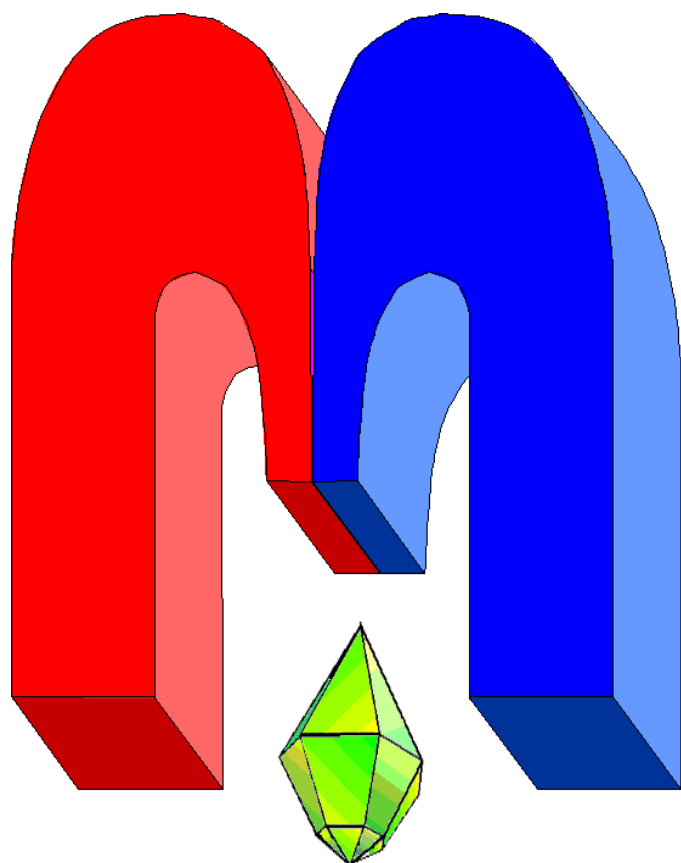


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In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Electronic and magnetic properties of $[\text{Fe}(\text{3-MeO-Qsal})_2]\text{Y}\cdot n$ solvent ($n = 0,1$) complexes

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$[\text{Fe}(\text{3-MeO-Qsal})_2]\text{Y}$ ($\text{Y} = \text{PF}_6, \text{BF}_4, \text{NCS}, \text{NO}_3, \text{BPh}_4$) compounds were synthesized using the diffusion method and studied by the electron spin resonance and the magnetic susceptibility methods in the temperature range (5-300) K. Coexistence of spatially separated high-spin and low-spin fractions in these compounds was observed. Low-spin fraction of all compounds reveals the antiferromagnetic correlations at low temperatures. High-spin fraction of complexes with $\text{Y} = \text{PF}_6$ demonstrate the weak ferromagnetic properties due to exchange interaction between complexes in whole temperature range. Influence of outer-sphere anion on the spin state, the electronic properties of low-spin Fe(III) complexes is demonstrated.

PACS: 75.20-g, 75.30.Et, 76.30.-v, 75.40Cx

Keywords: high-spin and low-spin state, intermolecular interactions, outer-sphere anions

Based on Qsal-containing Fe(III) complexes (N-(8-Quinoly)salicylaldimine), a number of compounds with interesting physical properties have been synthesized. The observed properties include the thermo-induced spin transition (spin-crossover), the spin state switching after irradiation with light (LIESST effect), and the coexistence of the hysteretic behavior of the conductive and spin properties in the same temperature range [1-4]. Recently Fe(III) complexes with substituted X-Qsal ligands begun to attract more and more attention. In previous works [5, 6] compounds with $\text{X} = \text{MeO}$ ($\text{MeO} = \text{methoxy substitute } (\text{CH}_3\text{O})$) in 4th and 5th positions of the phenyl ring and with different types of outer-sphere anions were investigated. It was demonstrated that magnetic properties of the complex are significantly affected by the position of the MeO in the phenyl ring and by the type of the outer-sphere anion. As for the compounds with MeO group in the 3rd position, only complexes with the outer-sphere anion PF_6 have been studied [7]. By changing synthesis conditions, complexes Fe(III) with different spin states were synthesized: low-spin (LS) Fe(III) complexes were obtained in unsolvated compounds (synthesis in inert atmosphere) and high-spin (HS) Fe(III) complexes were obtained in solvated compounds (synthesis in air). In these works [5-7] magnetic properties of Fe(III) complexes were characterized only by magnetic susceptibility measurements, the electron spin resonance (ESR) method has not been used. According to the X-ray diffraction data [5-7], in $[\text{Fe}(\text{X-Qsal})_2]\text{Y}$ complexes two three-dentate ligands coordinate towards the central Fe atom in almost perpendicular direction (Fig. 1). In the spatial unit cell complexes are positioned so, that the planes of quinoline and phenyl ring of neighboring complexes are almost parallel. This allows formation of π - π bonds between complexes, as well as hydrogenic C-H... π bonds between H-atoms of quinoline and the π -system of the quinoline or phenyl ring of the neighboring complex. Additional type C-H...R ($\text{R} = \text{F}, \text{O}$) hydrogenic bonds can be formed involving the outer-sphere anion Y, the MeO group, and molecules of solvent and/or water in solvated complexes. Schemes of possible inter-molecular bonds were suggested in [5-7] based on the X-ray diffraction data analysis only.

The purpose of this work was to synthesize $[\text{Fe}(\text{3-MeO-Qsal})_2]\text{Y}$ complexes and to study their spin variables properties, electronic structure and magnetic interactions between them in a series of compounds with different outer-sphere anions.

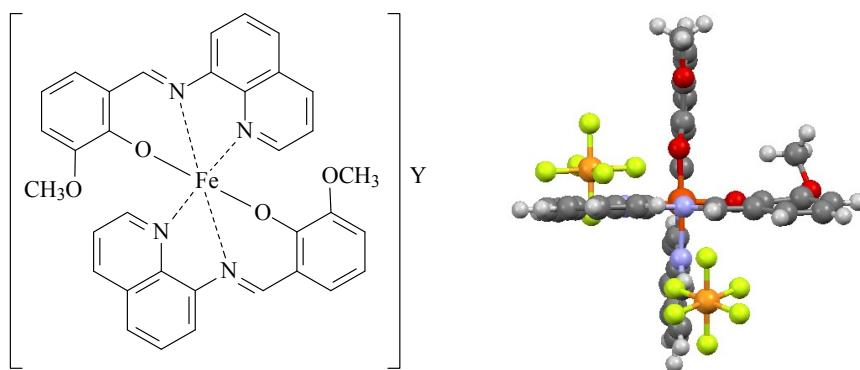


Figure 1. Structural scheme of complexes $[\text{Fe}(\text{3-MeO-Qsal})_2]\text{Y}$ and three-dimensional image of complexes $[\text{Fe}(\text{3-MeO-Qsal})_2]\text{PF}_6$.

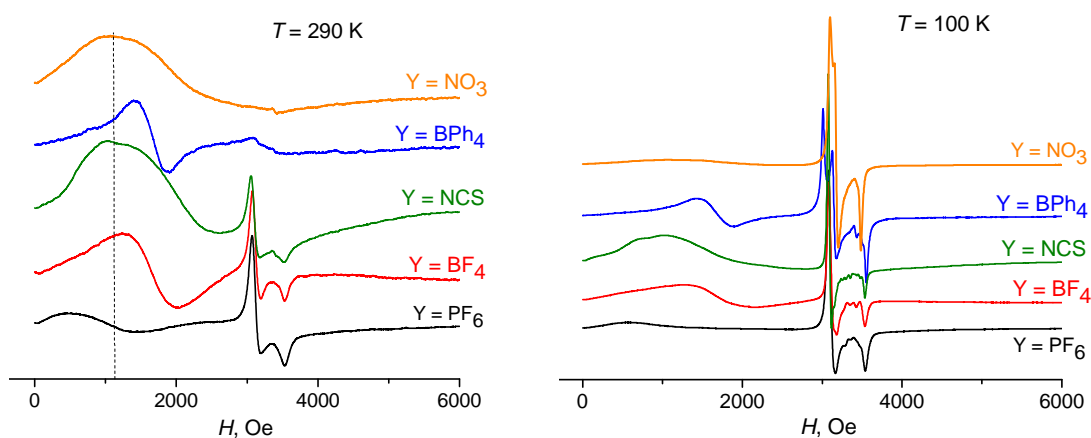


Figure 2. The ESR spectra of compounds $[\text{Fe}(\text{3-MeO-Qsal})_2]\text{Y}$; X-band.

In contrast to the previous work [7], where $[\text{Fe}(\text{3-MeO-Qsal})_2]\text{PF}_6$ was synthesized using standard methods (stirring and heating of components), in our work complexes $[\text{Fe}(\text{3-MeO-Qsal})_2]\text{Y}$ with $\text{Y} = \text{PF}_6, \text{BF}_4, \text{NCS}, \text{NO}_3, \text{BPh}_4$ (samples **1**, **2**, **3**, **4**, **5** respectively) were synthesized using the diffusion method, similar to the one described in [5, 6]. Diffusion method (slow diffusion of the iron salt solution on top of a ligand solution) allowed us to increase yield, purity and crystallinity of the product, as well as to avoid using elevated temperatures during the synthesis and, thus, to reduce the probability of formation of chains, oxides and other unwanted phenomena. Synthesized powdered compounds have been studied by the ESR and the magnetic susceptibility methods in the temperature range (5-300) K. ESR measurements were performed on the ESR spectrometer EMX-plus with temperature-prefix ER4131VT. Temperature and field dependences of magnetization was measured on the magnetometer PPMS-9 (Federal Center of Shared Facilities of Kazan federal university).

The ESR spectra of the investigated samples constitute superposition of signals from the HS and the LS Fe(III) complexes (Fig. 2). The signal of HS complexes ($S = 5/2$) is a broad line in the low-field range of the spectrum. Its shape can be described by the spin Hamiltonian, including the Zeeman and the spin-spin interactions with the values of the fine structure parameter $D > h\nu$ and with the width of individual lines of about 1000-1500 Oe. The position and shape of the line does not depend on the temperature up to 5 K. In the sample **1** for a satisfactory description of the HS signal it is necessary to introduce an additional effective magnetic field ≈ 750 Oe, which is created, apparently, due to ferromagnetic exchange interactions between the complexes [8]. At the same time, this additional field was not required to model the signal from the LS centers (Fig. 3). Hence, it can be argued that the HS and the LS fractions are spatially separated. As mentioned above, HS complexes $[\text{Fe}(\text{3-MeO-Qsal})_2]\text{PF}_6$ were observed in the solvates presence, but LS one in unsolvated

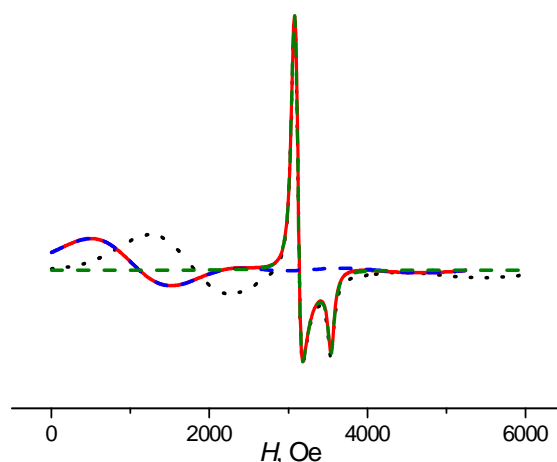


Figure 3. Simulated ESR spectrum of the sample **1**, $T = 290$ K with parameters: for LS center $g_1 = g_2 = 2.184$, $g_3 = 1.915$, $\Delta H_{LS} = 100$ Oe; for HS center $D = 3000$ Oe, $E/D = 0.22$, $\Delta H_{HS} = 1100$ Oe, $\Delta H_{fm} = 750$ Oe; weighting coefficients $K_{HS} = 0.81$ and $K_{LS} = 0.19$; green dotted line is LS component of the spectrum, the blue dotted line is HS component of the spectrum, the red line is the total spectrum; black dotted line shows a theoretical spectrum excluding shift of HS component due the ferromagnetic exchange interactions.

Table 1. Results of g -factors analysis on the complex Fe(III) in the investigated compounds.

Y	g_x	g_y	g_z	A	B	C	K	Δ , cm^{-1}	V , cm^{-1}	ΔE_{12} , cm^{-1}	ΔE_{13} , cm^{-1}
PF ₆	2.187	2.187	1.911	0.1307	0.9914	0.0000	0.603	884.5	0.000	2508	2925
BF ₄	2.184	2.184	1.915	0.1277	0.9918	0.0000	0.604	904.5	0.000	2566	2985
NCS	2.191	2.191	1.916	0.1264	0.9920	0.000	0.629	913.7	0.000	2594	3013
NO ₃	2.185	2.133	1.943	0.1039	0.9945	0.0121	0.6186	1118.9	140.0	2938	3877
BPh ₄	2.25	2.153	1.906	0.1326	0.991	0.0209	0.639	896.9	155.6	2248	3264

compound [7]. This allows us to assert that HS complexes are formed in the solvated fraction, and LS complexes in the unsolvated fraction. This interpretation is confirmed by the results of research complexes $[\text{Fe}(4\text{-MeO-Qsal})_2]\text{Y}$ ($\text{Y} = \text{PF}_6, \text{NO}_3, \text{ClO}_4$), where the presence of solvate in HS complexes has been established on the basis of X-ray study [6].

Intermolecular interactions are strongly dependent on the type of outer-sphere anion, its position, size, configuration. The shift of the HS complexes signal towards lower magnetic fields for the samples **2, 3, 4, 5** or absent (sample **2** and **4**) or considerably less, than for the sample **1**. It is not possible to reliably estimate a small shift from model calculations at large width of individual line (~ 1000 Oe).

The ESR spectra of LS complexes ($S = 1/2$) are described by temperature-independent parameters of the spin Hamiltonian g_i , given in Table 1. As the temperature decreases, the width of the individual lines is reduced, which manifests itself in improving the degree of resolution of g -tensor components. This is explained by the decrease of the relaxation contribution to the line width. The signals from the LS complexes were observed in the entire temperature range for samples **1, 2, 3**. In samples **4, 5** at temperatures above ~ 190 K signals from LS complexes were not detected due to strong relaxation broadening. Analysis of g -factors of the ESR spectra of the LS Fe(III) complexes **1-5** was performed using the single-electron approximation within the lower orbital triplet, as discussed in [9]. We took into account the spin-orbit interaction $\xi \hat{s}$ and the tetragonal Δ and the rhombic V components of the ligands field. The calculation results are shown in Table 1, where A , B and C are the coefficients of the wave functions of the orbital triplet, and K is the coefficient of the spin-orbit coupling suppression, ΔE_{12} , ΔE_{13} are the energy intervals between the levels of the orbital triplet.

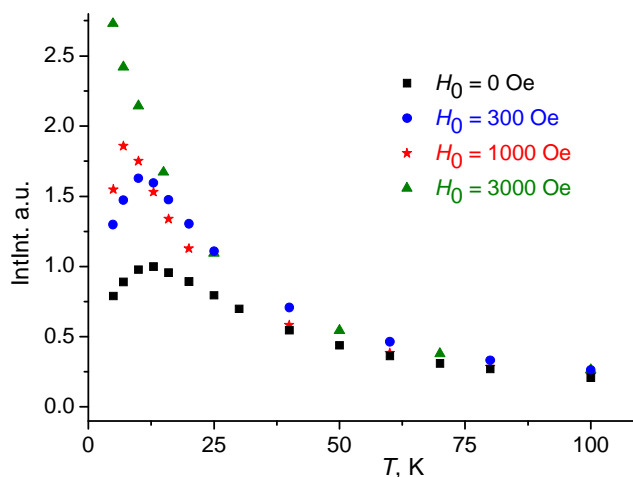


Figure 4. The temperature dependence of the ESR signal integral intensity of LS complexes Fe(III) for sample **1** after cooling in the constant magnetic field H_0 .

At low temperatures, the integral intensity of the LS center signal has a maximum at the temperatures $T_c = 12.5$ K, 11.3 K, 9.5 K, 11.0 K, 7.2 K for samples **1**, **2**, **3**, **4**, **5**, respectively. This indicates occurrence of antiferromagnetic interactions between LS complexes at low temperatures [10]. If the samples are pre-cooled in a nonzero magnetic field H_0 , the maximum T_c shifts towards lower temperatures and eventually disappears, if H_0 is large enough (Fig. 4). As mentioned above, the spatial orientation of ligands in compounds of this type allows formation different bonds. The regions with antiferromagnetic correlations appear at low temperatures due to indirect exchange bounds between the magnetic moments of the spins. The value of these interaction decreases with increasing temperature, which leads to the occurrence of the T_c maximum in the temperature dependence of the integral intensity of the ESR signal. After cooling in a nonzero magnetic field H_0 , antiferromagnetic correlations are hampered. In this case, compensation of the magnetic moments of correlated spins starts at a lower temperature and for a sufficiently large value H_0 may disappear.

Magnetic susceptibility measurements confirmed the coexistence of Fe(III) ions in HS and LS states in the investigated samples, and the absence of the spin transition. The product of the magnetic susceptibility and temperature, $(\chi_{\text{mol}} - \chi_0)T$, which is proportional to the effective magnetic moment squared, remains constant with changing the temperature. The value of the effective magnetic moment in the investigated samples is less than the magnetic moment corresponding to the pure HS state of Fe(III), and allows up to (15-30)% concentration of LS centers, for different outer-sphere anions Y. This is in agreement with estimations based on the ESR spectra analysis.

The temperature dependence of the inverse magnetic susceptibility is described by the Curie's law, taking into account the temperature-independent contribution, $\chi_{\text{mol}}^{-1} = T/(C + \chi_0 T)$. The sign of χ_0 is negative for samples **1** and **5**, and positive for samples **2**, **3**, **4** (Fig. 5). During the static magnetic susceptibility measurements, neither deviations from the Curie's law at low temperatures, nor magnetic susceptibility dependence on the thermo-magnetic history of the sample were not observed. The measurements were conducted similar to the ESR measurements, with precooling of samples in nonzero magnetic field. Observation of the antiferromagnetic correlations in the ESR experiments, and the absence of any of their manifestations in the time-averaged magnetic measurements, suggests that the antiferromagnetic correlations have a dynamic (fluctuational) nature [11].

Thus, this study shows that changing the spin state of complexes $[\text{Fe}(\text{3-MeO-Qsal})_2]\text{Y}$ and their cooperative properties (intermolecular interactions) can be achieved by modifying structure elements of ligands and outer-sphere anion. The results can be useful in the search for new systems with spin-crossover properties.

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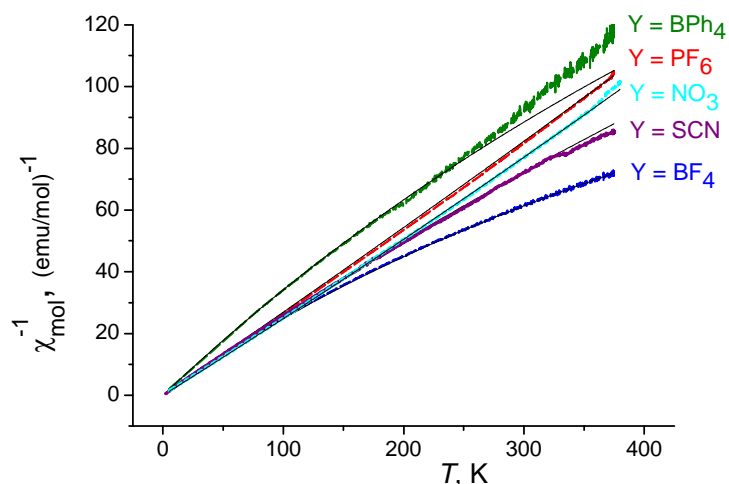


Figure 5. The temperature dependence of χ_{mol}^{-1} for complexes $[\text{Fe}(3\text{-MeO-Qsal})_2]\text{Y}$; black line is the results of the calculation according to the formula $\chi_{mol} = C/(T - Q) + \chi_0$: $C = 3.75$, $\chi_0 = -0.00035$, $Q = 0$ for sample **1**; $C = 3.22$, $\chi_0 = 0.0043$, $Q = 0$ for sample **2**; $C = 3.79$, $\chi_0 = 0.0015$, $Q = 0$ for sample **3**; $C = 2.70$, $\chi_0 = 0.0023$, $Q = 0$ for sample **4**; $C = 4.10$, $\chi_0 = -0.0007$, $Q = 0$ for sample **5**.

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