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Spin Crossover in Heteroligand Iron(II) Complexes with Tris(3,5-Dimethylpyrazol-1-yl)methane

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Abstract—Heteroligand iron(II) complexes with tris(3,5-dimethylpyrazol-1-yl)methane (HC(3,5-$Me_2Pz)_3$) are synthesized. Along with this ligand, the internal coordination sphere of Fe(II) of the new complexes includes other nitrogen-containing heterocycles, in particular, tetrazole (Tz), pyrazole (Pz), 3,5-dimethylpyrazole (3,5-Me_2Pz), and 3-amino-4-ethoxycarbonylpyrazole (Ametcpz), as well as ions NCS^- or $N(CN)_2^-$. Compounds $[Fe(HC(3,5\text{-}Me_2Pz)_3)(Tz)_3](NO_3)_2$ (**I**), $[Fe(HC(3,5\text{-}Me_2Pz)_3)(Tz)_3](ClO_4)_2$ (**II**), $[Fe(HC(3,5\text{-}Me_2Pz)_3)(Pz)_3](NO_3)_2$ (**III**), $[Fe(HC(3,5\text{-}Me_2Pz)_3)(Aecpz)(NCS)_2]$ (**IV**), and $[Fe(HC(3,5\text{-}Me_2Pz)_3)(3,5\text{-}Me_2Pz)(N(CN)_2)_2] \cdot 0.5H_2O$ (**V**) are isolated. The study of the temperature dependence $\mu_{eff}(T)$ shows the spin crossover $^1A_1 \Leftrightarrow {}^5T_2$ accompanied by thermochromism (the color changes from white to pink) in complexes **I**, **II**, and **IV**. The molecular and crystal structures of complex **V** are determined by X-ray diffraction analysis (CIF file CCDC 994626).

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INTRODUCTION

Spin crossover in coordination compounds of 3*d* metals with the electronic configuration d^4–d^7 and the octahedral structure of the coordination polyhedron attracts permanent attention of researchers and is widely used [1–10]. The spin multiplicity changes under the effect of temperature, pressure, or light irradiation with a certain wavelength. The syntheses and studies of new complexes with spin crossover are necessary for both the further development of the theory of this interesting phenomenon and practical use. Complexes of various iron(II) salts with polynitrogen-containing ligands are of special interest, because in many of these complexes the spin crossover is accompanied by a distinct change in the color, and this is of independent practical significance.

Tris(3,5-dimethylpyrazol-1-yl)methane (HC(3,5-$Me_2Pz)_3$, Pz is pyrazole) was used for the synthesis of a series of iron(II) complexes of the composition $[FeL_2]A_n$ ($A = BF_4^-$, I^-, NO_3^-, Cl^-, ClO_4^-, SO_4^{2-}; n = 1, 2). A number of these complexes exhibit a spin crossover. The sharp and complete transitions with a hysteresis in the $\mu_{eff}(T)$ curves are observed in the single-crystal phase of $[Fe(HC(3,5\text{-}Me_2Pz)_3)_2]I_2$ [11] and in the polycrystalline phase of $[Fe(HC(3,5\text{-}Me_2Pz)_3)_2](NO_3)_2$ [12]. The sharp but incomplete transitions are observed in complexes $[Fe(HC(3,5\text{-}Me_2Pz)_3)_2](BF_4)_2$ [13, 14] and $[Fe(HC(3,5\text{-}Me_2Pz)_3)_2](ClO_4)_2$ [15]. In $[Fe(HC(3,5\text{-}Me_2Pz)_3)_2]I_2$ and $[Fe(HC(3,5\text{-}Me_2Pz)_3)_2](ClO_4)_2$, spin crossovers are observed only in single crystals, while the polycrystalline phases exhibit no spin crossover. Note that two polymorphous modifications were observed for single crystals in the latter case. The spin crossover is observed in one modification isostructural to $[Fe(HC(3,5\text{-}Me_2Pz)_3)_2](BF_4)_2$, while no spin crossover is observed in the second modification [15].

It seemed reasonable to synthesize heteroligand iron(II) complexes with HC(3,5-$Me_2Pz)_3$ and to study the influence of the second ligand (in the cases where the internal sphere of the complex contains a nitrogen-containing anion, the influence of the third ligand is studied) on the possibility of manifestation and character of the spin crossover.

EXPERIMENTAL

The following reagents were used: $FeSO_4 \cdot 7H_2O$ (high-purity grade) recrystallized from an aqueous solution acidified with H_2SO_4; ascorbic acid (medicine grade); $Ba(NO_3)_2$, $Ba(ClO_4)_2$, and KNCS

Table 1. Elemental analysis results for heteroligand iron(II) complexes **I**–**V**

Compound	Empirical formula	Content (found/calculated), %			
		C	H	N	Fe
I	$C_{19}H_{28}FeN_{20}O_6$	35.2/33.1	4.6/4.1	39.8/40.7	8.1/8.1
II	$C_{19}H_{32}Cl_2FeN_{18}O_{10}$	28.0/28.5	5.3/4.0	33.1/33.5	
III	$C_{25}H_{34}FeN_{14}O_6$	44.3/44.0	5.5/5.0	28.1/28.7	8.0/8.2
IV	$C_{24}H_{32}FeN_{11}O_{2.5}S_2$	45.9/45.4	5.4/5.1	23.5/24.3	
V	$C_{25}H_{31}FeN_{14}O_{0.5}$	52.4/50.8	5.7/5.3	33.2/33.2	9.3/9.4

(reagent grade); tetrazole (Tz), pyrazole, 3-amino-4-ethoxycarbonylpyrazole (Aecpz), and $NaN(CN)_2$ (Aldrich); and tris(3,5-dimethylpyrazol-1-yl)methane was synthesized using an improved procedure similar to that described in [16].

Synthesis of complexes [Fe(HC(3,5-Me$_2$Pz)$_3$)(Tz)$_3$](NO$_3$)$_2$ (I), and [Fe(HC(3,5-Me$_2$Pz)$_3$)(Tz)$_3$](ClO$_4$)$_2$ · 2H$_2$O (II). To prepare solutions of salts $Fe(NO_3)_2$ or $Fe(ClO_4)_2$, $FeSO_4 \cdot 7H_2O$ (0.56 g, 0.002 mol) and ascorbic acid (0.2 g) were dissolved together on heating in hot water (10 mL). A weighed sample of the corresponding barium salt ($Ba(NO_3)_2$ (0.52 g, 0.002 mol) or $Ba(ClO_4)_2$ (0.67 g)) was dissolved on heating in water (10 mL). Then the hot solutions of the barium salts were slowly added with stirring to a hot solution of $FeSO_4$. The obtained solutions with a precipitate of $BaSO_4$ were kept at room temperature for 2 h, and the precipitates of $BaSO_4$ were filtered off and rejected. Weighed samples of HC(3,5-Me$_2$Pz)$_3$ (0.60 g, 0.002 mol) and tetrazole (0.84 g, 0.012 mol) were dissolved together in acetone (5–7 mL), and the solution was added to a solution of $Fe(NO_3)_2$ or $Fe(ClO_4)_2$. The obtained solutions were evaporated to ~1/2 of the initial volume and placed in an ice-cold bath, and cold acetone (5 mL) was added. The formed precipitates were filtered off, washed two times with acetone, and dried in air. Other substances after the synthesis were washed and dried similarly.

Synthesis of [Fe(HC(3,5-Me$_2$Pz)$_3$)(Pz)$_3$](NO$_3$)$_2$ (III) was carried out according to a procedure similar to the synthesis of complex **I**. Pyrazole (0.82 g, 0.012 mol) was added to a solution of $Fe(NO_3)_2$ obtained after $BaSO_4$ was separated.

Synthesis of [Fe(HC(3,5-Me$_2$Pz)$_3$)(Aecpz)(NCS)$_2$] · 0.5H$_2$O (IV). Weighed samples of $FeSO_4 \cdot 7H_2O$ (0.14 g, 0.5 mmol) and ascorbic acid (0.1 g) were dissolved in hot water (5–7 mL), and $Ba(NO_3)_2$ (0.13 g, 0.5 mmol) was dissolved in water (10 mL) on heating. A solution of $Fe(NO_3)_2$ was obtained as described in the synthesis of complex **I**. KNCS (0.29 g, 3 mmol) and a solution of a mixture of ligands (0.15 g (0.5 mmol) of HC(3,5-Me$_2$Pz)$_3$ and 0.078 g (0.5 mmol) of Aecpz) in acetone were added to the obtained solution. The resulting solution was evaporated to ~1/2 of the initial volume. The precipitate was formed after the solution was cooled in an ice-cold bath.

Synthesis of [Fe(HC(3,5-Me$_2$Pz)$_3$)(3,5-Me$_2$Pz)(N(CN)$_2$)$_2$] · 0.5H$_2$O (V). Weighed samples of $FeSO_4 \cdot 7H_2O$ (0.56 g, 0.002 mol), ascorbic acid (0.2 g), and $NaN(CN)_2$ (1.07 g, 0.012 mol) were dissolved together in hot water (10 mL). A weighed sample of HC(3,5-Me$_2$Pz)$_3$ (1.79 g, 0.006 mol) was dissolved in acetone (10 mL), and the solution was added to the solution of the salts. A precipitate was formed after ~1/2 of the solvent volume was removed and the solution was cooled. Single crystals of compound **V** suitable for X-ray diffraction analysis precipitated from the mother liquor upon slow crystallization.

The yields of complexes **I**–**V** were 30–35% of the theoretical value. All isolated precipitates were white at room temperature. Complexes **I**, **II**, and **IV** possessing thermochromism became pink when cooling to the temperature of liquid nitrogen.

Elemental analyses to C, H, and N were carried out at the Analytical Laboratory of the Nikolaev Institute of Inorganic Chemistry (Siberian Branch, Russian Academy of Sciences) on a EURO EA 3000 instrument (EuroVector, Italy). Iron was analyzed by complexonometric titration with sulfosalicylic acid as an indicator after the samples were decomposed on heating in a mixture of concentrated H_2SO_4 and $HClO_4$ (1 : 2). The elemental analysis data are presented in Table 1.

The diffractometric study of polycrystals of compound **V** was carried out on a Shimadzu XRD 7000 diffractometer at room temperature using the CuK_α radiation.

X-ray diffraction analysis of complex V. The crystallographic characteristics and details of the diffraction experiment for compound **V** are presented in Table 2. The diffraction data were obtained using a standard procedure. An absorption correction was applied semiempirically using the SADABS program. The structures were solved by a direct method and refined by full-matrix least squares in the anisotropic approximation (SHELX-97) [17]. The positions of the hydrogen atoms at the carbon atoms were calculated geometrically and refined in the rigid body approximation (riding model). The positions of the hydrogen atoms at the oxygen atoms of the water molecules were revealed from the difference electron density synthesis and refined with the fixed U_{iso} and bond length. Selected bond lengths are listed in Table 2. One of the dicyanamide ligands is disordered over two positions caused by rotation about the axis passing through the terminal nitrogen atoms. The weight of the major position was 63%.

The coordinates of atoms and other parameters for structure **V** were deposited with the Cambridge Crystallographic Data Centre (CCDC 994626); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

The static magnetic susceptibility of polycrystalline samples **I–III** was measured by Faraday's method in the temperature range 78–300 K at the intensity of the external magnetic field up to 9 kOe. The heating (cooling) rate in the region of spin crossover was 0.5 deg/min. The magnetic properties of polycrystalline samples **IV** and **V** were studied on an MPMS-*XL* SQUID magnetometer (Quantum Design) in the range 2–300 K in a magnetic field of 5 kOe. Diamagnetic corrections were applied according to the Pascal additive scheme when calculating the paramagnetic component of the molar magnetic susceptibility (χ). The effective magnetic moment (μ_{eff}) was determined in the paramagnetic region using the formula $\mu_{\text{eff}} = \left(\frac{3k}{N_A\mu_B^2}\chi T\right)^{1/2} \approx (8\chi T)^{1/2}$, where k is the Boltzmann constant, N_A is Avogadro's number, and μ_B is Bohr's magneton.

IR absorption spectra were recorded on Scimitar FTS 2000 and Vertex 80 spectrometers in the region 100–4000 cm^{-1}. The samples were prepared as suspensions in Nuiol, fluorinated oil, and polyethylene.

RESULTS AND DISCUSSION

Heteroligand complexes **I–V** containing HC(3,5-$Me_2Pz)_3$ and other nitrogen-containing ligands were isolated from aqueous-acetone solutions upon the reactions of the corresponding iron(II) salts, HC(3,5-$Me_2Pz)_3$, and L, where L is tetrazole, pyrazole, and 3-amino-4-ethoxycarbonylpyrazole. Iron(II) nitrate and perchlorate were synthesized by the exchange reaction upon mixing of solutions of $FeSO_4$ and the corresponding barium salt. Iron(II) thiocyanate and dicyanamide were obtained from solutions containing $FeSO_4$ and an excess of the corresponding salt (KSCN or $NaN(CN)_2$. All obtained Fe(II) salts were used for syntheses without isolation from solutions. Ascorbic acid was used as a reducing agent and an acidifying agent to prevent iron(II) oxidation.

According to the X-ray diffraction analysis data for compound **V**, ligand HC(3,5-$Me_2Pz)_3$ is coordinated according to 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

Table 2. Crystallographic characteristics and the experimental and refinement details for structure **V**

Parameter	Value
M	586.98
Temperature, K	100
Diffractometer	Bruker X8 Apex
Radiation (λ, Å)	MoK_α (0.71073)
Crystal system	Triclinic
Space group	$P\bar{1}$
Z	4
a, Å	13.9082(6)
b, Å	15.3560(7)
c, Å	16.2266(6)
α, deg	69.4330(10)
β, deg	64.8360(10)
γ, deg	79.9220(10)
V, Å^3	2935.4(2)
ρ(calcd), g/cm^3	1.328
μ, mm^{-1}	0.556
Crystal size, mm	0.35 × 0.05 × 0.05
Color	Colorless
θ Range of data collection	2.12–31.56
Measured reflections	33856
Independent reflections (R_{int})	15834 (0.0407)
Reflections with $I \geq 2\sigma(I)$	10477
Number of refined parameters	760
R_1 ($I > 2\sigma(I)$)	0.0533
wR_2 (all reflections)	0.1483
GOOF (all reflections)	1.022
Residual electron density (min/max), e/Å^3	–0.60/0.61

Table 3. Selected bond lengths in compound **V**

Bond	d, Å	Bond	d, Å
Fe(1)–N(1*A*)	2.222(2)	Fe(2)–N(1*B*)	2.216(2)
Fe(1)–N(3*A*)	2.195(2)	Fe(2)–N(3*B*)	2.204(2)
Fe(1)–N(5*A*)	2.221(2)	Fe(2)–N(5*B*)	2.202(2)
Fe(1)–N(7*A*)	2.141(2)	Fe(2)–N(7*B*)	2.137(2)
Fe(1)–N(31*A*)	2.133(3)	Fe(2)–N(31*B*)	2.121(2)
Fe(1)–N(41*A*)	2.110(2)	Fe(2)–N(41*B*)	2.107(2)

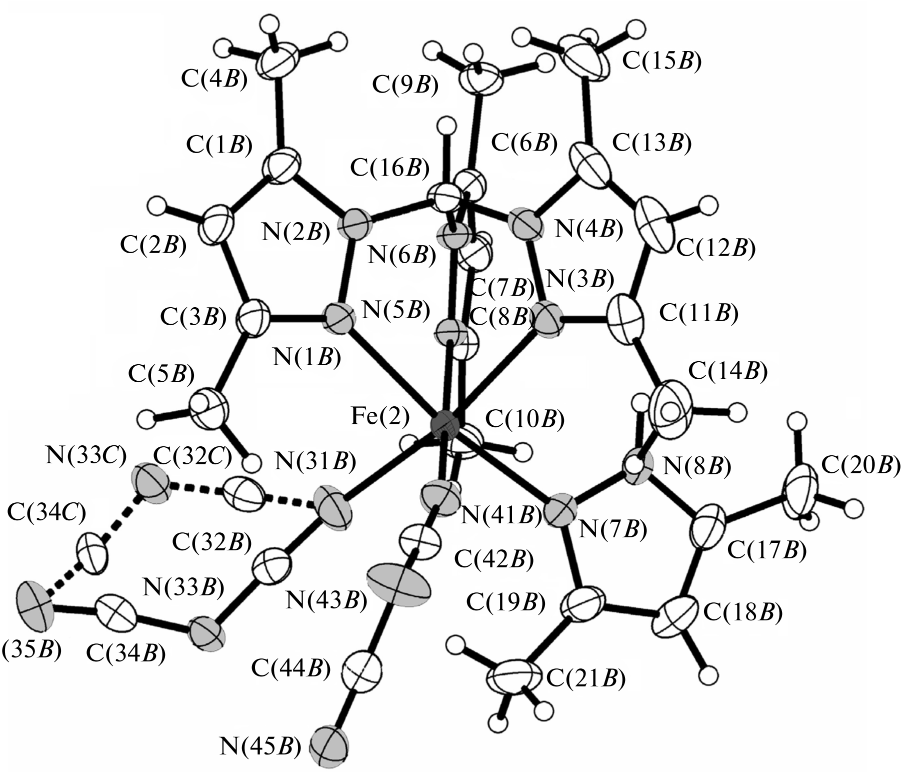


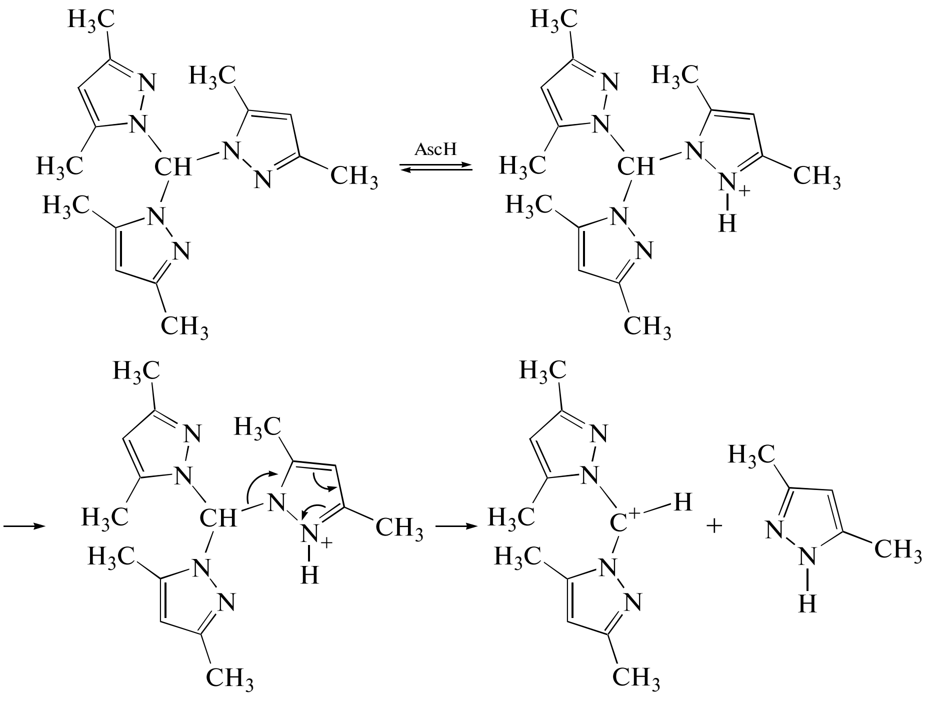
Fig. 1. Structure of a molecule of complex **V** (50% probability atomic displacement ellipsoids).

group (Fig. 1). The coordination polyhedron of the iron atom is added to a distorted octahedron by the nitrogen atom of ligand 3,5-Me_2Pz and two nitrogen atoms of the $N(CN)_2^-$, ions coordinated by the monodentate mode. The Fe–N bond lengths have values characteristic of the high-spin Fe^{2+} cation (Table 3).

Note that dicyanamide can be coordinated to the metal by both the monodentate and bidentate bridging mode. The synthesis of the iron(II) complex with tris(pyrazol-1-yl)methane ($HC(Pz)_3$) and $N(CN)_2^-$, in which this anion has a duel function was described [5]. In this complex, the distorted octahedron is formed due to $HC(Pz)_3$, which is coordinated, like $HC(3,5\text{-}Me_2Pz)_3$, via the tridentate cyclic mode by three nitrogen atoms (monodentate $N(CN)_2^-$ and two bidentate bridging $N(CN)_2^-$) connecting the iron(II) ions into the binuclear complex. In our case, the dicyanamide ions are coordinated through the monodentate mode.

The formation of individual compound **V** is confirmed by the elemental analysis data and also by the data of diffractometry of polycrystals. The diffraction pattern of the polycrystalline sample is consistent with the theoretical pattern calculated for compound **V** according to the X-ray diffraction analysis data taking into account a slight shift of the lines toward large values of 2θ angles due to a decrease in the unit cell parameters with the temperature change from 100 K (X-ray diffraction analysis) to room temperature.

In compound **V** 3,5-Me_2Pz is formed in the course of the synthesis of the complex from the iron(II) salt and $HC(3,5\text{-}Me_2Pz)_3$ molecules. It is known that substrate protonation precedes the elimination of amines, including the pyrazole molecule. The rearrangement of the protonated form of bis(pyrazol-1-yl)metane to bis(pyrazol-4-yl)methane including the elimination of the neutral pyrazole molecule was described [18]. A similar elimination of the 3,5-Me_2Pz molecule in the thermal rearrangement of the bis(3,5-dimethylpyrazol-4-yl)methane salt was found [19]. Probably, in our case, this process is favored by ascorbic acid present in the reaction mixture, leading to a fairly low pH ~2. It is most likely that the elimination of the 3,5-Me_2Pz molecule is preceded by the protonation of the nitrogen atom of the pyrazole cycle in the ligand. The synchronous electron shift (the formation of some bonds and the cleavage of other bonds) occurs in the formed quaternary ammonium salt, due to which the neutral 3,5-Me_2Pz molecule (highly leaving groups) is eliminated. The remained carbocation is trapped by either the ascorbic acid residue, or any anion from the reaction mixture



AscH is ascorbic acid.

Since this process is observed only in the synthesis of compound **V**, it can be assumed that a certain role belongs to the $N(CN)_2^-$ anion with the pronounced donor properties, which is present in the system. Due to this, the coordination node FeN_3NN_2 is formed in compound **V** due to three nitrogen atoms of the HC(3,5-Me_2Pz)$_3$ molecule, the nitrogen atom of the 3,5-Me_2Pz ligand, and two nitrogen atoms of two dicyanamide ions. The detailed study of the mechanisms of these processes is beyond the task of the present study, but we are planning to perform it elsewhere.

Selected vibration frequencies of complexes **I–V**, ligands, and anions **(VI–X)** are given in Table 4. The stretching vibration bands of the OH groups appear at 3590–3302 cm^{-1} in the high-frequency range of the spectra of complexes **II**, **IV**, and **V** containing water molecules. The broad structured bands at 3297–2100 cm^{-1} in the spectra of ligands **VII–X** can be assigned to the stretching vibrations of the NH groups involved in hydrogen bonds. Their character changes on going to the spectra of complexes **I–V**. However, the spectral pattern indicates that the nitrogen atoms of the imine groups are not involved in coordination.

The bands of stretching–bending vibrations of the ring sensitive to coordination appear in the region from 1590 to 1500 cm^{-1}. The spectrum of HC(3,5-Me_2Pz)$_3$ exhibits an intense R_{ring} band at 1561 cm^{-1}, whereas in the spectra of complexes **I–V** this band is shifted by 4–6 cm^{-1} to the high-frequency range. This indicates the coordination of the nitrogen atoms of the pyrazole rings to the metal ion. The R_{ring} bands are also observed at 1589–1501 cm^{-1} in the spectra of ligands **VII–X** (Table 4). Substantial changes in the number and position of these bands occur on going to the spectra of the complexes, indicating the coordination of ligands **VII–X** to Fe(II). The change in the spectral pattern for the spectrum of complex **V** in the range 2287–2169 cm^{-1} compared to the spectrum of $N(CN)_2^-$ is related to the coordination of this anion to Fe(II), which is confirmed by the X-ray diffraction analysis data for compound **V**. The position of the $\nu(NCS^-)$ band also suggests the coordination of the thiocyanate ion to Fe(II) [20]. On the contrary, the positions of the $\nu_3(NO_3^-)$, and $\nu_3(ClO_4^-)$, $\nu_4(ClO_4^-)$ bands in the spectra of compounds **I–III** indicate the outer-of-sphere position of these anions. New bands characteristic of $\nu(Fe-N_{ring})$ are observed at 270–220 cm^{-1} in the low-frequency region of the spectra of compounds **I–V**.

The curves of the $\mu_{eff}(T)$ dependences for complexes **I** and **II** are shown in Figs. 2a and 2b, respectively. It is seen that the gradual and incomplete spin crossover is observed in these complexes. The high value of the magnetic moment at low temperatures indicates a significant residual fraction of the high-spin forms of complexes **I** and **II**. The evaluation of the latter shows that only 50% of iron(II) ions are transformed into the high-spin form. This can be due to the initial presence of complexes of two types in crystal. Of these complexes, only one type undergoes the spin crossover. Another possible mechanism is related to a

Table 4. Selected vibration frequencies in the spectra of complexes **I–V**, ligands, and anions*

ν, cm^{-1}											Assignment
I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**	**X**	**XI**	
	3590 3426		3537 3472 3382 3302	3563 3482							$\nu(H_2O)$
3135 3097	3141 3106	3137 3055	3133	3137 3108 3044	3130	3155–2200 br	3140–2170 br	3297 3236 3203	3200–2100 br		$\nu(NH)$ $\nu(CH)_{ring}$
				2277 2229 2213 2169						2287 2233 2182	$\nu(N(CN)_2^-)$
			2080								$\nu(NCS^-)$
			1709 1696					1671			$\nu(CO)$
1565 1543	1566 1544 sh 1535	1565 1544 1529 1507	1566 1542 sh 1521 1534 1508	1580 1567	1561	1589 w 1561 sh 1523	1558 1537 1508 w 1495	1558 1522 1501	1595 1553		R_{ring}
1380		1370									$\nu_3(NO_3^-)$
	1101 624										$\nu_3(ClO_4^-)$ $\nu_4(ClO_4^-)$
271 245	271 245	272 246 225	267 236	267 253 241							$\nu(Fe–N)$

* **VI** contains $HC(3,5\text{-}Me_2Pz)_3$, **VII** contains tetrazole, **VIII** contains pyrazole, **IX** contains 3-amino-4-ethoxycarbonylpyrazole, **X** contains 3,5-dimethylpyrazole, and **XI** contains dicyanamide ion.

decrease in the crystal symmetry in the course of spin crossover, resulting in the formation of two crystallographically independent molecules of the complex: high-spin and low-spin. This situation was observed [13, 14] for complex $[Fe(HC(3,5\text{-}Me_2Pz)_3)_2](BF_4)_2$ and for the single-crystal phase of isostructural $[Fe(HC(3,5\text{-}Me_2Pz)_3)_2](ClO_4)_2$ [15]. The value of μ_{eff} for complex **III** remains nearly unchanged with the temperature change. This indicates that no spin transition occurs when a ligand of a weaker field compared to that of $HC(3,5\text{-}Me_2Pz)_3$ and tetrazole is introduced into the coordination sphere of the pyrazole complex.

The value of μ_{eff} of complex **IV** equal to 5.37 μ_B at 300 K decreases smoothly with a temperature decrease reaching a plateau at ~4.7 μ_B in the temperature range 190–45 K (Fig. 2c). In the region below 45 K, μ_{eff} decreases to 3.69 μ_B at 5 K. The high-temperature value of μ_{eff} is higher than the theoretical purely spin value equal to 4.90 μ_B for one paramagnetic center with the spin $S = 2$ at the g factor equal to 2. The decrease in μ_{eff} in the range 300–200 K is due, most likely, to the spin transition $Fe(II)_{HS}$ ($S = 2$) $\Leftrightarrow$ $Fe(II)_{LS}$ ($S = 0$). A decrease in μ_{eff} to ~4.7 μ_B corresponds to the transition of only ~24% of Fe^{2+} ions from the high- to low-spin state. The exchange interactions between the spins of the Fe^{2+} ions are weak and appear at temperatures lower than 45 K.

The dependence $\mu_{eff}(T)$ for complex **V** is shown in Fig. 2d. At 300 K μ_{eff} = 5.25 μ_B and remains almost unchanged when the temperature decreases to 50 K. For the further cooling, μ_{eff} gradually decreases to 4.05 μ_B at 5 K. The value of μ_{eff} in the temperature

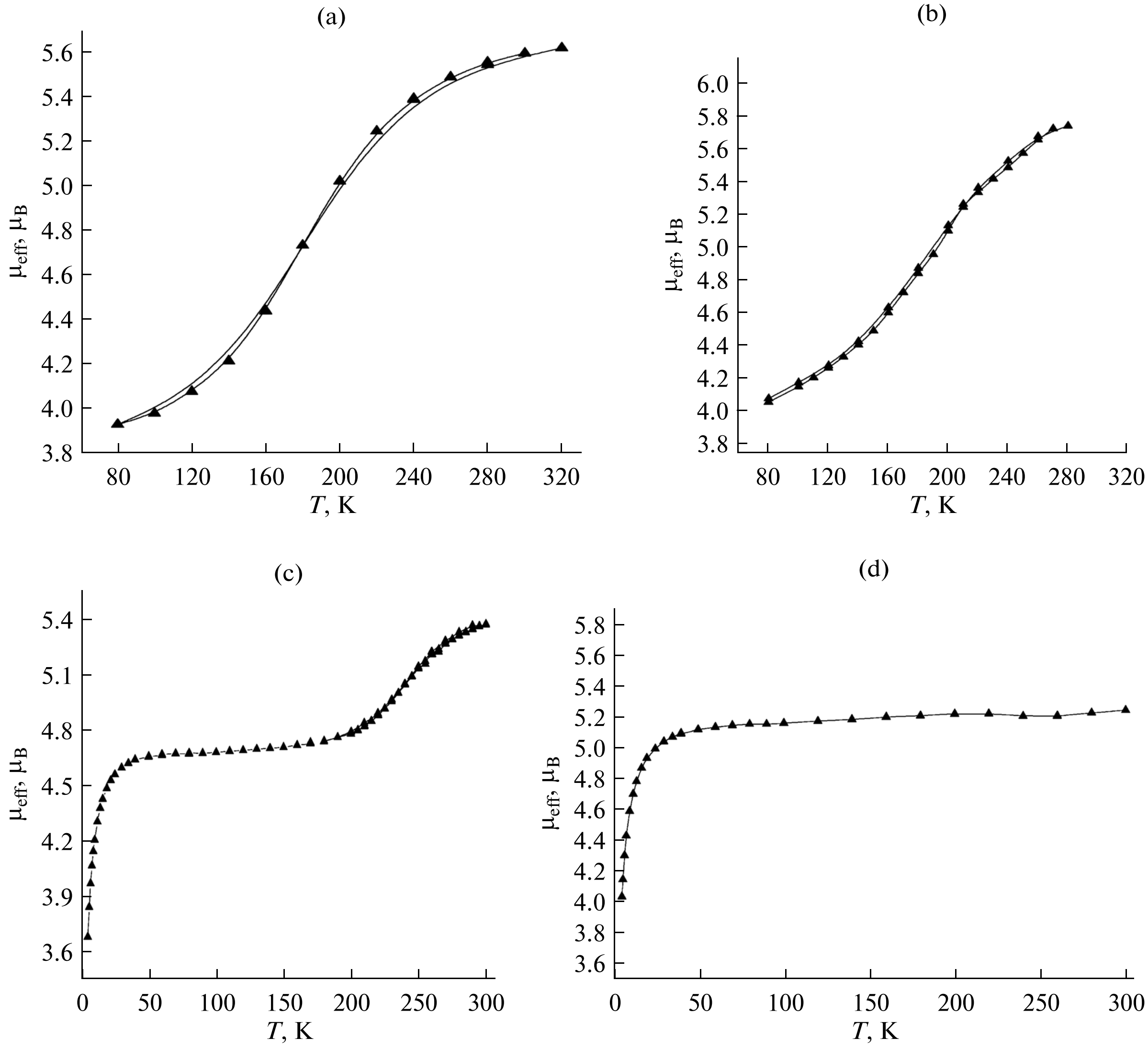


Fig. 2. Dependences $\mu_{\text{eff}}(T)$ for complexes (a) **I**, (b) **II**, (c) **IV**, and **V** (d).

range 300–50 K is close to the theoretical purely spin value equal to 4.90 μ_B for one paramagnetic center with the spin $S = 2$ at the g factor equal to 2, which corresponds to the Fe^{2+} ion in the high-spin state.

We synthesized and studied a series of new heteroligand iron(II) complexes (**I–V**) containing other nitrogen-containing ligands along with tris(3,5-dimethylpyrazol-1-yl)methane. It is shown that the gradual spin crossover is observed in complexes **I**, **II**, and **IV**, whereas exchange interactions of the antiferromagnetic character appear between the Fe^{2+} ions in complex **V** at low temperatures. As mentioned above, no spin crossover is observed in the polycrystalline phase of the iron(II) perchlorate complex with HC(3,5-$Me_2Pz)_3$, $[Fe(HC(3,5\text{-}Me_2Pz)_3)_2](ClO_4)_2$, while the spin crossover is observed in the synthesized heteroligand complex $[Fe(HC(3,5\text{-}Me_2Pz)_3)(Tz)_3](ClO_4)_2 \cdot 2H_2O$ ($T_c = 200$ K). Thus, the introduction of tetrazole into the coordination sphere of the iron(II) ion induced the spin crossover in the polycrystalline phase.

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