

Spin crossover in homo- and heteroligand iron(II) complexes with tris(pyrazol-1-yl)methane derivatives*

L. G. Lavrenova^{a,b}

^aA. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, 3 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.

Fax: +7 (383) 330 9489. E-mail: ludm@niic.nsc.ru

^bNovosibirsk State University,

2 ul. Pirogova, 630090 Novosibirsk, Russian Federation

The studies concerning coordination compounds of various salts of iron(II) with tris(pyrazol-1-yl)methane derivatives (HC(pz)₃) are discussed. The results of a number of studies on the synthesis and investigation of the homo- and heteroligand iron(II) complexes with tris(3,5-dimethylpyrazol-1-yl)methane (HC(3,5-Me₂pz)₃) are considered. The study of the temperature dependence $\mu_{\text{eff}}(T)$ showed that the spin crossover (SCO) $^1A_1 \leftrightarrow ^5T_2$ observed in a series of the compounds discussed is accompanied by thermochromism (color change pink (purple) \leftrightarrow colorless). Specific features of the SCO and their dependence on the outer-sphere anion in the iron(II) complexes are discussed. The data of the recently published work devoted to the synthesis of the iron(II) complexes with three *N*-substituted HC(pz)₃ derivatives (general formula ^xL , where $x = \text{H}$, $\text{CH}_2\text{C}_6\text{H}_5$ (Bn) and $p\text{-SO}_3\text{C}_6\text{H}_4\text{CH}_3$ (Ts)) are considered.

Key words: magnetic properties, spin crossover, coordination compounds, iron(II), tris(pyrazol-1-yl)methane derivatives.

Introduction

Spin crossover (spin transition) is observed in coordination compounds of 3d-metals with the electron configuration d^4-d^7 having an octahedral or pseudo-octahedral structure of the coordination polyhedron. Spin crossover is one of the most interesting phenomena in coordination chemistry and being attracted rapt attention of researchers for several years.^{1–8} Spin multiplicity changes in response to external conditions: temperature, pressure, or irradiation with the light of a certain wavelength. The synthesis and investigation of new complexes exhibiting SCO are necessary for both the development of the theory of this remarkable phenomenon and practical use of compounds of this class. The iron(II) compounds with polynitrogen ligands are of special interest because in many of them the spin transition is accompanied by a well discernible change in the color of the compounds, which substantially extends possibilities of their practical application. These complexes can be used for the development of systems of information recording and storage, thermochromic indicators and labels, electroluminescent devices, thermosensitive materials in magnetic resonance tomography, etc.^{9–15}

* Based on the materials of the XXVII International Chugaev Conference on Coordination Chemistry (October 2–6, 2017, Nizhny Novgorod, Russia).

Tris(pyrazol-1-yl)methane and its derivatives represent a promising class of compounds for the synthesis of new magnetically active coordination compounds of iron(II) with polynitrogen heterocyclic ligands in which the SCO $^1A_1 \leftrightarrow ^5T_2$ and (or) exchange interactions between paramagnetic Fe^{II} ions are observed.^{6,16–28} It is revealed that tris(pyrazol-1-yl)methanes coordinate to metal ions by three N(2) atoms of the pyrazole cycle *via* the tridentate cyclic mode¹⁶ (Fig. 1).

The SCO $^1A_1 \leftrightarrow ^5T_2$ observed in these compounds is accompanied by thermochromism: color change "purple \leftrightarrow colorless." The temperature of the SCO (T_c) depends substantially on the composition of the complex, in particular, on the outer-sphere anion. For example, in the complexes with the unsubstituted ligand [Fe{HC(pz)₃}₂]-A_m·nH₂O (A is anion, $m = 1, 2$, $n = 0-7$) the temperature of the transition (T_c) ranges from 310 to 470 K depending on the composition.¹⁶

In this review, we present the results of the works concerning the synthesis and investigation of the homo- and heteroligand coordination compounds of various iron(II) salts with the tris(pyrazol-1-yl)methane derivatives (HC(pz)₃), which have been published during the recent five years. Here we do not deal with the results of studies on the spin crossover in the Fe^{II} complexes with unsubstituted HC(pz)₃, since this representative data body needs special analysis.

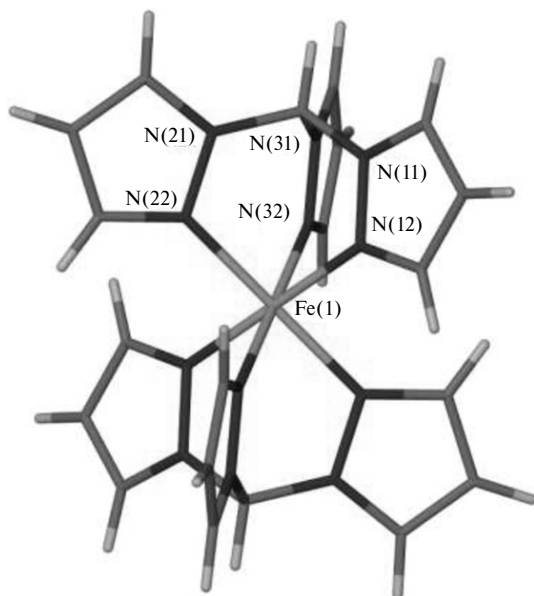


Fig. 1. Complex of tris(pyrazol-1-yl)methane with metal.

The results on the synthesis and investigation of the homo- and heteroligand complexes of various iron(II) salts with tris(3,5-dimethylpyrazol-1-yl)methane ($\text{HC}(3,5\text{-Me}_2\text{pz})_3$) were considered most completely. The study of the dependence $\mu_{\text{eff}}(T)$ showed that the spin crossover ${}^1A_1 \leftrightarrow {}^5T_2$ accompanied by thermochromism is observed in a number of compounds with $(\text{HC}(3,5\text{-Me}_2\text{pz})_3)$.^{23–28}

The complexes of iron(II) tetrafluoroborate $[\text{Fe}(\text{bnL})_2](\text{BF}_4)_2$, $[\text{Fe}(\text{tsL})_2](\text{BF}_4)_2$, and $[\text{Fe}(\text{hl})_2](\text{BF}_4)_2$ were obtained with new ligands having the substituent at one of the nitrogen atoms of the pyrazole cycle (${}^x\text{L}$).²⁹ Spin crossover was observed in complex $[\text{Fe}(\text{hl})_2](\text{BF}_4)_2$ and solvate $\text{Fe}(\text{bnL})_2(\text{BF}_4)_2 \cdot 2\text{CH}_3\text{CN}$. These are the first examples of the iron(II) compounds with substituted on the nitrogen atom $\text{HC}(\text{pz})_3$ derivatives exhibiting SCO.

Synthesis and properties of iron(II) complexes with tris(3,5-dimethylpyrazol-1-yl)methane

Tris(3,5-dimethylpyrazol-1-yl)methane ($\text{HC}(3,5\text{-Me}_2\text{Pz})_3$) was used for the synthesis of a series of iron(II) complexes of the general formula $[\text{FeL}_2]A_n$ ($A = \text{BF}_4^-$, I^- , NO_3^- , Cl^- , ClO_4^- , SO_4^{2-} ; $n = 1, 2$). The spin crossover ${}^1A_1 \leftrightarrow {}^5T_2$ was observed in the series of these compounds. For example, the sharp and complete SCO with hysteresis in the curves of the $\mu_{\text{eff}}(T)$ dependence is observed in single-crystal $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2]\text{I}_2$ ¹⁸ and in the polycrystalline phase of $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NO}_3)_2$.²⁴ The sharp but incomplete spin crossover appears in complexes $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{BF}_4)_2$ ^{6,17} and $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{ClO}_4)_2$.²³ In these compounds, spin crossover is observed only for single crystals, whereas SCO is absent in the polycrystalline phases. It should be mentioned that two polymorphous modifications were

found in $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{ClO}_4)_2$, and the SCO is observed only in one of the phases: isostructural to $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{BF}_4)_2$.

This series of compounds was extended owing to the synthesis of both homo- and heteroligand iron(II) complexes with $\text{HC}(3,5\text{-Me}_2\text{pz})_3$. The work was carried out to study the influence of the second ligand (or the third ligand in the cases where the nitrogen-containing anion coordinates to Fe^{II}) on the manifestation and characteristics of SCO.

Homoligand iron(II) complexes with tris(3,5-dimethylpyrazol-1-yl)methane

The properties of the series of the homoligand iron(II) compounds with tris(3,5-dimethylpyrazol-1-yl)methane and various outer-sphere anions were considered. The compounds were identified and characterized by the methods of elemental (CHN) analysis, X-ray diffractometry and X-ray diffraction analysis, electronic (diffuse reflectance spectra, DRS) and IR spectroscopy, and static magnetic susceptibility.

Structure and magnetic and thermodynamic properties of complex $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NO}_3)_2$

Coordination compound $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NO}_3)_2$ was isolated from an aqueous-acetone solution from the reaction of a freshly prepared aqueous solution of iron(II) nitrate and an acetone solution of $\text{HC}(3,5\text{-Me}_2\text{pz})_3$ at the molar ratio of the reactants equal to 1 : 3.²⁴ A solution of iron(II) nitrate was obtained by the exchange reaction between aqueous solutions of iron(II) sulfate and barium nitrate. The crystal structure of $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NO}_3)_2$ was determined at two temperatures: below ($T = 240$ K) and above ($T = 123$ K) the spin transition. It is revealed that at $T = 240$ K iron(II) exists in the high-spin (HS) and at $T = 123$ K in the low-spin (LS) states. The Fe–N distances are 2.14–2.18 Å ($\text{Fe}^{\text{HS}}\text{–N}$) and 1.97–1.99 Å ($\text{Fe}^{\text{LS}}\text{–N}$). The complex has a distorted octahedral structure of the coordination polyhedron with the FeN_6 mode (Fig. 2). The conclusion about the spin state of Fe^{II} can be made on the basis of the data on the Fe–N distances ($d^{\text{HS}} > 2.1$ and $d^{\text{LS}} < 2.0$ Å) or integral values of F and Σ that characterize the degree of distortion of the FeN_6 octahedron.³⁰ For the ideal octahedron, the F and Σ values are equal to zero. The more noticeable the distortion of the octahedron, the higher the F and Σ values. The typical high-spin state of Fe^{2+} is observed at $F > 3$ and $\Sigma > 60^\circ$, whereas the low-spin state is characterized by $F < 2$ and $\Sigma < 35^\circ$.³⁰ According to the X-ray diffraction data, in complex $[\text{Fe}(\text{HC}(3,5\text{-Mepz})_3)_2](\text{NO}_3)_2$ at 240 K Fe^{II} exists in the HS state.

In the high-frequency range of the IR spectrum of $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NO}_3)_2$, the absorption bands in

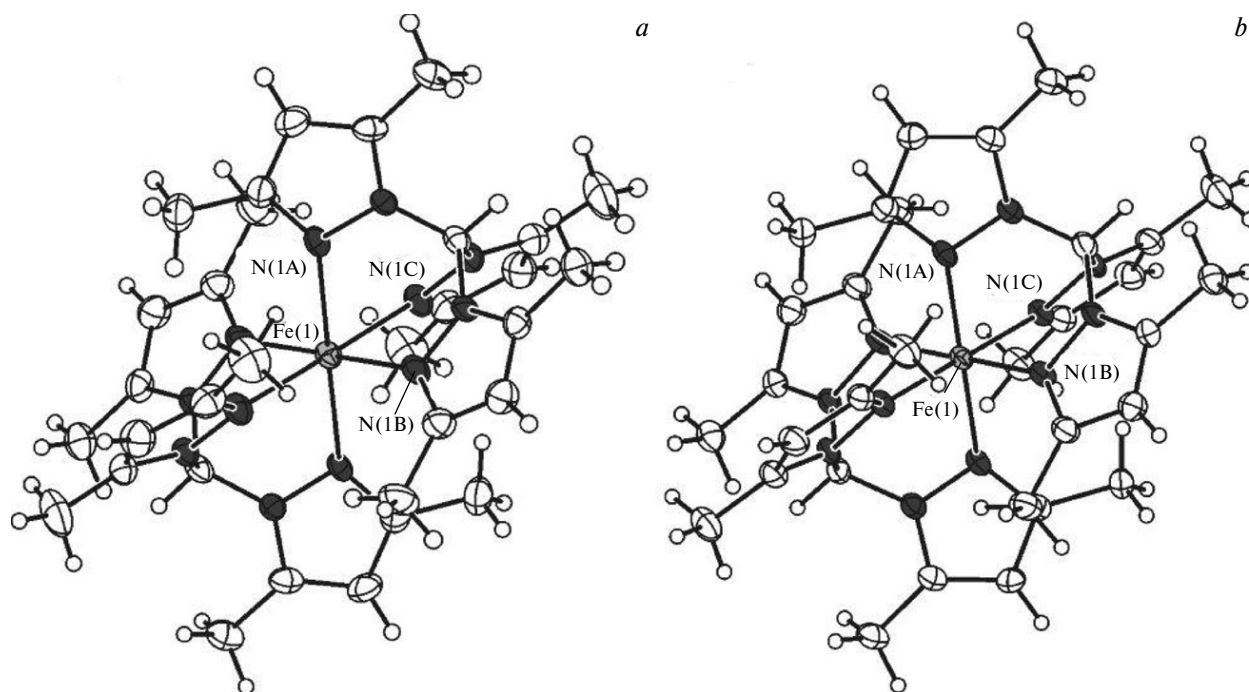


Fig. 2. Complex cation $[\text{Fe}(\text{HC}(3,5\text{-Mepz})_3)_2]^{2+}$ in the HS (a) and LS (b) forms.

a range of $2922\text{--}3120\text{ cm}^{-1}$ correspond to the $\nu(\text{CH})$ vibrations. The stretching and bending vibrations of the pyrazole ring sensitive to coordination appear at 1593 and 1561 cm^{-1} .^{17,20} The presence of the band at 1561 cm^{-1} in the spectrum of the complex indicates the coordination of pyrazole to the iron(II) ion by the N(2) atom of the pyrazole ring. The band at 1350 cm^{-1} in the spectrum of $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NO}_3)_2$ was assigned to the $\nu_3(\text{NO}_3^-)$ vibration and indicates the outer-sphere position of the nitrate ion.

The study of the magnetic properties of $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NO}_3)_2$ showed that the complex exhibited the thermally induced sharp and complete SCO $^1A_1 \leftrightarrow ^5T_2$ with the hysteresis of the $\mu_{\text{eff}}(T)$ dependence (Fig. 3). The temperatures of the forward (on heating, T_c^\uparrow) and backward (on cooling, T_c^\downarrow) transitions are 231 and 227 K , respectively. The spin crossover is accompanied by thermochromism: the change in color "colorless \leftrightarrow dark pink" is observed (Fig. 4).

The diffusion reflectance spectrum of $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NO}_3)_2$ obtained at ambient temperature contains the band at 685 nm assigned to the $d\text{--}d$ -transition $^5T_2 \rightarrow ^5E$, which indicates the high-spin form of the complex. It should be mentioned that this wavelength is typical of the HS forms of the octahedral iron(II) complexes with the FeN_6 coordination mode but is shifted to the high-frequency range compared to the spectra of the earlier studied Fe^{II} complexes with 1,2,4-triazoles.³¹

The temperature dependence of the heat capacity of complex $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NO}_3)_2$ was studied in the $100\text{--}300\text{ K}$ range by adiabatic calorimetry.²⁵ An

anomaly of the heat capacity (Fig. 5) was found in the temperature range corresponding to spin crossover. The temperatures of the forward ($T_c^\uparrow = 233\text{ K}$) and backward ($T_c^\downarrow = 223\text{ K}$) transitions, which were obtained from the thermodynamic data, are well consistent with the values detected by the method of static magnetic susceptibility.²⁴ The average deviation of the experimental heat capacity values from the smoothed curve $C_p(T)$ below 220 K and above 240 K was $\sim 3\%$. The enthalpy of the SCO was calculated from the obtained data: $\Delta_{\text{trs}}H = 5.53\text{ kJ mol}^{-1}$. The entropy of the SCO was calculated by the equation $\Delta_{\text{trs}}S = \Delta_{\text{trs}}H/T_{\text{trs}} - 5530/229.7 = 24.1\text{ J (mol K)}^{-1}$, since overheating/overcooling with the temperature hysteresis of $\approx 4.6\text{ K}$ characteristic of the phase transition of the first

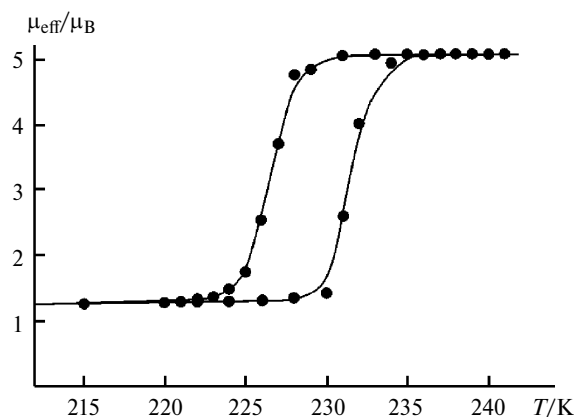


Fig. 3. Dependence $\mu_{\text{eff}}(T)$ for complex $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NO}_3)_2$.

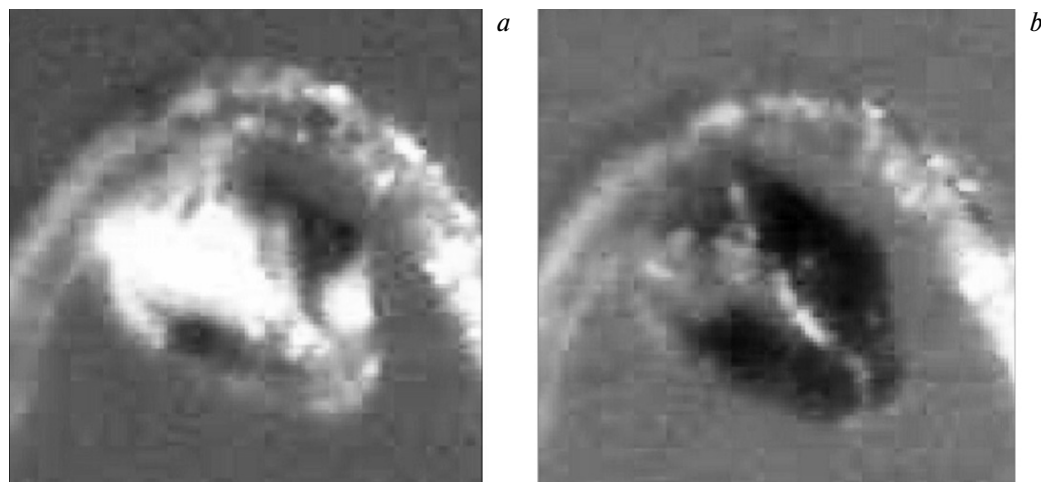


Fig. 4. Thermochromism of crystals $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NO}_3)_2$ observed on a Gemini R Ultra diffractometer at 237 K (a) and 123 K (b).

order were observed during DSC measurements. It should be mentioned that the excessive entropy is higher than the value corresponding to the electronic contribution ($13.4 \text{ J} (\text{mol K})^{-1}$). This fact and the hysteresis phenomena indicate the presence of strong cooperative interactions in the solid phase of the complex. Two SCO models were used for the quantitative estimation of cooperative effects: the Slichter–Drickamer (SD)³² and Sorai–Seki (SS)³³ models. The SCO temperatures and cooperative interaction parameters calculated using these models were as follows: $T_{1/2} = 231.8 \text{ K}$, $\Gamma = 4.38 \text{ kJ mol}^{-1}$, and $n = 96$, where $T_{1/2}$ is the temperature at which the number of domains in the HS and LS forms coincide, Γ is the cooperative interaction parameter, and n is the number of molecules of the complex in a domain. The Γ values exceeds the value of $2RT_{\text{trs}} = 3.85 \text{ kJ mol}^{-1}$, which is characteristic of com-

pounds with strong cooperative interactions. In this case, the fraction of Fe^{II} ions in the HS state and the Fe–N distance vary jumpwise. Thus, the mass of the obtained experimental data (the value of $\Delta_{\text{trs}}S$ exceeding the value of the electronic contribution, the presence of hysteresis phenomena on heating/cooling, and the value of cooperative interaction parameter Γ) allows one to conclude that the discovered anomaly of heat capacity at $T_{\text{trs}} = 229.7 \text{ K}$ in complex $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NO}_3)_2$ is the phase transition of the first kind.

Iron(II) thiocyanate complexes with tris(3,5-dimethylpyrazol-1-yl)methane

The compounds of iron(II) thiocyanate with tris(3,5-dimethylpyrazol-1-yl)methane $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NCS})_2$ and $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2][\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)(\text{NCS})_3]_2$ were synthesized.²⁷ Complex $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NCS})_2$ was isolated from an aqueous-acetone solution upon the reaction of iron(II) thiocyanate with $\text{HC}(3,5\text{-Me}_2\text{pz})_3$. An aqueous solution of $\text{Fe}(\text{NO}_3)_2$ was obtained in the first step of the synthesis by the exchange reaction between FeSO_4 and $\text{Ba}(\text{NO}_3)_2$. Iron(II) thiocyanate was obtained in a solution containing $\text{Fe}(\text{NO}_3)_2$ and KNCS in a threefold excess and was used without isolation from the solution. To avoid Fe^{II} oxidation and for weak acidification, ascorbic acid ($\text{pH} \sim 2$) was added to the solution. Single crystals of compound $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2][\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)(\text{NCS})_3]_2$ were obtained during an attempt to grow crystals of complex $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NCS})_2$. The structure of compound $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2][\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)(\text{NCS})_3]_2$ consists of discrete complex ions: centrosymmetric cation $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2]^{2+}$ (Fig. 6, a) and noncentrosymmetric anion $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)(\text{NCS})_3]^-$ (Fig. 6, b). In both cases, the Fe^{II} ion has the octahedral coordination mode.

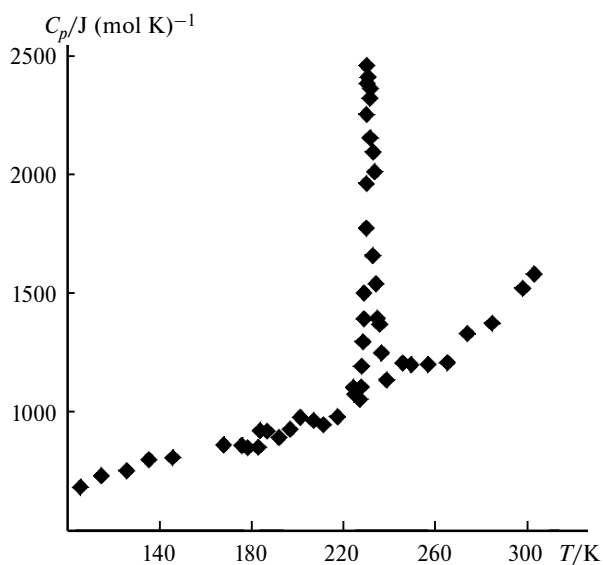


Fig. 5. Dependence $C_p(T)$ for complex $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NO}_3)_2$.

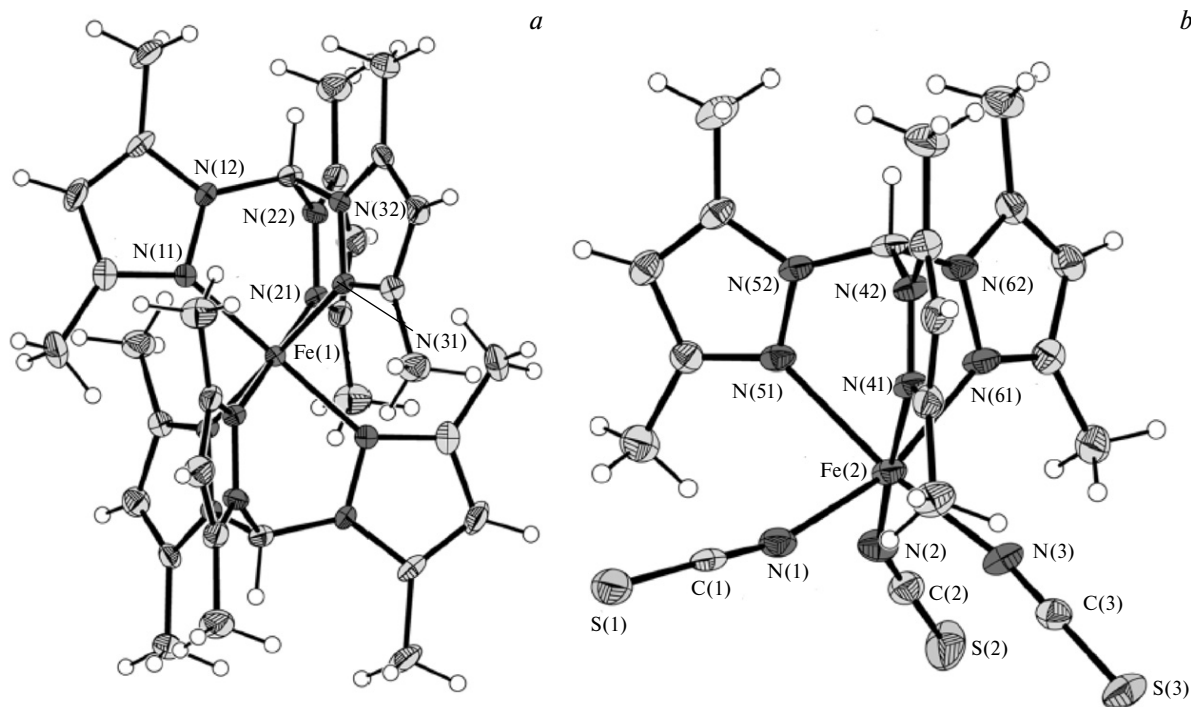


Fig. 6. Structures of the complex cation $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2]^{2+}$ (a) and anion $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)(\text{NCS})_3]^-$ (b) in compound $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2][\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)(\text{NCS})_3]_2$ (thermal ellipsoids are given with 50% probability).

The coordination mode in the cation is formed by six N atoms of two coordinated $\text{HC}(3,5\text{-Me}_2\text{pz})_3$ molecules, and that in the anion is formed by three N atoms of the $\text{HC}(3,5\text{-Me}_2\text{pz})_3$ molecule and three N atoms of three isocyanate groups. In both the cation and anion, tris(3,5-dimethylpyrazol-1-yl)methane coordinates *via* the tridentate cyclic mode to form three six-membered metallocycles—Fe—N—N—C—N—N— with two common atoms of iron and carbon of the CH group.

The bands of metal—ligand stretching vibrations appear in the low-frequency range ($600\text{--}100\text{ cm}^{-1}$) of the IR spectrum of $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NCS})_2$. The new bands in the spectrum of the complex in a range of $270\text{--}235\text{ cm}^{-1}$, which are absent from the spectrum of $\text{HC}(3,5\text{-Me}_2\text{pz})_3$ can be attributed to the $\nu(\text{Fe}\text{--}\text{N})$ vibrations, indicating the addition of the ligand to the metal. The coordination of NCS groups in 3d-metal complexes is performed most frequently by nitrogen atoms, and the $\nu(\text{CN})$ vibration band in the spectra of these complexes lies near 2050 cm^{-1} .¹³ The split $\nu(\text{CN})$ vibration band in the spectrum of $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NCS})_2$ with the center at 2057 cm^{-1} indicates the outer-sphere arrangement of the isocyanate ion.

The $\mu_{\text{eff}}(T)$ dependence for complex $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NCS})_2$ is presented in Fig 7. At 300 K the μ_{eff} value is $5.37\ \mu_{\text{B}}$ and almost does not change with temperature decreasing to 40 K. The μ_{eff} values decrease below 40 K reaching $4.04\ \mu_{\text{B}}$, which indicates exchange interactions of the antiferromagnetic character.

Iron(II) *closo*-borate complexes with tris(3,5-dimethylpyrazol-1-yl)methane

The complexes of iron(II) *closo*-borates with tris(3,5-dimethylpyrazol-1-yl)methane $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2]\text{-B}_{10}\text{H}_{10}\cdot\text{H}_2\text{O}$ and $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2]\text{B}_{12}\text{H}_{12}\cdot\text{H}_2\text{O}$ were synthesized and studied.²⁶ The compounds were prepared by the reaction of an aqueous solution of iron(II) *closo*-borate with a solution of the ligand in acetone at the ratio (Fe : $\text{HC}(3,5\text{-Me}_2\text{pz})_3$) = 1 : 4. Iron(II) *closo*-borates were synthesized by the reactions of aqueous solutions of

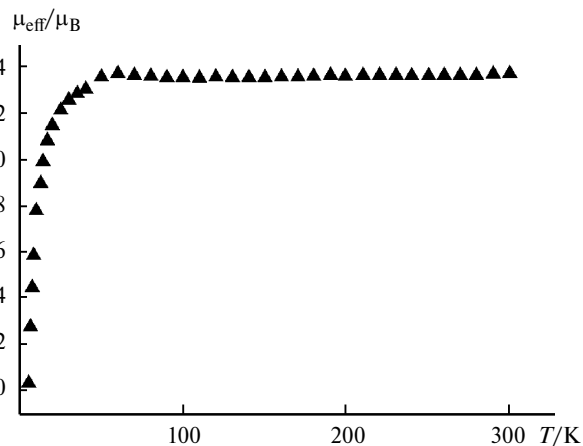


Fig. 7. Dependence $\mu_{\text{eff}}(T)$ for complex $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{NCS})_2$.

FeSO₄ with a 1.5-fold excess of K₂B₁₀H₁₀ or K₂B₁₂H₁₂. Ascorbic acid was used in all syntheses as a reducing and weakly acidifying agent. The compounds were identified and examined using the methods of elemental analysis, electronic (diffuse reflectance spectra, DRS) and IR spectroscopy, and static magnetic susceptibility.

A broad band at 3600–3300 cm⁻¹ corresponding to the ν(OH) vibration of water of crystallization is observed in the high-frequency range of the IR spectra. The bands sensitive to coordination and corresponding to stretching and bending vibrations of pyrazole rings are arranged in the spectrum of ligand HC(3,5-Me₂pz)₃ in a range of 1600–1550 cm⁻¹. The shift and change in the intensity of the absorption bands in the spectra of the complexes indicates the coordination of the nitrogen atoms of the pyrazole rings to the metal. In addition, the spectra of the complexes in this range resemble the spectra of compounds [Fe(HC(3,5-Me₂pz)₃)₂](ClO₄)₂, [Fe(HC(3,5-Me₂pz)₃)₂](NO₃)₂, and [Fe(HC(3,5-Me₂pz)₃)₂]I₂·H₂O, the structures of which were determined by X-ray diffraction analysis.^{18,23,24}

The vibration bands of the BH bonds of B₁₀H₁₀²⁻ and B₁₂H₁₂²⁻ at 2470 cm⁻¹ (ν(BH)) in the spectra of the complexes are not almost shifted compared to those in the spectra of the starting salts, indicating the outer-sphere position of these anions. The shift of the δ(BBH) vibration band at 1075 cm⁻¹ in the complexes with the low-frequency range by 5 cm⁻¹ is caused by a weak B–H···H–OH interaction.

A broad band with a maximum at 802 and 825 nm is observed in the DRS of [Fe(HC(3,5-Me₂pz)₃)₂]-B₁₀H₁₀·H₂O and [Fe(HC(3,5-Me₂pz)₃)₂]-B₁₂H₁₂·H₂O, respectively. These bands can be assigned to the ⁵T₂→⁵E transition in the weak distorted octahedral field of the ligands. The positions of these bands are typical of the spectra of the high-spin octahedral iron(II) complexes.³⁴ The values of the splitting parameters indicate that SCO in complexes [Fe(HC(3,5-Me₂pz)₃)₂]-B₁₀H₁₀·H₂O and [Fe(HC(3,5-Me₂pz)₃)₂]-B₁₂H₁₂·H₂O is theoretically possible on cooling, because Δ_{BC} ≤ 12 500 cm⁻¹.³⁵

Based on the obtained results and comparison of them with literature data, the tridentate cyclic coordination mode of the ligand and the distorted coordination structures of the coordination polyhedral in complexes [Fe(HC(3,5-Me₂pz)₃)₂]-B₁₀H₁₀·H₂O and [Fe(HC(3,5-Me₂pz)₃)₂]-B₁₂H₁₂·H₂O are concluded.

The temperature dependences of μ_{eff} for [Fe(HC(3,5-Me₂pz)₃)₂]-B₁₀H₁₀·H₂O and [Fe(HC(3,5-Me₂pz)₃)₂]-B₁₂H₁₂·H₂O are presented in Figs 8 and 9. The sharp decrease in μ_{eff} for [Fe(HC(3,5-Me₂pz)₃)₂]-B₁₀H₁₀·H₂O in the temperature range 300–80 K is caused by the SCO. The μ_{eff} value on the plateau corresponds to the transition of only 50% Fe^{II} ions from the HS to LS state.

For [Fe(HC(3,5-Me₂pz)₃)₂]-B₁₂H₁₂·H₂O, the μ_{eff} value at 325 K is equal to 4.40 μ_B and decreases with the temperature first gradually and more sharply when 30 K is

reached and achieves 2.20 μ_B at 2 K. The shape of the μ_{eff}(T) dependence for this complex indicates exchange interactions of the antiferromagnetic character between the iron(II) ions.

The range of complexes of various iron(II) salts with tris(3,5-dimethylpyrazol-1-yl)methane having the spin crossover ¹A₁↔⁵T₂ is much narrower than that for the Fe^{II} compounds with unsubstituted tris(pyrazol-1-yl)methane. It was repeatedly mentioned that the temperature and character of the SCO depend substantially on the outer-sphere anion.^{1–3,16,31} A representative series of the complexes containing outer-sphere anions of various nature, including cluster anions, was obtained for HC(pz)₃. These compounds are characterized by SCO with very high transition temperatures (depending on the anion, T_c varies from 340 to 470 K).¹⁶ It is most likely that such a strong dependence of T_c on the outer-sphere anion is explained by its influence on the strength of the ligand field. The introduction of methyl groups substantially decreases T_c.

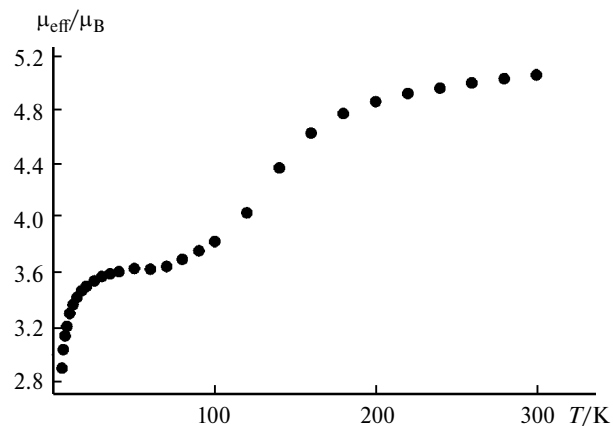


Fig. 8. Dependence μ_{eff}(T) for [Fe(HC(3,5-Me₂pz₃)₂]-B₁₀H₁₀·H₂O.

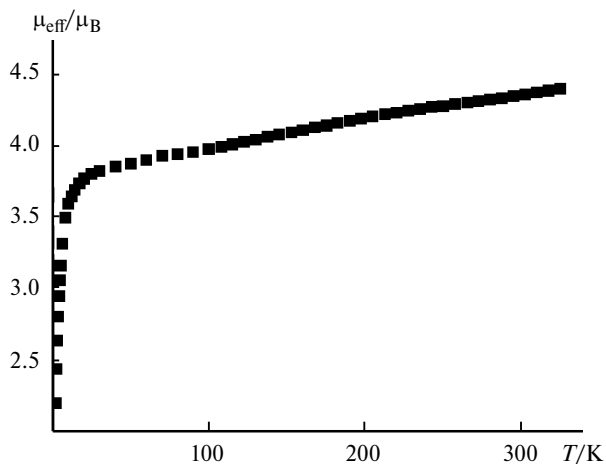


Fig. 9. Dependence μ_{eff}(T) for [Fe(HC(3,5-Me₂pz₃)₂]-B₁₂H₁₂·H₂O.

In authors' opinion,³⁶ this is related to steric hindrances for the coordination to the metal of the HC(pz)₃ derivatives bearing a substituent in position 3 of the pyrazole cycles. For the Fe^{II} compounds with tris(3,5-dimethylpyrazol-1-yl)methane, the T_c values vary in a range of 150–233 K. Among the complexes studied, the lowest SCO temperature is observed for [Fe(HC(3,5-Me₂pz)₃)₂]-B₁₀H₁₀·H₂O (150 K, gradual transition without hysteresis) and the highest temperature is observed for complex [Fe(HC(3,5-Me₂pz)₃)₂](NO₃)₂ (sharp transition with a slight hysteresis, T_c = 231 K and $T_c\downarrow$ = 227 K).

Heteroligand iron(II) complexes with tris(3,5-dimethylpyrazol-1-yl)methane

The heteroligand iron(II) complexes containing in the internal sphere other nitrogen-containing heterocycles, in particular, tetrazole (Tz), pyrazole (Pz), 3,5-dimethylpyrazole (3,5-Me₂pz), 3-amino-4-ethoxycarbonylpyrazole (Ametcpz), and phthalazine (Phz), as well as anions NCS⁻ or N(CN)₂⁻, along with tris(3,5-dimethylpyrazol-1-yl)methane were synthesized and studied.^{26,27} The influence of the second ligand (or the third ligand in the cases where the internal sphere of the complex contains the nitrogen-containing anion) on the possibility of manifestation and character of SCO is discussed.

Heteroligand compounds [Fe(HC(3,5-Me₂pz)₃)(Tz)₃](NO₃)₂ (**1**), [Fe(HC(3,5-Me₂pz)₃)(Tz)₃](ClO₄)₂ (**2**), [Fe(HC(3,5-Me₂pz)₃)(Pz)₃](NO₃)₂ (**3**), [Fe(HC(3,5-Me₂pz)₃)(Aetcpz)(NCS)₂] (**4**), [Fe(HC(3,5-Me₂pz)₃)(3,5-Me₂pz)(N(CN)₂)₂]·0.5H₂O (**5**),²⁶ and [Fe(HC(3,5-Me₂pz)₃)(Phz)(NCS)₂]·H₂O (**6**)²⁷ were synthesized. The study of the temperature dependence $\mu_{\text{eff}}(T)$ in the temperature range 2–350 K showed the spin crossover ¹A₁ ↔ ⁵T₂ accompanied by thermochromism (color change "colorless ↔ pink") in complexes **1**, **2**, and **4**. The single crystals were obtained and the molecular and crystal structures of complexes **5** and **6** were determined.

Heteroligand complexes **1–6** containing HC(3,5-Me₂pz)₃ and other nitrogen-containing ligands were isolated from aqueous-acetone solutions of the reactions of the corresponding iron(II) salts, ligand HC(3,5-Me₂pz)₃, and L, where L is tetrazole, pyrazole, 3-amino-4-ethoxycarbonylpyrazole, or phthalazine. Iron(II) nitrate and perchlorate were prepared by the exchange reaction mixing solutions of FeSO₄ and the corresponding barium salt. Iron(II) thiocyanate and dicyanamide were synthesized in a solution containing FeSO₄ and an excess of the corresponding salt (KSCN or NaN(CN)₂) and used without isolation from the solution. Ascorbic acid was applied as a reducing and weakly acidifying agent to prevent the oxidation of iron(II). The single crystals of compound **5** suitable for X-ray diffraction analysis were obtained from the mother liquor after the solid phase was separated by slow crystallization. The crystals of complex **6** were grown in a U-like tube by the reaction of an aqueous solution of

Fe(NCS)₂ and an acetone solution of a mixture of ligands HC(3,5-Me₂pz)₃ and Phz.

According to the X-ray diffraction data for compound **5**, the HC(3,5-Me₂pz)₃ ligand coordinates *via* the tridentate cyclic mode to form three six-membered metallocycles Fe–N–N–C–N–N with two common atoms: iron and carbon of the CH group (Fig. 10). The coordination polyhedron of the iron(II) ion is supplemented to a distorted octahedron by the nitrogen atom of ligand 3,5-Me₂pz and two nitrogen atoms of the N(CN)₂⁻ ions coordinated *via* the monodentate mode. The Fe–N bonds have the lengths characteristic of the high-spin Fe²⁺ cation. Note that dicyanamide can coordinate to the metal *via* both the monodentate and bidentate bridging mode. The synthesis of the binuclear heteroligand iron(II) complex with tris(pyrazol-1-yl)methane and N(CN)₂⁻, in which this anion perform a dual function, is described.³⁷ In this complex, the distorted octahedral polyhedron is formed due to HC(pz)₃, which, as HC(3,5-Me₂pz)₃, coordinates *via* the tridentate cyclic mode by three nitrogen atoms: of monodentate N(CN)₂⁻ and two bidentate bridging N(CN)₂⁻ linking the iron(II) ions into the binuclear complex. In our case, the dicyanamide ions coordinate *via* the monodentate mode.

In addition to the elemental analysis results, the formation of individual compound **5** is also confirmed by the data of X-ray diffractometry of polycrystals. The diffraction pattern of the polycrystalline sample is consistent with the theoretical one calculated for compound **5** by the X-ray diffraction data taking into account a slight shift of the lines toward high values of 2θ angles. The shift is caused by a decrease in the unit cell parameters with the temperature change from 100 K (X-ray diffraction analysis) to ambient temperature. In compound **5**, 3,5-dimethylpyrazole is formed during the synthesis of the complex from the iron(II) salt and HC(3,5-Me₂pz)₃ molecules. It is known that the elimination of amines, including a pyrazole molecule, is preceded by the protonation of the substrate. For example, the rearrangement of the protonated form of bis(pyrazol-1-yl)methane to bis(pyrazol-4-yl)methane including the elimination of the neutral pyrazole molecule is described.³⁸ A similar elimination of the 3,5-Me₂pz molecule during the thermal rearrangement of the *cis*-(3,5-dimethylpyrazol-4-yl)methane salt was found.³⁹ It can be assumed that this process is favored by the presence of ascorbic acid in the reaction mixture resulting in a fairly low pH ~ 2. It is most likely that the elimination of the 3,5-Me₂pz molecule is preceded by the protonation of the nitrogen atom of the pyrazole cycle in the ligand. The concurrent shift of electrons (formation of some bonds and cleavage of other bonds) occurs in the formed quaternary ammonium salt due to which the neutral 3,5-Me₂pz molecule (well leaving group) is detached. The remained carbocation is captured by either the ascorbic acid residue or any anion from the reaction mixture (Scheme 1).

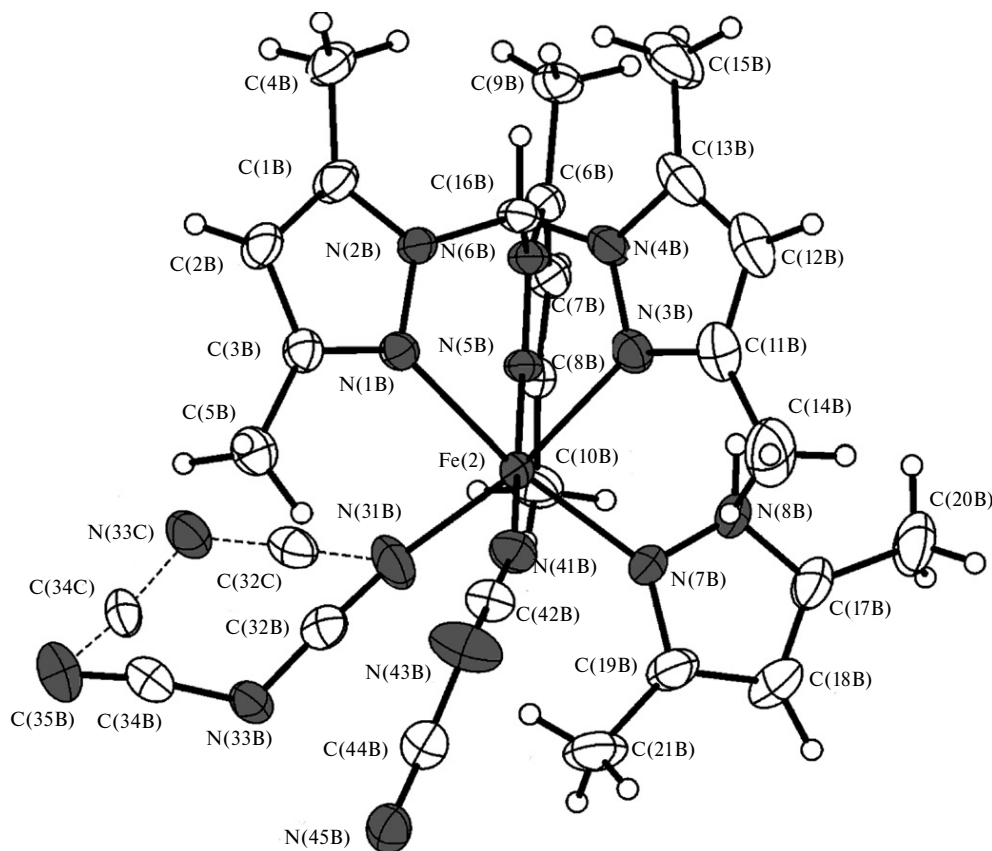


Fig. 10. Molecular structure of complex 5 (atomic shift ellipsoids of 50% probability).

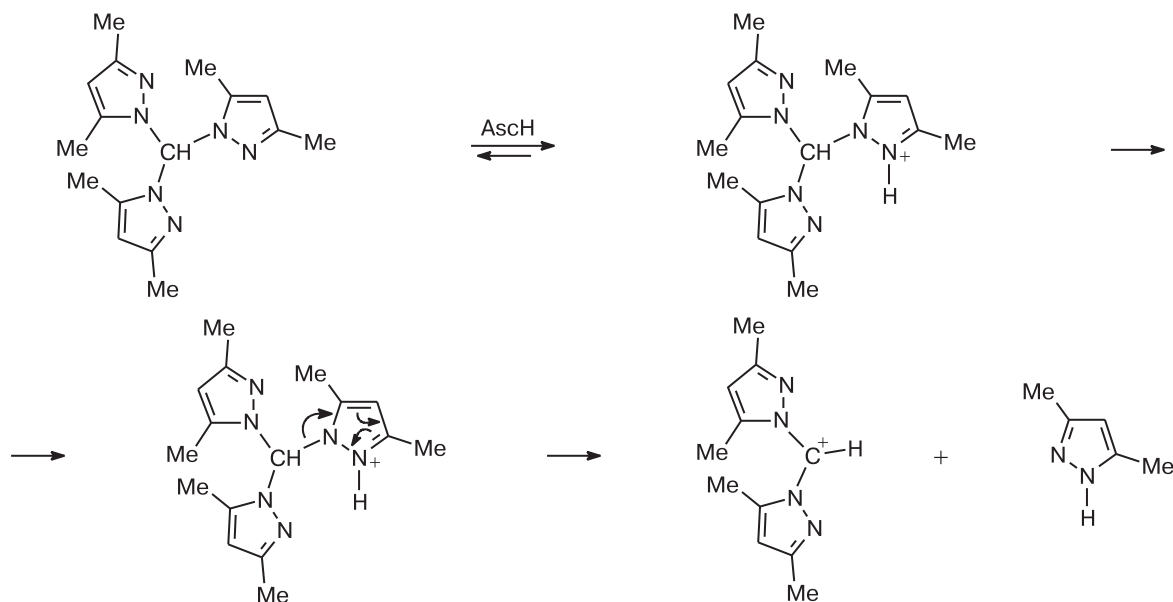
Since this process is observed only for the synthesis of compound **5**, it can be assumed that the presence of the $\text{N}(\text{CN})_2^-$ anion with pronounced donor properties in the system plays a certain role. Owing to this, the coordination mode FeN_3NN_2 is formed in compound **5** due to three nitrogen atoms of one $\text{HC}(3,5\text{-Me}_2\text{pz})_3$ molecule, one nitrogen atom of $3,5\text{-Me}_2\text{pz}$, and two nitrogen atoms of two dicyanamide ions.

The bands of stretching vibrations of OH groups are observed at $3590\text{--}3302\text{ cm}^{-1}$ in the high-frequency range of the IR spectra of complexes **2**, **4**, and **5** containing water molecules. The sensitive to coordination bands of stretching and bending vibrations of the ring are manifested in a range of $1590\text{--}1500\text{ cm}^{-1}$. The spectrum of $\text{HC}(3,5\text{-Me}_2\text{pz})_3$ contains the intense band of R_{ring} at 1561 cm^{-1} , which is shifted by $4\text{--}6\text{ cm}^{-1}$ to the high-frequency range in the spectra of complexes **1**–**5**. This indicates the coordination of the nitrogen atoms of the pyrazole rings to Fe^{II} . The bands of R_{ring} are also observed in a range of $1589\text{--}1501\text{ cm}^{-1}$ in the spectra of the ligands, *viz.*, tetrazole, pyrazole, $3,5\text{-dimethylpyrazole}$, $3\text{-amino-4-ethoxycarbonylpyrazole}$, and phthalazine. The change in the number and position of these bands on going to the spectra of the complexes indicates the coordination of the above listed ligands to Fe^{II} . The change in the spectrum of compound

5 in a range of $2287\text{--}2169\text{ cm}^{-1}$ compared to the spectrum of $\text{N}(\text{CN})_2^-$ is associated with the coordination of this anion to Fe^{II} , which is confirmed by the X-ray diffraction data for complex **5**. The position of the $\nu(\text{NCS}^-)$ vibration band also suggests the coordination of the thiocyanate ion to Fe^{II} .⁴⁰ On the contrary, the positions of the $\nu_3(\text{NO}_3^-)$ bands, as well as $\nu_3(\text{ClO}_4^-)$ and $\nu_4(\text{ClO}_4^-)$ bands, in the spectra of complexes **1**–**3** indicates the outer-sphere position of these anions. New bands characteristic of the $\nu(\text{Fe}\text{--}\text{N}_{\text{ring}})$ vibration were found in the low-frequency range of the spectra of complexes **1**–**5** in a range of $270\text{--}220\text{ cm}^{-1}$.

Figures 11 and 12 show the curves of the $\mu_{\text{eff}}(T)$ dependence of complexes **1** and **2**. It is seen that gradual and incomplete crossover is observed in these complexes. The high magnetic moment at low temperatures indicates a significant residual fraction of the high-spin forms in complexes **1** and **2**. The estimation of the latter showed that only 50% iron(II) ions transform into the high-spin form. This can be due to the initial presence of complexes of two types in the crystal, of which only one type undergoes SCO. Another possible mechanism is related to a decrease in the symmetry of the crystal during SCO, resulting in the appearance of two crystallographically independent molecules of the complex in the HS and LS

Scheme 1



AscH is ascorbic acid.

forms. This situation was observed^{6,17} for complex $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_2)(\text{BF}_4)_2]$ and for the single crystals of isostructural $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_2)(\text{ClO}_4)_2]$.²³ The μ_{eff} value of complex **3** remains almost unchanged with a change in temperature. This indicates that no spin transition occurs upon the introduction of pyrazole (ligand of a weaker field compared to $\text{HC}(3,5\text{-Me}_2\text{pz})_3$ and tetrazole) into the coordination sphere of the complex.

The μ_{eff} value of complex **4** equal to $5.37 \mu_{\text{B}}$ at 300 K decreases smoothly with a temperature decrease and reaches a plateau at $\sim 4.7 \mu_{\text{B}}$ in the temperature 190–45 K

(see Fig. 13). Below 45 K, μ_{eff} decreases to $3.69 \mu_{\text{B}}$ at 5 K. The high-temperature value of μ_{eff} is higher than the theoretical spin-only value of $4.90 \mu_{\text{B}}$ for one paramagnetic center with the spin $S = 2$ at the g -factor equal to 2. It is likely that the decrease in μ_{eff} in the temperature range from 300 to 200 K is caused by SCO. The decrease in μ_{eff} to $\sim 4.7 \mu_{\text{B}}$ corresponds to the transformation of only $\sim 24\%$ Fe^{II} ions from $\text{Fe}^{\text{II}}_{\text{HS}} (S = 2)$ into $\text{Fe}^{\text{II}}_{\text{LS}} (S = 0)$. The exchange interactions between spins of the Fe^{II} ions are weak and appear at the temperatures below 45 K. The study of the $\mu_{\text{eff}}(T)$ dependences for complexes **5** and **6** showed that they have no SCO, whereas exchange interactions of the antiferromagnetic character are observed in these complexes at the temperatures below 50 K.

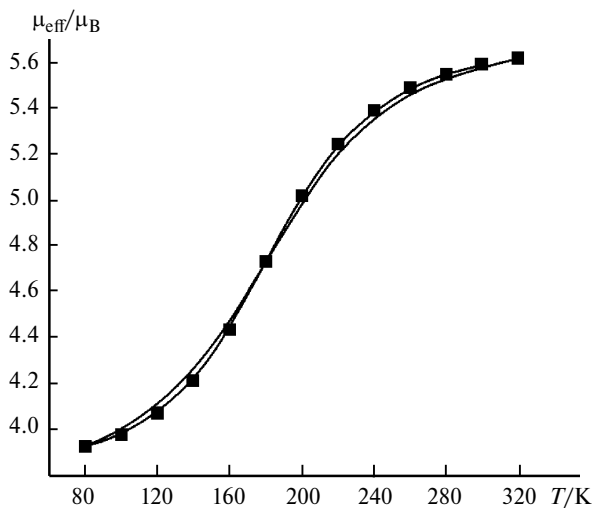


Fig. 11. Dependence $\mu_{\text{eff}}(T)$ for complex $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)(\text{Tz})_3](\text{NO}_3)_2$.

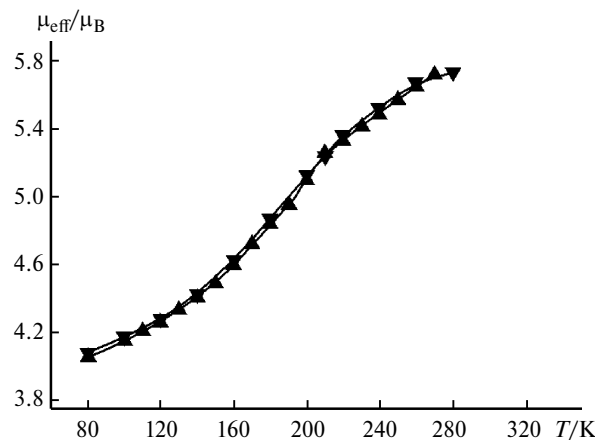


Fig. 12. Dependence $\mu_{\text{eff}}(T)$ for complex $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)(\text{Tz})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$.

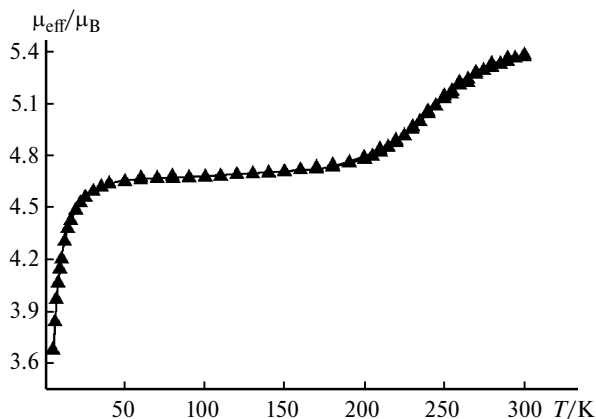


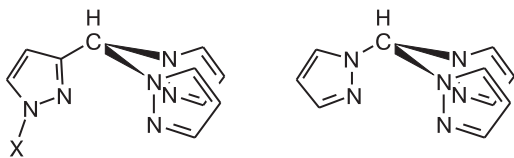
Fig. 13. Dependence $\mu_{\text{eff}}(T)$ for complex $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)(\text{Accpz})](\text{NCS})_2$.

It is mentioned²³ that no SCO is observed in the polycrystalline phase of the iron(II) perchlorate complex $\text{HC}(3,5\text{-Me}_2\text{pz})_3[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)_2](\text{ClO}_4)_2$, whereas the spin crossover ($T_c = 200$ K) is observed in the synthesized by us heteroligand complex $[\text{Fe}(\text{HC}(3,5\text{-Me}_2\text{pz})_3)(\text{tz})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. Thus, the introduction of tetrazole into the coordination sphere of the iron(II) ion resulted in the spin crossover in the polycrystalline phase.

Iron(II) tetrafluoroborate complexes with *N*-substituted tris(pyrazol-1-yl)methane derivatives

The authors developed²⁹ procedures for the synthesis of three new *N*-substituted derivatives of tris(pyrazol-1-yl)methane (^xL): $x = \text{H}$, $\text{CH}_2\text{C}_6\text{H}_5$ (Bn) and $p\text{-SO}_3\text{C}_6\text{H}_4\text{CH}_3$ (Ts). The ligands obtained represent the first examples of the class of *N*-substituted $\text{HC}(\text{pz})_3$ and were used for the synthesis and study of the structures and magnetic properties of the iron(II) tetrafluoroborate complexes. The formulas of *N*-substituted $\text{HC}(\text{pz})_3$ and standard tris(pyrazole-1-yl)methane are presented below.

Complexes $[\text{Fe}(\text{^xL})_2](\text{BF}_4)_2$ ($x = \text{Bn}$, Ts , H) were isolated from THF or acetone in the reaction of $[\text{Fe}(\text{H}_2\text{O})_6](\text{BF}_4)_2$ with ^xL at the ratio $\text{Fe} : \text{^xL} = 1 : 2$. The formed precipitates $[\text{Fe}(\text{BnL})_2](\text{BF}_4)_2$, $[\text{Fe}(\text{TsL})_2](\text{BF}_4)_2$, and $[\text{Fe}(\text{HL})_2](\text{BF}_4)_2$ were dried *in vacuo* to remove the solvents. The polycrystalline phases of complexes $[\text{Fe}(\text{BnL})_2](\text{BF}_4)_2$ and $[\text{Fe}(\text{TsL})_2](\text{BF}_4)_2$ are colorless and, according to the data of magnetochemical measurements, paramag-



N-substituted and standard tris(pyrazol-1-yl)methanes

netic. At ambient and lower temperatures, the solid phase of $[\text{Fe}(\text{HL})_2](\text{BF}_4)_2$ exhibits a pink color characteristic of the LS form of the Fe^{II} complexes having the FeN_6 coordination mode. The complex becomes colorless on heating to temperatures higher than 150 °C. The color transition is reversible: on cooling the complex again gains a pink color. The single crystals of this complex were obtained on the slow evaporation of an aqueous solution, and its structure was determined at 100 K. It follows from the X-ray diffraction data that *N*-substituted tris(pyrazol-1-yl)methanes coordinate *via* the same mode as standard derivatives: by three nitrogen atoms of the pyrazole cycles, so that two ligand molecules form a weakly distorted octahedral polyhedron.

The magnetochemical study in a temperature range of $100\text{--}400$ K showed the gradual SCO in $[\text{Fe}(\text{HL})_2](\text{BF}_4)_2$. The complex transforms completely into the LS form at the temperature about 200 K, and the incompleteness of the transition into the HS form at 400 K (curve of the $\mu_{\text{eff}}(T)$ dependence does not reach a plateau) is explained by instrumental restrictions. The transition temperature $T_{1/2}$ (50% HS form) was estimated: ≈ 360 K.

The authors isolated the crystals of disolvates $[\text{Fe}(\text{BnL})_2](\text{BF}_4)_2 \cdot 2\text{CH}_3\text{CN}$ and $[\text{Fe}(\text{TsL})_2](\text{BF}_4)_2 \cdot 2\text{CH}_3\text{CN}$ suitable for X-ray diffraction analysis from acetonitrile solutions of $[\text{Fe}(\text{BnL})_2](\text{BF}_4)_2$ and $[\text{Fe}(\text{TsL})_2](\text{BF}_4)_2$. On the whole, at 100 K the structures are similar to that for complex $[\text{Fe}(\text{HL})_2](\text{BF}_4)_2$. The average Fe—N distance in $[\text{Fe}(\text{BnL})_2](\text{BF}_4)_2 \cdot 2\text{CH}_3\text{CN}$ is $1.985(1)$ Å, which corresponds to the LS form of the complex. By contrast, the average Fe—N distance in $[\text{Fe}(\text{TsL})_2](\text{BF}_4)_2 \cdot 2\text{CH}_3\text{CN}$ at 100 K is $2.214(1)$ Å, indicating the high-spin form of this complex.

The magnetochemical study in a temperature range of $2\text{--}300$ K showed the SCO of the solvate $[\text{Fe}(\text{BnL})_2](\text{BF}_4)_2 \cdot 2\text{CH}_3\text{CN}$, unlike the initial complex. In the temperature range from 300 to 175 K, μ_{eff} is 5.1 μ_{B} . At the temperatures below 175 K, μ_{eff} gradually decreases to 1.7 μ_{B} (at 60 K). The question about the solvent effect on the temperature and character of SCO was repeatedly discussed.^{41–44} In particular, it was mentioned⁴³ that the hydration of the complex can result in both an increase and decrease in the spin transition temperature. There is an example of the formation of solvate of the starting complex resulting in the manifestation of the SCO, which was absent from the starting compound.

To conclude, the results of studying the magnetically active coordination compounds of iron(II) with the tris(pyrazol-1-yl)methane derivatives, which were published during the recent five years, are reviewed. In particular, the works considered concern the synthesis and investigation of the homo- and heteroligand iron(II) complexes with tris(3,5-dimethylpyrazol-1-yl)methane and various anions (both coordinated to the metal and outer-sphere). The study of the temperature dependence $\mu_{\text{eff}}(T)$ showed the spin crossover ${}^1A_1 \leftrightarrow {}^5T_2$ accompanied by ther-

mochromism in the series of the synthesized complexes. The results of the work on the synthesis of three new ligands of the "scorpionate" class, *N*-substituent derivatives of HC(pz)₃, ^xL, where x = H, CH₂C₆H₅ (Bn), and *p*-SO₃C₆H₄CH₃ (Ts), and the related iron(II) tetrafluoroborate complexes, are presented. The magnetochemical study revealed spin crossover in complexes [Fe(^HL)₂](BF₄)₂ and [Fe(^{Bn}L)₂](BF₄)₂ · 2CH₃CN. These compounds are characterized by thermochromism (color change "pink ↔ colorless").

This work was financially supported by the Russian Foundation for Basic Research (Project No. 16-53-00020 Bel_a).

References

1. *Spin Crossover in Transition Metal Compounds I–III*, Eds P. Gutlich, H. Goodwin, Springer, 2004, 233–235.
2. M. A. Halcrow, *Spin-Crossover Materials Properties and Applications*, Wiley&Sons, 2013, 562 p.
3. E. Konig, G. Ritter, S. K. Kulshreshtha, *Chem. Rev.*, 1985, **85**, 219.
4. A. Bousseksou, G. Molnár, L. Salmon, W. Nicolazzi, *Chem. Soc. Rev.*, 2011, **40**, 3313.
5. G. Aromi, L. A. Barrios, O. Roubeau, P. Gamez, *Coord. Chem. Rev.*, 2011, **255**, 485.
6. G. J. Long, F. Grandjean, D. L. Reger, *Top. Curr. Chem.*, 2004, **233**, 91.
7. M. Shatruk, H. Phan, B. A. Chrisostomo, A. Suleimenova, *Coord. Chem. Rev.*, 2015, **289–290**, 62.
8. S. Brooker, *Chem. Soc. Rev.*, 2015, **44**, 2880.
9. P. Gamez, J. S. Costa, M. Quesada, G. Aromi, *Dalton Trans.*, 2009, 7845.
10. O. Kahn, C. J. Martinez, *Science*, 1998, **279**, 44.
11. M. Matsuda, H. Isozaki, H. Tajima, *Chem. Lett.*, 2008, **37**, No 3, 374.
12. K. Sone, Y. Fukuda, *Inorganic Thermochromism*, Springer, Berlin, 1987.
13. R. N. Muller, V. Elst, S. Laurent, *J. Am. Chem. Soc.*, 2003, **125**, 8405.
14. J.-F. Letard, N. Daro, C. Aymonier, F. Cansell, S. Saint-Martin, EP Pat. 2391631, 2011.
15. A. Bousseksou, C. Vieu, J.-F. Letard, P. Demont, J.-P. Tuchagues, L. Malaquin, J. Menegotto, L. Salmon, EU Pat. 1430552, 2004.
16. L. G. Lavrenova, O. G. Shakirova, *Eur. J. Inorg. Chem.*, 2013, 670.
17. D. L. Reger, C. A. Little, A. L. Rheingold, M. Lam, L. M. Liable-Sands, B. Rhagitan, T. Concolino, A. Mohan, G. J. Long, V. Briois, *Inorg. Chem.*, 2001, **40**, 1508.
18. D. L. Reger, C. A. Little, M. D. Smith, A. L. Rheingold, K.-C. Lam, T. L. Concolino, G. J. Long, R. P. Hermann, F. Grandjean, *Eur. J. Inorg. Chem.*, 2002, 1190.
19. H. Paulsen, L. Duelund, A. Zimmermann, F. Averseng, M. Gerdan, H. Winkler, H. Toftlund, A. X. Trautwein, *Monat. Chem.*, 2003, **134**, 295.
20. O. G. Shakirova, L. G. Lavrenova, N. V. Kuratieva, D. Yu. Naumov, V. A. Daletskii, L. A. Sheludyakova, V. A. Logvinenko, S. F. Vasilevskii, *Russ. J. Coord. Chem.*, 2010, **36**, 275.
21. O. G. Shakirova, L. G. Lavrenova, V. A. Daletskii, E. A. Shusharina, T. P. Griaznova, S. A. Katsyuba, V. V. Syakaev, V. V. Skripacheva, A. R. Mustafina, S. E. Soloveva, *Inorg. Chim. Acta*, 2010, **363**, 4059.
22. O. G. Shakirova, V. A. Daletskii, L. G. Lavrenova, S. V. Trubina, S. B. Erenburg, K. Yu. Zhizhin, N. T. Kuznetsov, *Russ. J. Inorg. Chem.*, 2013, **58**, 656.
23. L. G. Lavrenova, A. D. Strelakova, A. V. Virovets, D. A. Piryazev, V. A. Daletskii, L. A. Sheludyakova, T. F. Michailovskaya, S. F. Vasilevskii, *Russ. J. Coord. Chem.*, 2012, **38**, 507.
24. L. G. Lavrenova, A. V. Virovets, E. V. Peresyphkina, A. D. Strelakova, D. A. Piryazev, V. A. Daletskii, L. A. Sheludyakova, S. F. Vasilevskii, *Inorg. Chim. Acta*, 2012, **382**, 1.
25. G. A. Berezovskii, V. A. Daletskii, D. P. Pishchur, A. D. Strelakova, L. G. Lavrenova, *Russ. J. Phys. Chem.*, 2013, **87**, 1272.
26. O. G. Shakirova, L. G. Lavrenova, A. S. Bogomyakov, K. Yu. Zhizhin, N. T. Kuznetsov, *Russ. J. Inorg. Chem.*, 2015, **60**, 786.
27. L. G. Lavrenova, A. D. Strelakova, A. I. Smolentsev, D. Yu. Naumov, A. S. Bogomyakov, L. A. Sheludyakova, S. F. Vasilevskii, *Russ. J. Coord. Chem.*, 2016, **42**, 675.
28. L. G. Lavrenova, A. D. Strelakova, A. S. Bogomyakov, E. V. Korotaev, A. V. Virovets, D. A. Piryazev, L. A. Sheludyakova, S. F. Vasilevskii, *Russ. J. Coord. Chem.*, 2015, **41**, 189.
29. J. R. Gardinier, A. R. Treleven, K. J. Meise, S. V. Lindeman, *Dalton Trans.*, 2016, **45**, 12639.
30. B. Moubaraki, B. A. Leita, G. J. Halder, S. R. Batten, P. Jensen, J. P. Smith, J. D. Cashion, C. J. Kepert, J. F. Letard, K. S. Murray, *Dalton Trans.*, 2007, **39**, 44136.
31. L. G. Lavrenova, S. V. Larionov, *Russ. J. Coord. Chem.*, 1998, **24**, 379.
32. C. P. Slichter, H. G. Drickamer, *J. Chem. Phys.*, 1972, **56**, 2142.
33. M. Sorai, S. Seki, *J. Phys. Chem. Solids*, 1974, **35**, 555.
34. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1984.
35. A. Hauser, *Adv. Polym. Sci. (Top. Curr. Chem.)*, 2004, **233**, 49.
36. M. A. Goodman, A. Y. Nazarenko, J. Barbara, B. J. Casavant, Z. Li, W. W. Brennessel, M. J. DeMarco, G. Long, M. S. Goodman, *Inorg. Chem.*, 2012, **51**, 1084.
37. S. R. Batten, J. Bjernemose, P. Jensen, B. A. Leita, K. S. Murray, B. Moubaraki, J. P. Smith, H. Toftlund, *Dalton Trans.*, 2004, 3370.
38. N. J. Wheate, J. A. Broomhead, J. G. Collins, A. I. Day, *Aust. J. Chem.*, 2001, **54**, 141.
39. A. S. Potapov, Doct. Sci. (Chem.) Thesis, Tomsk, 2012 (in Russian).
40. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1977.
41. V. V. Zelentsov, *Russ. J. Coord. Chem.*, 1992, **18**, 787.
42. V. N. Ikorskii, *Dokl. Phys. Chem.*, 2001, **377**, 77.
43. L. G. Lavrenova, E. V. Kirillova, V. N. Ikorskii, Yu. G. Shvedenkov, V. A. Varnek, L. A. Sheludyakova, S. V. Larionov, *Russ. J. Coord. Chem.*, 2001, **27**, 46.
44. M. B. Bushuev, D. P. Pishchur, I. V. Korolkov, K. A. Vinogradova, *Phys. Chem. Chem. Phys.*, 2017, **19**, 4056.

Received December 5, 2017;
in revised form February 21, 2018;
accepted May 5, 2018