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IRON CHELATE COMPLEXES INVESTIGATED BY THE MÖSSBAUER EFFECT METHOD

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The Mössbauer spectra for three groups of the Fe(III) and Fe(II) chelates of the different dentate ligands at temperatures 77° and 295°K were measured.

Non-typical values of the isomer shifts and weak temperature dependence of the quadrupole splittings obtained for the Fe(II) complexes by the "back, donation" effect are explained.

1. *Introduction*

In recent years the scope of application of the internal complex salts (metal chelate compounds) in chemical, medical, and biological research has been continually increasing. Hence, studies of the hyperfine interactions in these compounds by the Mössbauer effect seem to be interesting. They may give new information concerning the character of chemical bonding of the metal atom with organic ligands as well as the electronic structure of the central metal atom in the molecule of the chelate compound.

In the present work the measurements of the Mössbauer spectra for 14.4 keV γ-transition of ^{57}Fe in liquid nitrogen and room temperatures for three groups of the iron chelate compounds were carried out:

1. 8-hydroxyquinoline Fe(II) and Fe(III). These are chelates of the bidentate ligands and coordination number four or six. Abbr. Oxine-Fe(II) and Oxine-Fe(III), respectively.

2. Bis-salicylaldehydeethylenediimine Fe(II) and Fe(III)Cl and its derivate: Bis-3-methoxy-salicylaldehydeethylenediimine Fe(II). These are chelates of the quadridentate ligands and coordination number four. Abbr. BSEDI-Fe(II), BSEDI-Fe(IIICl) and B-3-MoxSEDI-Fe(II), respectively.

3. Salicylideneaminophenol Fe(II) and Fe(III). These are chelates of the tridentate ligands and coordination number six. Abbr. SAPh-Fe(II) and SAPh-Fe(III), respectively.

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The chemical structures of these chelates are given in Fig. 1. The crystalline structures, chemical properties, and magnetic moments of those type compounds have been investigated by many authors [1–6]. Some of them were also studied by Mössbauer experiments.

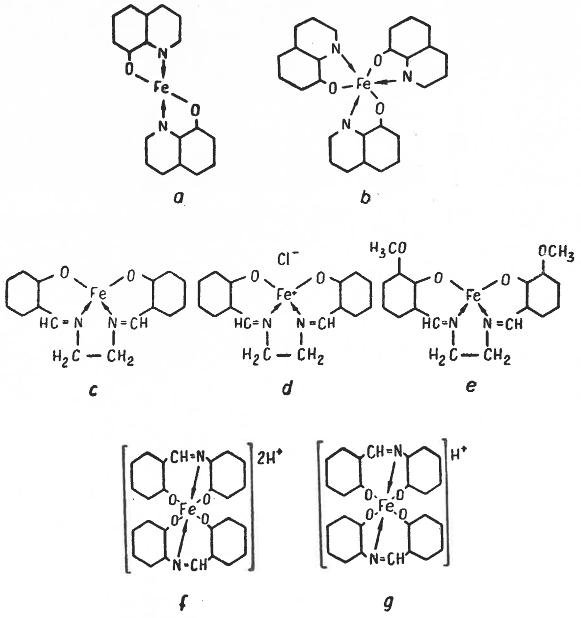

Fig. 1. The chemical structure of the chelate complexes. *a.* Oxine-Fe(II); *b.* Oxine-Fe(III); *c.* BSEDI-Fe(II); *d.* BSEDI-Fe(III) Cl; *e.* B-3-MoxSEDI-Fe(II); *f.* SAPh-Fe(II) and *g.* SAPh-Fe(III)

Takashima *et al.* investigated some groups of various organic iron chelates [7]. Stukan measured the Mössbauer effect in quadridentate Fe(II) and Fe(III) chelates [8]. Berrett *et al.* studied some chelates of Fe(III) [9].

The aim of our work was to study and compare the Mössbauer effect in Fe(III) and Fe(II) chelates of different dentate ligands.

2. *Experimental*

2.1. Samples preparation

All the investigated compounds were prepared from iron chloride. Some of them were additionally prepared from iron sulphate [BSEDI-Fe(II) and SAPh-Fe(II)], iron nitrate [(SAPh-Fe(III)], and iron bromide [(SAPh-Fe(II)].

The BSEDI and SAPh were obtained by reaction of 0.01 *g*-mole of suitable organic compounds dissolved depending on their solubility, in 500–600 ml hot ethanol (95 per cent) with 0.01 *g*-mole either of chloride, sulphate, nitrate, or bromide of divalent and trivalent iron also dissolved in hot ethanol. In synthesis of oxine 0.02 *g*-mole of oxine and 0.01 *g*-mole of Fe(II) or 0.03 *g*-mole oxine and 0.01 *g*-mole of Fe(III) salts were used.

The mixture of iron salts and organic ligands was heated in a water bath with reflux condensor for 1–2 hours. After cooling and partial evaporation of ethanol, the obtained solid preparation of chelates was purified by crystallization from the ethanol solution. Only in the synthesis of chelates from iron sulphate were salts dissolved in a mixture of ethanol and water (1 : 1).

The elementary chemical analysis carried out for these complexes indicates that the ratios M:L (metal-ligand) were: Oxine-Fe(III) 1 : 3, Oxine-Fe(II) 1 : 2, BSEDI 1 : 1 and SAPh 1 : 2.

2.2. Measuring technique

Measurements of the Mössbauer patterns were performed with the Intertechnique Mössbauer Spectrometer operated in time mode.

TABLE I

No	Compound *a)*	b) Prepared from	c) T(°K)	d) $\delta \frac{mm}{sec}$	e) $2\varepsilon \frac{mm}{sec}$	f) Ratio M : L
1	Oxine $(C_9H_6NO)_3Fe^{III}$	$FeCl_3$	77	0.61	0.84	1 : 3
			295	0.49	0.81	
2	$(C_9H_6NO)_2Fe^{II}$	$FeCl_2$	77	0.56	1.01	1 : 2
			295	0.49	0.95	
			363	0.48	0.80	
3	BSEDI $(C_{16}H_{14}O_2N_2)Fe^{III}Cl$	$FeCl_3$	77	0.59	1.03	1 : 1
			295	0.51	0.98	
4	$(C_{16}H_{14}O_2N_2)Fe^{II}$	$FeCl_2$	77	0.51	0.82	
			295	0.49	0.79	
5	$(C_{16}H_{14}O_2N_2)Fe^{II}$	$FeSO_4 \cdot 7H_2O$	77	0.55	0.99	
			295	0.47	0.93	
6	B-3-Mox-SEDI $(C_{18}H_{18}O_4N_2)Fe^{II}$	$FeCl_2$	77	0.51	0.89	
			295	0.43	0.87	
7	SAPh $(C_{26}H_{19}O_4N_2)Fe^{III}$	$FeCl_3$	77	0.60	1.16	1 : 2
			194	0.53	1.12	
			295	0.46	1.11	
			395	0.40	1.02	
8	$(C_{26}H_{19}O_4N_2)Fe^{III}$	$Fe_2(SO_4)_3 \cdot 7H_2O$	77	0.51	1.06	
			295	0.54	1.03	
9	$(C_{26}H_{19}O_4N_2)Fe^{III}$	$Fe(NO_3)_3$	77	0.63	0.87	
			295	0.50	0.85	
10	$(C_{26}H_{20}O_4N_2)Fe^{II}$	$FeCl_2$	77	0.59	1.29	
			295	0.50	1.28	
11	$(C_{26}H_{20}O_4N_2)Fe^{II}$	$FeBr_2$	77	0.53	1.24	
			295	0.41	1.14	

The source was ~5 mCi ^{57}Co embedded in a platinum lattice. The absorbers were prepared in the form of a uniform layer disc of crystalline synthetic powder of the above-mentioned samples and pressed between mica and aluminium sheets. The surface density of the absorbers was ca. 8 mg of natural Fe/cm^2.

Between the measurements the spectrometer was frequently calibrated with α-Fe_2O_3 absorber.

3. Results and discussion

The Mössbauer absorption spectra for all investigated iron chelate compounds taken at room and liquid nitrogen temperatures indicate quadrupole splittings and positive isomer shifts relative to stainless steel. Some of these spectra are shown in Figs 2 (*a–f*).

The investigated compounds (*a*), type of iron compounds used for the sample preparation (*b*), temperature of absorbers (the source in all measurements was held at room temperature) (*c*), isomer shifts $\delta(d)$, quadrupole splittings $2\varepsilon(e)$, and ratios metal-ligand (*f*) are presented in Table I.

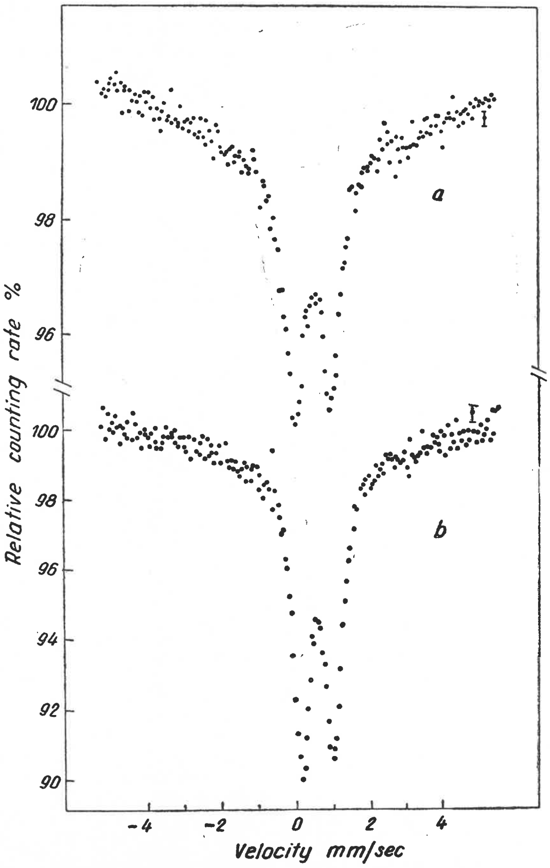

Fig. 2. Mössbauer spectra. *a*. Oxine-Fe (II) and *b*. Oxime Fe (III)

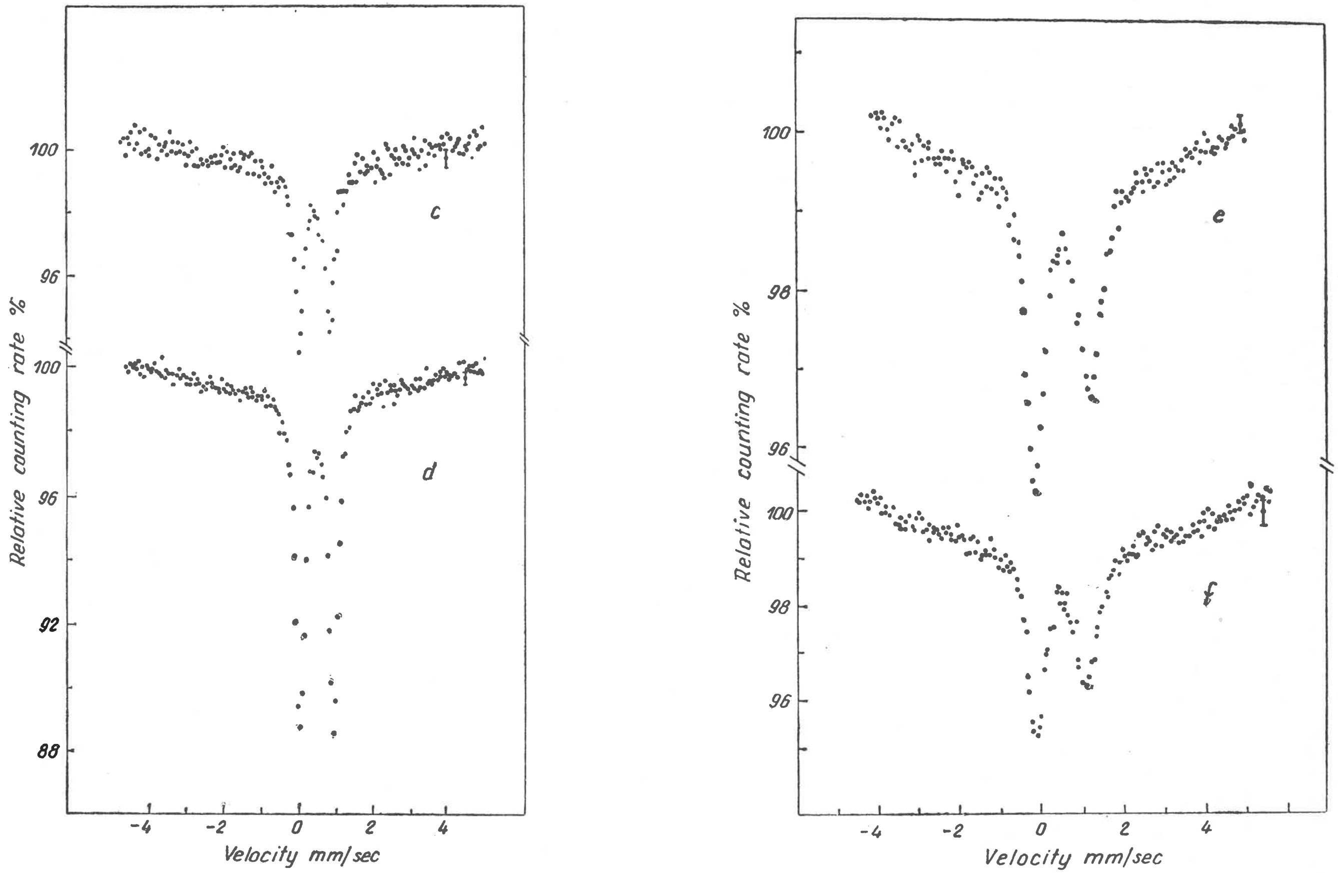

Fig. 2. Eössbauer spectra. *c.* BSEDI-Fe(II) and *d.* B-3-MoxSEDI-Fe(II). *e.* SAPh-Fe(II) and *f.* SAPh-Fe(III)

Two of these chelates BSEDI-Fe(III)Cl and BSEDI-Fe(II) were investigated by Mössbauer technique earlier [7–9]. The isomer shifts obtained in our measurements are in good agreement with other works [7, 8] but the quadrupole splittings are slightly lower than those reported by other authors [7, 9].

Some interesting and new conclusions may be drawn from the comparison of our results with Duncan–Golding's graph [10]. This diagram (Fig. 3) represents areas corresponding to Fe^{2+} and Fe^{3+} in high-spin as well as Fe^{II} and Fe^{III} in low-spin state compounds. They were formed from experimental results for a large number of different typical iron compounds. Our results (almost independently from the iron valency) form in this graph the fifth area. Their positions approach the area corresponding to Fe^{3+} in high-spin state. The high-spin state of iron ions for these chelates was also confirmed by magnetic susceptibility measurements [1, 11].

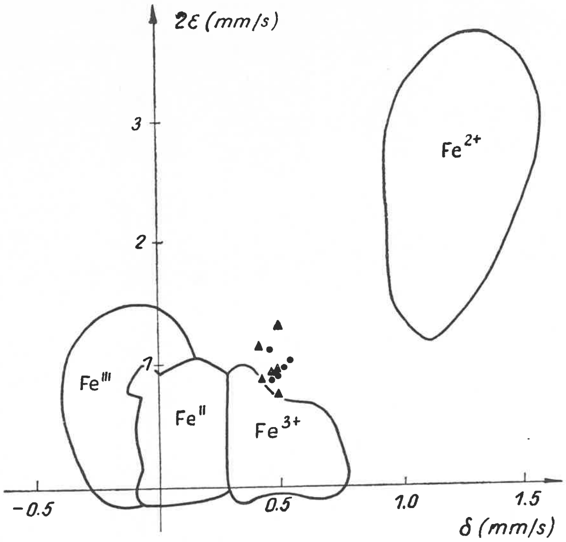

Fig. 3. Ducan-Golding's graph. Circles indicate the values for the Fe^{3+} and triangles those for Fe^{2+} investigated chelates

The lower than expected values of the isomer shifts in the investigated Fe^{2+} iron chelates indicate that the *s*-electron density at the nucleus of the Fe^{2+} chelates is increased. This may be due either to direct contribution from 4*s* bonding or to the indirect contribution from 3*d* bonding. The weak temperature dependence of the quadrupole splitting for the Fe^{2+} in the investigated chelates (Fig. 4 — triangle points) rather confirms the second possibility.

This indicates that the bonding of the iron d_π electrons to empty p_π ligand orbitals leads to a decrease in the *d*-electron density of the iron ion. This leads through the Hartree--Fock potential to an increase in the *s*-electron density at the nucleus and to a decrease in the observed isomer shifts.

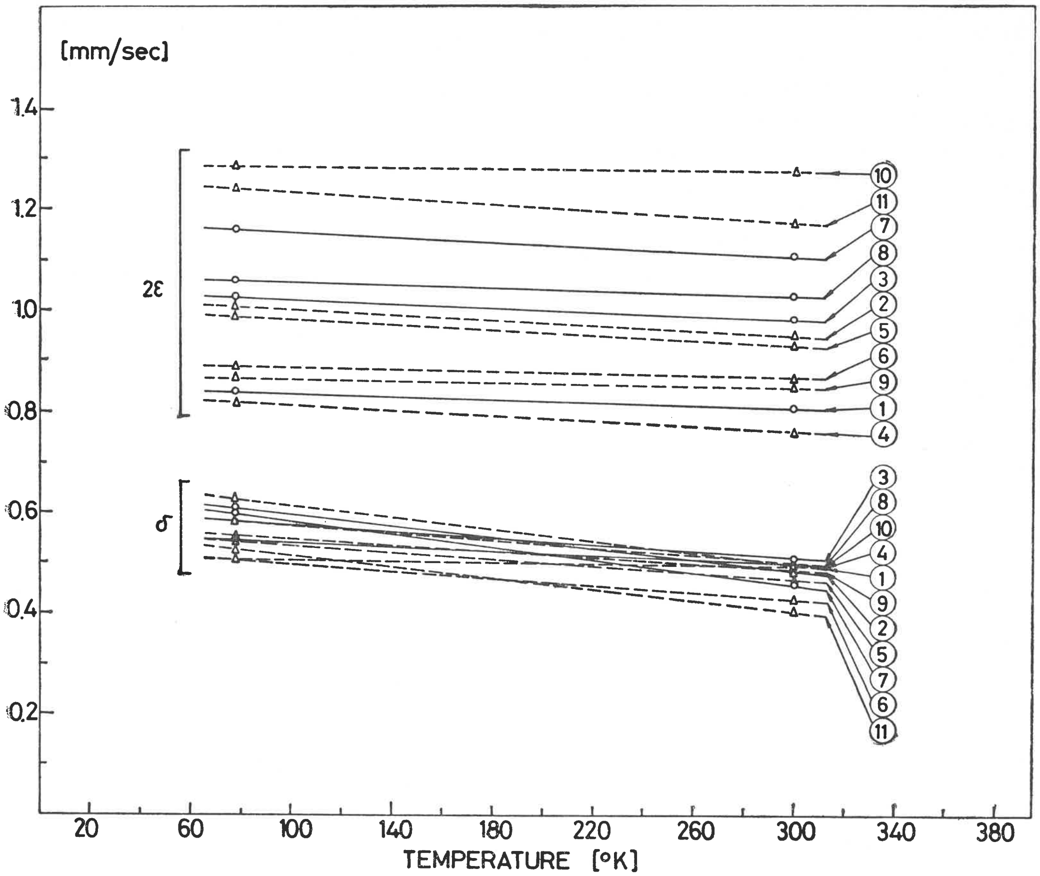

Fig. 4. The temperature dependence of the quadrupole splittings 2ε and isomer shifts δ. Circles (continuous lines) indicate Fe^{3+} and triangles (broken lines) Fe^{2+} chelates. The numeration is the same as in Table I

This effect, the so-called "back donation", is well known experimentally as well as theoretically in the case of the ferro- and ferricyanides [12].

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REFERENCES

[1] M. Calvin, C. M. Barkew, *J. Amer. Chem. Soc.*, **68**, 2267 (1946).
[2] V. Hovorka, *Chem. listy*, **52**, 1708 (1958).
[3] V. Hovorka, M. Krǎl, *Chem. listy*, **52**, 1710 (1958).
[4] I. Stroński, *Report INP* No 573/ C, Cracow 1967.
[5] A. V. Khedekar, J. Lewis, F. E. Mabbs, H. Weigold, *J. Chem. Soc.* (*A*), 1561 (1967).
[6] A. Earnshaw, E. A. King, L. F. Larkworthy, *J. Chem. Soc.* (*A*), 1048 (1968).

[7] Y. Takashima, Y. Tateishi, *Bull. Chem.. Soc. Japan*, 38, 1688 (1965).

[8] R. A. Stukan, *Thesis*, *Acad. of Sci. of USSR*, Inst. of Chem. Phys., Moscow 1965.

[9] R. R. Berrett, B. W. Fitzimons, A. A. Owusu, N. J. Seeley, A. W. Smith, *Progress in Coordination Chemistry*, Ed. M. Cais, Elsevier, Amsterdam 1968, p. 561.

[10] J. F. Duncan, R. M. Golding, *Quart. Rev. (London)*, **19**, 36 (1965).

[11] D. S. Kulgawczuk, Z. Obuszko, J. Sawicki, I. Stroński, *to be published*.

[12] R. G. Shulman, S. Sugano, *J. Chem. Phys.*, **42**, 39 (1965).