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Mono- and Heteroligand Iron(II) Complexes with Tris(3,5-Dimethylpyrazol-1-yl)methane

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Abstract—Coordination compounds of iron(II) thiocyanate with tris(3,5-dimethylpyrazol-1-yl)methane ($HC(3,5\text{-}Me_2Pz)_3$), $[Fe(HC(3,5\text{-}Me_2Pz)_3)_2](NCS)_2]$ (**I**) and $[Fe(HC(3,5\text{-}Me_2Pz)_3)(Phz)(NCS)_2] \cdot H_2O$ (**II**), where Phz is phthalazine, are synthesized. The complexes are studied by X-ray diffraction analysis, diffuse reflectance and IR spectroscopy, and static magnetic susceptibility measurements. The single crystals are obtained, and the molecular and crystal structures of complex **II** and compounds $[Fe(HC(3,5\text{-}Me_2Pz)_3)(3,5\text{-}Me_2Pz)(NCS)_2] \cdot C_2H_5OH$ (**III**), where 3,5-Me_2Pz is 3,5-dimethylpyrazole, and $[Fe(HC(3,5\text{-}Me_2Pz)_3)_2][Fe(HC(3,5\text{-}Me_2Pz)_3)(NCS)_3]_2$ (**IV**) are determined (CIF files CCDC 1415452 (**II**), 1415453 (**III**), and 1415454 (**IV**)). The study of the temperature dependence $\mu_{eff}(T)$ in a range of 2–300 K shows exchange interactions of the antiferromagnetic character between the iron(II) ions in complexes **I** and **II**.

Keywords: iron(II), tris(3,5-dimethylpyrazol-1-yl)methane, complexes, structure, magnetic properties

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INTRODUCTION

Significant attention is given to the search and study of complexes exhibiting spin crossover, since such compounds provide an enhanced response to a change in the external conditions: the spin multiplicity of the ground state changes under the influence of the temperature and pressure or irradiation with light with a certain wavelength [1, 2]. Tris(pyrazol-1-yl)methanes and their derivatives represent a promising class of compounds for the preparation of new magnetically active coordination iron(II) complexes with nitrogen-containing ligands in which spin crossover $^1A_1 \Leftrightarrow {}^5T_2$ and (or) exchange interactions between paramagnetic Fe(II) ions can be observed [3–8].

We have recently synthesized and studied the heteroligand iron(II) complexes with tris(3,5-dimethylpyrazol-1-yl)methane, whose internal coordination sphere contains $HC(3,5\text{-}Me_2Pz)_3$ and other nitrogen-containing ligands, in particular, tetrazole, pyrazole, 3,5-dimethylpyrazole, 3-amino-4-ethoxycarbonylpyrazole, and NCS^- or $N(CN)_2^-$ ions [9]. In some cases, the introduction of the second ligand favors the manifestation of spin crossover in the Fe(II) compounds with $HC(3,5\text{-}Me_2Pz)_3$, whereas no spin crossover was observed in the polycrystalline phase of the monoligand complex. It seemed reasonable to continue the work on the synthesis of the magnetically active iron(II) complexes with $HC(3,5\text{-}Me_2Pz)_3$ and their investigation.

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 (medical grade), salts $Ba(NO_3)_2$ and KNCS (reagent grade), phthalazine (Aldrich), and tris(3,5-dimethylpyrazol-1-yl)methane, which was synthesized according to a modified procedure similar to [10].

Synthesis of $[Fe(HC(3,5\text{-}Me_2Pz)_3)_2](NCS)_2$ (I). A solution of salt $Fe(NCS)_2$ was prepared from a solution of $FeSO_4$ in two stages. At the first stage, a solution of $Fe(NO_3)_2$ was obtained by the exchange reaction between $FeSO_4$ and $Ba(NO_3)_2$. Then $FeSO_4 \cdot H_2O$ (0.14 g, 0.5 mmol) and ascorbic acid (0.1 g) were dissolved together in hot water (3 mL). The stoichiometric amount of $Ba(NO_3)_2$ (0.13 g, 0.5 mmol) was dissolved in water (5 mL) on heating, and a solution of $Ba(NO_3)_2$ was slowly added with stirring to a solution of $FeSO_4$. The resulting solution with a precipitate was kept at room temperature for 2 h, and a precipitate of $BaSO_4$ was filtered and thrown away. For the preparation of $Fe(NCS)_2$, a threefold excess of KNCS (0.29 g, 3 mmol) was dissolved in a minimum amount of water, and this solution was added to the obtained solution of $Fe(NO_3)_2$. A weighed sample of HC(3,5-$Me_2Pz)_3)_2$ (0.45 g, 1.5 mmol) was dissolved in acetone (5–7 mL) on heating, and the solution was added to a hot solution of salt $Fe(NCS)_2$. A white precipitate was formed on cooling in an ice-cold bath. The precipitate was filtered off, washed with ethanol and acetone, and dried in air. Complexes **II** and **III** were washed and dried similarly. The yield of compound **I** was 0.18 g (47%).

For $C_{34}H_{44}FeN_{14}S_2$ (**I**)

anal. calcd., %:	C, 53.1;	H, 5.8;	N, 25.5.
Found, %:	C, 53.4;	H, 6.2;	N, 25.0.

Synthesis of [Fe(HC(3,5-$Me_2Pz)_3$)(Phz)$(NCS)_2$] · $0.5H_2O$ (II). A solution of salt $Fe(NCS)_2$ was obtained in the same way as that for the synthesis of compound **I**. To obtain complex **II**, an equimolar mixture of the ligands, HC(3,5-$Me_2Pz)_3)_2$ (0.5 mmol, 0.15 g) and Phz (0.5 mmol, 0.065 g), was dissolved in acetone (10 mL), and the obtained solution was added to a solution of $Fe(NCS)_2$. An orange precipitate was formed after a solvent excess was removed and the solution was cooled down in an ice-cold bath. The yield of compound **II** was 40%.

For $C_{26}H_{30}FeN_{10}OS_2$ (**II**)

anal. calcd., %:	C, 50.4;	H, 4.9;	N, 22.6.
Found, %:	C, 49.4;	H, 4.9;	N, 22.5.

Crystals of [Fe(HC(3,5-$Me_2Pz)_3$)(3,5-Me_2Pz)$(NCS)_2$] · C_2H_5OH (**III**) suitable for X-ray diffraction analysis precipitated from an ethanolic solution of complex **I** during slow crystallization. Single crystals of complex **II** were grown in a U-like tube upon the reaction of an aqueous solution of $Fe(NCS)_2$ and an acetone solution of a mixture of ligands HC(3,5-$Me_2Pz)_3$ and Phz. An attempt to use this method for growing single crystal crystals of the heteroligand complex [Fe(HC(3,5-$Me_2Pz)_3$)(Aecpz)$(NCS)_2$] · $0.5H_2O$ (Aecpz is 3-amino-4-ethoxycarbinolpyrazole), the synthesis procedure for which was published earlier [9], gave crystals of [Fe(HC(3,5-$Me_2Pz)_3)_2$][Fe(HC(3,5-$Me_2Pz)_3(NCS)_3]_2$ (**IV**).

Elemental analyses to C, H, and N were carried out on a EURO EA 3000 instrument (EuroVector, Italy) at the analytical laboratory of the Nikolaev Institute of Inorganic Chemistry (Siberian Branch, Russian Academy of Sciences).

The X-ray diffraction study of polycrystals of compounds **I–IV** was carried out on a Shimadzu XRD 7000 diffractometer (CuK_α radiation) at room temperature.

X-ray diffraction analyses of complexes **II–IV** were carried out using a standard procedure on a Bruker-Nonius X8 Apex automated four-circle diffractometer equipped with a 4K CCD two-coordinate detector (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 150(2) K. An absorption correction was applied empirically by intensities of equivalent reflections (SADABS) [11]. The structures were solved by a direct method and refined by least squares for F^2 in the anisotropic approximation for all non-hydrogen atoms (SHELXTL) [11]. The hydrogen atoms of the organic ligands were localized geometrically and refined by the riding model, and the hydrogen atoms of the crystallization water molecules were not localized. The crystallographic characteristics and details of diffraction experiments for compounds **II–IV** are presented in Table 1. Selected bond lengths and bond angles are given in Table 2. The coordinates of atoms and thermal parameters were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC 1415452 (**II**), 1415453 (**III**), 1415454 (**IV**); http://www.ccdc.cam.ac.uk/data_request/cif).

The magnetic properties of polycrystalline samples **I–III** were studied on a MPMS-*XL* SQUID magnetometer (Quantum Design) in a range of 2–300 K in a magnetic field of 5 kOe. For the calculation of the paramagnetic component of the molar magnetic susceptibility (χ), diamagnetic corrections were applied according to the Pascal additive scheme. The effective magnetic moment (μ_{eff}) was determined in the paramagnetic range using the equation $\mu_{eff} = \left(\frac{3k}{N_A\mu_B^2}\chi T\right)^{1/2} \approx (8\chi T)^{1/2}$, where k is the Boltzmann constant, N_A is Avogadro's number, and μ_B is the Bohr magneton.

Diffuse reflectance spectra were recorded on a UV-3101 PC scanning spectrophotometer (Shimadzu) at room temperature.

IR absorption spectra were measured on a Scimitar FTS 2000 and a Vertex 80 spectrometers in a range of 100–4000 cm^{-1}. The samples were prepared as suspensions in Nujol, fluorinated oil, and polyethylene.

RESULTS AND DISCUSSION

The iron thiocyanate complexes with tris(3,5-dimethylpyrazol-1-yl)methane and phthalazine were isolated from aqueous-acetone solutions upon the reactions of iron(II) thiocyanate with HC(3,5-$Me_2Pz)_3$ and Phz. Iron(II) thiocyanate was obtained

Table 1. Crystallographic characteristics and details of diffraction experiments and refinement for structures **II**, **III**, and **IV**

Parameter	Value		
	II	**III**	**IV**
Empirical formula	$C_{26}H_{29}FeN_{10}O_{0,5}S_2$	$C_{25}H_{36}FeN_{10}OS_2$	$C_{70}H_{88}Fe_3N_{30}S_6$
FW	609.55	612,61	1709.61
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	10.7553(4)	11.6707(6)	10.5054(6)
b, Å	15.9793(5)	14.3295(7)	10.9726(6)
c, Å	19.7741(6)	17.8191(7)	18.6233(10)
α, deg	90	90	91.137(2)
β, deg	118.582(2)	93.6720(10)	98.7570(10)
γ, deg	90	90	105.0700(10)
V, $Å^3$	2984.26(17)	2973.9(2)	2044.8(2)
Z	4	4	1
ρ_{calcd}, g cm^{-3}	1.354	1.368	1.388
$\mu_{MoK\alpha}$, mm^{-1}	0.681	0.685	0.739
Crystal size, mm	0.24 × 0.10 × 0.08	0.36 × 0.10 × 0.08	0.25 × 0.14 × 0.02
θ Range, deg	1.73–26.02	1.83–27.51	1.93–27.55
Ranges of indices *h*, *k*, *l*	$-13 \leqslant h \leqslant 13$, $-12 \leqslant k \leqslant 19$, $-22 \leqslant l \leqslant 24$	$-14 \leqslant h \leqslant 15$, $-18 \leqslant k \leqslant 17$, $-23 \leqslant l \leqslant 13$	$-12 \leqslant h \leqslant 13$, $-13 \leqslant k \leqslant 14$, $-23 \leqslant l \leqslant 24$
Number of reflections			
measured	18641	23524	14205
unique (*N*) [R_{int}]	5880 (0.0393)	6818 (0.0384)	9386 (0.0383)
observed ($I > 2\sigma(I)$) (N_o)	4464	4939	5995
Number of refined parameters	367	362	505
F(000)	1264	1288	892
R_1, wR_2 for N_o	0.0407, 0.1008	0.0463, 0.1230	0.0505, 0.1012
R_1, wR_2 for *N*	0.0603, 0.1066	0.0755, 0.1324	0.0993, 0.1122
GOOF	1.056	1.077	0.959
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e $Å^{-3}$	0.503; –0.264	1.368; –0.613	0.475; –0.555

from solutions containing $Fe(NO_3)_2$ and a KNCS excess. Salts $Fe(NO_3)_2$ and $Fe(NCS)_2$ were used for the syntheses without isolation from solutions. To avoid iron(II) oxidation, ascorbic acid (pH ~ 2) was used as a reducing and acidifying agent.

The crystals of compound **II** suitable for X-ray diffraction analysis 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 $HC(3,5\text{-}Me_2Pz)_3$ and Phz. The structure of compound **II** is formed by molecular complexes $[Fe\{HC(3,5\text{-}Me_2Pz)_3\}\{Phz\}(NCS)_2]$ containing central Fe(II) atoms in a weakly distorted octahedral environment (Fig. 1) and solvate water molecules. Tris(3,5-dimethylpyrazol-1-yl)methane coordinates to the Fe(II) atom via the tridentate cyclic mode. Along with three N atoms of tris(3,5-dimethylpyrazol-1-yl)methane, the coordination environment of the Fe(II) atom contains the N(Phz) atom and two N atoms of two thiocyanate groups. The Fe–N bond lengths somewhat differ depending on the ligand: for $HC(3,5\text{-}Me_2Pz)_3$ they range from 2.180(2) to 2.210(2) Å, whereas for the Phz and NCS^- groups they are 2.221(2), 2.109(2), and 2.114(2) Å, respectively.

Table 2. Selected bond lengths (Å) and angles (deg) in compounds **II**, **III**, and **IV***

Bond	*d*, Å	Bond	*d*, Å
		II	
Fe(1)–N(1)	2.109(2)	N(11)–N(12)	1.375(3)
Fe(1)–N(2)	2.114(2)	N(21)–N(22)	1.376(3)
Fe(1)–N(11)	2.2095(19)	N(31)–N(32)	1.373(2)
Fe(1)–N(21)	2.2018(19)	N(1)–C(1)	1.161(3)
Fe(1)–N(31)	2.180(2)	N(2)–C(2)	1.162(3)
Fe(1)–N(41)	2.221(2)	C(1)–S(1)	1.629(3)
		C(2)–S(2)	1.630(3)
		III	
Fe(1)–N(1)	2.108(2)	N(11)–N(12)	1.374(3)
Fe(1)–N(2)	2.092(2)	N(21)–N(22)	1.371(3)
Fe(1)–N(11)	2.209(2)	N(31)–N(32)	1.373(3)
Fe(1)–N(21)	2.229(2)	N(1)–C(1)	1.165(3)
Fe(1)–N(31)	2.223(2)	N(2)–C(2)	1.157(4)
Fe(1)–N(41)	2.164(2)	C(1)–S(1)	1.636(3)
		C(2)–S(2)	1.635(3)
		IV	
Fe(1)–N(11)	1.991(2)	N(11)–N(12)	1.372(3)
Fe(1)–N(21)	1.978(2)	N(21)–N(22)	1.377(3)
Fe(1)–N(31)	1.976(2)	N(31)–N(32)	1.377(3)
Fe(2)–N(1)	2.100(3)	N(41)–N(42)	1.378(3)
Fe(2)–N(2)	2.126(3)	N(51)–N(52)	1.373(3)
Fe(2)–N(3)	2.108(3)	N(61)–N(62)	1.387(3)
Fe(2)–N(41)	2.216(2)	N(1)–C(1)	1.164(4)
Fe(2)–N(51)	2.315(2)	N(2)–C(2)	1.160(4)
Fe(2)–N(61)	2.212(2)	N(3)–C(3)	1.160(4)
		C(1)–S(1)	1.630(3)
		C(2)–S(2)	1.640(3)
		C(3)–S(3)	1.636(3)
Angle	ω, deg	Angle	ω, deg
		II	
N(1)Fe(1)N(2)	95.86(8)	N(2)Fe(1)N(41)	87.19(8)
N(1)Fe(1)N(11)	91.13(8)	N(11)Fe(1)N(21)	81.33(7)
N(1)Fe(1)N(21)	171.63(8)	N(11)Fe(1)N(31)	83.33(7)
N(1)Fe(1)N(31)	91.89(8)	N(11)Fe(1)N(41)	95.79(8)
N(1)Fe(1)N(41)	88.01(8)	N(21)Fe(1)N(31)	83.69(7)
N(2)Fe(1)N(11)	172.51(8)	N(21)Fe(1)N(41)	96.30(8)
N(2)Fe(1)N(21)	91.52(8)	N(31)Fe(1)N(41)	179.11(8)
N(2)Fe(1)N(31)	93.71(8)		
		III	
N(1)Fe(1)N(2)	93.91(9)	N(2)Fe(1)N(41)	96.17(9)
N(1)Fe(1)N(11)	92.30(9)	N(11)Fe(1)N(21)	82.16(8)
N(1)Fe(1)N(21)	172.68(8)	N(11)Fe(1)N(31)	81.81(8)
N(1)Fe(1)N(31)	92.34(9)	N(11)Fe(1)N(41)	167.48(8)
N(1)Fe(1)N(41)	95.56(9)	N(21)Fe(1)N(31)	82.17(8)
N(2)Fe(1)N(11)	92.99(9)	N(21)Fe(1)N(41)	89.12(8)
N(2)Fe(1)N(21)	91.17(8)	N(31)Fe(1)N(41)	88.14(8)
N(2)Fe(1)N(31)	172.02(9)		

Table 2. (Contd.)

Angle	ω, deg	Angle	ω, deg
	IV		
N(11)Fe(1)N(21)	89.03(9)	N(1)Fe(2)N(61)	163.21(9)
N(11)Fe(1)N(21)*	90.97(9)	N(2)Fe(2)N(41)	174.27(10)
N(11)Fe(1)N(31)	88.96(9)	N(2)Fe(2)N(51)	96.37(10)
N(11)Fe(1)N(31)*	91.04(9)	N(2)Fe(2)N(61)	93.63(10)
N(21)Fe(1)N(31)	88.05(10)	N(3)Fe(2)N(41)	89.90(10)
N(21)Fe(1)N(31)*	91.95(10)	N(3)Fe(2)N(51)	171.29(10)
N(1)Fe(2)N(2)	95.72(10)	N(3)Fe(2)N(61)	93.80(10)
N(1)Fe(2)N(3)	100.06(11)	N(41)Fe(2)N(51)	82.96(9)
N(2)Fe(2)N(3)	90.24(10)	N(41)Fe(2)N(61)	80.65(9)
N(1)Fe(2)N(41)	89.89(10)	N(51)Fe(2)N(61)	80.17(9)
N(1)Fe(2)N(51)	84.95(9)		

* Symmetry transformations used to generate equivalent atoms: $-x$, $1 - y$, $1 - z$.

The crystals of compound **III** suitable for X-ray diffraction analysis were obtained by the slow crystallization of complex **I** from an ethanolic solution. The structure of compound **III** is formed by molecular complexes $[Fe\{HC(3,5\text{-}Me_2Pz)_3\}\{3,5\text{-}Me_2Pz\}(NCS)_2]$ containing the central Fe(II) atoms in an almost undistorted octahedral environment (Fig. 2) and solvate molecules of ethanol. Tris(3,5-dimethylpyrazol-1-yl)methane coordinates to the Fe atom via the tridentate cyclic mode. Along with three N atoms of tris(3,5-dimethylpyrazol-1-yl)methane, the coordination environment of the Fe(II) atom contains the N atom from 3,5-dimethylpyrazole and two N atoms of two thiocyanate groups. The Fe–N bond lengths somewhat differ depending on the ligand: for $HC(3,5\text{-}Me_2Pz)_3$ they lie in a range of 2.209(2)–2.229(2) Å, and for the 3,5-Me_2Pz and NCS^- groups they are 2.164(2), 2.108(2), and 2.092(2) Å, respectively. Thus, the thiocyanate ion in the internal coordination sphere of iron(II) favors an easy elimination of the 3,5-dimethylpyrazole molecule. We observed such a phenomenon for the complex formation of iron(II) dicyanamide with tris(3,5-dimethylpyrazol-1-yl)methane [9]. The reaction of iron(II) dicyanamide with two $HC(3,5\text{-}Me_2Pz)_3$ molecules affords complex $[Fe(HC(3,5\text{-}Me_2Pz)_3)(3,5\text{-}Me_2Pz)(N(CN)_2)_2] \cdot 0.5H_2O$. We assumed that the presence of anions with pronounced donor properties (in this case, thiocyanate ion) in the reaction mixture played an important role in the elimination of 3,5-Me_2Pz.

The crystals of compound **IV** were prepared by an attempt to crystallize complex $[Fe(HC(3,5\text{-}Me_2Pz)_3)(Aecpz)(NCS)_2] \cdot 0.5H_2O$, the synthesis of the polycrystalline phase of which was described [9]. 3-Amino-4-ethoxycarbonylpyrazole does not enter into the coordination sphere of Fe(II) in the course of slow crystallization, and single crystals of compound **IV** are formed. The structure of compound **IV** is built of discrete complex ions: centrosymmetric cations $[Fe\{HC(3,5\text{-}Me_2Pz)_3\}_2]^{2+}$ (Fig. 3a) and noncentrosymmetric anions $[Fe\{HC(3,5\text{-}Me_2Pz)_3\}(NCS)_3]^-$ (Fig. 3b). In both cases, the coordination polyhedron of the Fe(II) atoms is octahedron. The coordination

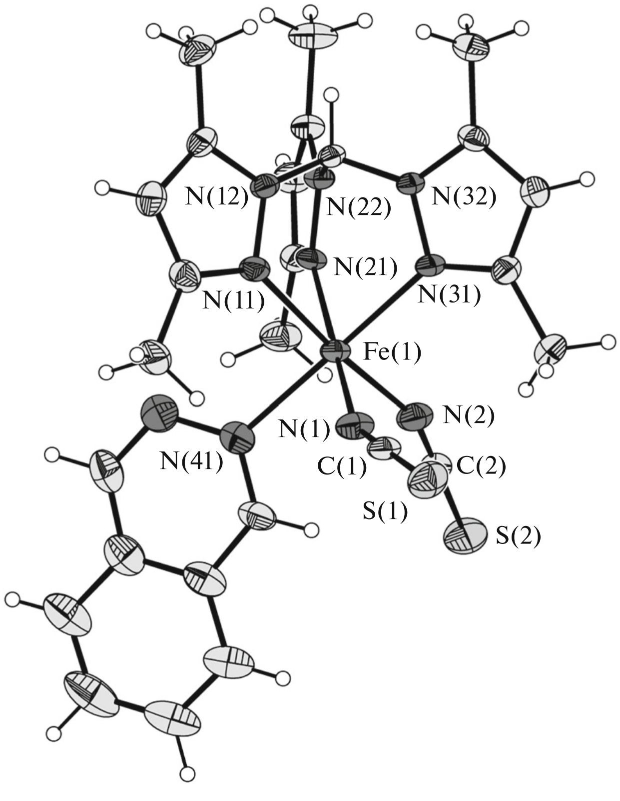

Fig. 1. Structure of molecular complex $[Fe(HC(3,5\text{-}Me_2Pz)_3)(Phz)(NCS)_2]$ in compound **II** (thermal ellipsoids of 50% probability).

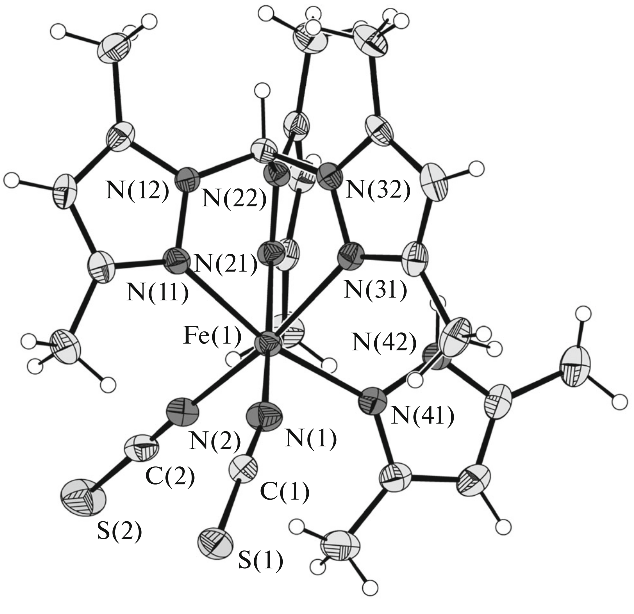

Fig. 2. Structure of molecular complex [Fe(HC(3,5-$Me_2Pz)_3)(3,5-Me_2Pz)(NCS)_2$] in compound **III** (thermal ellipsoids of 50% probability).

polyhedron in the cation is formed by six N atoms of two coordinated $HC(3,5-Me_2Pz)_3$ molecules, whereas that in the anion is formed by three N atoms of the $HC(3,5-Me_2Pz)_3$ molecule and three N atoms of three thiocyanate groups. Tris(3,5-dimethylpyrazol-1-yl)methane in both cation and anion is coordinated via the tridentate cyclic mode to form three six-membered metallocycles –Fe–N–N–C–N–N– with two common iron atoms and carbon of the CH group. In the $[Fe\{HC(3,5-Me_2Pz)_3\}_2]^{2+}$ cation, the Fe–N bond lengths lie in a range of 1.976(2)–1.991(2) Å, indicating the low-spin state of Fe(II). In the $[Fe\{HC(3,5-Me_2Pz)_3\}(NCS)_3]^-$ anion, these bonds are noticeably longer (2.212(2)–2.315(2) Å), which is characteristic of Fe(II) in the high-spin state. The Fe–N(NCS) bond lengths are 2.100(3), 2.108(3), and 2.126(3) Å.

The structures of compounds **II** and **III** are characterized by fairly weak directed intermolecular interactions. The structure of **II** contains hydrogen bonds between the crystallization water molecules and coordination phthalazine molecules (O···N 3.14 Å), as well as π–π-stacking interactions between the tris(3,5-dimethylpyrazol-1-yl)methane heterocycles and benzene rings of phthalazine (the distance between their planes is ~3.7 Å). A weak hydrogen bond N–H···S (N···S 3.51 Å) between the NH group of 3,5-dimethylpyrazole and the S atom of one of NCS^- groups of the adjacent molecular complex can be mentioned in the case of compound **III**. The presence of bonds of this type results in the formation of chains of molecular complexes parallel to the *z* axis (Fig. 4). The second NCS^- group participates in the hydrogen bond with the solvate molecule of ethanol (O···S 3.32 Å). Appreciable directed intermolecular interactions are absent from the structure of compound **IV**.

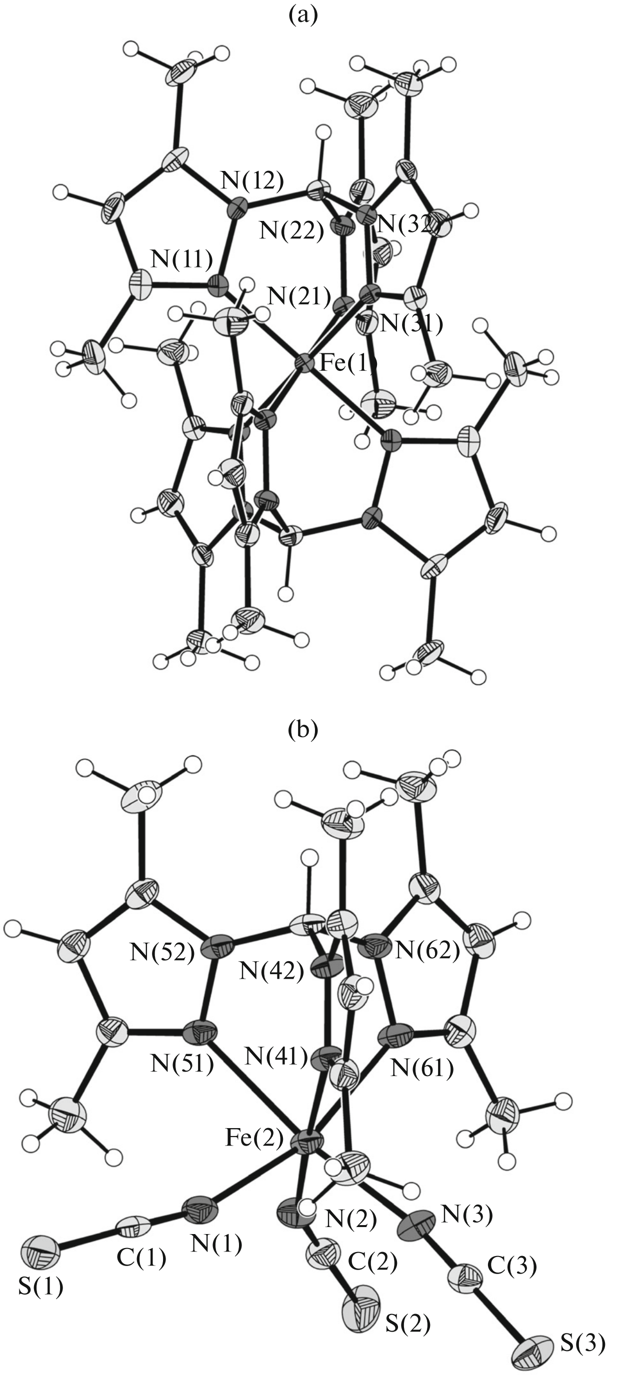

Fig. 3. Structures of the (a) $[Fe\{HC(3,5-Me_2Pz)_3\}_2]^{2+}$ complex cation and (b) $[Fe\{HC(3,5-Me_2Pz)_3\}(NCS)_3]^-$ anion in compound **IV** (thermal ellipsoids of 50% probability).

The diffuse reflectance spectra of complexes **I** and **II** contain one broad band each with maxima at ~860 cm^{-1}. The bands can be assigned to the $^5T_2 \rightarrow {}^5E$

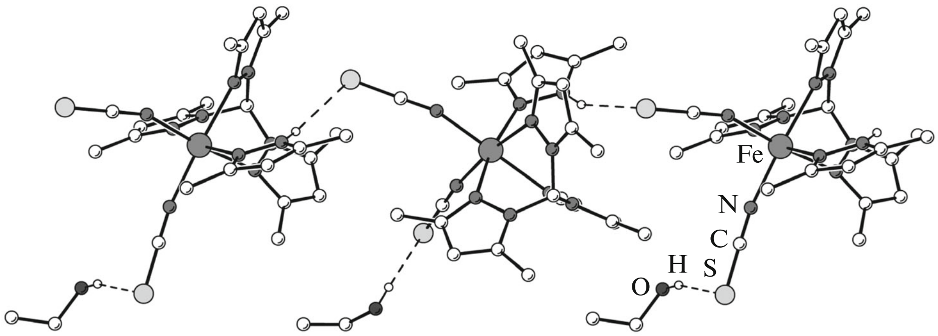

Fig. 4. Fragment of the chain formed by hydrogen bonds N–H···S (dashed lines) between complexes [Fe(HC(3,5-$Me_2Pz)_3$)(3,5-Me_2Pz)$(NCS)_2$] in structure **IV**. Hydrogen atoms that are not involved in hydrogen bonding are omitted for clarity.

transition in a weak distorted octahedral field of the ligands. Their position is characteristic of high-spin iron(II) complexes with the FeN_6 coordination mode, in particular, complexes of various iron(II) salts with 1,2,4-triazoles [12].

The main vibration frequencies in the spectra of complexes **I** and **II**, ligands HC(3,5-$Me_2Pz)_3$ and Phz, and thiocyanate ions are presented in Table 3. The band of stretching vibrations of the OH groups appears at 3644 cm^{-1} in the high-frequency range of the spectrum of compound **II** containing water molecules. The ν(CH) vibrations in the spectra of complexes **I** and **II** and ligands HC(3,5-$Me_2Pz)_3$ and Phz are observed in a range of 3160–2850 cm^{-1}.

The vibrations of the heterocycles are observed in the range 1610–1470 cm^{-1}. The R(ring) position in the spectrum of complex **I** remains almost unchanged compared to the spectrum of HC(3,5-$Me_2Pz)_3$, which can be explained by the influence of various factors during complex formation. The spectrum of complex **II** exhibits significant changes in the range of cycle vibrations, indicating the coordination of both HC(3,5-$Me_2Pz)_3$ and Phz to the metal.

The bands of stretching metal–ligand vibrations are observed in the low-frequency range of the spectra of the complexes (600–100 cm^{-1}). The new bands in the spectra of compounds **I** and **II** at 270–235 cm^{-1}, which are absent from the spectra of the ligands, can be assigned to ν(Fe–N), confirming the coordination of these nitrogen-containing ligands to the metal.

The results of X-ray diffraction analyses for a series of the iron(II) complexes with tris(pyrazol-1-yl)methanes [3–8] and those for compound **II** obtained in this work indicate that HC(3,5-$Me_2Pz)_3$ coordinates via the tridentate cyclic mode and three N(2) atoms of the pyrazole cycles add to the metal. Therefore, in complex **I** the FeN_6 coordination mode is formed by six nitrogen atoms of two HC(3,5-$Me_2Pz)_3$ molecules, and the thiocyanate ions are outer-sphere. The coordination of NCS groups in 3*d*-metal complexes occurs most frequently through nitrogen atoms, and the ν(CN) band in these complexes lies near 2050 cm^{-1} [13]. The split ν(CN) band in the spectrum of com-

Table 3. Selected vibration frequencies in the spectra of complexes **I** and **II**, molecules HC(3,5-$Me_2Pz)_3$ and Phz, and thiocyanate ion

ν, cm^{-1}					
I	**II**	HC(3,5-$Me_2Pz)_3$	Phz	NCS^-	Assignment
	3644				ν(OH)
2064 2050	2079 2066			2053	ν(CN)
1561	1607 1564	1561	1605 1577 1556 1488		R(ring)
271 256 234	267 243				ν(M–N)

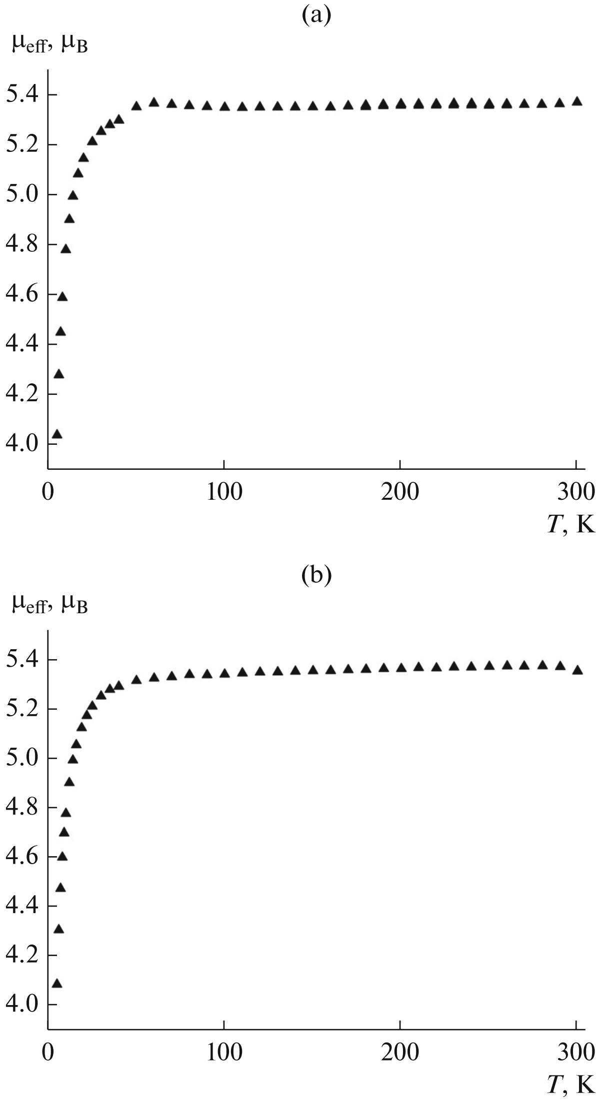

Fig. 5. Dependences $\mu_{\text{eff}}(T)$ for complexes (a) **I** and (b) **II**.

pound **I**, whose center is located at 2057 cm^{-1}, indicates the out-of-sphere position of the thiocyanate ion. According to the X-ray diffraction data for complex **II**, its three coordination sites are occupied by the nitrogen atoms of the HC(3,5-$Me_2Pz)_3$ molecule and one site is occupied by the nitrogen atom of monodentatly coordinated Phz. The coordination polyhedron of FeN_6 is supplemented to an octahedron by two nitrogen atoms of two thiocyanate ions. The IR spectrum of complex **II** exhibits the split ν(CN) band noticeably shifted to the high-frequency range compared to the spectrum of NCS^-, which is consistent with the out-of-sphere position of the thiocyanate ion. It is difficult to distinguish the ν(C=S) bands because of their overlapping with the vibration bands of the ligands.

The $\mu_{\text{eff}}(T)$ dependences for complexes **I** and **II** are similar (Fig. 5). At 300 K the values of μ_{eff} equal to 5.37 μ_B remain almost unchanged as the temperature decreases to 40 K. Below 40 K μ_{eff} decrease to achieve 4.04 μ_B for **I** and 4.90 μ_B for **II** at 5 K. The values of μ_{eff} in a temperature range of 300–40 K for compounds **I** and **II** are somewhat higher than the theoretical purely spin value, which is equal to 4.90 μ_B for one paramagnetic center with the spin $S = 2$ at a g factor of 2. The exchange interactions between spins of the iron(II) ions are weak and observed only below 40 K.

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