0	g	$-0.56\,yz$	$-0.40\,z$	$+0.38\,z$
27	2	−12.8	g	$-0.35\,xz$	$-0.31\,z$	$-0.33\,z$
28	2	−12.9	u		$0.33\,z$	$+0.34\,z$
29	2	−13.5	g		$0.41\,x$	$-0.30\,y$
30	2	−13.6	g	$0.45\,xy$		$+0.40\,x$
31	2	−14.9	u		$0.30\,x$	$-0.31\,x$
32	2	−15.4	u		$-0.34\,y$	$+0.36\,y$
40	2	−25.1	g		$0.36\,\mathrm{s}$	$-0.35\,\mathrm{s}$
41	2	−25.5	u		$-0.36\,\mathrm{s}$	$+0.35\,\mathrm{s}$

[a] A complete table may be obtained on request from the authors.

of $\mathcal{H}_{ii}$ (eq 6) yield more than 50% $3d_{xy}$ character. For lower values of the Wolfsberg–Helmholz constant K, the difference between the results from various charge-dependent $\mathcal{H}_{ii}$ is considerable, but for increasing K this difference is diminished. This is clearly demonstrated in Figure 3 where the LCAO coefficient $C_0^{3d_{xy}}$ 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 ($O_{\mathrm{Cu-S}}$) 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 $\mathcal{H}_{ii}$ and $K = 1.8$ ($q_{\mathrm{Cu}} = 1.41$; $q_{\mathrm{S(1)}} = -1.11$; $q_{\mathrm{S(2)}} = -1.12$; $O_{\mathrm{Cu-S(1)}} = 0.03$; $O_{\mathrm{Cu-S(2)}} = 0.03$ electron unit); an example of a nearly complete covalent bonding is the calculation with $k = 0.1$ and $K = 2.8$ ($q_{\mathrm{Cu}} = -0.16$; $q_{\mathrm{S(1)}} = -0.24$; $q_{\mathrm{S(2)}} = -0.22$; $O_{\mathrm{Cu-S(1)}} = 0.23$; $O_{\mathrm{Cu-S(2)}} = 0.24$ 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 $q_{\mathrm{Cu}} = 0.04$, $q_{\mathrm{S(1)}} = -0.28$, $q_{\mathrm{S(2)}} = -0.26$, $O_{\mathrm{Cu-S(1)}} = 0.22$, and $O_{\mathrm{Cu-S(2)}} = 0.22$ 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. **g Tensor.**—The computed Δg_{ii} values are plotted in Figure 1 as a function of K. The plots show that

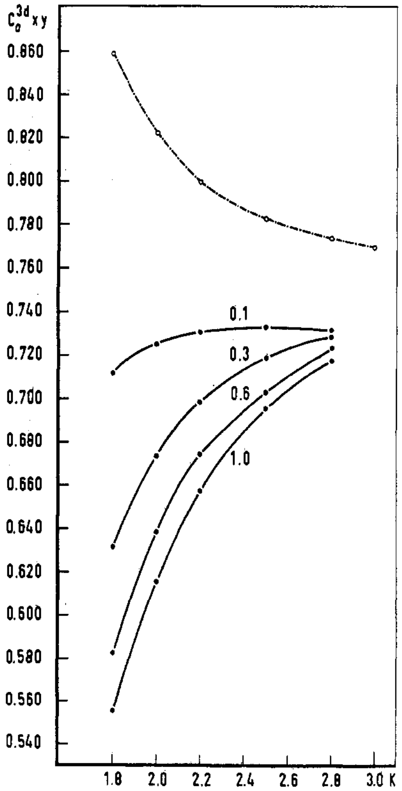


Figure 3.—The LCAO coefficient $C_0^{3d_{xy}}$ of the $3d_{xy}$ atomic orbital in the MO of the unpaired electron *vs.* the Wolfsberg–Helmholz parameter K. Solid lines refer to calculations with different values of the charge-dependency parameter k. The dashed–dotted line represents calculations with a point charge approximation for the charge dependency of the Hamiltonian matrix.

Δg_{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 $C_0^{3d_{xy}}$ and q_{Cu} on k also vanishes for $K \approx 2.8$.

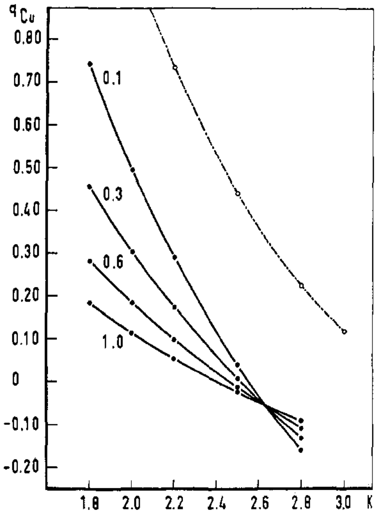


Figure 4.—Mulliken charges (in electron units) on the copper atom *vs.* the Wolfsberg–Helmholz parameter K. Details are given in the caption of Figure 3.

A comparison with the observed values indicates that the best results for Δg_{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 $\mathcal{H}_{ii}$ (eq 5) is largely diminished by the surrounding atoms. This is in agreement with the results obtained for $PtCl_4^{2-}$ by Cotton and Harris.[11] They found the best charge dependency of $\mathcal{H}_{ii}$ to be between 1 and 2 eV/unit charge, whereas our values for different orbitals lie between 0.75 and 1.5.

For low values of K the point charge approximation for $\mathcal{H}_{ii}$ yields much too large Δg_{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 Δg_{xx} and Δg_{zz} arise from excitations from MO's 19 and 20, respectively. This is due to the fact that these MO's have mainly $3d_{xz}$ or $3d_{x^2-y^2}$ character. The main contributions to Δg_{yy} arise from excitations from MO's 18 and 26 which have mainly $3d_{yz}$ 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 Δg_{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^{4s} (eq 10) has been computed to vary between 0.0021 and 0.0050, a_{iso} varies between 0.24×10^{-4} and 1.35×10^{-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 79×10^{-4} cm^{-1}. For instance, a surplus of 4×10^{-6} β spin in the copper 2s orbital would be enough to explain this hfc.

4. Anisotropic Hyperfine Coupling Tensor, $\overline{\overline{A}}$.—Figure 2 shows the principal values A_{ii} of $\overline{\overline{A}}$ 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_{yy} is not plotted in Figure 2.

As may be deduced from eq 11, A_{ii} is proportional to $(C_0^{3d_{xy}})^2$, 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]

$$A_{xx}(\mathrm{SO}) = P\left(\frac{2}{3}\Delta g_{xx} - \frac{23}{42}\Delta g_{yy} - \frac{1}{3}\Delta g_{zz}\right) = -8.8 \times 10^{-4}\ \mathrm{cm}^{-1}$$

$$A_{yy}(\mathrm{SO}) = P\left(-\frac{23}{42}\Delta g_{xx} + \frac{2}{3}\Delta g_{yy} - \frac{1}{3}\Delta g_{zz}\right) = -6.9 \times 10^{-4}\ \mathrm{cm}^{-1}$$

$$A_{zz}(\mathrm{SO}) = P\left(-\frac{5}{42}\Delta g_{xx} - \frac{5}{42}\Delta g_{yy} + \frac{2}{3}\Delta g_{zz}\right) = +15.7 \times 10^{-4}\ \mathrm{cm}^{-1}$$

where $A_{ii}(\mathrm{SO})$ is the contribution to A_{ii} from the spin–orbit coupling and $P = g_e\beta_e g_N\beta_N\langle \mathrm{Cu\ 3d}|1/r_{Cu}^3|\mathrm{Cu\ 3d}\rangle = 315.98\ 10^{-4}$ cm^{-1}. Adding these corrections to the first-order values of A_{ii}, we obtained, for $K = 2.5$ and $k = 0.1$, $A_{xx} = 39.7 \times 10^{-4}$ cm^{-1}, $A_{yy} = 41.6 \times 10^{-4}$ cm^{-1}, and $A_{zz} = -81.3 \times 10^{-4}$ 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 $A_{xx} = 44.8 \times 10^{-4}$ cm^{-1}, $A_{yy} = 47.1 \times 10^{-4}$ cm^{-1}, and $A_{zz} = -91.8 \times 10^{-4}$ 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.

---

[21] W. Windsch and M. Welter, *Z. Naturforsch. A*, **22**, 1 (1967).

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 redox 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_2Cl_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.).

[22] J. G. M. van der Linden and H. G. J. van de Roer, *Inorg. Chim. Acta*, **5**, 254 (1971).

CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY,
UNIVERSITY OF NIJMEGEN, NIJMEGEN, THE NETHERLANDS

Extended Hückel Calculation of the Quadrupole Splitting in Iron Dithiocarbamate Complexes

BY J. L. K. F. DE VRIES, C. P. KEIJZERS, AND E. DE BOER*

Received August 2, 1971

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*-diethyldithiocarbamato)iron(III) chloride and bis(*N*,*N*-diethyldithiocarbamato)iron(II), is mainly caused by covalency effects. Some other contributions to the electric field gradient are also discussed.

Introduction

Bis(*N*,*N*-diethyldithiocarbamato)iron(III) chloride, $Fe(dtc)_2Cl$, has been extensively investigated with the aid of Mössbauer spectroscopy.[1-6] 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 (EFG) arising from the 3d valence electrons[3,7] in the spin quartet ground state to be zero. The influence of thermal excitations and spin–orbit coupling is also expected to be unimportant, because of the rather large distances between the energy levels.[4,7] Finally the lattice contribution to the EFG, calculated from a point charge model, is also too small to account for the observed QS.[3,5]

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 $Fe(dtc)_2Cl$ 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 $Cu(dtc)_2$.

From the charge distribution, resulting from this MO calculation, the EFG was computed and found to be in good agreement with the experimental value. Similar calculations were carried out for $[Fe(dtc)_2]_2$, a five-coordinated iron(II) dithiocarbamate complex with a fifth sulfur atom at the apical position. Here too agreement with the experimental value was obtained.

Experimental Section

The Mössbauer spectra of iron(III) dithiocarbamates have been reported.[4,5,8-10] The spectrum of $[Fe(dtc)_2]_2$ 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 Na_2SO_4 was removed by a washing procedure. All these operations were carried out under vacuum conditions, since the compound proved to be very air sensitive. The composition was checked by C, H, N, and Fe analyses, whereby oxidation of the complex could not be prevented. It is assumed that 2.5% of the sample contains impurities like oxygen and unremoved Na_2SO_4. *Anal.* Calcd: C, 33.33; H, 5.59; N, 7.77; Fe, 15.50. Found: C, 33.33; H, 5.67; N, 7.67; Fe, 15.15. In the ir spectrum all the peaks of the dtc ligands were clearly present.

---

[1] H. H. Wickman and A. M. Trozzolo, *Phys. Rev. Lett.*, **15**, 156 (1965); **16**, 162 (1966).

[2] H. H. Wickman, A. M. Trozzolo, H. J. Williams, and F. R. Merritt, *Phys. Rev.*, **155**, 563 (1967).

[3] H. H. Wickman and F. R. Merritt, *Chem. Phys. Lett.*, **1**, 117 (1967).

[4] H. H. Wickman and A. M. Trozzolo, *Inorg. Chem.*, **7**, 63 (1968).

[5] L. M. Epstein and D. K. Straub, *ibid.*, **8**, 560 (1969).

[6] H. H. Wickman and C. F. Wagner, *J. Chem. Phys.*, **51**, 435 (1969).

[7] R. L. Ake and G. M. Harris Loew, *ibid.*, **52**, 1098 (1970).

[8] E. Frank and C. R. Abeledo, *Inorg. Chem.*, **5**, 1453 (1966).

[9] L. M. Epstein and D. K. Straub, *ibid.*, **8**, 784 (1969).

[10] J. L. K. F. de Vries, J. M. Trooster, and E. de Boer, *ibid.*, **10**, 81 (1971).

[11] J. L. K. F. de Vries, J. M. Trooster, and E. de Boer, *J. Chem. Soc. D*, 604 (1970).