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Abstract

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MÖSSBAUER SPECTRA OF COMPLEX COMPOUNDS OF IRON WITH DIACETYLTHIOSEMICARBAZONE OXIME

In work (^{1}), one of us described derivatives of diacetylthiosemicarbazone oxime ($DTOH_2$) and thiosemicarbazone of the O-methyl ether of diacetyl monoxime (DTOMe) with Fe (II), the structures of which are shown in Fig. 1.

Compound I is the product of addition of $DTOH_2$ to $FeCl_2$ (II). When two protons are detached from the oximide groups (= NOH), the inner complex salt $Fe(DTOH)_2$ (II) is formed. The compound $Fe(DTOMe)_2$ (III) is also an inner complex salt, but with detachment of protons from the thiosemicarbazone groupings ($= N \cdot NH \cdot CS \cdot NH_2$); most probably, from the imino group.

Fig. 1. Structural formulas of the compounds studied

Although in the three compounds indicated the nearest environment of the central atom—iron—remains unchanged, the detachment of protons leads to a redistribution of electron density in the molecules. It is of interest to determine how changes in the composition of the ligands are reflected in the properties of the electric field in the region where the central iron atoms are located.

To investigate this question, we studied the Mössbauer absorption spectra of the listed iron compounds. The experiments on observing these spectra were carried out on an apparatus of the Institute of Chemical Physics of the Academy of Sciences of the USSR, providing uniformly accelerated motion of the absorber relative to the source. The source of 14.4-keV gamma quanta was the isotope Co^{57}, introduced into chromium by electrolysis and subsequent thermodiffusion at 800° in a hydrogen atmosphere.

After the β-decay of Co^{57}, in the course of cascade emission of gamma quanta, an excited state of Fe^{57} nuclei arises, which serves as the resonant Mössbauer emitter.

For detection of the gamma quanta, a scintillation counter with a NaJ(Tl) crystal 1 mm thick was used. The resonance absorption spectra were recorded by means of an AI-100 hundred-channel amplitude analyzer. The Co^{57} source in chromium was at room tempera-

ture, while the absorbers were measured both at room temperature and under cooling with liquid nitrogen (78°K).

The appearance of the Mössbauer spectra is shown in Fig. 2. A summary of the principal results is given in Table 1.

A common property of all three spectra, as well as of the spectra of other iron complex compounds studied in (^{2}), is the absence of Zeeman splitting of the ground and excited levels of Fe^{57}, indicating the absence of local magnetic fields in the region where the iron nuclei are located in these complexes. Direct measurements showed that these compounds are diamagnetic.

At the same time, in the spectra of the complex compounds studied by us and in (^{2}), as well as in the spectrum of ferrocene (^{2}, ^{3}), a rather strong quadrupole splitting is observed.

Table 1

Values of the chemical shifts and quadrupole splittings of Mössbauer spectral lines for iron(II) complexes with $DTOH_2$ and DTOHMe at various temperatures

No.	Compound	Chemical shift δ, mm/sec	Chemical shift δ, mm/sec	Quadrupole splitting Δ, mm/sec	Quadrupole splitting Δ, mm/sec
		78°K	300°K	78°K	300°K
I	$[Fe(DTOH_2)_2]Cl_2$	0.47	0.42	0.65	0.66
II	$[Fe(DTOH)_2]$	0.29	0.22	2.02	2.02
III	$[Fe(DTOMe)_2]$	0.50	0.45	0.88	0.88

Note. 1 mm/sec = $4.8 \cdot 10^{-8}$ eV; the error of measurements of δ and Δ is everywhere $±$0.01 mm/sec.

As is evident from Fig. 1 and the data of Table 1, upon going from I to III the chemical shift remains unchanged, and only a small increase in the quadrupole splitting is observed; on going to compound II, however, the quadrupole splitting increases sharply and the chemical shift noticeably decreases. Speaking of the closeness of the quadrupole splitting in I and II, we assume here that the sign of the splitting is the same in all the compounds we studied. A more detailed consideration shows, however, that this may not be the case. A detailed

Fig. 2. Mössbauer spectra. The upper curves for each of the three compounds were obtained at room temperature, the lower ones at the temperature of liquid nitrogen.

Figure 2: Fig. 2. Mössbauer spectra. The upper curves for each of the three compounds were obtained at room temperature, the lower ones at the temperature of liquid nitrogen.

analysis of the data, taking into account the possibility of a change in the sign of the splitting on going from compounds I to II and III, will be reported later. In addition, in the spectrum of compound II obtained at 78°K, two additional minima are suggested; their existence and origin are subject to further verification and clarification.

Fig. 2. Mössbauer spectra. The upper curves for each of the three compounds were obtained at room temperature, the lower ones at the temperature of liquid nitrogen.

Certain changes arising in the Mössbauer spectra of iron upon removal of protons, especially from the oximino group, indicate a difference in the field of the electron shells in the vicinity of the iron nuclei even in those cases when all bonds of iron with neighboring atoms remain, as before, governed by hybridization of atomic orbitals d^2sp^3. Therefore, for a correct description of the properties of the complexes we studied, one should

make use not of atomic, but of molecular orbitals. The difference between compounds I and III, which give spectra with close values of the chemical shifts and quadrupole splittings, is manifested in the character of two Fe–S bonds: in I they are donor-acceptor bonds, in III covalent ones. However, such a change in the bonds does not affect the general character of the molecular symmetry: the z axis (S–Fe–S) still remains a fourfold symmetry axis, and the octahedron structure in both cases I and III belongs to the symmetry group D_{4h} (in contrast to the regular octahedron O_h, in which all six bonds are identical). Accordingly, the Mössbauer spectra of compounds I and III differ relatively little.

Table 2

Compounds I and III, symmetry group D_{4h}: irreducible representation	Compounds I and III, symmetry group D_{4h}: atomic orbitals of iron	Compound II, symmetry group D_{2h}: irreducible representation	Compound II, symmetry group D_{2h}: atomic orbitals of iron
A_{1g}	s; d_{z^2} $d(\sigma)$-band	A_{1g}	s; d_{z^2}
A_{2u}	p_z	B^*_{1g}	$d_{x^2-y^2}$; d_{xy}
B_{1g}	$d_{x^2-y^2}$ $d(\delta)$-band	B_{1u}	p_z
B^*_{2g}	d_{xy} $d(\delta)$-band	B^*_{2g}	d_{xz}

Compounds I and III, symmetry group D_{4h}: irreducible representation	Compounds I and III, symmetry group D_{4h}: atomic orbitals of iron	Compound II, symmetry group D_{2h}: irreducible representation	Compound II, symmetry group D_{2h}: atomic orbitals of iron
E_g^*	d_{xz}; d_{xz} $d(\pi)$-band	B_{2u}	p_y
E_u	p_x; p_y	B_{3g}^* B_{3u}	d_{yz} p_x

In compound II the character of two Fe—N bonds changes: if in I and III all four of these bonds were donor-acceptor bonds, now two of them turn out already to be covalent. The z axis (S—Fe—S) is here a twofold symmetry axis, and the octahedron structure belongs to another symmetry group—D_{2h}.

The decrease in the degree of symmetry is accompanied by a sharp increase in the inhomogeneity of the electric field in the region where the central nucleus Fe is located—the quadrupole splitting of spectrum II increases by more than a factor of three in comparison with spectrum I. The character of the molecular orbitals in the compounds studied is illustrated by Table 2, where the index * marks the d_{xy}, d_{xz}, and d_{yz} orbitals that do not participate in the formation of bonds with nitrogen and sulfur.

In all the compounds studied, the $d_{z^2}d_{x^2-y^2}sp^3$ orbitals of iron participate in the formation of the six σ-bonds of the complex. In the four Fe—N bonds there is hybridization $d_{x^2-y^2}sp_{xp}y$, and in the two Fe—S bonds, hybridization $d_{z^2}p_z$.

The change in the character of two Fe—N bonds affects the electrons of the $d(\sigma)$-band ($d_{x^2-y^2}$-orbital), which give a positive contribution to the quadrupole splitting. The increase in the splitting speaks in favor of the fact that, on going from I and III to II, the contribution of this orbital to the structure of the atomic orbitals of iron increases. The simultaneous decrease in the chemical shift indicates an increase in compound II also of the contribution of the s-orbital to the atomic orbitals of iron.

These are the principal qualitative results of our experiments. For their quantitative interpretation it is desirable to carry out a determination of the eff-

effective charges of the iron atoms in all the compounds studied and calculations of the molecular orbitals.

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