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INTERPRETATION OF EXPERIMENTAL QUADRUPOLE SPLITTINGS OF IRON CONTAINING COMPLEXES USING MOLECULAR ORBITAL THEORY (*)

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Résumé. — Nous étudions sur la base de calculs d'orbitales moléculaires plusieurs arrangements tridimensionnels des ligands autour du fer dans des complexes du fer-pentacyanure, dans FeOCl et dans des hèmes désoxygénés. Nous calculons les tenseurs de gradient de champ électrique (GCE) pour les diverses structures moléculaires étudiées et nous en déduisons les éclatements quadripolaires, le paramètre d'asymétrie et les orientations de la composante V_{zz} du GCE dont les valeurs sont comparées aux données expérimentales.

Abstract. — On the basis of molecular orbital calculations we study several three dimensional arrangements of ligands with respect to iron in iron-pentacyanide complexes, in FeOCl, and in deoxygenated heme compounds. For the various molecular structures under study we derive electric field gradient (EFG) tensors, from which we calculate quadrupole splittings, asymmetry parameter, and orientations of the EFG component V_{zz} , which are compared with experimental data.

1. Quadrupole splitting and electric field gradient tensor. — Experimental quadrupole splittings, ΔE_Q^{exp} are compared with theoretical estimates of

$$\Delta E_Q^{\text{calc}} = \frac{1}{2} e Q V_{zz} (1 + \frac{1}{3} \eta^2)^{1/2}. \quad (1)$$

The quantity e represents the (positive) elementary charge, and the nuclear quadrupole moment Q is taken to be -0.21 b [1-4]. The main component of the Electric Field Gradient (EFG) tensor, V_{zz} , being defined by $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ and the asymmetry parameter $\eta = \frac{|V_{xx} - V_{yy}|}{|V_{zz}|}$, result from diagonalizing the (EFG) tensor V_{pq} ($p, q = x, y, z$). The aim of the present work is to derive V_{pq} from the calculated

electronic structure of several iron containing complexes.

Many-electron molecular orbital (MO) wave functions are obtained by theoretical approaches as described elsewhere [1]. The matrix elements of the EFG tensor components V_{pq} for two many-electron states $|l'\rangle$ and $|l\rangle$ follow from [5]:

$$\begin{aligned} \langle l' | V_{pq} | l \rangle = & \sum_{h', h} C_{(l'l)(h'h)} \langle \psi_{h'} | V_{pq} | \psi_h \rangle + \\ & + \sum_{h', h''} (C_{(l'l)(h'h'')} + C_{(l'l)(h''h)}) \langle \psi_{h'} | V_{pq} | \psi_{h''} \rangle + \\ & + \sum_{h'', h'''} C_{(l'l)(h''h''')} \langle \psi_{h''} | V_{pq} | \psi_{h'''} \rangle, \end{aligned} \quad (2)$$

where the states $|\psi\rangle$ are atomic orbitals (AO's), the coefficients C are their corresponding bond order matrix elements, the indices h, h' stand for Fe AO's, and h'', h''' for ligand AO's, respectively. The matrix elements $\langle \psi_{h'} | V_{pq} | \psi_{h''} \rangle$ are cross-terms between iron AO's and ligand AO's and can be transformed

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by introducing a completeness relation of orthogonal terms $|\psi_h^- \rangle$, which contain the iron AO's $|\psi_h \rangle$, into

$$\begin{aligned} \langle \psi_{h'} | V_{pq} | \psi_{h''} \rangle &= \\ &= \sum_h \langle \psi_{h'} | V_{pq} | \psi_h^- \rangle \langle \psi_h^- | \psi_{h''} \rangle. \end{aligned}$$

Since V_{pq} does not lead out of the subspace of $|\psi_h \rangle$, the summation can be restricted to iron orbitals and we get:

$$\langle \psi_{h'} | V_{pq} | \psi_{h''} \rangle = \sum_h \langle \psi_{h'} | V_{pq} | \psi_h \rangle S_{hh''}, \quad (3)$$

with $S_{hh''}$ representing overlap integrals between iron AO's ψ_h and ligand AO's $\psi_{h''}$. With the use of eq. (2) and (3) we distinguish two parts of the tensor V_{pq} , (i) the so-called valence contribution

$$\begin{aligned} \langle I' | V_{pq}^{\text{val}} | I \rangle &= \sum_{h',h} [C_{(I')}(h'h) + \\ &+ \sum_{h''} (C_{(I')}(h'h'') + C_{(I')}(h''h')) S_{hh''}] \langle \psi_{h'} | V_{pq} | \psi_h \rangle, \end{aligned} \quad (4)$$

and (ii) the so-called lattice contribution

$$\langle I' | V_{pq}^{\text{lat}} | I \rangle = \sum_{h'',h'''} C_{(I')}(h''h''') \langle \psi_{h''} | V_{pq} | \psi_{h'''} \rangle. \quad (5)$$

Assuming the ligand charges q_a to be localized at lattice points (R_{xa}, R_{ya}, R_{za}) we approximate V_{pq}^{lat} of eq. (5) by

$$\begin{aligned} \langle I' | V_{pq}^{\text{lat}} | I \rangle &= \\ &= (1 - \gamma_\infty) \sum_a q_a (3 R_{pa} R_{qa} - \delta_{pq} R_a^2) / R_a^5, \end{aligned} \quad (6)$$

where q_a and (R_{xa}, R_{ya}, R_{za}) are the charge and the cartesian coordinates of the a th ligand, and $(1 - \gamma_\infty)$ represents the Sternheimer antishielding correction: $(1 - \gamma_\infty) = 10.1$. From MO calculations the information concerning $C_{(I')}(h'h)$, $C_{(I')}(h'h'')$, $C_{(I')}(h''h')$, and $S_{hh''}$ is available. For the evaluation of V_{pq} from eq. (4) and (6) it remains therefore to derive the matrix elements $\langle \psi_{h'} | V_{pq} | \psi_h \rangle$ from

$$\begin{aligned} \langle \psi_{h'} | V_{pq} | \psi_h \rangle &= \\ &= \langle \| \text{EFG} \| \rangle e(1 - R) \langle r^{-3} \rangle \times \\ &\quad \times \langle \psi_{h'} | l_{pq} | \psi_h \rangle. \end{aligned} \quad (7)$$

In eq. (7) the reduced matrix element $\langle \| \text{EFG} \| \rangle$ takes the value 2/7 for d electrons, 6/5 for p electrons, and 0 for s electrons. The quantity e represents the (positive) elementary charge, and $\langle r^{-3} \rangle$ is the radial factor resulting from taking the expectation value of $(3z^2 - r^2)/r^5$. The $\langle r^{-3} \rangle_{3d}$ are taken from estimates [6] based on Clementi's [7] atomic Hartree-Fock wavefunctions: 4.49 a. u. for Fe configuration $3d^7$, 5.09 a. u. for $3d^6$, and 5.73 a. u. for $3d^5$. The actual value of $\langle r^{-3} \rangle_{3d}$ is determined for each compound

from its calculated Fe 3d orbital occupancy by interpolation between the foregoing values. The Sternheimer shielding correction is taken as $(1 - R) = 0.68$. For Fe 4p electrons the quantity $(1 - R)_{4p} \langle r^{-3} \rangle_{4p}$ is taken to be $\frac{1}{3}$ of the corresponding quantity for the 3d electrons [3, 8]. Finally the single-electron operator l_{pq} is given by

$$l_{pq} = \frac{1}{2}(l_p l_q + l_q l_p) - \frac{1}{3}l(l+1)\delta_{pq}. \quad (8)$$

Thus the problem of calculating ΔE_Q , η and the orientation of V_{zz} is solved straight-forward by diagonalizing the tensor V_{pq} and using eq. (1).

2. Temperature independent quadrupole splittings. —

The compounds presently under study are the diamagnetic clusters $\text{Fe}(\text{CN})_5\text{NOC}_6\text{H}_5^{-3}$, $\text{Fe}(\text{CN})_5\text{NO}_2^{-4}$, $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{-3}$, $\text{Fe}(\text{CN})_5\text{NH}_3^{-3}$, and the paramagnetic ($S = \frac{5}{2}$) cluster $\text{FeO}_4\text{Cl}_2^{-7}$. Since the experimental quadrupole splittings of these compounds are temperature independent over a wide temperature range, we feel justified in limiting our MO calculations to self-consistent-field studies which ignore the effect of low-lying excited electronic states. This has the simple consequence that we are concerned in eq. (2) only with diagonal matrix elements: $\langle I | V_{pq} | I \rangle$.

The molecular geometries for which calculations were made are described in Table I. In Table II we give calculated electronic configurations and we compare ΔE_Q^{exp} with ΔE_Q^{calc} . For compounds I to V we find good agreement between experimental and calculated quadrupole splittings. Since compound V (FeOCl) was investigated in single-crystalline form [14] we have the advantage to compare additional parameters:

$$\eta^{\text{exp}} = 0.32 \pm 0.03 \quad \text{and} \quad \eta^{\text{calc}} = 0.23,$$

$$V_{zz}^{\text{exp}} < 0 \quad \text{and} \quad V_{zz}^{\text{calc}} < 0, \quad V_{zz}^{\text{exp}} // V_{zz}^{\text{calc}}.$$

Compounds VI and VII are identical, respectively, to compounds I and II, except that in VI and VII the non-axial ligands (C_6H_5^- and NO_2^-) have been rotated relative to their position in I and II. Our results show that this rotation has a substantial effect upon the Fe 3d charge density, and that the calculated quadrupole splittings have moved away from their corresponding experimental values. We therefore conclude that the orientation of (C_6H_5^- and NO_2^-) relative to the iron-pentacyanide complex are described better by compounds I and II than by VI and VII.

3. Temperature dependent quadrupole splittings. —

In deoxygenated myoglobin (MO) or hemoglobin (Hb) are concerned with electronic states

$$|I\rangle = |I, \gamma, S, \gamma_S\rangle$$

which are energetically close by, and which are characterized by irreducible representations I and by total spin $S = 2$. All irreducible representations of the regarded symmetry group C_{2v} (Fig. 1) are one-dimen-

TABLE I

Geometries used for iron-pentacyanide complexes and for FeOCl. Geometry for $\text{Fe}(\text{CN})_5^{-3}$ based on $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot \text{H}_2\text{O}$ (see ref. [1]). Symmetry axis of $\text{Fe}(\text{CN})_5^{-3}$ taken in z direction. Geometry of 6th ligand in cartesian coordinate (Å) relative to Fe.

I. $\text{Fe}(\text{CN})_5\text{NOC}_6\text{H}_5^{-3}$. N : (0, 0, 1.63) ; O : (0, 0, 2.42) ;

C_1 : (− 0.986, 0, 2.616) ; C_2 : (− 1.476, 0.49, 3.106) ;
 C_3 : (− 1.476, − 0.49, 3.106) ; C_4 : (− 2.457, 0.49, 0.087) ;
 C_5 : (− 2.457, − 0.49, 4.087) ; C_6 : (− 2.947, 0, 4.577) ;
 H_1 : (− 1.476, 2.06, 3.106) ; H_2 : (− 1.476, − 2.06, 3.106) ;
 H_3 : (− 2.457, 2.06, 4.087) ; H_4 : (− 2.457, − 2.06, 4.087) ;
 H_5 : (− 4.046, 0, 5.676).

Coordinates of benzol (ref. 9). Fe-N and N-O distance same as in $\text{Fe}(\text{CN})_5\text{NO}^{-2}$. N-C distance in NOC_6H_5 from compounds like $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$ (ref. [9]).

II. $\text{Fe}(\text{CN})_5\text{NO}_2^{-4}$. O_1 : (0.742, 0.742, 2.519) ;

O_2 : (− 0.742, − 0.742, 2.519) ; N : (0, 0, 1.960).

Coordinates of NO_2^- from compounds containing NO_2 (ref. [9]). Fe-N distance from $\text{Ag}[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$ (ref. [9]).

III. $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{-3}$. O : (0, 0, 2.09) ; H_1 : (0, 0.8, 2.618) ;

H_2 : (0, − 0.8, 2.618).

Coordinates of H_2O (ref. [9]). Fe-O distance from $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$ (ref. [10]).

IV. $\text{Fe}(\text{CN})_5\text{NH}_3^{-3}$. N : (0, 0, 1.96) ; H_1 : (0.955, 0, 2.289) ;

H_2 : (− 0.477, 0.827, 2.289) ; H_3 : (− 0.477, − 0.827, 2.289).

N-H distance from NH_3 (ref. [11]). NH_3 angles same as those for CH_3 in $\text{CH}_3\text{CH}_2\text{Br}$ (ref. [9]). Fe-N distance from Co-N compounds (ref. [9]).

V. FeOCl. Fe : (0, 0, 0) ; Cl_1 : (1.651, − 1.651, 0) ; Cl_2 : (− 1.651, − 1.651, 0) ; O_1 : (1.651, 1.315, 0) ; O_2 : (− 1.651, 1.315, 0) ; O_3 : (0, 0.575, 1.89) ; O_4 : (0, 0.575, − 1.89).

Coordinates taken from (ref. [12]).

VI. $\text{Fe}(\text{CN})_5\text{NOC}_6\text{H}_5^{-3}$. Same as compound I but with C_6H_5^- rotated by 90° around the N- C_1 - C_6 - H_5 axis.

VII. $\text{Fe}(\text{CN})_5\text{NO}_2^{-4}$. Same as compound II but with NO_2^- rotated by 45° around the z axis.

TABLE II

Calculated electronic configurations $3d^m 4s^n 4p^0$ and experimental and theoretical quadrupole splittings for the complexes specified in Table I. ΔE_Q^{calc} is calculated as described in the text

Compound	I	II	III	IV	V	VI	VII
m, n, o	6.89, 0.15, 0.74	6.88, 0.15, 0.73	6.99, 0.15, 0.65	6.98, 0.14, 0.66	5.67, 0.19, 0.70	6.7, 0.13, 0.69	6.88, 0.15, 0.73
E_Q^{exp} (mm/s)	1.32 ± 0.03 ^(a)	0.85 ± 0.03 ^(a)	0.75 ± 0.03 ^(a)	0.65 ± 0.03 ^(a)	0.916 ± 0.001 ^(b)		
E_Q^{calc} (mm/s)	1.24	0.71	0.68	0.64	0.828	2.55	1.11

^(a) Taken from reference [13].

^(b) Taken from reference [14].

FIG. 1. — Stereostuctural models for Mb or Hb : (I) $a = 0.4 \text{ \AA}$, $b = 2.09 \text{ \AA}$; (II) $a = 0.4 \text{ \AA}$, $b = 2.34 \text{ \AA}$; (III) $a = 0.8 \text{ \AA}$, $b = 2.34 \text{ \AA}$.

sional and thus γ can be omitted. The five-fold spin degeneracy of each state Γ is lifted by spin-orbit interaction, $H_{s.o.} = -\lambda L \cdot S$, with the coupling constant λ being related to the free ion value, $\lambda_0 = 103 \text{ cm}^{-1}$, by a reduction factor α^2 : $\lambda = \alpha^2 \lambda_0$. The eigenvectors $|e_\alpha\rangle$ of this problem, having energies E_α , are certain linear combinations of the base vectors $|\Gamma, S, \gamma_S\rangle$:

$$|e_\alpha\rangle = \sum_{\Gamma, \gamma_S} C_{\Gamma, \gamma_S}^\alpha |\Gamma, S, \gamma_S\rangle. \quad (9)$$

Since we are interested in quadrupole splittings we calculate for each state $|e_\alpha\rangle$ its relevant EFG tensor:

$$V_{pq}^\alpha = \langle e_\alpha | V_{pq} | e_\alpha \rangle. \quad (10)$$

By use of eq. (9) and

$$\begin{aligned} \langle \Gamma' | V_{pq} | 1 \rangle &= \langle \Gamma', \gamma_S' | V_{pq} | \Gamma, \gamma_S \rangle \\ &= \langle \Gamma' | V_{pq} | \Gamma \rangle \delta_{\gamma_S' \gamma_S}, \end{aligned}$$

V_{pq}^α can be written as a sum of matrix elements $\langle \Gamma' | V_{pq} | 1 \rangle$, which have been defined in section 1. In order to evaluate the temperature dependence of the EFG one must average the components V_{pq}^α of the individual substates $|e_\alpha\rangle$ according to Boltzmann-statistics:

$$\langle V_{pq} \rangle_T = \sum_\alpha V_{pq}^\alpha \exp(-E_\alpha/kT) / \sum_\alpha \exp(-E_\alpha/kT). \quad (11)$$

Diagonalization of $\langle V_{pq} \rangle_T + V_{pq}^{\text{lat}}$ leads to $V_{zz}(T)$, to $\eta(T)$, to the orientation of $V_{zz}(T)$, and finally through eq. (1) to $\Delta E_Q(T)$.

For each of the three models of figure 1 we then calculate the above parameters. The final $\Delta E_Q(T)$ - and $\eta(T)$ -curves together with their corresponding energies $E(^5A_2)$, $E(^5B_1)$ and $E(^5B_2)$ [15] and with experimental $\Delta E_Q(T)$ -data for Mb and Hb are shown in figure 2 for model I. For models II and III no ΔE_Q -fit curve was

FIG. 2. — Temperature dependent quadrupole splittings, $E_Q(T)$, and asymmetry parameters, $\eta(T)$, for model I of figure 1. $\lambda = -75 \text{ cm}^{-1}$. Experimental $E_Q(T)$ data for frozen Mb solution (ref. [19]) are indicated by closed circles, for a Mb single crystal (ref. [17]) by «X» and errors bars, and for frozen Hb (rat, ph 10) solution (ref. [20]) by open circles and error bars. Energies for 5B_2 , 5B_1 , and 5A_2 in cm^{-1} corresponding to $E_Q(T)$ - and $\eta(T)$ -curves are: a) 0, 150, 150; b) 0, 150, 175; c) 0, 150, 200.

obtained. A low lying 1A_1 state has negligible influence on $\Delta E_Q(T)$ and $\eta(T)$, and a low lying 3E state is ruled out by the fact that a low-energy term scheme including intermediate spin states does not correspond to the experimental susceptibility data, $\chi(T)$, for Mb of Nakano *et al.* [16], whereas the term scheme related to curve b, figure 2, nicely fits the experimental $\chi(T)$ data. Further, we find from our calculations $V_{zz} > 0$ and V_{zz} being oriented along the heme axis y (Fig. 2), in reasonable agreement with our recent findings from Mössbauer investigation of Mb single crystals at 77 K [17]. A most recent computational analysis of our former Mb single crystal Mössbauer data by Y. Maeda (private communication, 1974) indicates that an orientation of V_{zz} parallel to the hemeplane is consistent also with an η -parameter in the range $0 \leq \eta \leq 0.7$.

4. Conclusion. — All compounds under study here exhibit covalent bonding to varying degrees and therefore may appropriately be handled by methods based on molecular-orbital theory rather than by crystal-field methods. Still, the present MO interpretation of experimental quadrupole splittings of the various complexes is approximative in the sense that the clusters which are specified by Table I and figure 1 are models only for the real compounds, and further, that the MO procedure itself is approximative to the extend described in

ref. [1]. These simplifications, however, are believed to be secondary for the present attempt to derive a gross description of the structural situation around the iron. From the present work we therefore conclude that the MO interpretation of experimental quadrupole split-

tings consistently agrees with the three dimensional structures of compounds I to V in Table I, and also agrees with the assumption that the heme iron in Mb and Hb is pentacoordinated and significantly out of the *hemeplane* (by $\approx 0.4 \text{ \AA}$).

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