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Spin Crossover Properties of Fe (III) Complexes in [Fe(bzacen)(tvp)]BPh₄·nSolv Chain Structures. EPR study.

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Abstract

Two types of Fe (III) polynuclear iron (III) 1D-chain coordination compounds of the general formula [Fe(L)(tvp)]BPh₄·nSolv, where L = dianion of N,N'-ethylenebis(benzoylacetylaceton)2,2'-imine (bzacen), tvp = 1,2-di(4-pyridyl)ethylene were synthesized and studied by the EPR and magnetic susceptibility methods in the temperature range (100-300) K. Two types of spin-variable complexes are formed depending on the time of precipitation of the complexes from the same solution leading to differently solvated species. They have different characteristics of the local ligand field and the spin transition behavior. The thermodynamic parameters of spin transitions were determined from the temperature dependence of the EPR signals integral intensity. The energy levels splitting values obtained by analyzing g-factors of low-spin Fe (III) centers evidenced not only on the crucial role of low-symmetry distortions on the principal possibility of spin-crossover processes, but also on the temperature peculiarities of spin transitions.

KEYWORDS

EPR spectroscopy, Iron (III) complexes, spin-crossover transition, local ligand field

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INTRODUCTION

The synthesis of coordination compounds of Fe (III) with spin-crossover properties and characteristics necessary for practical application is an actual problem. The search of a relationship between the chemical structure and properties of the spin state of Fe (III) complexes is most important for its decision. There are many factors which determine the spin state of these Fe (III) complexes: the composition and ligand structure, the orientation of the equatorial and axial ligands, the type of anion, the presence or absence of a solvate in the complex and the nature of intermolecular interactions between the complexes.^[1-6] The research results show that each of these causes lead to the redistribution of electron density on ligands and affects the strength and symmetry of the ligand field, which can lead to a change of Fe (III) ions spin-variable properties. However, the conclusions made are actual only for specific ligand systems, and their use requires a more detailed study of the changes in the local ligand field at the Fe (III) ion. EPR spectroscopy provides detailed information on the local symmetry and electronic structure of the spin-crossover Fe (III) complexes.^[7-10]

The Fe (III) complexes with N4O2 coordination are of great interest because they are potentially favored for manifestation of spin-variable properties.^[11-13] The influence of the configuration of the tetradentate equatorial N2O2 donating Schiff base ligand (L) in a series of mononuclear Fe (III) complexes of the composition $[\text{FeLX}_2]\text{Y}$ with $\text{X} = \text{Him}$ and $\text{Y} = \text{BPh}_4$ was studied in Ref..^[1, 14, 15] The variation of L in the series salen - acen - bzacen, happen, salacen led to a change in the spin state of the complexes: high spin (HS) - low spin (LS) - spin transition. According to the authors, the spin state of the Fe (III) ion is determined mainly by the strength of the ligand field of the N4O2 coordination site: salen provides a weak ligand field, acen provides a strong ligand field, bzacen, happen ligands and an asymmetric salacen ligand - an intermediate ligand field. At the same time, based on the results of studying $[\text{Fe}(\text{X-SalEen})_2]\text{Y}$ complexes by EPR and Mossbauer spectroscopy, concluded that the asymmetry of the local ligand field on the Fe (III) ion also plays an important role in the formation of a spin transition.^[16] The large splitting of low-spin ${}^2\text{T}_{2g}$ terms in this case lead to possibility of spin transition between the lower Kramers doublet of this multiplet and the excited high-spin multiplet ${}^6\text{A}_{1g}$.

Not only monomolecular Fe (III) complexes are important, but also polynuclear systems that collectively respond to external influences. Schiff tetradentate N2O2 bases L tend to form 1-D chains when the $[\text{Fe}(\text{III})(\text{L})]^+$ fragment is combined with a bridged bidentate

ligand. The interconnection between ligand conformation L and magnetic properties of Fe (III) complexes in a 1-D polymeric materials of the general formula $[\text{Fe(III)L(X)}]^+$, where L = acen, salen, salphen, X = bidentate N - donating bridging ligand, were studied in by methods of X-ray analysis and magnetic susceptibility.^[17] In compounds with the bridging ligand X = tvp and the equatorial ligand L = salen, which contains aromatic groups, Fe (III) ions were in a high-spin state. Replacing the equatorial ligand with L = acen, in which only aliphatic groups are present, led to a change of the spin state of Fe (III) ions to a low-spin one; incomplete spin transition was observed only at temperatures above 250 K.

In our opinion, the use of equatorial ligands L = bzacen, happen, or salacen, combining both aromatic and aliphatic fragments, is very likely to create favorable conditions for the realization of the spin transition in this class of compounds.

In order to obtain a complex with spin-changing properties, the compound $[\text{Fe(L)(tvp)}]\text{BPh}_4$ with the equatorial ligand L = dianion of N,N'-ethylenebis(benzoylacetylacetonate)2,2'-imine (bzacen) and a bidentate ligand tvp = 1,2-di(4-pyridyl)ethylene were synthesized, characterized and studied by EPR and magnetic susceptibility methods. EPR spectroscopy allowed to obtain information on the energy levels and wave functions of Fe (III), the local symmetry of the ligand field of spin-crossover complexes, and also on the thermodynamic parameters characterizing the spin-transition process.

EXPERIMENTAL

The composition of the synthesized compounds were confirmed by the elemental analysis. Elemental analysis was performed on the EuroVector EA3000 CHNS-O Elemental Analyzer. Powder X-ray diffraction patterns were recorded on a DRON-7 diffractometer with $\text{CuK}\alpha$ radiation with a β - filter. The EPR spectra were recorded by means of EPR CW spectrometer Bruker EMXplus (X-band) with temperature console ER4131VT in the temperature range of 100-340 K. The simulation of the obtained EPR spectra was performed by means of the EasySpin software package.^[18] Temperature-dependent magnetic susceptibility was measured on the equipment (a PPMS-9 magnetometer) of the Federal Shared Facilities Center for Physicochemical Investigations of Kazan Federal University over a temperature range of 100 to 300 K. All measurements were made on polycrystalline solids.

Synthesis of the complexes

All the chemicals and solvents used for the syntheses were purified by recrystallization or distillation and dehydration until their constants coincided with data from literature. Freshly prepared Schiff bases ligands were used to synthesize Fe (III) complexes. The ligands were synthesized by mixing equivalent amounts of aldehydes with ethylene diamine in ethanol, followed by heating with stirring and crystallization while cooling to room temperature. The products were recrystallized from ethanol twice. During the synthesis, it was found that, depending on the time of crystallization of the complexes from the solution, two types of compounds are formed.

[Fe(bzacen)(tvp)]BPh₄·2CH₃OH·CHCl₃ (sample **1**). A tvp solution (58.2 mg, 0.32 mmol) was added to a solution of [Fe(bzacen)Cl] (140 mg, 0.32 mmol) in 40 ml of chloroform/methanol mixture (1:1). This mixture was stirred at 60°C to dissolve and was filtered, while hot, into a freshly prepared methanol solution (5 ml) of NaBPh₄ (109.1 mg, 0.32 mmol). The resulting mixture was stirred 24 hours at room temperature. Gray-green fine-crystalline precipitate was filtered, washed with cold methanol and dried in air. Yield: 128 mg, 37%. Calculated: C 67.39; H 5.66; N 5.15 C₆₁H₆₁BFeN₄O₄Cl₃. Found: C 67.48; H 5.55; N 5.06.

[Febzacen(tvp)]BPh₄ CH₃OH (sample **2**) was prepared by the same procedure as the sample **1**, only the stirring time at room temperature was 1 hour. Dark-green fine-crystalline precipitate was filtered, washed with cold methanol and dried in air. Yield: 20%. Calculated: C 75.73; H 6.03; N 5.99 C₅₉H₅₆BFeN₄O₃ Found: C 74.98; H 6.11; N 6.26.

According to the elemental analysis, the composition of complexes **1** and **2** contains a different number of solvent molecules used in the synthesis in the form of a solvate.

Although synthesis products **1** and **2** were in the form of fine crystalline precipitates, single crystals of these compounds could not be grown. The powder X-ray diffraction patterns of the synthesized samples are shown in Fig. 2. The peaks on the X-ray diffraction pattern of sample **2**, indicated by asterisks, are absent on the X-ray diffraction pattern of sample **1**. This shows that the considered compounds have different structures.

RESULTS AND DISCUSSION

EPR spectroscopy and magnetic susceptibility data

In the EPR spectra of samples **1** and **2** two types of signals were observed. Type A signals are located in the weak-field part of the spectrum and have effective parameters $g_{\text{eff}}=4.2$ and $\Delta H_{\text{eff}}\approx 600$ Oe, corresponding to the HS Fe (III) centers ($S = 5/2$) with a large value of the fine structure parameter ($D>h\nu$) and strong rhombic distortions ($E/D \sim 1/3$). In the central part of the spectrum, we observed signals of type B. Type B signals have a shape which is characteristic for the spectrum of orthorhombic symmetry with $S = 1/2$ and were assigned to the LS Fe (III) complexes (Fig 3). However, the temperature dependence of the spectra of samples **1** and **2** is significantly different.

At low temperatures, the HS signal A from the sample **1** is not observed up to ~ 220 K; it arises and increases sharply with further temperature rise (Fig. 3a). The temperature dependence of the integrated intensity of this signal indicates the existence of an incomplete spin transition in the sample in the temperature range (200-320) K (Fig. 5a). The intensity of the LS signal B in this temperature range decrease sharply (Fig. 3a). Spectrum B is described by temperature-independent parameters $g_1=2.313$; $g_2=2.073$; $g_3=1.947$. With increasing temperature, smoothing of the characteristic peculiarities of the spectrum B was observed (up to the transition to a single almost isotropic line), as a result of the increase of the relaxation contribution to the width of the individual line.

The peculiarities of the temperature dependence of the EPR spectra of the sample **2** indicate the existence of a spin transition in it in the temperature range (130 - 230) K. The integrated intensity of the HS signal A increases, as the temperature rises from ~ 130 K to ~ 230 K (Fig. 5b), while the decrease of the integral intensity of the LS signal B is faster than expected by Curie-Weiss law. Spectrum B is described by temperature independent parameters $g_1= 2.355$, $g_2=2.090$, $g_3=1.924$, and is also characterized by an increase of the width of the individual line with temperature increase. The differences in the parameters of the LS centers for the samples **1** and **2** indicates a change in the properties of the nearest environment of the Fe (III) ion, which perhaps is due to the different conformation of the complexes in the samples.

To determine the relative content of HS and LS fractions, decomposition of experimental spectra into HS and LS components was carried out. An example of modeling the experimental spectrum of sample **2**, measured at a temperature of 190 K, is shown in Fig.

4. The I_{HS} and I_{LS} values of the integrated intensities of the HS and LS signals were obtained by double integration of the HS and LS components of the simulated spectrum. The relative content of the HS centers N_{HS} at a given temperature, N_{HS} was defined as the ratio of the integral intensity I_{HS} of the HS signal to the sum $I_{HS}+I_{LS}$ of the integral intensities of the HS and LS signals. The temperature dependence of the normalized integrated intensity of the EPR signal of the HS complexes for samples **1** and **2** is shown in Fig. 5

The temperature dependence of the effective magnetic moment (expressed in units of Bohr magnetons) of samples **1** and **2** in the range (100–300) K is presented in Fig. 6. The value of ca. $2.0\mu_B$ is characteristic of the Fe (III) ions in the LS state, while the value of $5.91\mu_B$ corresponds to the Fe (III) ions in the HS state. For sample **1** $\mu_{eff}(T)$ show a sharp increase in the value of μ_{eff} from $2.53\mu_B$ at 200 K to $5.12\mu_B$ at 300 K. This property is due to the thermally induced incomplete spin transition between HS and LS states in this temperature range. For sample **2** $\mu_{eff}(T)$ spin-crossover properties are manifested in the lower temperature range. The plot of the effective magnetic moment vs. temperature of complexes **2** indicated the sharp increase in μ_{eff} from $3.08\mu_B$ to $5.33\mu_B$ with increasing temperature from 130 K to 230 K. The magnetic susceptibility data are in agreement with the results of analysis of the temperature dependence of the EPR spectra shown in Fig. 5.

Thermodynamic characteristics of the spin transition

As noted earlier, in the samples **1** and **2** in a certain temperature range, we observed an anomalous increase of the integrated intensity of the HS signal A for paramagnetic centers, which is due to existence of the spin transition. The changes in enthalpy and entropy, causing the spin transition, were determined from analysis of the temperature dependence of the integral intensity. When spin transition is absent, the integral intensity of the HS isolated paramagnetic centers obeys the Langeven's law and in the high-temperature approximation is inversely proportional to temperature. The population of the HS state also decreases with increasing temperature according to the Boltzmann's law of the population of energy levels. At the same time, in the spin transition temperature range, the relative content of the HS centers of the $N_{HS}(T)$ centers increases with temperature. Given the described processes, a change in the integral intensity of signal A is represented by the equation

$$I_{HS} = I_0 \cdot N_{HS}(T) \cdot \delta/kT \cdot (1 - \exp(-\Delta E/kT)) / (1 + \exp(-\Delta E/kT)), \quad (1)$$

where ΔE is the energy interval between the ground and excited HS states of the system, I_0 is the normalization factor, $\delta = \hbar\nu$ is the interval between levels, which are involved in the formation of the EPR signal.

The change of relative content of HS fraction $N_{HS}(T)$ during spin transition corresponds to the thermodynamic ratio:^[19]

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

where ΔH is the change of enthalpy, ΔS is the entropy change, Γ is the interaction parameter, r is the residual HS fraction, which is present at low temperatures in the LS fraction, $R=8.31 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is the gas constant.

Satisfactory agreement was obtained when describing the temperature dependence integrated intensity of signal A of samples **1**, **2** by equations (1), (2) (Fig.5a, 5b). The optimal values of fitting parameters are presented in table 1.

Analysis of the electronic structure of the complexes

The g - factors of the EPR spectra of low-spin Fe (III) complexes observed in samples **1** and **2** were analyzed using the one-electron approximation in the framework of the lower orbital triplet, similarly to Ref..^[16, 20, 21] The coefficients of the wave functions of the lower triplet A, B, C and the coefficient of suppression of the spin-orbit coupling K were calculated taking into account the spin-orbit interaction $\xi \hat{I} \hat{s}$, tetragonal Δ , and orthorhombic V components of the ligand field. The values of E_i , Δ and V were determined by substituting the obtained values into the energy matrix and solving the corresponding system of linear equations; the value of ξ was assumed to be 460 cm^{-1} . The obtained data are given in table 2.

The wave functions of the ground doublet, presented in the basis of real wave functions, have the form

$$\begin{aligned} \psi_1 &= a |d_{yz}^+\rangle + b |d_{xy}^-\rangle + c |d_{xz}^+\rangle \\ \psi_2 &= a |d_{yz}^-\rangle - b |d_{xy}^+\rangle - c |d_{xz}^-\rangle \end{aligned} \quad (3)$$

Their coefficients and the obtained values A, B, and C are related by the relations

$$a = -i(A+C)/\sqrt{2}; \quad b = iB; \quad c = (C - A)/\sqrt{2} \quad (4)$$

For the obtained values of A, B, C, the coefficient c of $|d_{xz}\rangle$ state has a maximum value in the basis of real wave functions ($c=0.995$ for sample **1** and $c=0.992$ for sample **2**). The $|d_{xz}\rangle$ state is the ground state of the Fe (III) ion for samples **1** and **2**.

The difference of the parameters of the LS centers in samples **1** and **2** indicates a change of the properties of the nearest environment of the Fe (III) ion.

To obtain a diagram of the energy levels of the $[\text{Fe}(\text{bzacen})(\text{tvp})]\text{BPh}_4$ complexes exhibiting spin-crossover properties, the following considerations should be taken into account. From general thermodynamic considerations, it follows that the main energy level should be LS, and the level of the HS state should be higher by a relatively small value (of the order of kT). The results of analysis of g -factors of LS complexes of Fe (III) of the studied compounds in Table 2 indicate a large value of splitting of the lower orbital triplet (several thousand cm^{-1}). It is possible to neglect the splitting of the multiplet ${}^6\text{A}_1$ HS in the crystal field. It does not exceed a few cm^{-1} , since this term has an orbital moment $L = 0$. Thus, the HS ${}^6\text{A}_1$ term involved in the spin transition, should be located above the lower level of the split LS ${}^2\text{T}_2$ term. A similar arrangement of the energy levels participating in the spin transition was considered in Ref..^[16, 22, 23]

The analysis of the experimental g -factors for the LS centers of samples **1** and **2** made it possible to identify the difference in the magnitude of the low-symmetry distortions of the ligand field and to determine the corresponding energy level of the lower orbital triplet E_1 , E_2 , E_3 (Table 2). Calculations showed that the LS splitting of the orbital triplet is significantly larger than the magnitude of the “pure spin-orbit splitting” (690 cm^{-1}). In Fig.7, E_1 , E_2 and E_3 , indicate the energy levels of the split LS orbital triplet t_{2g} , and E_{HS} indicates the energy of the excited HS multiplet.

The nearest environment N4O2 of the Fe (III) ion (up to the second coordination sphere) has the same configuration. Therefore, the energy of the term ${}^6\text{A}_{1g}$ is assumed to be the same for samples **1** and **2**. Then, the decrease in the temperature of the spin transition T_C in sample **2** (208.4 K) compared to **1** (285.8 K) is explained by a decrease in the orbital triplet splitting for the LS configuration and, accordingly, a decrease in the energy interval $E_{\text{HS}}-E_1$ between the main LS and HS energy levels (Fig. 7).

Effect of solvation on the spin-variable properties of Fe (III) complexes

It is well known that in coordination compounds the solvent content has a strong effect on the spin state of Fe (III) complexes and the parameters of the spin transition.^[13, 24, 25]

As the authors of Ref.^[24] note, there are many examples of decreasing the temperature of the spin transition upon desolvation of a sample or simply the appearance of spin-crossover properties in previously solvated compounds with only low-spin states. Analyzing data on recent spin-crossover systems, the authors of Ref.^[13] concluded that most often different solvents modify the behavior of the spin-crossover transition rather than not responsible for its occurrence. A typical example of such a system is [Fe(qsal-I)₂]OTf and [Fe(qsal-I)₂]OTf·MeOH compounds. X-ray structural analysis and magnetic susceptibility measurements showed that a loss of solvent leads to a decrease in the spin transition temperature and the hysteresis width.^[26] The authors explain these changes by an increase in intermolecular interactions due to the formation of additional π - π and hydrogen bonds with increasing degree of solvation.

Based on the elemental analysis data, the observed differences in the electronic structure and magnetic resonance properties of the Fe (III) complexes in samples **1** and **2** can be attributed to structural differences caused by a change in the crystal packing for complexes with different concentrations of solvent molecules. The temperature of spin transition is lower in complexes **2**, which include a smaller number of solvent molecules. That correlates with the tendency to decrease the temperature of the spin transition upon desolvation of the sample described in Ref.^[24–26] The powder diffraction patterns shown in Fig. 2 demonstrate the structural differences between samples **1** and **2**.

CONCLUSION

Two types of spin-crossover complexes [Fe(bzacen)(tvp)]BPh₄·nSolv obtained at different times of crystallization from solution were found. They differ in the local ligand field characteristics and in the spin-crossover transition parameters. Measurements of the EPR spectra temperature dependence with their subsequent decomposition into low-spin and high-spin components made it possible to estimate the relative content of the high-spin and low-spin fractions and obtain information on the thermodynamic parameters of spin transition and spin-crossover processes.

The EPR data analysis of compounds with equatorial ligand bzacen led to the conclusion: if the spin state in highly symmetric Fe (III) complexes is determined by the energy interval between the ²T₂ and ⁶A₁ terms, then in the pseudo-octahedral complexes the splitting of ²T₂ energy levels due to low-symmetry components of the crystal field and spin-orbit interaction play a significant role in the realization of spin-crossover processes.

The degree of solvation rather strongly influenced on the electronic structure, on magnetic and resonance parameters of Fe (III) samples **1** and **2**. A decrease of the spin transition temperature in sample **2** with a smaller number of solvent molecules in the complex correlates with tendency to decrease the spin transition temperature upon sample desolvation.

Note that the our investigation of two different modifications of spin-crossover complexes extracted in different time of their crystallization from solution show large capabilities of the EPR method in studying the kinetics of Fe (III) complexes formation and their thermodynamic stability.

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REFERENCES

- [1] B. J. Kennedy, A. C. McGrath, K. S. Murray, B. W. Skelton, A. H. White, *Inorg. Chem.* **1987**, 26, 483.
- [2] T. Fujinami, M. Koike, N. Matsumoto, Y. Sunatsuki, A. Okazawa, N. Kojima, *Inorg. Chem.* **2014**, 53, 2254.
- [3] M. Koike, K. Murakami, T. Fujinami, K. Nishi, N. Matsumoto, Y. Sunatsuki, *Inorg. Chim. Acta* **2013**, 399, 185.
- [4] T. A. Ivanova, O. A. Turanova, I. V. Ovchinnikov, L. V. Mingalieva, I. F. Gil'mutdinov, V. A. Shustov, L. G. Gafiyatullin, *Rus. J. Inorg. Chem.* **2017**, 62, 476.
- [5] J. C. Dias, B. Vieira, L. C. J. Pereira, V. D. Gama, *Inorg. Chim. Acta* **2008**, 362, 2076.
- [6] W. Phonsri, P. Harding, L. Liu, S. G. Telfer, K. S. Murray, B. Moubaraki, T. M. Ross, G. N. L. Jameson, D. J. Harding, *Chem. Sci.* **2017**, 8, 3949.
- [7] I. V. Ovchinnikov, T. A. Ivanova, O. A. Turanova, G. I. Ivanova, L. V. Mingalieva, A. A. Sukhanov, *Rus. J. Coord. Chem.* **2013**, 39, 598.
- [8] N. E. Domracheva, A. V. Pyataev, V. E. Vorobeva, M. S. Gruzdev, E. M. Zueva, *J. Phys. Chem. B* **2013**, 117, 7833.

- [9] T. A. Ivanova, O. A. Turanova, I. F. Gil'mutdinov, L. V. Mingalieva, I. V. Ovchinnikov, *Rus. J. Inorg. Chem.* **2019**, *64*, 520.
- [10] M. Mazur, L. Pogany, B. Brachňakova, I. Šalitraš, *Chemical Papers*, DOI: 10.1007/s11696-019-00781-2.
- [11] P. J. Koningsbruggen, Y. Maeda, H. Oshio, in *Spin Crossover in Transition Metal Compounds I, Top. Curr. Chem.* (Eds.: P. Gülich, H. A. Goodwin), Springer-Verlag, Berlin, Heidelberg, **2004**, *233*, pp. 259 - 324.
- [12] T. Nihei, Y. Shiga, Y. Maeda, H. Oshio, *Coord. Chem. Rev.* **2007**, *251*, 2606.
- [13] D. J. Harding, P. Harding, W. Phonsri, *Coord. Chem. Rev.* **2016**, *313*, 38-61.
- [14] Y. Nishida, S. Oshio S, Kida S. *Bull Chem Soc Jpn.* **1977**, *50*, 119.
- [15] N. Matsumoto, K. Kimoto, A. Ohyoshi, Y. Maeda, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3307-3311.
- [16] M. S. Haddad, W. D. Federer, M. W. Lynch, D. N. Hendrickson, *Inorg. Chem.* **1981**, *20*, 123.
- [17] T. M. Ross, S. M. Neville, D. R. Turner, B. Moubaraki, K. S. Murray, *Dalton Trans.* **2010**, *39*, 149.
- [18] S. Stoll, A. Schweiger, *J. Magn. Reson.* **2006**, *178*, 42.
- [19] J.-P. Martin, J. Zarembowitch, A. Bousseksou, A. Dworkin, J. G. Haasnoot, F. Varret, *Inorg. Chem.* **1994**, *33*, 6325.
- [20] M. M. Bhadbhade, D. Srinivas, *Polyhedron.* **1998**, *17*, 2699.
- [21] T.A. Ivanova, I.V. Ovchinnikov, A.Turanov, *Phys. Solid State*, **2007**, *49*, 2132.
- [22] H. Oshio, Y. Maeda, Y. Takashima, *Inorg. Chem.* **1983**, *22*, 2684.
- [23] R. Boca, I. Nemeč, I. Šalitraš, J. Pavlik, R. Herchel, F. Renz, *Pure Appl. Chem.* **2009**, *81*, 1357.
- [24] I. Nemeč, R. Herchel, Z. Trávníček, *Dalton Trans.* **2015**, *44*, 4474.
- [25] W. Phonsri, D. S. Macedo, C. G. Davies, G. N. L. Jameson, B. Moubarakia, K. S. Murray, *Dalton Trans.* **2017**, *46*, 7020.
- [26] D. J. Harding, W. Phonsri, P. Harding, I. A. Gass, K. S. Murray, B. Moubaraki, J. D. Cashion, L. Liud, S. G. Telfer, *Chem. Commun.* **2013**, *49*, 6340.

Table 1.

Thermodynamic characteristics of the complexes [Fe(bzacen)(tvp)]BPh₄.

Compound	T _C , K (N _{HS} =N _{LS})	ΔH, kJ·mol ⁻¹	ΔS, J·mol ⁻¹ ·K ⁻¹	Γ, kJ·mol ⁻¹	r
Sample 1	285.8	26.8	93.9	0.0	0.0
Sample 2	208.4	16.4	78.9	0.0	0.02

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Table 2.

The results of the analysis of the g-factors of LS Fe (III) complexes in the studied compounds.

Compound	E1, cm ⁻¹	E2, cm ⁻¹	E3, cm ⁻¹	Δ , cm ⁻¹	V/ Δ	K	A	B	C
Sample 1	-3299	-847	4147	-2065	0.194	0.823	0.772	0.034	-0.635
Sample 2	-2617	-508	3126	-1551	0.221	0.803	0.782	0.044	-0.621

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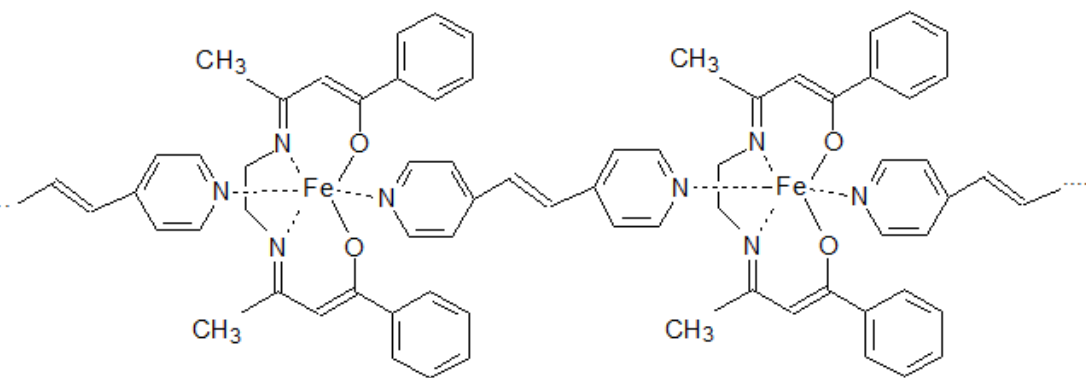


FIGURE 1 Schematic representation of the structure for complexes $[\text{Fe}(\text{bzacen})(\text{tvp})]\text{BPh}_4$

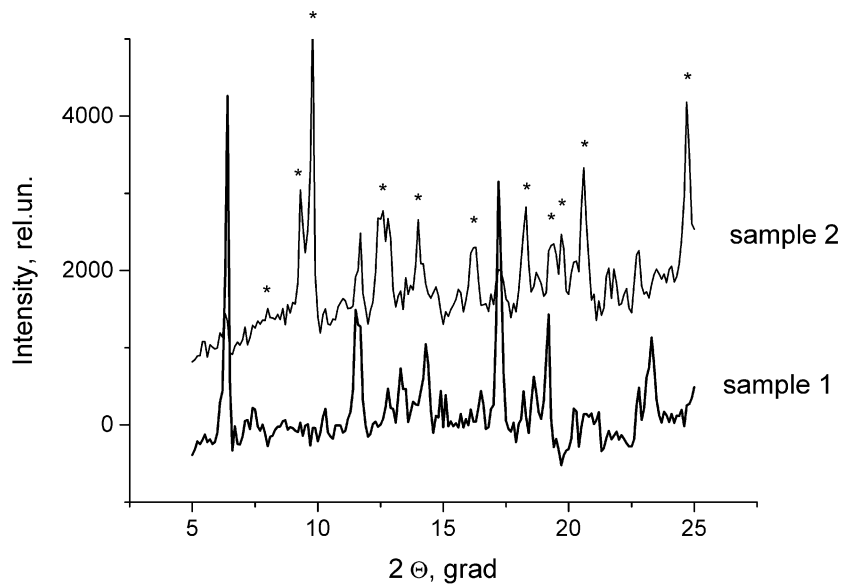


FIGURE 2 X-ray powder diffraction patterns of samples 1 and 2

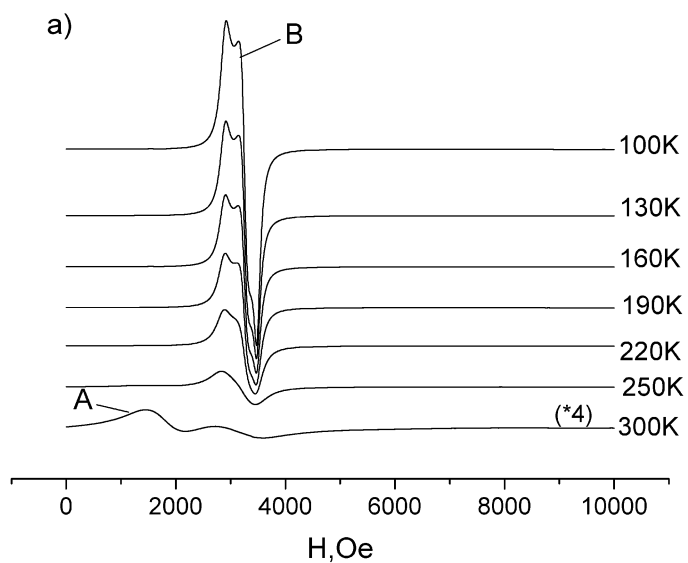


FIGURE 3 The temperature dependence of the EPR spectra for samples 1 (a) and 2 (b); $\nu=9.47$ GHz

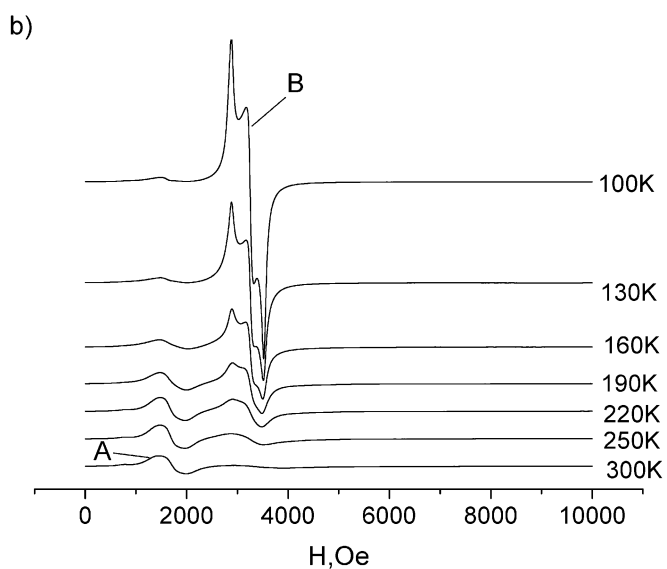


FIGURE 3 The temperature dependence of the EPR spectra for samples 1 (a) and 2 (b); $\nu=9.47$ GHz

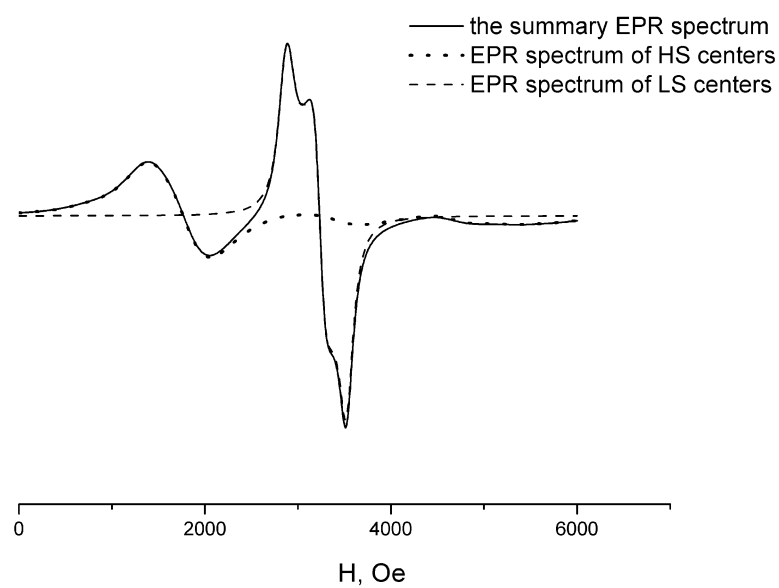


FIGURE 4 Experimental EPR spectrum of sample 2 at 190 K presented as a superposition of the signals of HS and LS centers with the relative content of HS centers $N_{HS} = 0.58$

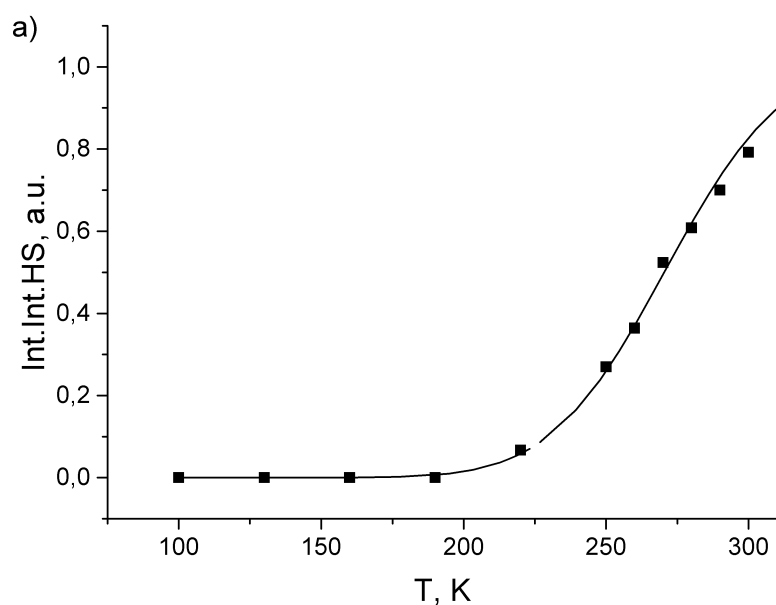


FIGURE 5 The temperature dependence of normalized integrated intensity of the EPR signal of HS samples 1 (a) and 2 (b). ■ experiment; ___ calculating using equations (1), (2) with thermodynamic parameters given in table 1

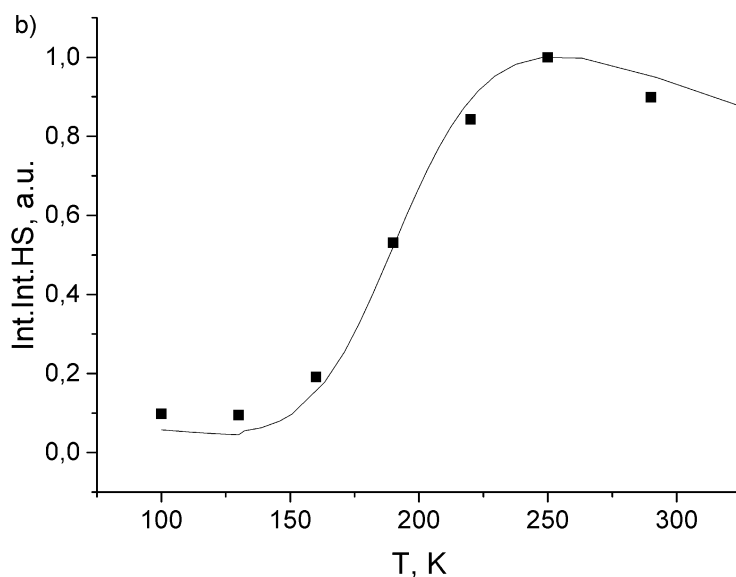


FIGURE 5 The temperature dependence of normalized integrated intensity of the EPR signal of HS samples 1 (a) and 2 (b). ■ experiment; ___ calculating using equations (1), (2) with thermodynamic parameters given in table 1

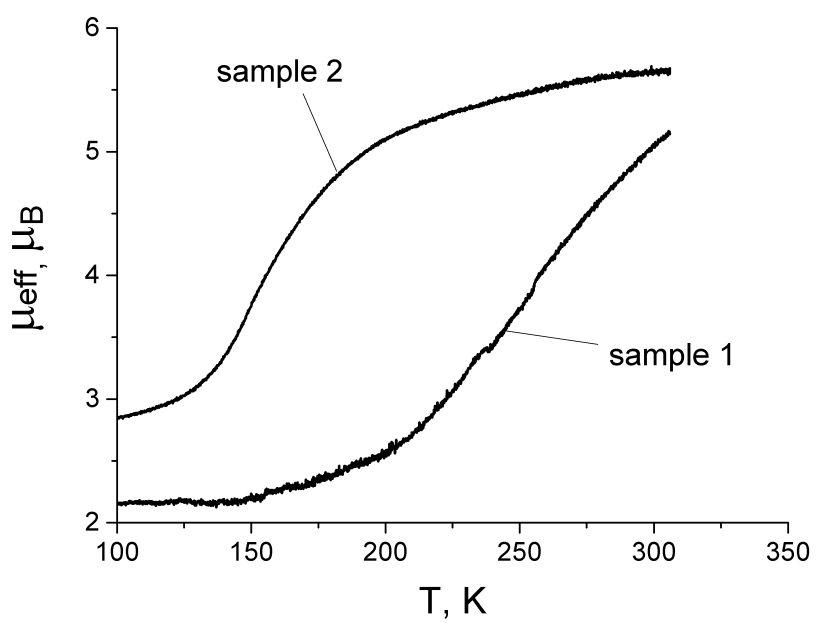


FIGURE 6 The temperature dependence of the effective magnetic moment of samples 1 and 2

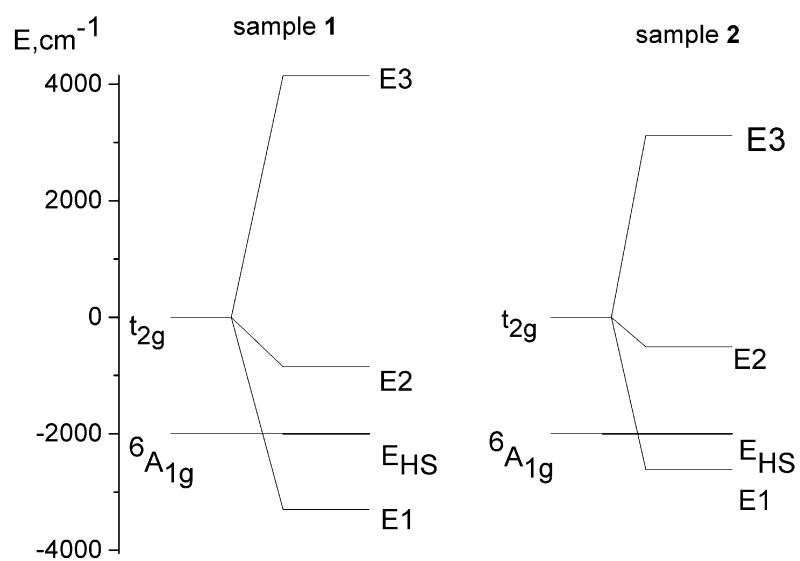
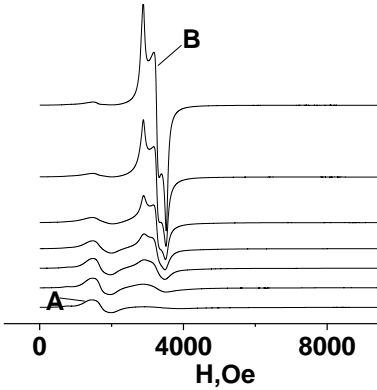


FIGURE 7 Supposed energy levels diagram for samples 1 and 2

<p>Two types of complexes [Fe(benzacen)(tvp)]BPh₄·nSolv are synthesized and studied by the EPR and magnetic susceptibility methods. The thermodynamic parameters of spin transitions were determined from the temperature dependence of the EPR signals integral intensity. Estimation of the splitting of the energy levels of these complexes by analyzing g-factors of low-spin Fe (III) centers showed a large role of low-symmetry deformation of the ligand field in the implementation of spin-crossover processes.</p>		<p>Spin Crossover Properties of Fe(III) Complexes in [Fe(benzacen)(tvp)]BPh₄·nSolv Chain Structures</p> <p>T.A. Ivanova, I.V. Ovchinnikov, O.A. Turanova*, L.V. Bazan, V.A. Shustov, R.G. Batulin, M.A. Cherosov</p>
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