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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*-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, $\text{Fe}(\text{dtc})_2\text{Cl}$, 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 $\text{Fe}(\text{dtc})_2\text{Cl}$ 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 $\text{Cu}(\text{dtc})_2$.

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 $[\text{Fe}(\text{dtc})_2]_2$, 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 $[\text{Fe}(\text{dtc})_2]_2$ has not been measured before. This compound was prepared from iron(II) sulfate and $\text{Na}(\text{dtc})$ 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.

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TABLE I
MÖSSBAUER PARAMETERS (MM SEC⁻¹) AT LIQUID NITROGEN
AND ROOM TEMPERATURE

	100°K		300°K	
	IS	QS	IS	QS
Fe(dtc) ₂ Cl	0.70 ^a	2.67 ^a	0.64 ^b	2.63 ^b
[Fe(dtc) ₂] ₂	1.16	4.16	1.02	4.01

^a Reference 10. ^b Reference 5.

The Mössbauer parameters are listed in Table I (the isomer shift (IS) values are given with respect to sodium nitroprusside). The QS of [Fe(dtc)₂]₂ is the largest one observed for an iron(II) compound. It has been measured with a constant-acceleration spectrometer, with ⁵⁷Co in palladium as a source. The accuracy of our measurements is 0.04 mm sec⁻¹.

The Molecular Orbital Calculation

The MO's were calculated by means of the LCAO-MO extended Hückel method.¹² As in I the computer program used was based on the self-consistent charge procedure.

1. **Structure.**—The cartesian coordinates of the atoms were calculated using crystal structures which are discussed in the sections dealing with the different compounds.

2. **Atomic Wave Functions.**—To limit the number of atomic wave functions in all complexes, the dtc ethyl groups were replaced by hydrogen atoms, the N-H distance being 1.01 Å. As a basis for our calculations we took into account all valence orbitals: iron 3d, 4s, 4p; sulfur and chlorine 3s, 3p; carbon and nitrogen 2s, 2p; hydrogen 1s. As in I the radial part of the atomic wave functions were the double exponent (3d functions) or single exponent (all the other functions) Slater-type orbitals given in ref 13–15. These functions were used to calculate the overlap matrix. For the derivation of the $\langle r^{-3} \rangle$ values, necessary for the calculation of the EFG, the core-orthogonalized Slater-type orbitals¹⁴ were used.

3. **\mathcal{H} Matrix.**—As in I, the diagonal elements \mathcal{H}_{ii} were approximated by

$$\mathcal{H}_{ii} = -\alpha_i - k\beta_i q_A \quad (0 \leq k \leq 1) \quad (1)$$

and the off-diagonal elements \mathcal{H}_{ij} by the Wolfsberg-Helmholz approximation

$$\mathcal{H}_{ij} = KS_{ij}(\mathcal{H}_{ii} + \mathcal{H}_{jj})/2 \quad (2)$$

For the meaning of the symbols we refer to I and for the parameters K and k the values 2.5 and 0.1 are taken, respectively. As has been demonstrated in I, they give the best agreement between the calculated and experimental g values and hyperfine couplings of Cu(dtc)₂. The α_i and β_i values are taken from ref 16 and 17.

Calculation of the EFG

The diagonal elements V_{ii} of the EFG tensor at nucleus A in a polyatomic system have the form¹⁸

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$$V_{ii}^A = \frac{e}{4\pi\epsilon_0} \left\{ \sum_{B \neq A} [Z_B(3(X_i)_{AB}^2 - R_{AB}^2)/R_{AB}^5] - \left\langle \psi \left| \sum_{k=1}^n [(3(x_i)_{Ak}^2 - r_{Ak}^2)/r_{Ak}^5] \right| \psi \right\rangle \right\} \quad (3)$$

where \vec{R}_{AB} is the radius vector connecting the nuclei A and B, $(X_i)_{AB}$ is its component along the chosen molecular i axis, \vec{r}_{Ak} is the radius vector connecting the nucleus A and the electron k , and $(x_i)_{Ak}$ is its i th component. The core charge of the atom B is given by eZ_B , the charge of an electron is given by $-e$, and ψ is the ground-state molecular wave function. For ψ a single configuration function is taken, composed of one or more Slater determinants. The one-electron MO's are linear combinations of atomic orbitals

$$\Phi_u = \sum_{a=1}^m C_{au}\phi_a \quad (4)$$

where Φ_u is the u th MO and the sum is taken over the m atomic orbitals. Substituting the expression for Φ into ψ , the electronic part of eq 3 may be written

$$V_{ii}^A(\text{el}) = - \sum_{u=1}^m N_u \sum_{a=1}^m \sum_{b=1}^m C_{au} C_{bu} \langle \phi_a | v_{ii}^A(\text{el}) | \phi_b \rangle \quad (5)$$

where N_u is the occupation number of the u th MO, C_{au} and C_{bu} are the LCAO coefficients of the atomic orbitals ϕ_a and ϕ_b , and $v_{ii}^A(\text{el})$ is the EFG operator

$$v_{ii}^A(\text{el}) = \frac{e}{4\pi\epsilon_0} \frac{3x_i^2 - r^2}{r^5} \quad (6)$$

Equation 5 may be split up in terms, involving a different number of centers

$$V_{ii}^A(\text{el}) = - \sum_u N_u \left[\sum_{a,a'}^A C_{au} C_{a'u} \langle \phi_a | v_{ii}^A(\text{el}) | \phi_{a'} \rangle + 2 \sum_a^A \sum_{B \neq A} \sum_b^B C_{au} C_{bu} \langle \phi_a | v_{ii}^A(\text{el}) | \phi_b \rangle + \sum_{B \neq A} \sum_{b,b'}^B C_{bu} C_{b'u} \langle \phi_b | v_{ii}^A(\text{el}) | \phi_{b'} \rangle + \sum_{B \neq A} \sum_{C \neq A} \sum_{B \neq C}^B \sum_c^C C_{bu} C_{cu} \langle \phi_b | v_{ii}^A(\text{el}) | \phi_c \rangle \right] \quad (7)$$

O'Konski and Ha showed for the EFG on the nitrogen atom in HCN and NH₃ that the last term, which is a three-center contribution, is negligibly small.¹⁸

White and Drago pointed out in a recent paper,¹⁹ for nuclei of the third row and higher, that the sum of the two-center nuclear and electronic contributions (being opposite in sign) to the EFG is small in comparison to the one-center contribution, so that for practical purposes the semiempirical relationship

$$V_{ii}^A = - \sum_u N_u \sum_a^A C_{au}^2 V_{ii}^{aa} - 2 \sum_u N_u \sum_{a < a'}^A C_{au} C_{a'u} V_{ii}^{aa'} \quad (8)$$

can be used. In this equation we made the substitution

$$V_{ii}^{ab} = \langle \phi_a | v_{ii}^A(\text{el}) | \phi_b \rangle \quad (9)$$

We wish to calculate this one-center contribution, which we call the valence contribution. The effect of

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neglecting the sum of the multicenter contributions will be discussed later.

Utilizing the atomic orbital net populations according to Mulliken²⁰

$$n(a) = \sum_u N_u C_{au}^2 \quad (10)$$

and defining

$$n(a, a') = \sum_u N_u C_{au} C_{a'u} \quad (11)$$

we may rewrite eq 8

$$V_{ii}^A = -\sum_a n(a) V_{ii}^{aa} - 2 \sum_{a < a'} n(a, a') V_{ii}^{aa'} \quad (12)$$

In this equation V_{ii}^{aa} is the contribution to the EFG of one electron in the atomic orbital a , which is zero for the spherically symmetric functions. In our calculations we are dealing with the iron valence orbitals 3d, 4s, and 4p. From the nondiagonal elements only the $V_{ii}^{aa'}$ between 3d functions are important. The other non-zero elements between 4s and 3d_{z²} and between 4s and 3d_{x²-y²} can be neglected since the value of $\langle R_{3d}(r) | r^{-3} | R_{4s}(r) \rangle$ turned out to be very small compared to $\langle r^{-3} \rangle_{3d}$. The EFG at the nucleus, due to an electron in a valence orbital, is modified by polarization of the inner closed shells.²¹ Thus eq 12 becomes

$$V_{ii}^{Fe} = (1 - R_{3d}) V_{ii}^{Fe}(3d) + (1 - R_{4p}) V_{ii}^{Fe}(4p) \quad (13)$$

where R is the Sternheimer shielding factor.

From eq 13 the following relevant formulas may be deduced

$$(V_{zz})_{3d} = -\frac{4}{7} \frac{e}{4\pi\epsilon_0} \langle r^{-3} \rangle_{3d} (1 - R_{3d}) \times \left[n(3d_{z^2}) - n(3d_{x^2-y^2}) + \frac{1}{2} n(3d_{zz}) + \frac{1}{2} n(3d_{yz}) - n(3d_{xy}) \right] \quad (14)$$

$$(V_{zz})_{4p} = -\frac{4}{5} \frac{e}{4\pi\epsilon_0} \langle r^{-3} \rangle_{4p} (1 - R_{4p}) \times \left[n(4p_z) - \frac{1}{2} n(4p_x) - \frac{1}{2} n(4p_y) \right] \quad (15)$$

$$(V_{xx} - V_{yy})_{3d} = \frac{1}{7} \frac{e}{4\pi\epsilon_0} \langle r^{-3} \rangle_{3d} (1 - R_{3d}) \times [6n(3d_{yz}) - 6n(3d_{zz}) + (8\sqrt{3})n(3d_{z^2}, 3d_{x^2-y^2})] \quad (16)$$

$$(V_{xx} - V_{yy})_{4p} = \frac{6}{5} \frac{e}{4\pi\epsilon_0} \langle r^{-3} \rangle_{4p} (1 - R_{4p}) \times [n(4p_y) - n(4p_x)] \quad (17)$$

From the resulting V_{zz} and $V_{xx} - V_{yy}$, obtained by summing the 3d and 4p contributions, the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ can be deduced.

As eq 14-17 show, the nondiagonal terms only contribute to $(V_{xx} - V_{yy})_{3d}$. Thus for axially symmetric EFG tensors ($\eta = 0$), only diagonal terms have to be considered.

The QS is calculated from

$$QS = \frac{1}{2} e V_{zz} Q \sqrt{1 + \eta^2/3} \quad (18)$$

Q being the nuclear quadrupole moment of the ⁵⁷Fe first excited nuclear state. For the core-orthogonalized Slater-type orbitals $\langle r^{-3} \rangle_{3d} = 32.0 \text{ \AA}^{-3}$ and $\langle r^{-3} \rangle_{4p} = 11.6 \text{ \AA}^{-3}$. The value of $\langle r^{-3} \rangle_{3d}$ is in excellent agreement with the Hartree-Fock value of 32.5 \AA^{-3} .²²

The Sternheimer factor R_{3d} was calculated by Freeman and Watson to be 0.32.²³ The 4p Sternheimer factor R_{4p} is not known and was taken equal to R_{3d} . For Q we used the value $Q = 0.21 \pm 0.03 \text{ barn}$.²⁴

Results and Discussion

a. The Quadrupole Splitting. 1. $\text{Fe}(\text{dtc})_2\text{Cl}$.—The structure of $\text{Fe}(\text{dtc})_2\text{Cl}$ has been published recently by Hoskins and White²⁵ and is depicted in Figure 1. The z axis of the coordinate system has been taken

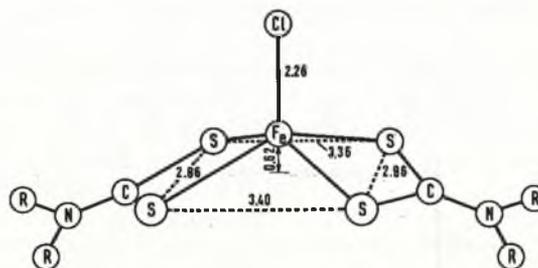


Figure 1.—Molecular structure diagram of bis(*N,N'*-diethyl-dithiocarbamato)iron(III) chloride.²⁵ Distances are given in angstroms.

along the direction Fe-Cl, and the x axis, in the plane of the atoms Fe, Cl, and C and parallel to the plane of the four sulfur atoms. Figure 2a gives the energy levels of the MO's of interest. MO's 17-21 correspond to the 3d atomic orbitals. They have mainly metal character, whereas all the others have considerable ligand character. Figure 2b shows the spectral excitation energies, derived from the electronic absorption spectrum of $\text{Fe}(\text{dtc})_2\text{Cl}$.¹⁰ There exists fair agreement with the calculated energy levels, bearing in mind the approximate nature of the extended Hückel method. The sequence of MO's 17-21 is exactly the one expected on the basis of esr measurements.²⁶ The high energy of the "3d_{xy}" molecular orbital accounts for the spin pairing of the fifth d electron.

In Table II the 3d and 4p coefficients are listed for the MO's of interest. From this table it can be seen that the covalency is strongly direction dependent.

The second row of Table III gives the net populations of the 3d and 4p atomic orbitals. The net electronic distribution is quite different from the one assumed in a crystal field model, given in row 1. For 3d_{y²-x²} the deviation is negligible; 3d_{z²}, 3d_{zz}, and 3d_{yz} contain about 10% more electronic charge as a consequence of "donation" effects. The most striking feature is that

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TABLE II
 MO COEFFICIENTS CALCULATED FOR $\text{Fe}(\text{dtc})_2\text{Cl}^a$

MO no.	Orbital type	$3d_{xy}$	$3d_{z^2}$	$3d_{yz}$	$3d_{xz}$	$3d_{x^2-y^2}$	$4p_x$	$4p_y$	$4p_z$
17	$3d_{xy}$	0.818	0	0	0	0	0	0	0
18	$3d_{z^2}$	0	0.924	0	0	-0.083	0	0	-0.205
19	$3d_{yz}$	0	0	0.941	0	0	0	0.107	0
20	$3d_{xz}$	0	0	0	0.959	0	0.098	0	0
21	$3d_{x^2-y^2}$	0	0.091	0	0	0.994	0	0	-0.024

^a Calculations performed with $K = 2.5$ and $k = 0.1$.

 TABLE III
 NET ORBITAL POPULATIONS OF $\text{Fe}(\text{dtc})_2\text{Cl}$ AND RESULTING EFG AND QS, FOR DIFFERENT VALUES OF K AND k

K	k	Net orbital populations										$3d^a$		$3d + 4p^b$	
		$3d_{xy}$	$3d_{z^2}$	$3d_{yz}$	$3d_{xz}$	$3d_{x^2-y^2}$	$4p_x$	$4p_y$	$4p_z$	V_{zz}^c	η^d	QS ^e	V_{zz}^c	η^d	QS ^e
2.5	0.1	f 0	1	1	1	2	0	0	0	1.05	0.66	2.46 ± 0.35	1.07	0.68	2.52 ± 0.36
2.5	0.1	g 0.8836	1.0949	1.1367	1.0798	1.9899	0.3204	0.5005	0.3807	1.20	0.58	2.77 ± 0.40	1.23	0.76	2.94 ± 0.42
2.5	1.0	0.7279	1.1154	1.1546	1.1139	2.0048	0.1995	0.1926	0.1683	0.87	0.59	2.01 ± 0.29	0.89	0.57	2.05 ± 0.29
2.0	1.0	0.8065	1.1578	1.2159	1.1498	2.0048	0.1502	0.1260	0.1003	0.84	0.62	1.96 ± 0.28	0.88	0.55	2.02 ± 0.29
2.0	0.6	0.8253	1.1454	1.2151	1.1373	2.0043	0.1498	0.1277	0.1014	0.91	0.65	2.13 ± 0.30	0.95	0.59	2.20 ± 0.31

^a Values calculated, taking into account only the contribution of 3d atomic orbital populations to the EFG. ^b Values calculated, taking into account the contribution of all iron valence orbitals to the EFG. ^c Z component of EFG in 10^{22} V m^{-2} . ^d Asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. ^e Quadrupole splitting in mm sec^{-1} , calculated with $Q = 0.21 \pm 0.03$ barn. The indicated error is due to the uncertainty in Q only. ^f Atomic orbital populations and resulting EFG and QS in a crystal field model. ^g Atomic orbital gross populations and resulting EFG and QS.

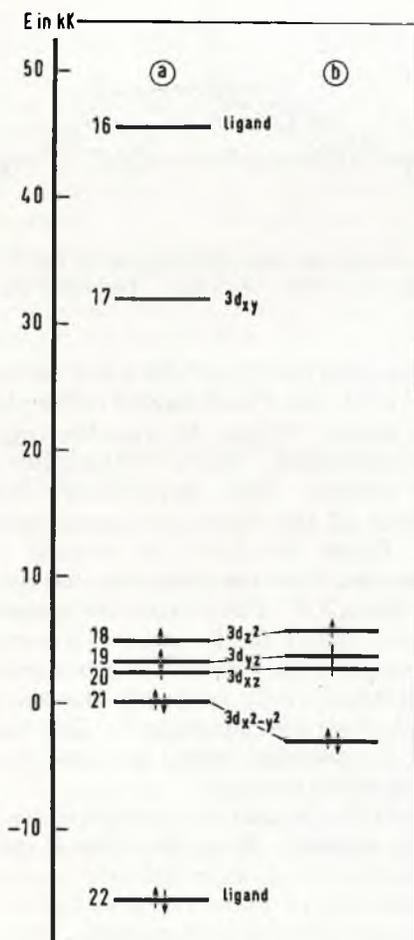


Figure 2.—Calculated relative energies ($1000 \text{ cm}^{-1} = 1 \text{ kK}$) of the most important MO's (a) and spectral excitation energies derived from the electronic absorption spectrum¹⁰ (b) of bis-(N,N' -diethyldithiocarbamato)iron(III) chloride. The zero energy level points are taken arbitrarily.

the $3d_{xy}$ orbital, which points to the sulfur ligand atoms, is not empty at all but is occupied by 0.7 electronic charge. This result is not unexpected because an electron transport from the negative dtc^- ligands

to the Fe^{3+} ion will take place *via* the initially empty, σ bonding $3d_{xy}$ orbital. Furthermore it is clear that the 4p orbitals have to be taken into account because they substantially participate in the bonding.

Using eq 18 the QS was calculated to be $+2.52 \pm 0.36 \text{ mm sec}^{-1}$ (where the indicated error is due to the uncertainty in Q only), in reasonable agreement with the observed QS of $+2.67 \text{ mm sec}^{-1}$ at liquid nitrogen temperature.¹⁰ The calculated sign is correct but the calculated asymmetry parameter $\eta = 0.68$ does not agree with the experimental value $\eta = 0.16$.⁴

The results of our calculations warrant the conclusion that covalency effects are primarily responsible for the observed large QS in $\text{Fe}(\text{dtc})_2\text{Cl}$.

It is important to know how strongly this calculated QS depends on structural data and the empirical parameters K and k . Therefore we have given in Table III the results of calculations in which the numerical values of the parameters have been changed: row 4 contains the results for $K = 2.5$ and $k = 1.0$, row 5 for $K = 2.0$ and $k = 1.0$, and row 6 for $K = 2.0$ and $k = 0.6$. Considering the calculated EFG and QS values, one may conclude that a change of the parameters causes a change in EFG and QS of at most 20%. The influence of the interatomic distances used was estimated from a calculation in which the Fe-S distance was increased by 0.1 \AA ; the QS turned out to decrease by 8% and the relative energy of the " $3d_{xy}$ " MO dropped by 6 kK.

A rough estimate of the effect of neglecting the sum of the multicenter contributions (eq 7) can be obtained by assuming a multicenter integral to be proportional to the corresponding overlap integral,¹⁸ e.g.

$$V_{ii}^{ab} = \frac{1}{2} S_{ab} (V_{ii}^{aa} + V_{ii}^{bb}) \quad (19)$$

This approximation is probably an overestimation of these $\langle r^{-8} \rangle$ type integrals.

With this approximation, V_{ii}^A becomes (see eq 3 and 7)

$$V_{ii}^A = -\sum_u N_u \left[2 \sum_{a < a'}^A C_{au} C_{a'u} V_{ii}^{aa'} + \sum_a^A V_{ii}^{aa} \times \right. \\ \left. \left\{ C_{au}^2 + \sum_{B \neq A} \sum_b^B S_{ab} C_{au} C_{bu} \right\} + \sum_{B \neq A} \sum_b^B V_{ii}^{bb} \times \right. \\ \left. \left\{ C_{bu}^2 + \sum_{C \neq B} \sum_c^C S_{bc} C_{bu} C_{cu} + \sum_a^A S_{ab} C_{au} C_{bu} \right\} \right] + \\ \frac{e}{4\pi\epsilon_0} \sum_{B \neq A} Z_B (3(X_i)_{AB}^2 - R_{AB}^2) / R_{AB}^5 \quad (20)$$

Defining the Mulliken "gross" population of atomic orbital b by²⁰

$$N(b) = \sum_u N_u \left(C_{bu}^2 + \sum_{a \neq b} S_{ab} C_{au} C_{bu} \right) \quad (21)$$

Equation 20 may be rewritten

$$V_{ii}^A = -\left[2 \sum_{a < a'}^A n(a, a') V_{ii}^{aa'} + \sum_a^A N(a) V_{ii}^{aa} + \right. \\ \left. \sum_{B \neq A} \left\{ \sum_b^B N(b) V_{ii}^{bb} - \frac{e}{4\pi\epsilon_0} Z_B (3(X_i)_{AB}^2 - R_{AB}^2) / R_{AB}^5 \right\} \right] \quad (22)$$

Setting V_{ii}^{bb} equal to $-(e/4\pi\epsilon_0)(3(X_i)_{AB}^2 - R_{AB}^2)/R_{AB}^5$ (point charge model) and defining the Mulliken gross atomic charge by

$$q_B = eZ_B - \sum_b^B eN(b) \quad (23)$$

Equation 22 becomes

$$V_{ii}^A = -2 \sum_{a < a'}^A n(a, a') V_{ii}^{aa'} - \sum_a^A N(a) V_{ii}^{aa} + \\ \frac{1}{4\pi\epsilon_0} \sum_{B \neq A} q_B (3(X_i)_{AB}^2 - R_{AB}^2) / R_{AB}^5 \quad (24)$$

The first two terms represent the valence contribution to the EFG and the third term represents the lattice contribution ($V_{ii}^A(\text{latt})$). Taking into account the polarization of the electronic shells, the components of the EFG on the iron nucleus are

$$V_{ii}^{\text{Fe}} = -2 \sum_{a < a'}^{\text{Fe}} (1 - R_a) n(a, a') V_{ii}^{aa'} - \\ \sum_a^{\text{Fe}} (1 - R_a) N(a) V_{ii}^{aa} + (1 - \gamma_\infty) V_{ii}^{\text{Fe}}(\text{latt}) \quad (25)$$

where γ_∞ is the Sternheimer correction factor, equal to -9.14 ,²⁷ which represents the effect on the EFG of the polarization of the atomic electrons. In the third row of Table III the gross populations of the iron orbitals and the resulting valence contribution to the EFG and QS values are listed. The calculated QS due to the valence electrons is $2.94 \pm 0.42 \text{ mm sec}^{-1}$. The lattice contribution to the EFG has been calculated using the computed Mulliken charges of the ligand atoms: sulfur, -0.17 ; carbon, 0.31 ; nitrogen, -0.22 ; hydrogen, 0.21 ; chlorine, -0.48 electron charge. It was found that the lattice contribution to the EFG components was small: V_{zz} was lowered from 1.23 to $1.16 \times 10^{22} \text{ V m}^{-2}$, η increased from 0.76 to 0.87 , and QS became $2.84 \pm 0.28 \text{ mm sec}^{-1}$. The extended Hückel method, however, yields atomic charges which

(27) R. M. Sternheimer, *Phys. Rev.*, **130**, 1423 (1963).

are rather small. We have also calculated the lattice contribution to the EFG by assuming that all charges of the dte^- ligands are concentrated on the sulfur atoms; that means a charge of -0.5 on the sulfur atoms and of -1.0 at the chlorine atom. In this case the lattice contribution is still small. The total EFG components are $V_{zz} = 1.19 \times 10^{22} \text{ V m}^{-2}$ and $\eta = 0.73$. The resulting QS is $2.83 \pm 0.40 \text{ mm sec}^{-1}$, which does not deviate significantly from the QS calculated with the Mulliken charges.

In general spin-orbit coupling tends to diminish the QS by mixing the various orbitals.²⁴ In our case, however, splittings between adjacent energy levels amount to more than 1000 cm^{-1} , which is large compared to the spin-orbit coupling constant ($\lambda^{\text{Fe}_{3d}} 104 \text{ cm}^{-1}$). Also the small temperature dependence of QS points to a small influence of spin-orbit coupling.

Taylor²⁸ and Sawatzky²⁹ discussed the influence on the EFG of the so-called overlap effect, caused by the nonorthogonality of the wave functions of the basis set. This effect is automatically taken into account in our calculations. However, only valence orbitals were considered in our calculations, assuming that closed-shell contributions to the EFG are negligible. To estimate the contribution of the core orbitals to the EFG, we have performed a calculation with $3p$, $3d$, and $4s$ orbitals on the iron atom; the resulting net populations of the $3p$ orbitals were $n(3p_x) = 2.00664$, $n(3p_y) = 2.00488$, and $n(3p_z) = 2.00278$.

We calculated $\langle r^{-3} \rangle_{3p}$ from the Hartree-Fock function given by Clementi³⁰ as 366 \AA^{-3} , very large compared to the corresponding $4p$ and $3d$ values.

The EFG components arising from $3p$ electrons can be calculated from formulas similar to (15) and (17). Assuming $(1 - R)_{3p} = 0.7$, the $3p$ contributions to the EFG were $V_{zz} = 0.263$ and $(V_{zz} - V_{yy}) = 0.2333 \times 10^{22} \text{ V m}^{-2}$. This correction changes the calculated QS from 2.84 ± 0.28 to $3.44 \pm 0.49 \text{ mm sec}^{-1}$.

2. $[\text{Fe}(\text{dte})_2]_2$.—From the X-ray powder spectra it is known that $[\text{Fe}(\text{dte})_2]_2$ occurs in the dimeric form, with a five-coordinated iron atom.³¹ In order to get an idea about the EFG in this iron(II) compound, we have performed calculations on the monomeric unit, placing at the apical position a Cl^- ion, so that the atomic wave functions and the structural parameters of $\text{Fe}(\text{dte})_2\text{Cl}$ can be used. From the results given in Table IV one notices that the order and the position of

TABLE IV
MO SCHEME OF $[\text{Fe}(\text{dte})_2]_2^a$

MO no.	Orbital type	$S = 1$		$S = 2$	
		Energy ^b	N_u^c	Energy ^b	N_u^c
16	Ligand	40,580	0	24,055	0
17	$3d_{xy}$	26,500	0	17,900	1
18	$3d_{z^2}$	3,940	1	3,252	1
19	$3d_{yz}$	2,610	1	2,330	1
20	$3d_{xz}$	1,730	2	1,430	1
21	$3d_{x^2-y^2}$	0	2	0	2
22	Ligand	-20,450	2	-9,262	2

^a Calculations performed with parameters $K = 2.5$ and $k = 0.1$. ^b Relative energy in cm^{-1} . ^c Occupation number of the MO's.

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TABLE V
 NET ORBITAL POPULATIONS OF $[\text{Fe}(\text{dte})_2]_2$ AND RESULTING EFG AND QS^a

	2S + 1 ^b	Net orbital populations							3d ^a			3d + 4p ^b			
		3d _{xy}	3d _{z²}	3d _{yz}	3d _{xz}	3d _{x²-y²}	4p _x	4p _y	4p _z	V _{zz} ^c	η ^d	QS ^e	V _{zz} ^c	η ^d	QS ^e
[Fe(dte) ₂] ₂	3	0.6318	1.0303	1.0780	1.9789	2.0025	0.1995	0.1788	0.1540	0.14	-14.23	2.54 ± 0.36	0.17	-11.62	2.53 ± 0.36
	f	0	1	1	2	2	0	0	0	-0.90	3	3.9			
	5	1.3971	1.0517	1.1308	1.0827	2.0038	0.1461	0.1138	0.0881	2.25	0.26	4.98 ± 0.71	2.29	0.23	5.06 ± 0.72
	f	1	1	1	1	2	0	0	0	1.80	0	3.9			

^a See caption of Table III. ^c Calculations of $[\text{Fe}(\text{dte})_2]_2$ performed with parameters $K = 2.5$ and $k = 0.1$. ^b Spin multiplicity.

the MO's with mainly 3d character is the same as in $\text{Fe}(\text{dte})_2\text{Cl}$. Unfortunately we were unable to record the electronic absorption spectrum and to measure reliably the susceptibility, so that the spin multiplicity of the ground state could not be determined. Therefore we calculated the QS for both the triplet and the quintet ground states. The results are listed in Table V and may be compared with the experimental QS value of 4.16 mm sec⁻¹ at 100°K. Taking into account the assumed molecular structure and the unknown multiplicity of the ground state one may conclude that also here covalency contributes significantly to the observed QS. In both spin configurations the calculated 3d_{xy} AO population strongly deviates from the value expected on the basis of a crystal field model. In the high-spin configuration, which cannot be excluded on the basis of the energy of the "3d_{xy}" MO, the QS according to the crystal field model is entirely caused by the sixth electron in the "3d_{x²-y²}" MO. Covalency increases mainly the electron charge in the "3d_{xy}" MO and therefore enhances the QS. This explains why the observed QS of $[\text{Fe}(\text{dte})_2]$ is larger than the maximum QS expected for common ionic ferrous compounds (about 3.9 mm/sec).

b. Isomer Shift.—The observed IS's of $\text{Fe}^{\text{III}}(\text{dte})_2\text{Cl}$ and $\text{Fe}^{\text{II}}(\text{dte})_2$ are respectively 0.70 and 1.16 mm sec⁻¹. One should expect that this difference in IS is correlated with the different orbital net populations of the compounds.

The 4s net orbital populations of $\text{Fe}^{\text{III}}(\text{dte})_2\text{Cl}$ and high-spin $[\text{Fe}^{\text{II}}(\text{dte})_2]_2$ are 0.2172 and 0.1720, respectively (with parameters $K = 2.5$ and $k = 0.1$). Both compounds have about the same total 4p net population (0.5554 and 0.5323, respectively). The total net population of the 3d shell increases from 5.9760 for the iron(III) compound to 6.6461 for the iron(II) compound. Both differences give rise to a lower electronic charge at the iron nucleus of $[\text{Fe}^{\text{II}}(\text{dte})_2]_2$ and, conse-

quently, to a larger IS, as is observed. If $[\text{Fe}(\text{dte})_2]_2$ occurs in the intermediate spin state, the 3d and 4s populations are 6.7215 and 0.2050, respectively, which lead to the same conclusion.

Conclusions

The results of the semiempirical extended Hückel method depend on the parameters chosen. This introduces a certain amount of arbitrariness in the outcome of the calculation. To eliminate this to a certain extent we have chosen those parameters (K and k) which gave good agreement between the theoretical and the experimental g values and hyperfine couplings of $\text{Cu}(\text{dte})_2$ (see preceding article). With this set of parameters we have calculated another physical quantity, the electric field gradient. Our calculations show that the large EFG in five-coordinated iron dithiocarbamate complexes is primarily caused by covalency effects and is almost entirely due to the valence iron electrons.

The treatment followed gives only useful results for crystals, in which distinct molecules can be discerned; hence ionic crystals are excluded. If, in addition, these molecules possess low symmetry, the results of the calculation become more reliable, since then effects of spin-orbit coupling and thermal mixing of states are negligible. Therefore we suggest that meaningful results also can be obtained for other five-coordinated complexes with intermediate spin state, such as bis(maleonitriledithiolato)iron and bis(toluenedithiolato)iron, which all have unusually high QS values.

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