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Ferrocenoylhydrazone of 2-*N*-Tosylaminobenzaldehyde: Structure, Properties, and Complexing Ability

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Abstract—2-*N*-Tosylaminobenzaldehyde ferrocenoylhydrazone was synthesized. The crystal structure of the hydrazone was shown to include two independent molecules differing in mutual orientation of the tosyl and ferrocene fragments. Quantum-chemical simulation of the hydrazone tautomerism was performed. Its complexes with Cu(II), Ni(II), Zn(II), and Cd(II) were synthesized and investigated.

Keywords: ferrocenoylhydrazones, electronic spectroscopy, tautomerism, X-ray diffraction analysis, density functional theory, complex formation

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Acylhydrazones of polyfunctional carbonyl compounds is one of the most studied ligand systems in modern coordination and supramolecular chemistry [1–4], which is due to both their biological activity [5–7] and a high complexing ability [8, 9]. Among compounds of this type, hydrazones containing ferrocenyl fragment are of special interest, some of which show second order non-linear optical properties [10–12] or biological activity [13–15]. Numerous complexes based on hydrazones of carbonyl ferrocene derivatives were described [16–24], whereas ferrocenoylhydrazones of carbonyl compounds are much less studied [25–29]. In particular, so far, only one ferrocenoylhydrazone was investigated by X-ray diffraction analysis (XRD) method [30]. The literature data on the hydrazones of 2-*N*-tosylaminobenzaldehyde are also scarce [31–34].

In continuation of studies on complexing properties of ferrocene-containing ligands [35–37] we have synthesized and investigated ferrocenoylhydrazone of 2-*N*-tosylaminobenzaldehyde (**I**) and a number of its metal complexes. Compound **I** can exist in the form of two main tautomers: hydrazone form **Ia** and α-oxyazine form **Ib** [38] (Scheme 1).

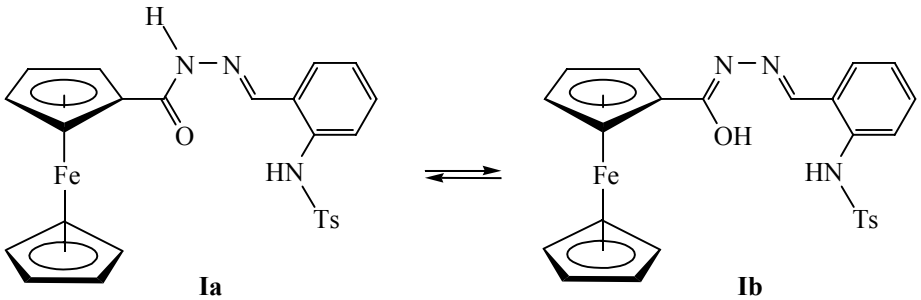
In the IR spectrum of compound **I** the absorption bands are present from the stretching vibrations of the N–H bonds of the hydrazone and tosylamino groups, and the C=O and C=N bonds. In the short-wave region of the spectrum two absorption bands are observed, which are characteristic of ferrocene-containing structures and belong to torsional vibrations of cyclopentadienyl ligands.

The ^{1}H NMR spectrum of compound **I** shows an upfield singlet of the methyl group. The signal of the unsubstituted cyclopentadienyl ring appears as a singlet. The signals of the substituted cyclopentadienyl ring protons are shifted downfield with respect to this singlet and are non-split. Two singlets of the imine groups appear downfield. The most downfield signal was assigned to the imine proton of the hydrazone group, which was proved by investigating model compounds (2-*N*-tosylaminobenzaldehyde and benzaldehyde ferrocenoylhydrazone). These data allow to suggest that compound **I** exists mainly in the hydrazone form **Ia** [8, 9].

To prove this assumption we have performed quantum-chemical calculations of the electronic and spatial structure of tautomers **Ia, Ib** at the density functional theory level (DFT) in the gas phase and in ethanol solution. The polarized continuum model

† Deceased.

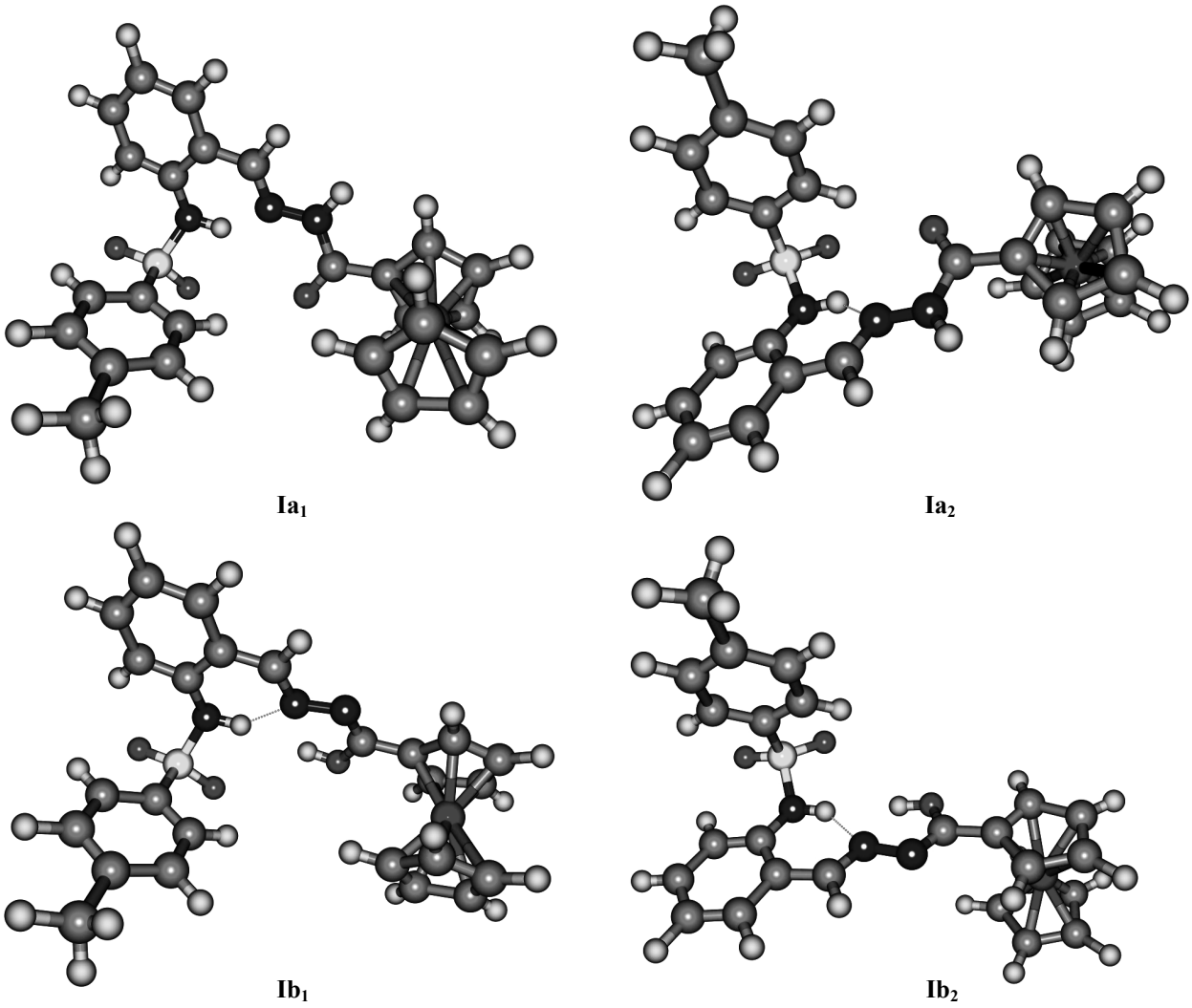
Scheme 1.



Ia **Ib**

(PCM) was used to take into account the solvent effect [39]. The hybrid exchange-correlation functional B3LYP [40–42] with extended valence-split basis set 6-311+G(*d,p*) was employed. The geometry of the molecules was fully optimized without symmetry restrictions. The minima on the potential energy surface were identified for each structure by calculation of the force constants matrix and normal modes.

The structure of tautomers **Ia, Ib** is shown in Fig. 1; their total energies and relative stabilities are given in Table 1. For both tautomers the local energy minima



Ia_1 **Ia_2**

Ib_1 **Ib_2**

Fig. 1. Molecular structure of tautomeric forms of compound **I** in the gas phase.

Table 1. Total energy E (au) and relative stability (ΔE, kcal/mol) of tautomeric forms of compound **I**

Structure	E, a.u.		ΔE, kcal/mol	
	vacuum	ethanol	vacuum	ethanol
Ia$_1$	–3018.66046	–3018.69764	0.83	1.0
Ia$_2$	–3018.66177	–3018.69923	0	0
Ib$_1$	–3018.65573	–3018.67854	3.79	13.0
Ib$_2$	–3018.65600	–3018.67911	3.62	12.6

are shown for the conformations corresponding to the location of the tosyl group and the ferrocene fragment at the same (**Ia$_1$** and **Ib$_1$**) or the opposite (**Ia$_2$** and **Ib$_2$**) sides of the hydrazone group C–N–N–C. The energy of the *trans*-conformers is somewhat lower both in the gas phase and in the solution, but ΔE does not exceed 1 kcal/mol (Table 1). In all cases, the hydrazone form **Ia** is more stable than the α-oxyazine form **Ib** , and in ethanol the ΔE value increases from 3.6 to 12.6 kcal/mol.

The structure of compound **I** in the crystal was determined by XRD analysis. The single crystal was obtained by slow crystallization from the solution in DMF. In the crystal, compound **I** exists in the hydrazone tautomeric form. Selected interatomic distances and bond angles are given in Table 2.

The unit cell contains two independent molecules, **A** and **B**, with close geometric parameters (Fig. 2). The main difference between **A** and **B** consists in different mutual orientation of the tosyl group and the ferrocene fragment: at different sides of the hydrazone group $C^{11}N^1N^2C^{12}$ in molecule **A**, and at the same side of the analogous group $C^{36}N^4N^5C^{37}$ in molecule **B**.

The ferrocene fragment in molecule **B** has the eclipsed conformation; its conformation in molecule **A** is also close to the eclipsed, but the cyclopentadienyl rings are turned by the angle of ca. 7º. The hydrazone fragment in molecule **A** is slightly distorted being turned about the N^1–N^2 bond; the dihedral angle between the averaged planes of the phenyl and the cyclopentadienyl rings is 13.56(11)º. In molecule **B**, the hydrazone fragment is practically planar.

Along with the aforementioned distortion, there is a difference in the conformation of the tosylamino group resulting in a substantial difference in the geometric characteristics of intramolecular hydrogen bonds

Table 2. Principal interatomic distances and bond angles in the molecule of compound **I**

Bond	d, Å	Angle	ω, deg
S^1–O^3	1.429617	$O^3S^1O^2$	119.7011
S^1–O^2	1.435117	$O^3S^1N^3$	109.9610
S^1–N^3	1.638717	$O^2S^1N^3$	104.629
O^1–C^{11}	1.2372	$O^3S^1C^{19}$	108.3711
N^1–C^{11}	1.3602	$O^2S^1C^{19}$	108.1911
N^1–N^2	1.3642	$N^3S^1C^{19}$	105.0410
N^2–$C1^2$	1.2812	$C^{11}N^1N^2$	117.9315
N^3–C^{18}	1.4193	$C^{12}N^2N^1$	118.3916
S^2–O^5	1.431216	$C^{18}N^3S^1$	125.0214
S^2–O^6	1.431715	$O^5S^2O^6$	119.5610
S^2–N^6	1.630417	$O^5S^2N^6$	110.5110
O^4–C^{36}	1.2332	$O^6S^2N^6$	103.979
N^4–C^{36}	1.3492	$O^5S^2C^{44}$	107.639
N^4–N^5	1.3732	$O^6S^2C^{44}$	109.2710
N^5–C^{37}	1.2832	$N^6S^2C^{44}$	104.979
N^6–C^{43}	1.3982	$C^{36}N^4N^5$	117.7914
		$C^{37}N^5N^4$	117.0115
		$C^{43}N^6S^2$	127.8913

formed between the tosylamino NH groups and the azomethine atoms N^2 and N^5. In molecule **B**, the six-membered ring closed by hydrogen bond is practically planar, thus favoring the optimal characteristics of the hydrogen bond (N^6–H^{6B} 0.88, $H^{6B}\cdots N^5$ 1.92, $N^6\cdots N^5$ 2.637(2) Å, $N^6H^{6B}N^5$ 137º). In molecule **A**, the atoms of sulfur and hydrogen H^{3B} are significantly out-of-plane due to the rotation about the C^{18}–N^3 bond, which substantially impairs the formation of the hydrogen bond (N^3–H^{3B} 0.88, $H^{3B}\cdots N^2$ 2.22, $N^3\cdots N^2$ 2.657(2) Å, $N^3H^{3B}N^2$ 110º). The tosyl groups are turned with respect to the S^1–N^3 and S^2–N^6 bonds so that the S^1=O^2 and N^3–H^{3B} and the S^2=O^6 and N^6–H^{6B} bonds become coplanar in pairs.

The hydrazone NH group in each molecule **A** and **B** forms intermolecular hydrogen bonds with the carbonyl oxygen of the hydrazide group in the adjacent crystallographic position, so that molecules **A** are linked with molecules **B** and vice versa. Molecule of

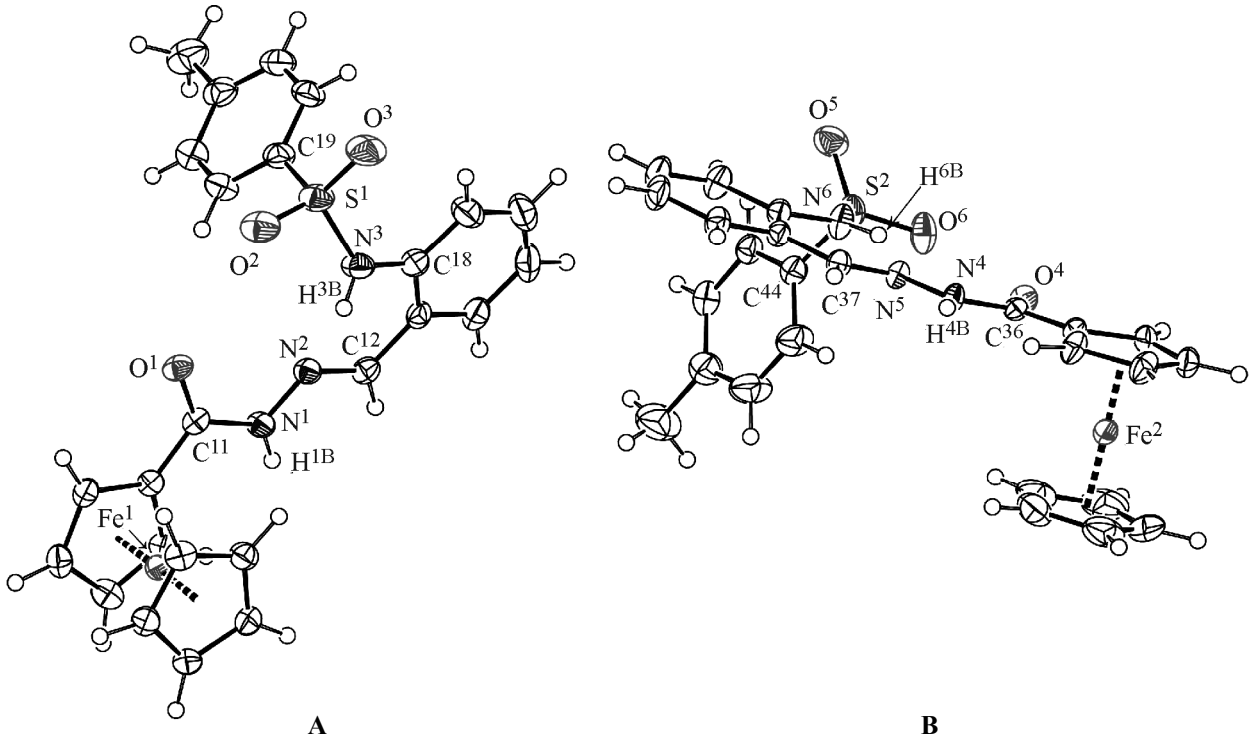


Fig. 2. Structure of two independent molecules of compound **I** with atoms presented as thermal ellipsoids of 50% probability.

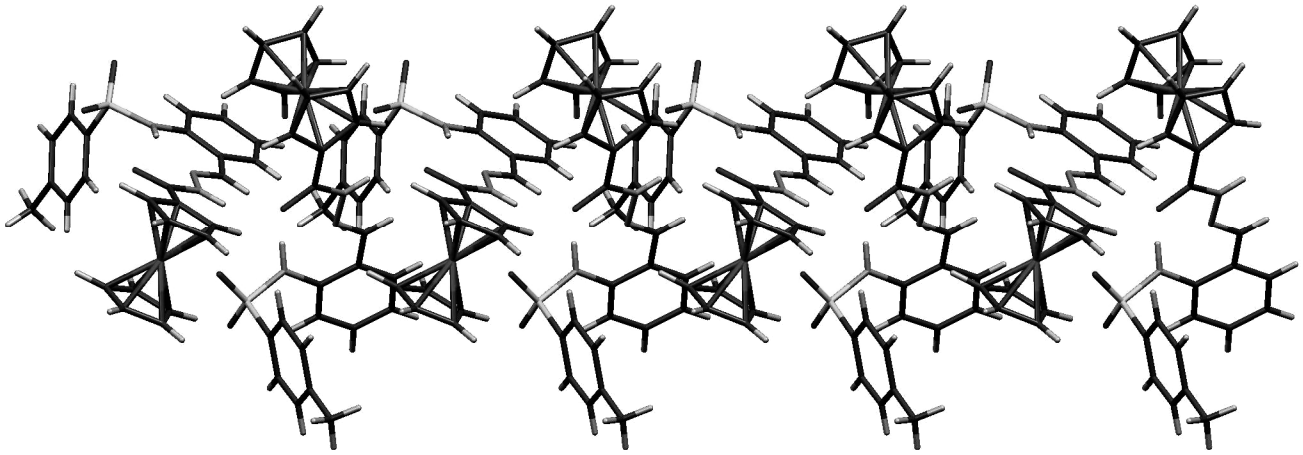


Fig. 3. Linear chains of molecules of compound **I** in crystal (view along the crystallographic axis *c*).

the type **A** forms two bonds with the following characteristics: N^1–H^{1B} 0.88, $H^{1B}\cdots O^{4i}$ 1.94, $N^1\cdots O^{4i}$ 2.777(2) Å, $N^1H^{1B}O^{4i}$ 157°; and $N4^{ii}$–$H4B^{ii}$ 0.88, $O^1\cdots H^{4Bii}$ 1.96, $O^1\cdots N^{4ii}$ 2.786(2) Å, $N^{4ii}H^{4Bii}O^1$ 155°; symmetry codes: (i) $2-x, -2-y, 2-z$; (ii) $1-x, -2-y, 2-z$. Similar bonds are formed also with participation of molecules of the type **B**; as a result, in the single crystal of compound **I** independent infinite linear chains are formed, stretched along crystallographic axis *a,* in which the molecules in conformations **A** and **B** are alternating (Fig. 3).

Note that the results of quantum chemical simulation of the spatial structure of the hydrazone tautomer of compound **I** nicely agree with the XRD data. The difference between the experimental and calculated lengths of the C–C, C–O and C–N bonds in all cases (in gas phase or in ethanol) does not exceed

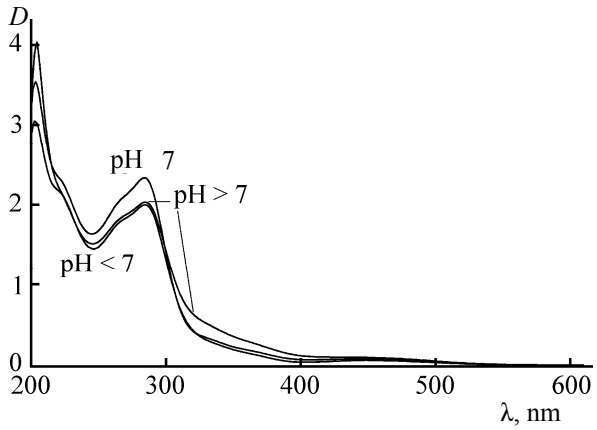


Fig. 4. UV spectra of 2-*N*-tosylaminobenzaldehyde ferrocenoylhydrazone in methanol at various pH.

0.02 Å. The best agreement with the experiment is observed for the geometry calculated in ethanol. The calculated energy of conformer **A** (**Ia$_1$**) is by 0.83 kcal/mol in the gas phase and by 1.00 kcal/mol in ethanol lower than that of conformer **B** (**Ia$_2$**) (Table 1).

The electron absorption spectrum of hydrazone **I** in methanol (Fig. 4) shows absorption bands at 284 nm (ε 23300 L cm^{-1} mol^{-1}) and 445 nm (ε 7900 L cm^{-1} mol^{-1}); in aqueous ethanol the position of the long-wave band remains practically unchanged (448 nm, ε 7800 L cm^{-1} mol^{-1}).

In acidic and alkaline media the extinction of the most short-wave band, which was observed also in the starting *o*-tosylaminobenzaldehyde and was assigned to the π–π* transition, is reduced by 15%. For the most long-wave absorption band assigned to the *d*–*d** transitions of the iron atom in the sandwich fragment [43], the decrease in the solution pH causes a hypochromic effect, although the position of the band in the spectrum virtually does not depend on the acidity of the solution.

The hypochromic effect can be attributed to the protonation of ferrocene, which can occur both at the iron atom and at the π-system of the cyclopentadiene ring. The absence of the red shift of the long-wave absorption band can serve as an indirect indication of the protonation of the cyclopentadienyl ring. As was shown earlier [44], the wedge-shaped distortion of the sandwich fragment (caused, in particular, by protonation of ferrocene at the iron atom) results in a distortion of the MO of the sandwich moiety, which must produce in a substantial red shift of the band under consideration.

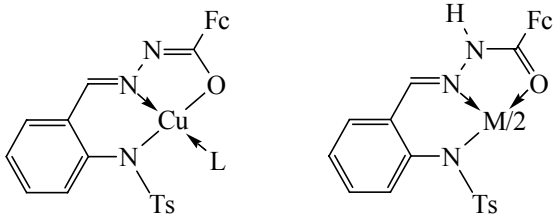
With Cu(II) acetate, hydrazone **I** forms complex **II** of the composition CuL·CH$_3$OH. In the IR spectrum of compound **II** as compared to **I** the bands ν(NH) and ν(C=O) disappear, and the ν(C=N) absorption band is split in two components, one of which is shifted to low frequencies. At the same time, in the IR spectrum of complex **II** a wide absorption band at 3380 cm^{-1} was observed, which was assigned to the stretching vibrations of the OH group of the coordinated molecule of methanol. The effective magnetic moment of complex **II** at room temperature is 1.81 μB, which is close to the pure-spin value and is characteristic of Cu(II) complexes with square-planar surrounding of the central ion [45]. Cooling to 77.4 K practically does not change the value of μ_{eff} of complex **II** (1.79 μB), which is indicative of its mononuclear structure. These data allow assigning the complex of Cu(II) with hydrazone **I** the structure of the type **II** (Scheme 2).

Note however, that complexes of Cu(II) with hydrazones and azomethins of 2-*N*-tosylaminobenzaldehyde are usually characterized by the presence of a weak [*d*(Cu–O) ~2.7 Å] coordination of one of the sulfonyl oxygens, complementing the coordination polyhedron of the copper atoms to a strongly distorted square pyramid (4 + 1) [34].

With Ni(II), Zn(II), and Cd(II) acetates, hydrazone **I** forms complexes of the composition M(HL)$_2$ (see Experimental). Disappearance of one of the ν(NH) absorption bands in the IR spectra of these complexes and a low-frequency shift of the ν(C=O) and ν(C=N) bands is indicative of the tridentate coordination of the ligand in the monodeprotonated form. Taking into account the composition, the Ni(II), Zn(II), and Cd(II) complexes can be assumed to have the structure of the type **III–V** with the octahedral surrounding of the central ion.

In the diffuse reflection spectra of the Ni complex the bands of six transitions were registered (Table 3).

Scheme 2.



II, L = CH$_3$OH; **III** (M = Ni), **IV** (M = Zn), **V** (M = Cd).

The least long-wave transitions correspond to the *d*–*d** transitions of the iron ion in ferrocene, and the band at 903 nm, apparently, is the band of charge transfer from the ligand to the metal. Also, three transitions were observed, whose frequencies are typical of electronic transitions of Ni(II) ion in an octahedral surrounding.

Special consideration should be given to the ^{1}H NMR spectra of Cd(II) complex. In general, they agree well with the suggested structure of the type **V**. The signal of the methine proton appears in the ^{1}H NMR spectrum of the complex as a singlet with satellites caused by the splitting on the cadmium ion with the vicinal coupling constant ^3J = 19.5 Hz. The presence of such a splitting proves participation in the coordination of the azomethine nitrogen atom. The spectrum contains an upfield singlet of the methyl group. The signals of aromatic protons are well resolved, which made it possible to make a complete assignment. The signals of the *p*-substituted aromatic ring appear as doublets with coupling constants of 7.8 Hz. The protons in the third and forth positions of the *o*-substituted ring are split into triplets with the averaged constant 7.3 Hz. The signals of the protons in the *o*-positions appear as a doublet and a broadened singlet, apparently, due to intramolecular hydrogen bond with the sulfonyl group.

However, an unusual behavior was observed in the ferrocenyl protons. Thus, instead of three singlets typical of monosubstituted ferrocenes (as a rule, the protons of the substituted ring are not split), six signals are observed with total integral intensity corresponding to monosubstituted ferrocene (9H). The proton signals of the Cd(II) complex are significantly shifted with respect to the original hydrazone **I**, which allows to exclude the presence of the latter in the sample. The character of the spectrum allows suggesting the release of magnetic equivalence of all four protons of the substituted cyclopentadiene ring; note the dependence of the difference of the chemical shifts of the chemically equivalent (in pairs) protons on the degree of their removal from the carbon atom in the first position of the ring. This phenomenon could be due to a strong π-conjugation of the carbonyl group with the substituted ring, in which the *ortho*-protons appear in different regions (Scheme 3).

The question which also deserves consideration is different type of binding of the two ligands with the metal (since the intensities of the signals are similar). However, the character of the splitting of the protons of the unsubstituted ring allows a conclusion that the latter suggestion is incorrect. For the total integral intensity of 5H, the signal of the free ring consists of the two components with the intensities of 1H and 4H. The only assumption allowing for this fact is the release of magnetic equivalence of one of protons of the unsubstituted ring due to specific influence of its closest nonchemical surrounding. This effect may have steric nature connected with hindrances suffered by a bulky ligand upon coordination with the central ion. However, the question of the reasons of retaining the equivalence of other protons needs further consideration.

Table 3. Parameters of diffuse reflection spectra of complex **III**

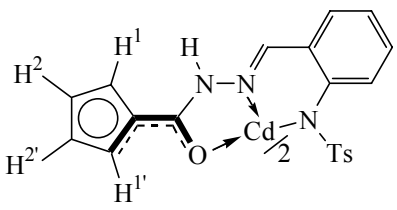
Band	*D*	ν, cm^{-1}	Transition
1	0.53	28980	*d*–*d**
2	0.45	20000	$^3A_{2g}\rightarrow{}^3T_{1g}$
3	~0.30	18870	$^3A_{2g}\rightarrow{}^3T_{1g}$(P)
4	0.25	10300	CT band
5	0.10	8000	$^3A_{2g}\rightarrow{}^3T_{2g}$

EXPERIMENTAL

For the synthesis of 2-*N*-tosylaminobenzaldehyde ferrocenoylhydrazone **I** the hydrazide of ferrocenecarboxylic acid and 2-*N*-tosylaminobenzaldehyde prepared by the known procedures [35, 46] were used.

IR spectra were taken on a Varian Scimitar 1000 FT-IR instrument in the range 400–4000 cm^{-1}; the samples were prepared as suspensions in mineral oil. Electron absorption spectra and spectra of diffuse reflection were recorded on a Varian Cary 5000 spectrophotometer in the range 200–800 nm. ^{1}H NMR spectra were registered in DMSO-d_6 solution on a Varian Unity 300 spectrometer (300 MHz). Elemental analysis was performed on a Perkin Elmer 240C instrument. Specific magnetic susceptibility was determined by the Faraday method in the temperature range 77.4–300 K.

Scheme 3.



Quantum chemical calculations were performed on WSD cluster of the Computing Center of Southern Federal University, using Gaussian'03 program [47]. For processing of the data, graphical presentation, and visualization of the results the ChemCraft program was used [48].

Hydrazone (I). To a hot solution of 2 mmol of 2-*N*-tosylaminobenzaldehyde in 10 mL of ethanol a hot solution of 2 mmol of hydrazide of ferrocenecarboxylic acid in 10 mL of ethanol was added. The reaction mixture was refluxed for 4 h and left overnight. The precipitate was filtered off, washed with ethanol, dried in a vacuum, and crystallized from the mixture ethanol–DMF (1 : 1). Yield 0.50 g (50%), mp >250 ºC. IR spectrum, ν, cm^{-1}: 3400, 3209 (NH), 1637 (C=O), 1608 (C=N), 1167, 1091 (SO_2), 515, 496 π(Cp–Fe). ^{1}H NMR spectrum, δ, ppm: 11.42 s (1H, NH), 11.16 s (1H, NH), 8.46 s (1H, CH=N), 7.65 d (2H, CH_{arom}, J = 7.8 Hz), 7.55 d (2H, CH_{arom}, J = 6.9 Hz), 7.30 d (2H, CH_{arom}, J = 7.8 Hz), 7.16 m (2H, CH_{arom}), 4.98 s (2H, CH_{Fc}), 4.50 s (2H, CH_{Fc}), 4.24 s (5H, CH_{Fc}), 2.30 s (3H, CH_3). Found, %: C 60.3, H 4.49, N 8.61. $C_{25}H_{23}FeN_3O_3S$. Calculated, %: C 59.9, H 4.62, N 8.38.

Complex II. To a hot solution of 0.5 mmol of compound **I** in 10 mL of methanol a hot solution of 0.5 mmol of copper(II) acetate in 10 mL of methanol was added. The reaction mixture was refluxed for 1 h, the precipitate was filtered off, washed with methanol, dried in a vacuum, and crystallized from methanol. Yield 0.09 g (30%), mp > 250 ºC. IR spectrum, ν, cm^{-1}: 3380 (OH), 1616, 1597 (C=N), 1138, 1084 (SO_2), 507, 493 π(Cp–Fe). M_{eff} 1.81 μB (298 K), 1.79 μB (77.4 K). Found, %: C 52.3; H 4.09; N 7.21. $C_{26}H_{25}CuFeN_3O_4S$. Calculated, %: C 52.5; H 4.24; N 7.06.

Complexes III–V. To a hot solution of 1 mmol of compound **I** in 10 mL of methanol a hot solution of 0.5 mmol of nickel(II), zinc(II), or cadmium(II) acetate, respectively, in 10 mL of methanol was added. The reaction mixture was refluxed for 1 h, the precipitate was filtered off, washed with methanol, dried in a vacuum, and crystallized from methanol.

Complex III. Yield 0.17 g (30%), mp > 250ºC. IR spectrum, ν, cm^{-1}: 3193 (NH), 1608 (C=O), 1598 (C=N), 1128, 1086 (SO_2), 508, 496 π(Cp–Fe). μ_{eff} 2.94 μB (298 K), 2.91 μB (77.4 K). Found, %: C 56.5; H 4.45; N 7.92. $C_{51}H_{47}Fe_2N_6NiO_7S_2$. Calculated, %: C 56.2; H 4.34; N 7.71.

Complex IV. Yield 0.22 g (40%), mp > 250ºC. IR spectrum, ν, cm^{-1}: 3200 (NH), 1610 (C=O), 1602 (C=N), 1134, 1082 (SO_2), 520, 505 π(Cp–Fe). ^{1}H NMR spectrum, δ, ppm: 11.53 s (1H, NH), 8.27 s (1H, CH=N), 7.73 d (2H, CH_{arom}, J = 8.1 Hz), 7.30 m (4H, CH_{arom}), 7.06 d (2H, CH_{arom}, J = 8.1 Hz), 4.78 s (2H, CH_{Fc}), 4.33 s (2H, CH_{Fc}), 4.17 s (5H, CH_{Fc}), 2.31 s (3H, CH_3). Found, %: C 55.3; H 4.21; N 7.41. $C_{51}H_{47}Fe_2N_6O_7S_2Zn$. Calculated, %: C 55.8; H 4.32; N 7.66.

Complex V. Yield 0.20 g (35%), mp > 250ºC. IR spectrum, ν, cm^{-1}: 3257 (NH), 1606 (C=O), 1598 (C=N), 1127, 1080 (SO_2), 501, 482 π(Cp–Fe). ^{1}H NMR spectrum, δ, ppm: 11.68 s (1H, NH), 8.45 s (1H, CH=N), 7.88 d (2H, CH_{arom}, J = 7.8 Hz), 7.42 br.s (1H, CH_{arom}), 7.23 d (1H, CH_{arom}, J = 7.5 Hz), 7.18 d (2H, CH_{arom}, J = 7.8 Hz), 7.08 t (1H, CH_{arom}, J = 7.3 Hz), 6.76 t (1H, CH_{arom}, J = 7.3 Hz), 5.01 s (1H, CH_{Fc}), 4.93 s (1H, CH_{Fc}), 4.74 s (1H, CH_{Fc}), 4.54 s (1H, CH_{Fc}), 4.23 br.s (1H, CH_{Fc}), 4.07 s (4H, CH_{Fc}), 2.27 s (3H, CH_3). Found, %: C 53.1; H 4.30; N 7.52. $C_{51}H_{47}CdFe_2N_6O_7S_2$. Calculated, %: C 53.5; H 4.14; N 7.34.

X-Ray diffraction analysis. Single crystals of compound **I** were obtained by slow crystallization from the solution in DMF. Brown prismatic crystals (M = 501.37), triclinic, parameters at 150 K: a = 9.4453(4) Å, b = 11.6977(5) Å, c = 23.4047(11) Å, α = 77.4728(7)º, β = 82.1968(7)º, γ = 66.5253(7)º, V = 2311.93(18) $Å^3$, space group P-1, Z = 4, d_{calc} = 1.440 g/cm^3. Parameters of the unit cell and intensities of 28053 reflections were measured on a Bruker Apex II diffractometer [l(MoK_a)= 0.71073 Å, graphite monochromator, ω-scanning, $2\theta_{max}$ = 60.6°] for the crystal of 0.33×0.11×0.09 mm^3 size. The original array of the measured intensities was treated using the programs SAINT [49], SADABS [50]. The structure was solved by the direct method and refined by full-matrix least-square method in anisotropic approximation for nonhydrogen atoms with respect to F^2_{hkl}. Hydrogen atoms were placed in the geometrically calculated positions and refined by the use of the *rider* model [U_{iso}(H) = nU_{eq}(C), where n = 1.5 for the carbon atoms of the methyl groups, n = 1.2 for the other carbon atoms]. Final divergence factors R_1 = 0.0408 and wR_2 = 0.1191 for 10491 independent reflections with $I > 2s(I)$, R_1 = 0.0612 and wR_2 = 0.1362 for all 28053 independent reflections, 595 refined parameters, GOOF = 1.001. All calculations were performed by the use of the SHELXL-97 program complex [51]. Atomic

coordinates and temperature factors were deposited in the Cambridge Crystallographic Data Center (CCDC 981876).

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