

SPIN-CROSSOVER IN COORDINATION COMPOUNDS OF IRON(II) WITH tris(PYRAZOL-1-YL)METHANE AND CLUSTER ANIONS

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Synthesis procedures for new coordination compounds of iron(II) with tris(pyrazol-1-yl)methane (HC(pz)₃), containing cluster anions in the outer sphere, of the composition [Fe{HC(pz)₃}₂][Mo₆Cl₁₄]·2H₂O (**I**), [Fe{HC(pz)₃}₂][Mo₆Br₁₄]·H₂O (**II**), and [Fe{HC(pz)₃}₂][Re₆S₈(CN)₆]·2H₂O (**III**) are developed. The compounds are studied by static magnetic susceptibility, electronic, IR, and Mössbauer spectroscopic methods. The magnetochemical study shows that in the polycrystalline phases of all compounds the spin-crossover $^1A_1 \leftrightarrow ^5T_2$ is observed which is accompanied by thermochromism.

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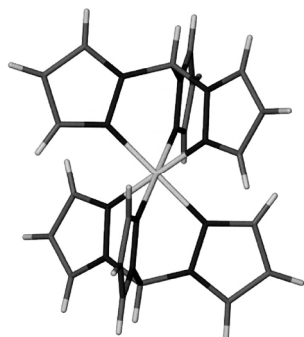
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Spin-crossover (SCO) in 3d metal coordination compounds with the d^4 – d^7 electron configuration attracts constant interest of researchers. This theme was considered in monographs [1, 2] and a number of reviews [3–5]. SCO (spin transition) is observed in octahedral or pseudo-octahedral complexes with ligands having a certain field force. Spin multiplicity changes under the effect of the temperature, pressure, or light irradiation with a certain wavelength. These complexes are of interest for practical application, in particular, as materials for displays and storage systems [6–11]. Complexes of iron(II) with polynitrogen-containing ligands, in which SCO is accompanied by thermochromism, are of special interest because this phenomenon itself has practical application. These compounds can be used as temperature indicators, thermochromic labels, temperature-sensitive materials in magnetic resonance tomography [12, 13] and so on.

Tris(pyrazol-1-yl)methanes are the ligand class promising for the synthesis of complexes having SCO [5, 14–17]. It is shown that tris(pyrazol-1-yl)methane is coordinated to metal ions by three N(2) atoms of three pyrazole rings in the tridentate chelating mode [16] (Scheme 1).

Such a ligand coordination results in the formation of an octahedral polyhedron with the FeN₆ coordination core. For iron complexes this is a prerequisite for SCO. SCO in iron(II) complexes with tris(pyrazol-1-yl)methane is, as a rule, observed at high temperatures in the range of 310–470 K [5]. In a number of cases, this hinders the achievement of the plateau of the $\mu_{\text{eff}}(T)$ dependence. The SCO temperature (T_c) is known to significantly depend on the composition of a compound, the

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Scheme 1.

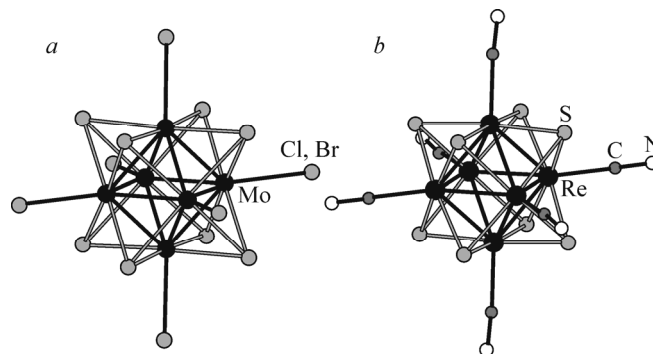


Fig. 1. Structures of cluster anion complexes $[\text{Mo}_6\text{X}_{14}]^{2-}$ (a) and $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$ (b).

nature of a ligand and an outer-sphere anion, the occurrence and number of crystallization water molecules. We have obtained a representative series of iron(II) complexes with tris(pyrazol-1-yl)methane, including a number of closo-borates and carboranes as outer-sphere anions [5, 18-20]. Most of them have SCO that is accompanied by thermochromism: a magenta (pink) \leftrightarrow white color change. It seemed reasonable to continue the study of iron(II) compounds with $\text{HC}(\text{Pz})_3$, to extend the group of Fe(II) complexes synthesized with this ligand by introducing new anions, in particular, cluster $[\text{Mo}_6\text{Cl}_{14}]^{2-}$, $[\text{Mo}_6\text{Br}_{14}]^{2-}$, and $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$ anions into the outer sphere.

These anions are typical representatives of the family of cluster complexes $[\{\text{M}_6(\mu_3\text{-X})_8\}\text{L}_6]$ with the octahedral cluster core $\{\text{M}_6(\mu_3\text{-X})_8\}^{n+}$, where $\text{M} = \text{Mo}$, $\text{X} = \text{Cl}$, Br , $n = 4+$ or $\text{M} = \text{Re}$, $\text{X} = \text{S}$, $n = 2+$. These complexes are an octahedron of six metal atoms inscribed into a cube of eight X atoms so that each X atom is above the triangular faces of the M_6 octahedron. Each metal atom is additionally coordinated by the terminal ligand L (Cl or Br atom for $\text{M} = \text{Mo}$) or the CN ligand for $\text{M} = \text{Re}$ (Fig. 1).

EXPERIMENTAL

For the synthesis we used $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (chemical pure grade) recrystallized from an acidified aqueous solution and ascorbic acid (pharmaceutical grade). tris(Pyrazol-1-yl)methane was synthesized by the procedure given in [16]. $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Cl}_{14}]$, $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Br}_{14}]$, $\text{K}_4[\text{Re}_6\text{S}_8(\text{CN})_6]$ were obtained by the procedures given in [21-23].

Synthesis of $[\text{Fe}(\text{HC}(\text{pz})_3)_2][\text{Mo}_6\text{Cl}_{14}] \cdot 2\text{H}_2\text{O}$ (I) and $[\text{Fe}(\text{HC}(\text{pz})_3)_2][\text{Mo}_6\text{Br}_{14}] \cdot \text{H}_2\text{O}$ (II). A weighed portion of 28.7 mg, 0.1 mmol of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ salt was dissolved in 0.5 ml of distilled water acidified with 0.01 g of ascorbic acid. To the obtained solution a solution of 42.8 mg, 0.2 mmol of $\text{HC}(\text{pz})_3$ in 0.5 ml of water was slowly added with stirring, and then a solution of 0.1 mmol, 155.7 mg of $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Cl}_{14}]$ or 217.9 mg of $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Br}_{14}]$ in 2 ml of acetone. Immediately after the mixing in the dark magenta solution a light yellow (I) or yellow (II) precipitate formed which was kept in the solution for half an hour with magnetic stirring. The precipitates were filtered off, washed three times with 1 ml of acetone, and dried in the air.

For **I** found, %: C 15.2, H 1.5, N 10.1. For $\text{C}_{20}\text{H}_{24}\text{Cl}_{14}\text{FeMo}_6\text{N}_{12}\text{O}_2$ calculated, %: C 15.1, H 1.5, N 10.6.

For **II** found, %: C 11.2, H 1.1, N 7.3. For $\text{C}_{20}\text{H}_{22}\text{Br}_{14}\text{FeMo}_6\text{N}_{12}\text{O}$ calculated, %: C 10.9, H 1.0, N 7.7.

Synthesis of $[\text{Fe}(\text{HC}(\text{pz})_3)_2]_2[\text{Re}_6\text{S}_8(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ (III). A weighed portion of 0.14 g, 0.5 mmol of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 2 ml of distilled water acidified with 0.05 g of ascorbic acid. To the obtained solution a solution of 0.22 g, 1 mmol of $\text{HC}(\text{pz})_3$ in 3 ml of water was slowly added; the solution became magenta due to the formation of the $[\text{Fe}(\text{HC}(\text{pz})_3)_2]\text{SO}_4$ complex. To this solution 0.42 g, 0.25 mmol of $\text{K}_4[\text{Re}_6\text{S}_8(\text{CN})_6]$ in 10 ml of water was added. Immediately after the mixing in the dark magenta solution a rose-beige precipitate formed which was kept in the solution for half an hour with magnetic stirring. The precipitate was filtered off, washed several times with water and hot hexane, and dried in the air.

For **III** found, %: C 21.7, H 1.8, N 16.1, Fe 10.1. For $C_{46}H_{44}Fe_2N_{30}O_2Re_6S_8$ calculated, %: C 21.8, H 1.8, N 16.6, Fe 10.1.

Yields of compounds **I**, **II**, and **III** were 97%, 89%, and 63% respectively.

On cooling in liquid nitrogen the compounds exhibit thermochromism; color changes are: yellow \leftrightarrow pink (**I**), yellow \leftrightarrow orange (**II**), beige \leftrightarrow orange (**III**).

The C, H, N elemental analysis was carried out on a EURO EA 3000 analyzer (EuroVector, Italy) in the laboratory at the Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences. The iron content in complex **III** was determined trilonometrically after the decomposition of samples of the complexes on heating in a mixture of concentrated H_2SO_4 and $HClO_4$ (1:2).

Polycrystals of the compounds were analyzed on a Shimadzu XRD 7000 diffractometer at room temperature with the use of CuK_{α} radiation.

The static magnetic susceptibility of the polycrystalline samples was measured by the Faraday method in the temperature range of 80-500 K at an external magnetic field strength up to 9 kOe. The heating (cooling) rate in the SCO region was 0.5 deg/min. Temperatures of the forward (T_c^{\uparrow}) and backward (T_c^{\downarrow}) transitions were found from the condition $d^2(\chi T)/dT^2 = 0$.

IR absorption spectra were measured on Scimitar FTS 2000 IR Fourier and Vertex 80 spectrometers in the ranges 400-4000 cm^{-1} and 100-400 cm^{-1} respectively at room temperature. The samples were prepared as suspensions in paraffin and fluorinated oils. The main characteristic frequencies in the IR spectra of the ligand, anion salts, and complexes are listed in Table 1. Diffuse reflectance spectra were measured on a scanning UV-3101 PC spectrometer (Shimadzu) at room temperature.

Mössbauer spectra of the complexes were measured at 78 K on an NP-610 spectrometer with a ^{57}Co (Rh) source. Due to a heavy matrix of the samples these complexes turned out to be extremely complicated objects of the study as a result of which the measurement time of one spectrum was approximately two days. The resonance absorption effect for the separate spectral lines did not exceed 1% (this fact hampered the measurement of the spectra at 295 K and higher temperatures). The spectra were processed by decomposing them in two quadruple doublets, one of which corresponded to low-spin (LS) state 1A_1 and another to high-spin (HS) state 5T_2 . As a result of the processing of the spectra the isomeric shift δ (with respect to α -Fe) was found along with the quadruple splitting ε and the doublet line width $\Gamma_{1,2}$. From the ratios of the doublet line areas to the total area of the spectra the relative concentration of iron atoms in LS and HS states (%) were also found in the assumption of the equality of the probabilities of the Mössbauer effect for iron atoms in LS and HS states, which is a quite satisfactory assumption for the spectra measured at 78 K.

TABLE 1. Main Vibrational Frequencies (cm^{-1}) in the Spectra of $HC(Pz)_3$ and Complexes **I-III**

Assignment	$HC(Pz)_3$	I	II	III
$\nu(O-H)$		3553	3429	3401
$\nu(C-H)$	3117	3129	3126	3118
	2983	2959	2955	2969
		2932	2930	2926
R(Pz)	1604	1618	1619	1567
	1574	1520	1518	1518
	1517			
$\nu(Fe-N)$		270	296	285
$\nu(Mo-Hal)$		331	243	

RESULTS AND DISCUSSION

Iron(II) complexes with tris(pyrazol-1-yl)methane and cluster outer-sphere anions were isolated from water-acetone (**I**, **II**) or aqueous (**III**) solutions at the molar ratio $\text{Fe}:\text{HC}(\text{Pz})_3 = 1:2$. In order to avoid the oxidation of Fe(II) ascorbic acid was added to the solutions as a reducing and weakly acidifying reagent.

Powder XRD data indicate the crystallinity of the obtained compounds, however, we failed to grow a single crystal suitable for the X-ray crystallographic analysis. Diffraction patterns of **I** and **II** practically coincide, which gives evidence that these complexes are isostructural.

Table 1 lists the main vibrational frequencies (cm^{-1}) in the IR spectra of $\text{HC}(\text{pz})_3$ and complexes **I-III**. In the high-frequency spectral region broad bands ($3560\text{-}3400\text{ cm}^{-1}$) are observed, which belong to the stretching vibrations of the O–H bond of crystal water. In the region of $\nu(\text{C-H})$ vibrations a shift of bands is observed in comparison with the spectrum of $\text{HC}(\text{Pz})_3$, which is likely to be due a change in the geometry of the alkane moiety of the ligand during the complexation. In the spectrum of the ligand in the range $1600\text{-}1400\text{ cm}^{-1}$ the bands of stretching-bending vibrations of pyrazole rings are located, which are sensitive to the coordination. In the spectra of complexes **I-III** these bands are noticeably shifted as compared to the spectrum of the ligand, which indicates the coordination of nitrogen atoms of the ligand pyrazole rings to the iron(II) ion. This conclusion is confirmed by the character of the IR spectra of the complexes in the low-frequency range ($600\text{-}100\text{ cm}^{-1}$). The spectra of **I-III** contain the bands at 270 cm^{-1} , 296 cm^{-1} , and 285 cm^{-1} respectively, which can be assigned to Fe–N stretching vibrations. The bands at 331 cm^{-1} and 243 cm^{-1} in the spectra of **I** and **II** are assigned to Mo–Cl and Mo–Br stretching vibrations respectively.

In each SCO of complexes **I-III** two broad absorption bands are observed in the visible and near IR range. Bands with the maxima at 835 nm (**I**), 840 nm (**II**), and 860 nm (**III**) can be assigned to the $d-d$ -transition ${}^5T_2 \rightarrow {}^5E$ in a weakly distorted octahedral ligand field. The position of these bands is typical of the spectra of HS octahedral complexes of iron(II) with nitrogen-containing ligands [19]. From these data it is possible to easily calculate the values $\nu = \Delta_{\text{HS}}$, where Δ_{HS} is the splitting parameter in the crystalline field of HS Fe(II) complexes (Table 2). The splitting parameters indicate that in complexes **I-III** SCO is theoretically possible on cooling because $11000\text{ cm}^{-1} \leq \Delta_{\text{HS}} \leq 12500\text{ cm}^{-1}$ [24].

In the range $450\text{-}550\text{ nm}$ in SCO of **I-III** an absorption band with the maxima at 570 nm (**I**, **II**) or 560 nm (**III**) are observed, which can be assigned to the $d-d$ transition ${}^1A_1 \rightarrow {}^1T_1$ in the strong distorted octahedral ligand field, FeN_6 chromophore. Using the approximations $\nu = \Delta_{\text{LS}} - C + 86B^2/\Delta_{\text{LS}}$ [25]; $\Delta_{\text{HS}} \approx 19B$ [24]; $C = 4.41B$ [26], we calculated the splitting parameters for **I-III** (Table 2). Note that the condition of the SCO appearance on heating $19000 \leq \Delta_{\text{LS}} \leq 22000\text{ cm}^{-1}$ [24] seems to be not strict; in our case, it is satisfied within a 3% relative error.

The ratio $\Delta_{\text{LS}}/\Delta_{\text{HS}} = (r_{\text{HS}}/r_{\text{LS}})^{5+6} \cong 1.6\div 1.8$ [27] is $1.54\div 1.59$. This indicates a 8-10% relative elongation of the Fe–N bond at SCO and agrees well with the experimental data for a series of iron(II) complexes with tris(pyrazol-1-yl)methane [5].

The dependences $\chi T(T)$ for complexes **I**, **II** were studied in the temperature ranges of $80\text{-}400\text{ K}$ and $300\text{-}460\text{ K}$ for complex **III**. It is found that in complexes **I-III** ${}^1A_1 \leftrightarrow {}^5T_2$ SCO with a small hysteresis is observed (Fig. 2a-c). The analysis of the dependences $d^2(\chi T)/dT^2$ (insets in Fig. 2a-c) made it possible to estimate the transition temperature. In complex **I** the forward transition on heating occurs at $T_c^\uparrow = 271\text{ K}$; the backward one on cooling occurs at $T_c^\downarrow = 268\text{ K}$. For complex **II** $T_c^\uparrow = 270\text{ K}$, $T_c^\downarrow = 268\text{ K}$; for complex **III** $T_c^\uparrow = 383\text{ K}$, $T_c^\downarrow = 379\text{ K}$. SCO in **I-III** is accompanied by thermochromism: yellow \leftrightarrow pink (**I**), yellow \leftrightarrow orange (**II**), and beige \leftrightarrow orange (**III**) color changes.

TABLE 2. SCO Parameters of **I-III** and Calculated Δ_{HS} , Δ_{LS} , and B Values (cm^{-1})

Complex	$\lambda({}^1A_1 = {}^1T_1)$, nm	$\lambda({}^5T_2 = {}^5E)$, nm	Δ_{HS}	B	Δ_{LS}	$\Delta_{\text{LS}}/\Delta_{\text{HS}}$
I	570	835	11976	630	18475	1.54
II	570	840	11905	627	18480	1.55
III	560	860	11628	612	18847	1.59

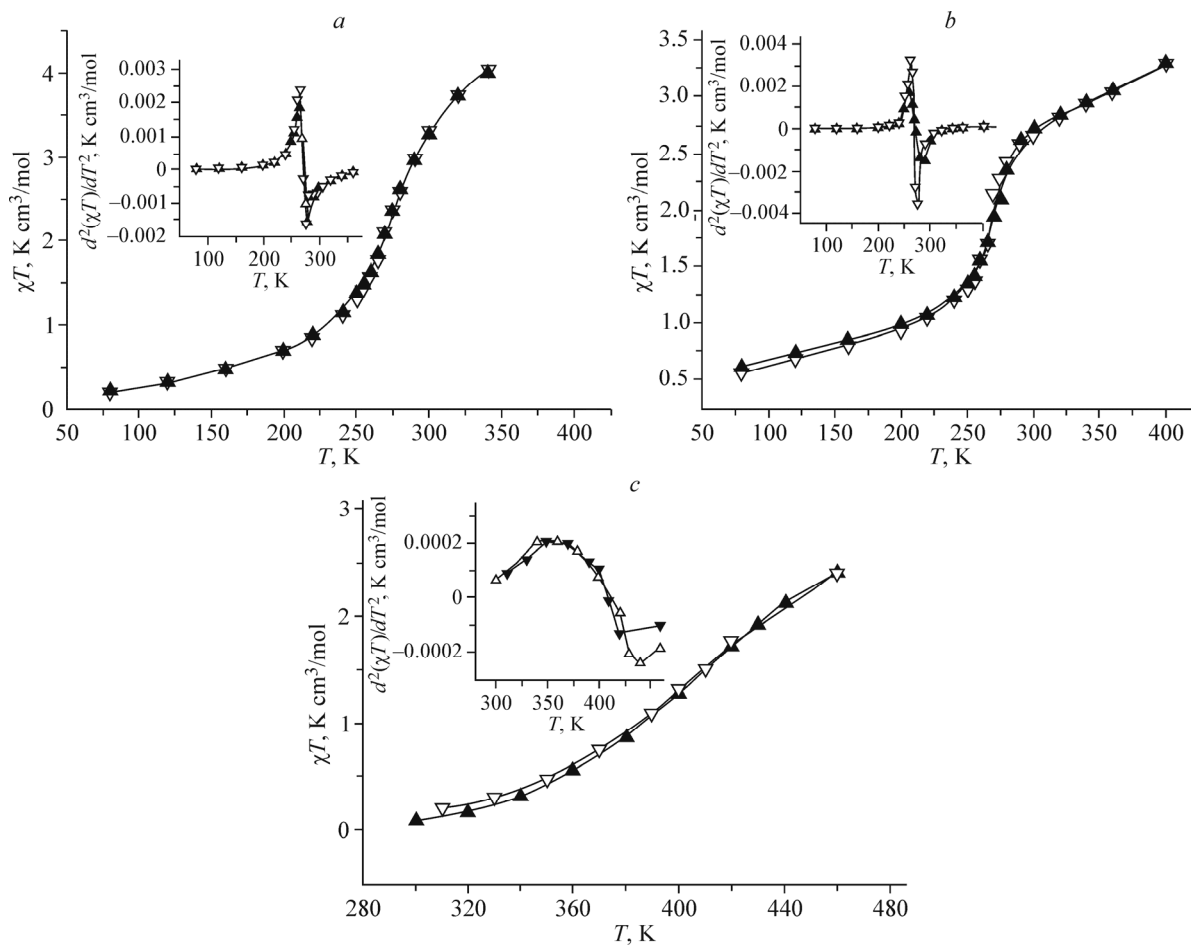


Fig. 2. Temperature dependence χT for $[\text{Fe}\{\text{HC}(\text{pz})_3\}_2][\text{Mo}_6\text{Cl}_{14}]\cdot 2\text{H}_2\text{O}$ (a), $[\text{Fe}\{\text{HC}(\text{pz})_3\}_2][\text{Mo}_6\text{Br}_{14}]\cdot \text{H}_2\text{O}$ (b), and $[\text{Fe}\{\text{HC}(\text{pz})_3\}_2]_2[\text{Re}_6\text{S}_8(\text{CN})_6]\cdot 2\text{H}_2\text{O}$ (c) complexes. \blacktriangle – heating, ∇ – cooling.

Mössbauer spectra of the studied complexes are shown in Fig. 3, where partial spectra of LS and HS forms are also depicted. The spectral parameters and the fraction of iron atoms for each of these forms are given in Table 3. It is essential that complexes **I-III** contain a large fraction of iron atoms in the HS state. The fraction of the HS state in complexes **II** and **III** proves to be obviously overestimated in comparison with the estimate obtained from the analysis of $\chi T(T)$ curves. The reason for this inconsistency we tentatively associate with that under the effect of high-energy radiation with an energy of 122 keV during the long-term measurement of the Mössbauer spectra of the complexes irreversible transitions from LS to HS states are observed. This hypothesis is confirmed by that in complexes **II** and **III**, which were long under the effect of

TABLE 3. Parameters of the Mössbauer Spectra of Complexes **I-III**

Complex	Form	%*	δ , mm/s	ε , mm/s	$\Gamma_{1,2}$, mm/s
[Fe{HC(pz) ₃ } ₂][Mo ₆ Cl ₁₄] \cdot 2H ₂ O	LS	85	0,500	0,341	0,275
	HS	15	1,395	3,570	0,340
[Fe{HC(pz) ₃ } ₂][Mo ₆ Br ₁₄] \cdot H ₂ O	LS	44	0,476	0,279	0,226
	HS	56	1,363	3,383	0,365
[Fe{HC(pz) ₃ } ₂] ₂ [Re ₆ S ₈ (CN) ₆] \cdot 2H ₂ O	LS	43	0,486	0,323	0,285
	HS	57	1,197	3,201	0,523
		± 5	$\pm 0,010$	$\pm 0,020$	$\pm 0,030$

* Fractions of LS and HS forms in the sample.

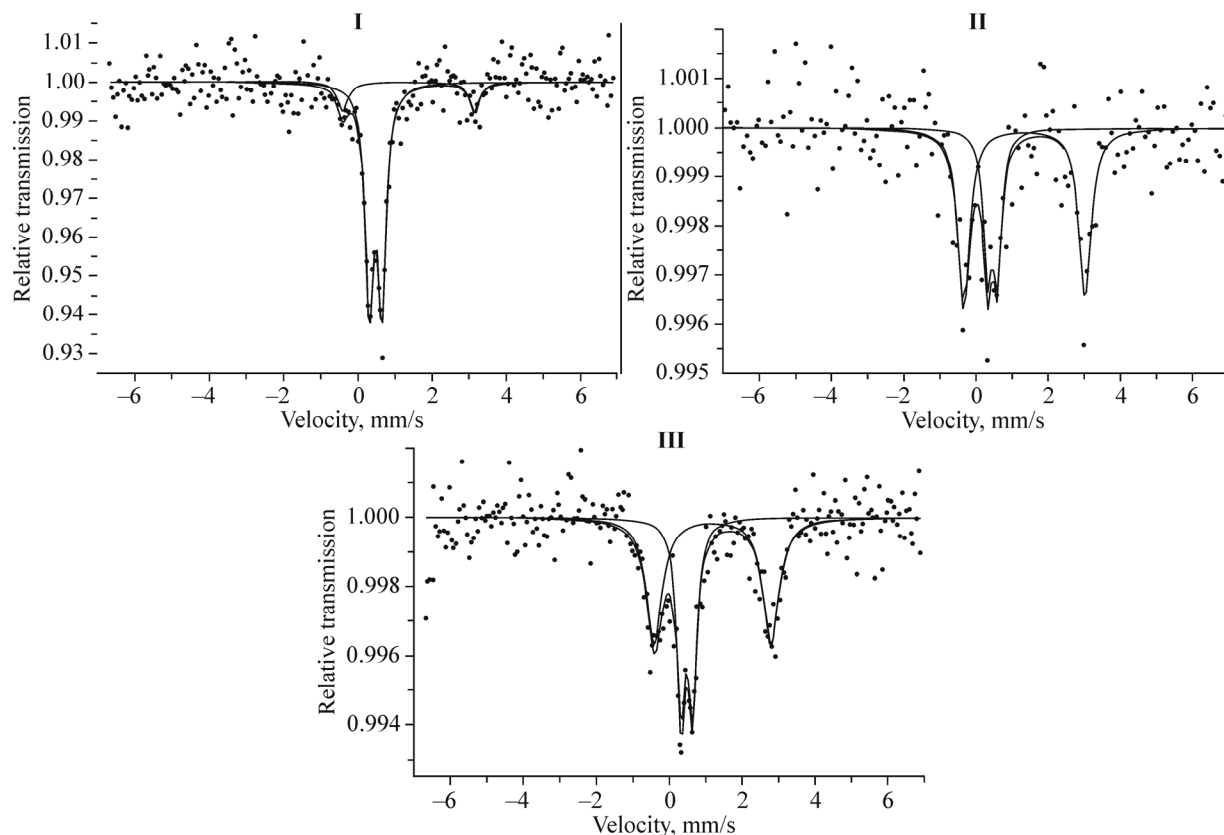


Fig. 3. Mössbauer spectra of complexes **I-III**.

radiation during the measurement of the spectra in preliminary experiments at 295 K, the fraction of HS forms is much higher than that in complex **I** with which these experiments were not performed. In order to reveal the nature of the discovered effect it is planned to perform further investigations.

Thus, three new iron(II) complexes with tris(pyrazol-1-yl)methane containing cluster ions in the outer sphere and having SCO and thermochromism were synthesized and studied.

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