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Thermo- and Photoinduced Properties of the Fe(III) Complexes with the Pentadentate Ligand According to the EPR Data

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Abstract—Compounds [Fe(Salten)L]BPh$_4$ (Salten = *N*,*N*-bis[(2-oxyphenyl)methylene]-4-azaheptane-1,7-diamine; L = Him (**I**) and Pic (**II**)) were studied by the EPR method in the temperature range from 5 to 300 K. The thermoinduced spin transition is observed in compound **II**. Its thermodynamic parameters and parameters of the ground electronic low-spin state were determined. The effect of decreasing the intensity of the stationary EPR signal upon laser pulse irradiation at λ = 532 nm was observed in the studied samples.

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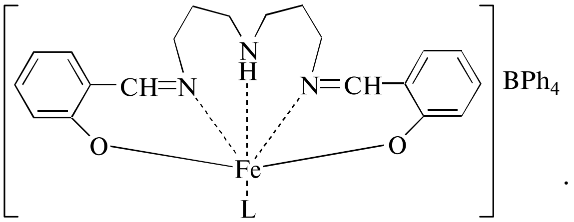
INTRODUCTION

Polyfunctional molecular systems, whose physical properties are switched over by weak external effects, are interesting from both purely scientific and practical points of view [1]. Among these systems are compounds of Fe(III) ions ($3d^5$ electronic configuration) with the closely arranged electron terms of different spin multiplicity $^6A_1$ and $^2T_2$, whose spin state changes ($S = 5/2 \rightleftharpoons S = 1/2$) upon the action of temperature and/or irradiation with light (spin crossover situation) [2–4]. Photoeffects in the region of *d*–*d* transitions or charge-transfer states or in the region of *cis*–*trans* isomerization of ligands are of significant interest due to the possibility of photocontrolling the magnetic, optical, and other properties of the substance [5].

The following compounds were chosen as objects of the EPR study of the specific temperature and dynamic properties of spin-variable compounds: [Fe(Salten)L]BPh$_4$ (Salten = *N*,*N*-bis[(2-oxyphenyl)methylene]-4-azaheptane-1,7-diamine; L = Him (imidazole) (**I**), Pic (4-methylpyridine) (**II**). The Fe(III) ions are coordinated by the pentadentate Salten ligand of the N,O-donor type and monodentate ligand L that supplements the coordination mode of the Fe(III) ion to 6.



The use of various monodentate ligands makes it possible to control the value of crystalline splitting on the central ion and to affect the spin state of the Fe(III) complex. According to the results of measuring the magnetic susceptibility in compounds of this class, the Fe(III) complexes containing pyridine derivatives as the sixth ligand L exhibit the thermally induced spin transition [6], whereas the spin state usually remains unchanged for other types of L. According to these criteria, a compound with L = Pic should possess the spin-variable properties, and that with L = Him should remain high-spin in the whole temperature range. In this work, the spin-transition properties of the Fe(III) complexes with the temperature change and under pulse light irradiation were studied by the EPR method for the first time.

EXPERIMENTAL

The hexacoordinate complexes [Fe(Salten)L]BPh$_4$ were synthesized according to [6] by the reaction of the [Fe(Salten)Cl] precursor with imidazole (Him) or pyridine derivatives (Pic) taken in equivalent amounts. Commercial reagents (Aldrich) were used as Pic and Him ligands. All reagents and solvents used were purified by recrystallization or distillation until their constants coincided with literature data. The compositions and structures of the synthesized compounds were determined by elemental analysis, ^{1}H NMR spectroscopy, UV spectroscopy, and MALDI-TOF mass spectrometry.

EPR measurements were performed in the X range at temperatures from 5 to 300 K on an EMXplus spectrometer (Bruker). The effect of light irradiation was studied on an Elexsys E580 spectrometer upon the laser irradiation at λ = 532 nm with pulses with the maximum energy $G = 10$ mJ, duration $\tau = 15$ ns, and repetition rate $\nu = 20$ Hz.

RESULTS AND DISCUSSION

Spin state of Fe(III) ions in the range from 5 to 300 K. The spectra of complex **I** exhibit signals of the A type with $g_{\mathrm{eff}} \approx 4.2$. They belong to the Fe(III) ions in the high-spin (HS) state (electronic configuration d^5, $S = 5/2$) and are described by the spin-Hamiltonian

$$\hat{H} = g\beta HS + D[\hat{S}_Z^2 - (1/3)S(S+1)] + E(\hat{S}_X^2 - \hat{S}_Y^2).$$

The energy levels at the frequency $\nu \sim 9.3$ GHz and $D \gg 0.3$ cm^{-1} represent three particular doublets. The EPR signal inside each of them can be described by an effective spin of 1/2 and values of the effective g factor described by a known procedure [7, 8]. The observed intense, almost isotropic line A is due to the transition between the sublevels of the medium doublet, and its effective parameters correspond to the Fe(III) centers with a high value of the fine structure parameter ($D > h\nu$) and strong orthorhombic distortions ($E/D \sim 1/3$). The transition between the sublevels of the lowest doublet in powdered systems is considerably less intense because of its high anisotropic width and manifests itself as a "shoulder" of the main signal A from weak fields with $g_{\mathrm{eff}} \approx 9$ (Fig. 1a). The signal A is observed in the whole temperature range, so that an analysis of the temperature dependence of its integral intensity (I_{int}) makes it possible to unambiguously judge about the presence or absence of a spin transition. For **I**, the integral intensity of the A signal obeys the Curie–Weiss law (Fig. 1b), indicating the absence of a spin transition. The line width (from peak to peak) remains unchanged with an increase in the signal intensity with the temperature decrease.

Two types of signals were observed for **II** when passing a temperature range of 290–5 K (Figs. 2a and 2b). As can be seen from Fig. 2c, the temperature dependence of the integral intensity of the A signal for **II** is not monotonic. A decrease in the integral intensity with the temperature decrease to ~70 K is due to a decrease in the amount of the HS centers and indicates the existence of the spin transition in this temperature range. An increase in the integral intensity of the A signal with the further temperature decrease is caused by the presence of a residual HS fraction that experiences no spin transition. The signal of this fraction increases with the temperature decrease according to Boltzmann's law of energy level population. A decrease in the line width of the A signal observed in the 250–70 K temperature range is also explained by the existence of the spin transition: in the spin transition range, the contribution to the line width from the dipole–dipole interactions decreases because of a decrease in the number of HS of neighbors with $S = 5/2$ and, accordingly, of an increase in the number of low-spin (LS) neighbors with $S = 1/2$.

The B signal appears in the spectrum from the side of a strong magnetic field and its intensity increases when the temperature decreases. The shape of the spectrum is characteristic of the spectrum of orthorhombic symmetry with $S = 1/2$ and can be assigned to the LS complexes. The B spectrum is described by the temperature-independent parameters $g_1 = 3.024$, $g_2 = 1.861$, $g_3 = 1.545$. Smoothing of characteristic singularities of the B spectrum (up to the transition to the single almost isotropic line) observed with the temperature increase is due to an increase in the relaxation contribution to the width of an individual line.

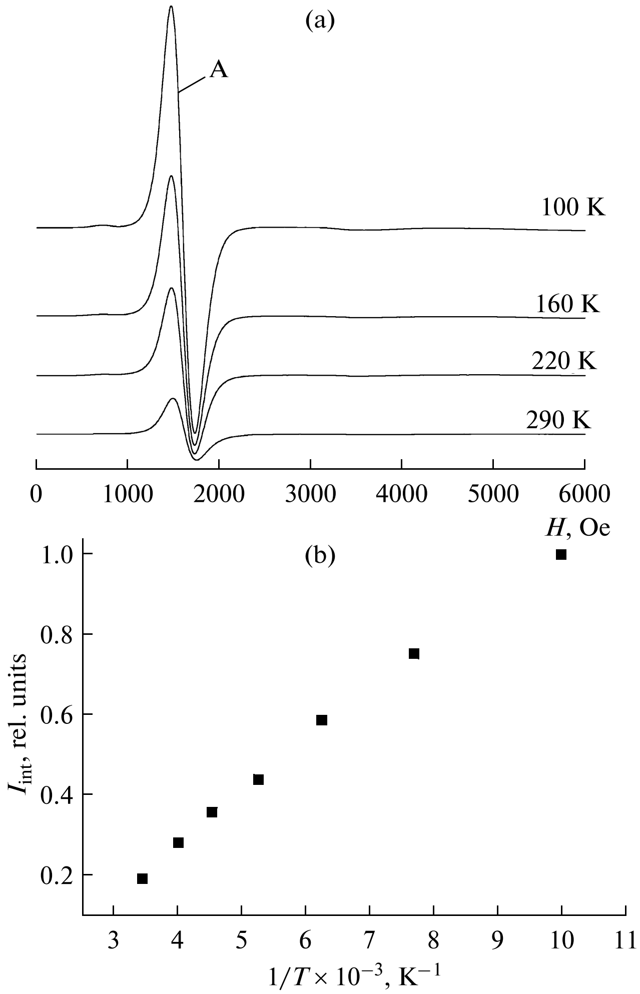


Fig. 1. Temperature plots of (a) the EPR spectra of complex **I** and (b) the integral intensity of the **A** signal of HS complex **I**.

In order to determine the wave functions of the ground state of the LS Fe(III) complexes and values of energy ranges between the sublevels of the lowest orbital triplet, we examined the experimental g factors in the one-electron approximation according to a described procedure [9–11]. A system of nonlinear equations that describe the experimental values of g factors was solved to find the wave function coefficients of the ground Kramers doublet (in the representation of angular moments) A, B, and C and the covalency parameter K. Substituting the obtained values of

A, B, C, and K into the energy matrix that takes into account the tetragonal Δ and orthorhombic V components of the crystalline field and spin-orbital interactions $\xi \hat{l}\hat{s}$ and solving the corresponding system of linear equations, we determined the values of E, Δ, and V. The calculation results are given below

g_x	g_y	g_z	A	B	C	K	Δ/ξ	V/ξ	$\Delta E_{12}/\xi$	$\Delta E_{13}/\xi$
–1.861	1.545	–3.024	0.8862	0.0658	–0.4586	0.905	–2.861	–0.248	1.820	9.578

In the basis set of real wave functions for the found values of A, B, and C, the wave functions of the ground doublet can be written as

$$\begin{aligned}\psi_1 &= -0.3024\mathrm{i}\left|d_{yz}^{+}\right\rangle + 0.0658\mathrm{i}\left|d_{xy}^{-}\right\rangle + 0.9509\left|d_{xz}^{+}\right\rangle,\\ \psi_2 &= -0.3024\mathrm{i}\left|d_{yz}^{-}\right\rangle - 0.0658\mathrm{i}\left|d_{xy}^{+}\right\rangle - 0.9509\left|d_{xz}^{-}\right\rangle.\end{aligned} \qquad (1)$$

It is seen that the orbital $|d_{xz}\rangle$ makes the main contribution to the ground state with the E_1 energy. The above presented values of axial Δ and orthorhombic V distortions of the complexes and the values of energy ranges ΔE_{12} and ΔE_{13} show that the LS complexes in **II** are characterized by small orthorhombic distortions and, hence, a smaller splitting between the E_1 and E_2 levels of the triplet compared to the range to the E_3 level.

Thermodynamic characteristics of the spin transition. As mentioned above, two processes result in the nonmonotonic change in the observed signal A from the HS complexes in sample **II**. According to Boltzmann's distribution law, the population of the HS state changes with the temperature decrease. At the same time, the amount of the HS complexes decreases due to the spin transition.

The character of changing the integral intensity of the A signal in the 5–300 K temperature range observed in **II** can satisfactorily be described with allowance for these two processes (Fig. 2c). The temperature change in the relative integral intensity of the observed HS signal was determined by the difference in populations between the levels involved in the formation of the EPR signal and by the number of complexes in the HS state N_{HS} and was described by the equation

$$\begin{aligned}I_{\mathrm{HS}} &= I_{\mathrm{o}} N_{\mathrm{HS}}(T)\delta/kT\\ &\times \exp(-\Delta E/kT)/(1 + 2\exp(-\Delta E/kT)),\end{aligned} \qquad (2)$$

where ΔE is the energy difference between the ground (LS) and excited (HS) states of the system, I_{o} is the normalization factor, and $\delta = \hbar\nu$ is the effective interval between the levels involved in the formation of the EPR signal. The number of particles N_{HS} does not remain unchanged but has a temperature dependence corresponding to the thermodynamic equation (3) that describes the change in the content of the HS fraction during the spin transition [12]:

$$\ln\left(\frac{1 - N_{\mathrm{HS}}}{N_{\mathrm{HS}} - r}\right) = \frac{\Delta H + \Gamma(1 + r - 2N_{\mathrm{HS}})}{RT} - \frac{\Delta S}{R}. \qquad (3)$$

Here ΔH and ΔS are the changes in the enthalpy and entropy between the HS and LS states, respectively; Γ is the parameter of interaction between the HS and LS fractions; r is the residual content of the HS fraction that is present at low temperature; and R is the gas constant. The optimum values of fitting parameters are given in the caption to Fig. 2c. The calculation results show that the incomplete spin transition with $T_{\mathrm{c}} \approx 200$ K and a small amount of the residual HS fraction takes place in **II**.

Influence of laser irradiation on the EPR spectra. Laser irradiation resulted in a decrease in the integral intensity of the EPR signals from Fe(III) in the HS state (signal A) in **I** and signals from Fe(III) in the LS and HS states in **II** (signals A and B). Since all samples were black nontransparent powders, irradiation was carried out in capillaries ~1.8 mm in diameter, so that the fraction of the irradiated complexes was estimated by us as ~10–15%. The time of EPR spectra recording was 2.8 min. The typical pattern of changing the signal intensity is shown in Fig. 3a. The signal from the resonator (the line with $g = 3.930$ and $\Delta H = 22$ Oe) was used as a calibration signal to monitor the identical conditions of measurements for the quantitative estimation of the effect. Figure 3a shows that laser pulse irradiation results in a decrease in the observed A signal, and this effect appears already during the first spectrum recording, i.e., ~2 min after the beginning of irradiation, and somewhat increases (by additional ~20–30%) 7 min after the beginning of irradiation. No further decrease in the signal was observed, as a rule, with an increase in the irradiation duration to 10–15 min. The signal intensity recovered on laser switching-off, but the recovery was incomplete in several cases. An increase in the recovery time more than 7 min exerts no effect on the degree of recovery. The signal intensity decreased under irradiation in the range from 5 to 300 K. It is seen from Fig. 3b that in **II**, where the HS and LS EPR signals are simultaneously observed at $T = 40$ K, the effect is observed for both signals. The dependence of the effect on the laser power was checked and showed some threshold value of the power, below which no effect was observed (Fig. 3c).

Note that the effect described was observed both in **II** prone to the thermoinduced spin transition and in **I**

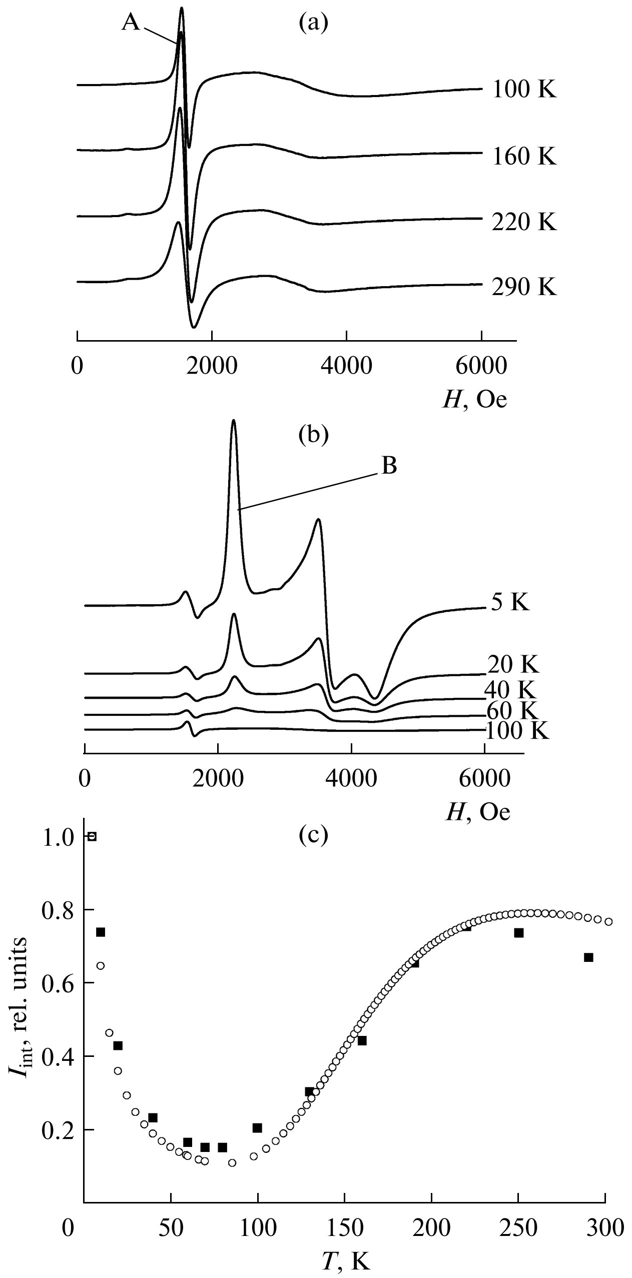


Fig. 2. Temperature plots of (a), (b) the EPR spectra of complex **II** and (c) the integral intensity of the **A** signal of HS complex **II**; ■ is experiment, and ○ is calculation. Parameters of the calculated dependence: $\Delta E = 3.5$ cm^{-1}, $\Delta H/R = 750$, $\Delta S/R = 3.5$, $\Gamma/R = 0$, $r = 0.025$, $R = 8.31$ J K^{-1} mol^{-1}.

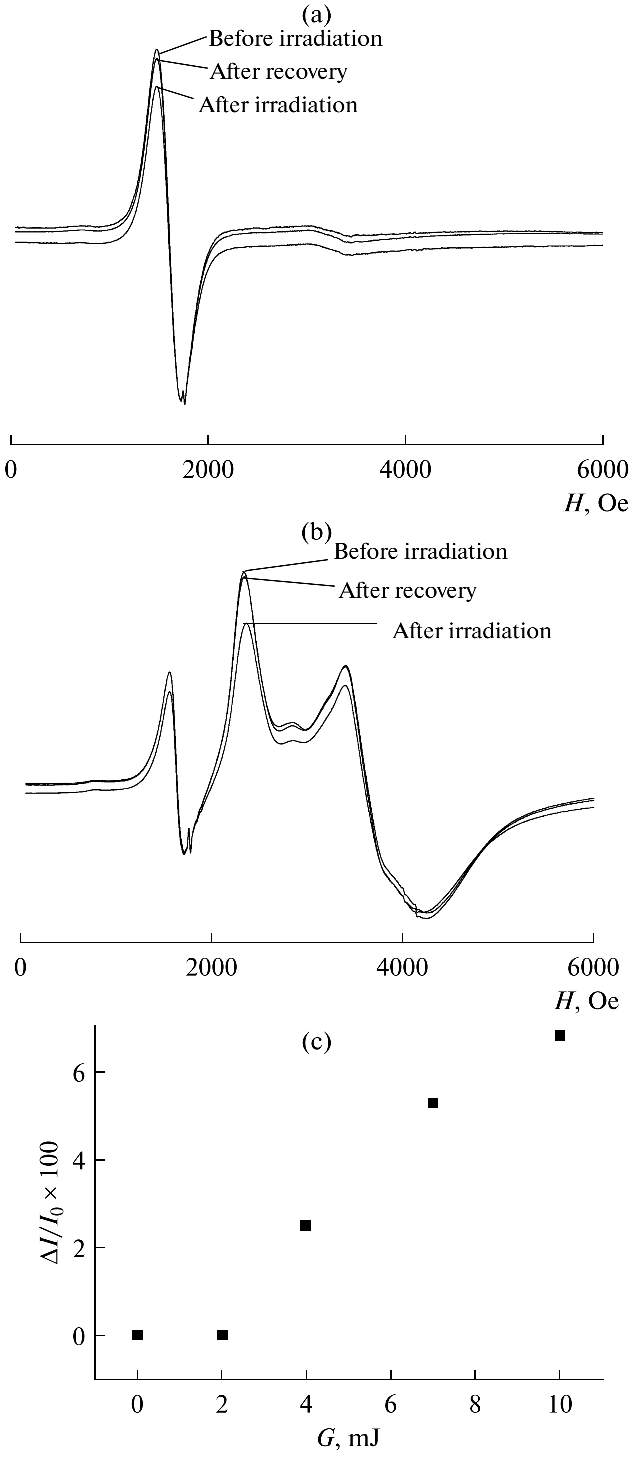


Fig. 3. Changes in the EPR signal upon the laser irradiation of the complexes: (a) **I** at $T = 200$ K and (b) **II** at $T = 40$ K; (c) the decrease in the relative intensity of signals at different laser pulse powers for complex **II**, $T = 250$ K.

without a thermoinduced transition. At the same time, no change in the EPR signal intensity during irradiation was observed for the irradiation of the described [13] $[Fe(Qsal)_2]CF_3SO_3$ sample with the same laser. A possible thermal heating by laser irradiation does not explain all specific features of the observed effect. It is not excluded that the effect is caused by processes of structural reorganization of the complex in combination with relaxation effects. Further studies including experiments in the time-resolved mode are being performed to elucidate the mechanism of the observed photoeffect.

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