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Fig. 1

Figure 1: Fig. 1

Abstract

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INTERPRETATION OF THE RESONANCE ABSORPTION OF γ-QUANTA BY CERTAIN COMPLEX COMPOUNDS OF IRON, TAKING INTO ACCOUNT BOND COVALENCY AND INDUCTIVE EFFECTS

In work ([1]), Mössbauer spectra were obtained for three complex compounds of iron(II) with thiosemicarbazone diacetyloxime:

$$\begin{array}{c} CH_3 - C = NOH \\ \quad\quad\quad | \\ CH_3 - C = N - NH \cdot CS \cdot NH_2 \end{array} \qquad (DTOH_2):$$

$[Fe(DTOH_2)_2]Cl_2$ (I), $[Fe(DTOH)_2]$ (II) and $[Fe(DTOMe)_2]$ (III).

As is evident from Fig. 1 and from the structural formulas given here and in ([1]), the environment nearest to the iron is the same in all three compounds, and they differ only by changes of higher order ([2]). In particular, the transition from compound I to II is associated with the removal of two protons from the NOH groups, while the transition from I to III is associated with the removal of two protons from the NH groups (and, at the same time, with the substitution —unimportant for our problem—of two hydrogen atoms in the NOH groups by methyl radicals).

Fig. 1

Despite the identity of the environment nearest to the iron, the Mössbauer spectra of these compounds—namely, the quadrupole splitting of the lines Δ and their chemical shift δ—are different (see Table 1). Thus, here a definite influence of higher-order changes on the Mössbauer spectra is revealed. It is of interest to give an interpretation of this influence, characterizing changes in the structure of the electron cloud of the bonds ([3]).

First of all, we note that all compounds (I), (II), and (III) are diamagnetic ([1]), so that the complexes are low-spin. In this case, a more complete description of them is possible only on the basis of the molecular-orbital method ([4]). Figure 2 gives a qualitative scheme for the formation of the molecular σ-orbitals of the complex from the orbitals of the central iron(II) atom and the orbitals of the nitrogen and sulfur atoms closest to it. In this treatment the formation of π-bonds is neglected, and it is assumed that the pairs of atoms sulfur S 1—4, nitrogen N′ 2—5, and nitrogen N 3—6 are different; the symmetry of the system will be D_{2h}. Twelve ligand electrons and six iron(II) electrons fill only the bonding and nonbonding orbitals, while the antibonding orbitals remain empty. The electronic configuration of all three complexes I, II, and III will be*

$$(a_g)^2(b_{3u})^2(b_{2u})^2(b_{1u})^2(b_{3g})^2(b_{2g})^2(d_{xy})^2(d_{xz})^2(d_{yz})^2$$

—the term ^1A_g.

The expressions for the wave functions of the bonding orbitals in the approximation of the molecular-orbital method—linear combinations of atomic orbitals

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* In the transition from I to II or from I to III, i.e., upon removal of protons, the formal filling of the orbitals does not change. Otherwise, upon adding two electrons to antibonding orbitals, the configuration would become paramagnetic.

(MO LCAO) have the form:

$$\Psi_1(a_g) = \alpha_1 s + \beta_1(\sigma_1 + \sigma_4) + \gamma_1(\sigma_2 + \sigma_5) + \delta_1(\sigma_3 + \sigma_6), \tag{1}$$

$$\Psi_2(b_{1u}) = \alpha_2 p_z + \beta_2(\sigma_1 - \sigma_4), \tag{2}$$

$$\Psi_3(b_{2u}) = \alpha_3 p_x + \beta_3(\sigma_2 - \sigma_5), \tag{3}$$

$$\Psi_4(b_{3u}) = \alpha_4 p_y + \beta_4(\sigma_3 - \sigma_6), \tag{4}$$

$$\Psi_5(b_{3g}) = \alpha_5 d_{z^2} + \beta_5(\sigma_1 + \sigma_4) - \gamma_5(\sigma_2 + \sigma_5) - \delta_5(\sigma_3 - \sigma_6), \tag{5}$$

Fig. 2: orbital energy scheme showing iron orbitals, molecular sigma orbitals, and ligand orbitals

Figure 2: Fig. 2: orbital energy scheme showing iron orbitals, molecular sigma orbitals, and ligand orbitals

$$\Psi_6(b_{2g}) = \alpha_6 d_{x^2-y^2} + \beta_6(\sigma_2 + \sigma_5) - \gamma_6(\sigma_3 + \sigma_6). \tag{6}$$

Here s, p_x, p_y, p_z, d_{z^2}, and $d_{x^2-y^2}$ denote the wave functions of the iron atom, and $\sigma_1, \sigma_2, \ldots, \sigma_6$ are the σ-functions of the ligands. The constants $\alpha_i, \beta_i, \gamma_i, \delta_i$ are related to one another and to the overlap integrals of the functions of different atoms by means of the normalization conditions. Therefore the constant α_i^2, characterizing the share of participation of the iron atom in the i-th molecular orbit, may serve as a certain measure of the degree of covalency of the metal-ligand bond.

Fig. 2

Using functions (1)–(6), one can calculate the gradient of the electric field q created by the outer electron shell near the Fe nucleus. Adopting the assumption usual for such cases that, near the iron nucleus, the ligand σ-functions are equal to zero, it is easy to obtain the general expression:

$$q = 2\alpha_1^2 q_{4s} + \left[(\alpha_2^2 - \alpha_3^2) + (\alpha_2^2 - \alpha_4^2)\right] q_{4p_z} + 2(\alpha_5^2 - \alpha_6^2) q_{3d_{z^2}}, \tag{7}$$

where q_{4s}, q_{4p_z}, and $q_{3d_{z^2}}$ are the gradients of the electric fields at the nucleus created by one excess $4s$-, $4p_z$-, and $3d_{z^2}$-electron, respectively.

Formula (7) does not contain the very small contributions to the electric-field gradient caused by deformations of closed shells (the outer t_{2g}^6 and the inner shells) due to differences in the electrostatic field of different ligands. From it, in particular, it is seen that if all ligands are identical, $\alpha_2 = \alpha_3 = \alpha_4$ and $\alpha_5 = \alpha_6$ (i.e., for O_h symmetry), $q = 0$, since $q_{4s} = 0$ (s-electrons do not create an electric-field gradient at the nucleus). Consequently, the observed quadrupole splitting can arise only from differences in the ligands, more precisely, from differences in the degrees of covalency of the bonds with them.

For further simplification of formula (7), let us note that $q_{3d_{z^2}}$ is approximately an order of magnitude smaller than q_{4p_z} [5]. Taking into account further that the molecular orbitals b_{1u}, b_{2u}, and b_{3u} are more bonding than b_{2g} and b_{3g} (see Fig. 2), we may assume that the constants α_2^2, α_3^2, and α_4^2 are greater than α_5^2 and α_6^2. At the same time, the differences $\alpha_2^2 - \alpha_3^2$ and $\alpha_2^2 - \alpha_4^2$ must also be greater than $\alpha_5^2 - \alpha_6^2$, since the more bonding orbitals are more sensitive to the nature of the atoms being bonded. Therefore, without impairing the subsequent conclusions, we may neglect the last term in (7), which contains $q_{3d_{z^2}}$. Then we obtain

$$q \approx [(\alpha_2^2 - \alpha_3^2) + (\alpha_2^2 - \alpha_4^2)]\, q_{4p_z}. \tag{8}$$

It is seen from this that the principal role in creating the electric-field gradient at the nucleus is played by the distribution of the electron cloud over three molecular orbitals in which the iron 4*p*-orbitals participate.

This distribution is characterized by three constants α_2^2, α_3^2, and α_4^2, corresponding to the three pairs of equivalent atoms S, N′, and N. Depending on the donor properties of these atoms, which in turn depend on the groups attached to them, the constants α_i^2 and their differences may take different values, changing the magnitude and sign of the quadrupole splitting.

In complex I all bonds are donor–acceptor bonds, and it may be assumed that the nitrogens N′ and N are equivalent (symmetry D_{4h}). Then $\alpha_3^2 \simeq \alpha_4^2$, and

$$q_{\mathrm{I}} \simeq 2(\alpha_{2\mathrm{I}}^2 - \alpha_{3\mathrm{I}}^2) q_{4p_z}. \tag{9}$$

From this equality, knowing q_{I} and q_{4p_z}, one can determine $\alpha_{2\mathrm{I}}^2 - \alpha_{3\mathrm{I}}^2$. Let us note, however, that experiment gives only the absolute value of the quadrupole splitting $\Delta = \frac{1}{2}|eQq|$; the sign of the splitting can be determined only on the basis of additional data, which is what we shall attempt to do.

Knowing that, in the coordinated state, the donor properties of nitrogen are greater than the donor properties of sulfur, we may suppose that $\alpha_{3\mathrm{I}}^2 > \alpha_{2\mathrm{I}}^2$. In this case it follows that $q_{\mathrm{I}} < 0$. Taking for the quadrupole moment of the excited state of Fe^{57} $Q = 0.15 \cdot 10^{-24}$ cm^2 ([6]), and for q_{4p_z} the gradient produced by an excess 4*p*-electron, for example in Ga ([7]), $q_{4p_z} = 7.5 \cdot 10^{15}$ CGSE, we readily obtain $\alpha_{3\mathrm{I}}^2 - \alpha_{2\mathrm{I}}^2 = 0.092$.

On going from compound I to II, the removal of protons from the NOH groups leads to a substantial displacement of charge toward the iron atom through the pair of nitrogen atoms N′. Such an inductive effect may be characterized by an increase of the coefficient $\alpha_{3\mathrm{II}}^2$ in comparison with $\alpha_{3\mathrm{I}}^2$, i.e., $\alpha_{3\mathrm{II}}^2 > \alpha_{3\mathrm{I}}^2$. On the other hand, writing formula (8) for cases II and I and taking their difference, we obtain (assuming that the remaining orbitals, apart from b_{2u}, do not change):

$$q_{\mathrm{I}} - q_{\mathrm{II}} = (\alpha_{3\mathrm{II}}^2 - \alpha_{3\mathrm{I}}^2) q_{4p_z}. \tag{10}$$

It is seen from this that $q_{\mathrm{I}} > q_{\mathrm{II}}$. But from the experimental data it follows that $|q_{\mathrm{I}}| < |q_{\mathrm{II}}|$ (see Table 1). Therefore $q_{\mathrm{II}} < 0$. Taking also $q_{\mathrm{I}} < 0$ (see above), we obtain: $\alpha_{3\mathrm{II}}^2 - \alpha_{3\mathrm{I}}^2 = 0.39$. This value characterizes, to some extent, the magnitude of the inductive effect under consideration.

In complex III, as compared with I, protons are removed from the NH groups. In this case the inductive effect on the iron atom can proceed only through the sulfur atoms, since charge transfer through the N atoms lying on the diagonal

3-6 is associated with overcoming a potential barrier, because all the ordinary bonds of these atoms are occupied. Hence it follows that $\alpha^2_{2\text{III}} > \alpha^2_{2\text{I}}$. Further, similarly to (10), we have:

$$q_{\text{III}} - q_{\text{I}} = 2(\alpha^2_{2\text{III}} - \alpha^2_{2\text{I}})q_{4p_z}, \tag{11}$$

so that $q_{\text{III}} > q_{\text{I}}$. But from the experimental data $|q_{\text{III}}| > |q_{\text{I}}|$. Consequently, $q_{\text{III}} > 0$. For $q_{\text{I}} < 0$ we can obtain the estimate: $\alpha^2_{2\text{III}} - \alpha^2_{2\text{I}} = 0.216$.

Thus, the changes in the magnitude of the quadrupole splitting of the excited state of the Fe^{57} nucleus in going from one iron compound to another find an explanation on the basis of the assumption of bond covalency and of inductive effects on the central atom that accompany changes in the long-range order, in particular the removal of a proton. In this case the signs of the quadrupole splitting $q_{\text{II}} < 0$ and $q_{\text{III}} > 0$ are obtained as a direct consequence of the entirely justified assumption concerning the direction of the inductive effects. As for the sign of q_{I}, it is obtained as negative on the basis of the assumption concerning differences in the donor

properties of nitrogen and sulfur, which is less strict. But if we assume $q_I > 0$, then we obtain $\alpha^2_{3II} - \alpha^2_{3I} = 0.76$ and $\alpha^2_{2II} - \alpha^2_{2I} = 0.032$, i.e., significant differences in the magnitudes of the inductive effects in the transitions from I to II and from I to III. Apart from the low probability of such differences, they would have had to lead to substantial changes in the magnitudes of the screening of the s-shells of the iron atom and, consequently, of the chemical shift δ, which, however, is not observed (see Table 1).

Table 1

Compound	Δ, mm/sec, $T = 300°$K	Δ, mm/sec, $T = 78°$K	δ, mm/sec, $T = 300°$K	δ, mm/sec, $T = 78°$K
I	0.66	0.65	0.42	0.47
II	2.02	2.02	0.22	0.29
III	0.88	0.88	0.45	0.50

Note. The errors of the measurements are everywhere ± 0.01 mm/sec; 1 mm/sec $= 4.8 \cdot 10^{-8}$ eV; the values of δ are given relative to Fe in Cr.

Moreover, from the form of the Mössbauer absorption spectra of these compounds ([1]) one can conclude that the two peaks of the quadrupole splitting are unequal: one is stronger than the other. This difference between the peaks is especially pronounced in compound I; comparing I and II with III, we even note a certain inversion of the intensity of the splitting components. Following the explanation given in ([8]) for the asymmetry of the quadrupole splitting of the Mössbauer spectra of isotropic polycrystalline samples, it may be assumed that the inversion of the intensity of the two splitting components is caused by a

change in the sign of the electric-field gradient in the region of the nucleus, i.e., that $q_I < 0$.

For an additional experimental verification of the conclusions about the change of sign of q in passing from I and II to III, it would be highly desirable to study the influence of a magnetic field on the shape of both splitting components of the spectral lines in all the compounds studied.

The estimates obtained for the differences of the squares of the constants α_i^2 may also be used in carrying out more complete calculations of the molecular orbitals in the complexes under consideration.

As for the chemical shift δ, without taking into account that part of it which depends on temperature and is determined by the quadratic Doppler effect, it depends on the density of the electron charge at the Fe^{57} nucleus. The latter, in turn, is proportional to the sum of the quantities $|\psi_{1s}(0)|^2$, $|\psi_{2s}(0)|^2$, $|\psi_{3s}(0)|^2$, and $|\Psi_{d_g}(0)|^2 = \alpha_1^2|\psi_{4s}(0)|^2$. When charge is shifted toward the iron nucleus due to inductive effects, α_1^2 increases, while the values $|\psi_{ns}(0)|^2$ decrease owing to the increased screening of the s-electrons by $4p$- and $3d$-electrons. Therefore the density of the electron cloud at the origin, and with it (and moreover in the opposite direction) the chemical shift δ, may either increase or decrease, as is indeed observed in going from I to II and III. Quantitative estimates, similar to those given above for the quadrupole splitting, appear, however, to be difficult.

The considerations presented are an additional illustration of the new possibilities opened by the Mössbauer effect for studying the structure of the electron cloud of bonds in complex molecular systems.

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Note: Figure translations are in progress. See original paper for figures.