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Synthesis and Spectroscopic Features of Iron(II) 1-Aryl-5-benzothiazol-2-ylformazanates

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Abstract—New iron(II) coordination compounds with 1-aryl-5-(benzothiazol-2-yl)formazans were prepared. Their compositions and structures were determined by electronic spectroscopy, mass spectrometry, single crystal X-ray diffraction analysis, and magnetochemical measurements.
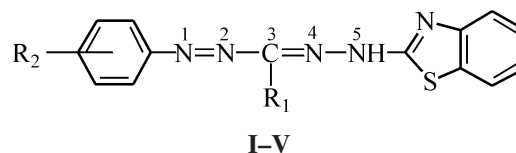
Iron coordination compounds with polydentate nitrogen-containing heterocyclic ligands are unique chemical systems. The specific features of their properties and structure are determined by the nature of the coordination core and by the steric arrangement of side functional groups.

Iron chelates has demonstrated good performance as effective catalysts of not only industrial (synthesis of ammonia, dehydrogenation of hydrocarbons, etc.) [1–3] but also biochemical processes [4]. Many of these compounds are characterized by exchange interactions of both ferro- (ferri-) and antiferromagnetic type, which lead under the action of certain external factors (temperature, pressure, irradiation at a definite wavelength) to transitions into a magnetically ordered state or to spin transitions $S = 5/2 \rightleftarrows S = 1/2$ [5–7] and make the iron complexes attractive objects for molecular electronics. In this context, synthesis and study of structural features of new coordination compounds of iron with ambidentate ligands are of both scientific and practical interest.

Among such ligands are, in particular, hetarylformazans, for which both bridging and chelate coordination is typical. The polydenticity and high flexibility of the formazan molecule, as well as the ability of such compounds to act as both bi-, tri-, and tetradentate ligands and also the possibility of controlling their properties through the substituent effect make them attractive for design of organometallic complexes with required stereochemistry [8, 9].

This study is concerned with synthesis of iron coordination compounds with formazans **I–V** and with the substituent effect on the composition, structure, and spin state of the metal complexes.

I–V

EXPERIMENTAL

The compounds were prepared from $FeCl_3 \cdot 6H_2O$ of analytically pure grade. 1-Aryl-5-benzothiazol-2-yl-formazans were synthesized by the procedures described in [10–13]. The purity of the metal complexes was verified by TLC on Silufol UV-254 plates.

Iron 1-(4-sulfophenyl)-3-methyl-5-(benzothiazol-2-yl)formazanate (IFe). A solution of 0.3 mmol of iron (III) chloride in 15 ml of water was added dropwise with continuous stirring at $40 \pm 5°C$ to a solution of 0.9 mmol of formazan in 100 ml of aqueous ethanol (1 : 1). The resulting mixture was stirred for 30 min and evaporated to a volume of 10 ml. The precipitate

Table 1. Elemental analyses and melting points of iron(II) formazanate complexes

Ligand	R_1	R_2	Complex	Empirical formula	T_m, °C	Found, % / Calculation, %		
						C	H	N
I	CH_3	$4\text{-}SO_3H$	**IFe**	$C_{30}H_{24}N_{10}S_4O_6Fe \cdot 3H_2O$	>250	$\underline{41.93}$ 41.96	$\underline{3.61}$ 3.53	–
II	$CH=CH\text{–}CH_3$	H	**IIFe**	$C_{34}H_{28}N_{10}S_2Fe$	180	$\underline{59.79}$ 58.61	$\underline{4.28}$ 4.06	$\underline{19.68}$ 20.11
III	$CH(CH_3)_2$	H	**IIIFe**	$C_{34}H_{32}N_{10}S_2Fe$	245	$\underline{58.30}$ 58.27	$\underline{4.63}$ 4.61	$\underline{19.75}$ 19.99
IV	$CH(CH_3)_2$	$4\text{-}OCH_3$	**IVFe**	$C_{36}H_{36}N_{10}S_2O_2Fe$	190	$\underline{56.45}$ 56.83	$\underline{4.97}$ 4.78	$\underline{18.06}$ 18.41
V	C_6H_5	H	**VFe**	$C_{40}H_{28}N_{10}S_2Fe$	215	$\underline{62.61}$ 62.52	$\underline{3.64}$ 3.71	$\underline{18.21}$ 18.18

was filtered off, washed with a small amount of distilled water, and dried in air.

Iron 1-phenyl-3-(propen-1-yl)-5-(benzothiazol-2-yl)-formazanate (IIFe). A solution of 0.3 mmol of iron(III) chloride in 15 ml of acetone was added dropwise with continuous stirring at $40 \pm 5°C$ to a solution of 0.9 mmol of formazan in 100 ml of acetone. The resulting mixture was stirred for 30 min and evaporated to a volume of 10 ml. The precipitate was filtered off, washed with warm distilled water and ethanol, and dried in air. Iron formazanates **IIIFe**, **IVFe**, and **VFe** were prepared similarly. The compositions of the ligands and complexes obtained are listed in Table 1.

The electronic absorption spectra of the ligands and their metal complexes in aqueous ethanol (1 : 1) for **I** or acetone for **II–V** were recorded on a Beckman UV-5260 double-beam spectrophotometer in the wavelength range 350–800 nm. The compositions of the complexes and equilibrium concentrations were determined from the plots of the optical densities of solutions vs. the volume of the salt solution added. The equivalence point corresponded to the salt solution volume required to attain the saturation. From these data, the stoichiometric composition of the complexes formed was calculated.

An elemental analysis was performed on a CHN PE2400SII automatic analyzer (Perkin–Elmer Instruments, the United States). The metal content was determined by express gravimetric analysis with a device produced by Khimlaborpribor Joint-Stock Company (Klin, Moscow oblast, Russia).

The IR spectra of the ligands and complexes obtained were recorded with a Specord 75-IR spectrophotometer in KBr pellets in the range 400–4000 cm^{-1}.

Mass spectra of iron formazanates were measured in the electron impact ionization mode on an MAT-ZPA device (Varian) with the reverse configuration in the design of magnetic and electrostatic analyzers, which allowed the spectra of metastable ions to be obtained directly. The spectra were measured under standard conditions: accelerating voltage 3 kV, cathode emission current 300 μA, and ionizing electron energy 70 eV. The samples were introduced into the ion source using the direct inlet system.

The magnetic characteristics of the compounds were measured with a Quantum Design 5-XL SQUID magnetometer in the temperature range 0–300 K in magnetic fields of strength 30 and 50 kOe.

Single-crystal X-ray diffraction analysis of complex **IVFe** was performed at 295(2) K with an Xcalibur 3 autodiffractometric system equipped with a CCD detector. Crystals of **IVFe** ($C_{36}H_{36}N_{10}O_2S_2Fe$, red prisms) belong to the monoclinic system. Unit cell parameters: $a = 10.3951(18)$, $b = 21.968(2)$, $c = 15.9281(16)$ Å; $\alpha = 90.00°$, $\beta = 99.347(11)°$, $\gamma = 90.00°$; $V = 3589.0(8)$ Å^3; $\rho_{calc} = 1.408$ g cm^{-3}; $M = 760.72$; $Z = 4$; space group $P2(1)/n$. The experiment completeness at $\theta \leq 26.38°$ was 99.5% (ω-scanning at 1° step and 10-s exposure per frame, crystal–detector distance 50 mm). A total of 7299 unique reflections were measured, including 2515 reflections with $I > 2\sigma(I)$. The absorption correction was ne-
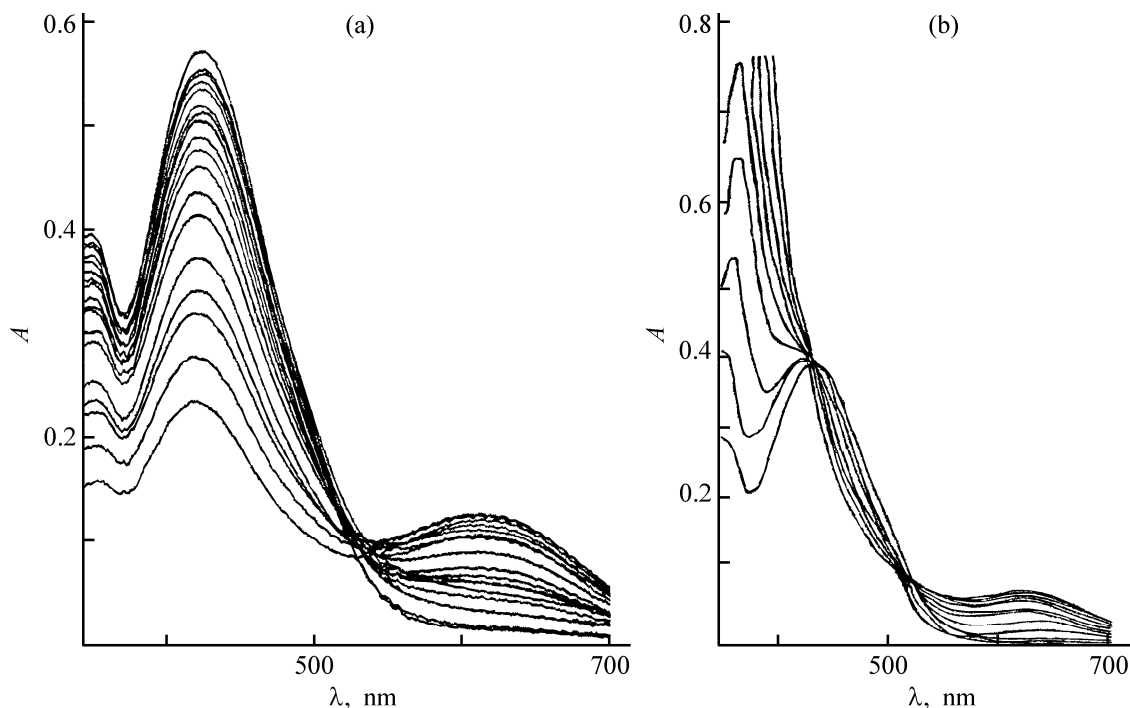
Fig. 1. Electronic spectra of formazan **IV** in acetone, recorded in the course of titration with a solution of (a) nickel(II) nitrate ([**IV**] = 2.85×10^{-5}, [Ni(NO$_3$)$_2$] = 10^{-3} M) and (b) iron(III) chloride ([**IV**] = 2.85×10^{-5}, [FeCl$_3$] = 1×10^{-2} M) in acetone. (*A*) Absorption and (λ) wavelength.

glected because of its insignificance (μ = 0.585 mm^{-1}). To collect and edit the experimental data and refine the unit cell parameters, we used the CrysAlis CD program [14]. The structure was solved by the direct method using the SHELX-97 program package [15]. The hydrogen atoms were placed in calculated positions and included in refinement in the rider model with dependent thermal parameters. The structure was solved by the least-squares method in the anisotropic approximation for nonhydrogen atoms and isotropic approximation for H atoms. The final divergence factors were $R_1 = 0.0670$, $wR_2 = 0.0803$ [$I > 2\sigma(I)$] at goodness-of-fit $S = 0.994$.

Depending on the structure of the initial formazan group, the ligands can coordinate M^{2+} and M^{3+} ions either in the tridentate fashion via N^1 and N^4 atoms of the formazan chain and nitrogen atom of the heteroring to give complexes ML$_2$ with a nitrogen-containing coordination core, or, if the aryl fragment contains an additional *o*-OH or *o*-COOH group, in the tridentate or tetradentate fashion to give complexes ML$_2$ or ML with N$_x$M or N$_x$O$_y$M coordination cores, depending on the synthesis conditions [8].

The variations in the mode of coordination of hetarylformazans in their complexes with metal ions, to give coordination compounds with diverse struc-

tures and properties are determined not only by the set of donor atoms in the ligand structure, but also by the electronic configuration of the central metal ion.

For example, in complexation of tridentate formazan **IV** with nickel(II) nitrate in an acetone solution, the intensity of the absorption band of the starting formazan at λ_{max} = 430 nm gradually decreases, and an absorption band of the metal complex appears at λ_{max} = 630 nm. The spectral pattern is characterized by the presence of one isobestic point, which suggests that only two formazan species are involved in the process: the starting formazan and the forming nickel(II) formazanate.

With iron(III), a metal ion with a variable oxidation state, the spectral pattern (Fig. 1) observed in the course of titration is more complicated. A decrease in the intensity of the absorption band of formazan is mainly associated with its tranformation into a product with λ_{max} < 350 nm. Apparently, formazan is oxidized into a tetrazolium salt (a well-known reaction of formazans [8]), with Fe(III) acting as oxidant. A weak absorption band appearing at 625 nm can be assigned to Fe(II) formazanate. This behavior has been already noted for complexation of some benzazolylformazans with Fe(III) and Mn(III) ions [16, 17].

The reactions of ethanol solutions of iron(III) chloride with benzothiazolylformazans **I–V** yielded

Table 2. Data furnished by electronic spectroscopy, mass spectrometry, and magnetochemical measurements for iron (II) complexes

Com-plex	M	m/z (I, %)	λ_{max}, nm	μ_{eff}, μ_B (μ_{eff}^2)
IFe	858.64	–	670, 490	2.09 (4.4)
IIFe	696.72	696 (32.26)	675, 510	1.97 (3.9)
IIIFe	700.76	700 (100)	670, 520	0.22 (0.05)
IVFe	760.82	760 (100)	675, 490	0.45 (0.2)
VFe	768.78	768 (100)	680, 495	1.18 (1.4)

crystalline iron complexes **I**Fe–**V**Fe, which have, according to the analytical data (Table 1), electronic spectra, and mass spectra (Table 2), the composition L_2Fe.

For formazanate **I**Fe, we failed to detect the molecular ion and recorded only weak peaks of fragmentation ions.

In the electronic spectra of the iron-containing complexes, we observed, along with the major absorption bands at 670–680 nm, weak bands at 490–520 nm.

In the IR spectra of the iron formazanates, absorption bands assignable to ν(Fe–N) vibrations [18, 19]

Fig. 2. Structure of iron 1-(4-methoxyphenyl)-3-isopropyl-5-(benzothiazol-2-yl)formazanate **IV**Fe. Selected bond lengths, Å: Fe(1)–N(1) 1.933(4), Fe(1)–N(5) 1.997(4), Fe(1)–N(10) 1.850(4), N(5)–C(7) 1.313(5), N(6)–N(1) 1.321(4), N(6)–C(10) 1.364(6), N(9)–C(7) 1.346(5), N(10)–N(9) 1.366(5), N(10)–C(10) 1.332(6), N(5)–C(16) 1.373(5), C(7)–S(1) 1.745(5), C(10)–C(15) 1.500(6), N(1)–C(20) 1.411(5). Selected bond angles, deg: N(3)–Fe(1)–N(7) 79.27(18), N(3)–Fe(1)–N(8) 78.48(19), N(10)–Fe(1)–N(1) 78.80(18), N(10)–Fe(1)–N(5) 78.81(19).

appear at about 745 and 500 cm^{-1}. In the IR spectra of the initial ligand, these bands are lacking.

The measured effective magnetic moments μ_{eff} of the metal complexes **III**Fe, **IV**Fe, and **V**Fe, containing bulky substituents in the 3-position of the formazan molecule, are as low as 0.22, 0.45, and 1.18 μ_B, respectively, which suggests formation of Fe(II) complex compounds predominantly in the low-spin (LS) state [20, 21].

For the metal complexes **I**Fe and **II**Fe containing alkyl substituents in the 3-position of the formazan molecule, μ_{eff} was 2.09 and 1.97 μ_B, respectively, which, according to [21], can be attributed to the presence of low- and high-spin (HS) iron(II) complexes and an admixture of Fe(III) complexes. Formazans with the alkyl substituent at the C^3 atom are oxidized to the tetrazolium salt somewhat more difficultly. Therefore, the probability of formation of impurity iron(III) complexes is higher.

The structure of the metal chelate core formed in complexation of formazans **I–V** with iron(III) chloride solutions was finally confirmed by single-crystal X-ray diffraction analysis for **IV**Fe as an example.

The general view of the molecule of **IV**Fe is shown in Fig. 2. The structure of **IV**Fe is, on the whole, similar to that of 1,3-diphenyl-5-(benzothiazol-2-yl) formazanate **V**Fe prepared previously [16].

The molecule of the iron complex occupies a special position on a twofold axis. Two formazan ligands are coordinated in the tridentate fashion via N^1 and N^4 atoms of the formazan chain and nitrogen atom of the heteroring to form the metal complex L_2Fe with the N_6Fe coordination core. The angle between the planes of the formazan ligands in the complex is 81.93°.

The N(8)FeN(7) (157.77°) and N(5)FeN(1) (157.66°) angles correspond to the meridional (*mer*) isomer; in the facial (*fac*) isomer this angle would be 90°. The iron coordination polyhedron is a distorted octahedron. Despite that all the vertices of the coordination polyhedron are occupied by nitrogen atoms, the Fe–N bonds noticeably differ in the length and can be subdivided into three groups, each with two bonds. The shortest Fe–N bonds, 1.850 and 1.856 Å, are formed by the N(10) and N(3) atoms occupying the vertex positions, i.e., the octahedron is compressed along the N(10)···N(3) axis. The intermediate-length Fe–N bonds, 1.933 and 1.942 Å, are formed with the N(1) and N(7) atoms, and the N(5) and N(8) atoms are the most remote from the Fe atoms: 1.997 and 2.003 Å, respectively.
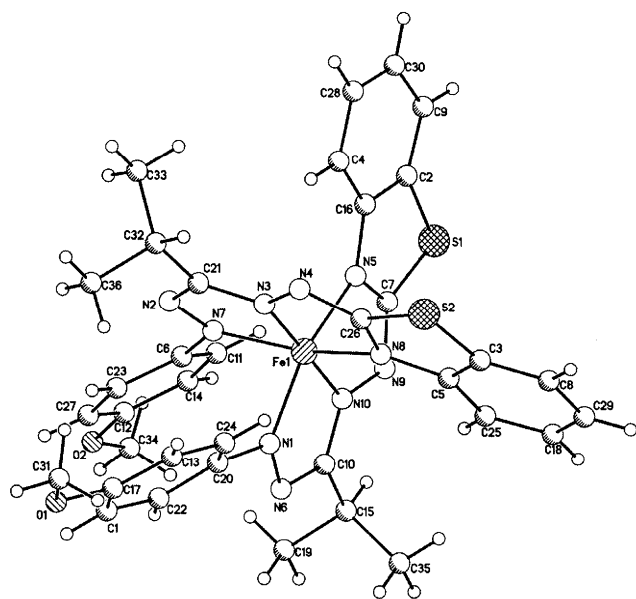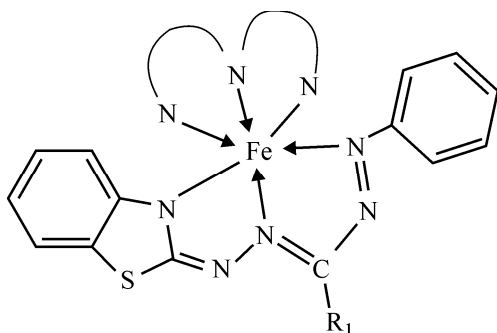
The hetaryl nitrogen atom involved in the coordination behaves like an additional complexing group. The complexation leads to changes in the electronic structure of the initial ligand, which is in the amino form with the *EEZ* configuration of the formazan ring. The molecular configuration also changes significantly: in the formazanate, the ligand is in the imino form, with the open *EZE* configuration.

The above spectral data suggest that compounds **III**Fe–**V**Fe are metal complexes containing Fe(II) predominantly in the LS state with the coordination configuration similar to that in **IV**Fe:

CONCLUSION

In the course of synthesis of coordination compounds from tridentate benzothiazolylformazans and solutions of iron(III) chloride, formazan is oxidized to tetrazolium salts, iron(III) is reduced, and, as a result, iron(II) formazanates are formed with various spin states of Fe(II).

ACKNOWLEDGMENTS

REFERENCES

1. Malina, N.K., *Raznitie issledovanii v oblasti sinteza ammiaka* (Progress of Studies in the Field of Ammonia Synthesis), Moscow: Nauka, 1983.
2. Arutyunov, V.S., *Katal. Prom–sti.*, 2003, no. 3, pp. 31–38.
3. Borutskii, P.N. and Podkletnova, N.M., *Katal. Prom–sti.*, 2003, no. 2, pp. 57–61.
4. Ulakhovich, N.A., *Soros. Obraz. Zh.*, 1997, no. 8, pp. 27–32.
5. Lavernova, L.G., Ikorskii, V.N., Larionov, S.V., et al., *Zh. Neorg. Khim.*, 1993, vol. 28, no. 9, pp. 1517–1525.
6. Stassen, A.F., Kooijman, H., Spec, A.L., et al., *Inorg. Chem.*, 2002, vol. 41, no. 24, pp. 6468–6471.
7. Shvedenkov, Yu.G., Virovets, A.V., and Lavrenova, L.G., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2003, no. 6, pp. 1281–1288.
8. Buzykin, B.I., Lipunova, G.N., Sysoeva, L.P., and Rusinova, L.I., *Khimiya formazanov* (Chemistry of Formazans), Moscow: Nauka, 1992.
9. Lipunova, G.N., Rusinova, L.I., and Maslakova, T.I., *Ross. Khim. Zh.*, 1996, vol. 40, nos. 4–5, pp. 148–154.
10. Bednyagina, N.P. and Lipunova, G.N., *Khim. Geterotsikl. Soedin.*, 1968, no. 5, pp. 902–910.
11. Petrova, G.M., Bednyagina, N.P., Malkina, T.G., and Podchainova, V.N., *Khim. Geterotsikl. Soedin.*, 1968, no. 4, pp. 709–715.
12. Lipunova, G.N., Lekomtseva, E.G., Sharova, L.I., et al., *Zh. Obshch. Khim.*, 1985, vol. 55, no. 4, pp. 895–899.
13. Validuda, G.I., Lipunova, G.N., Garnovskii, A.D., et al., *Zh. Obshch. Khim.*, 1986, vol. 56, no. 4, pp. 827–833.
14. CrysAlis CCD, Oxford Diffraction Ltd., Version 1.171.29.9 (release 23-03-2006 CrysAlis 171. NET).
15. Sheldrick, G.M., SHELX-97: A Software Package for the Solutions and Refinement of X-ray Data, Univ. of Göttingen (Germany), 1997.
16. Brown, D., Bogge, H., Lipunova, G.N., et al., *Inorg. Chem.*, 1998, vol. 280, pp. 30–38.
17. Muller, A., Bogge, H., Diemann, E., et al., *Naturwiss.*, 1994, vol. 81, pp. 136–137.
18. Nakanishi, K., *Infrared Absorption Spectroscopy*, San Francisco: Holden-Day, 1962.
19. Nakamoto, K., *Infrared Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1963.
20. El-Sawaf, A.K., West, D.X., El-Saied, F.A., et al., *Synth. Inorg. Met.-Org. Chem.*, 1997, vol. 27, no. 8, pp. 1127–1134.
21. Bushuev, M.B., Lavrenova, L.G., Ikorskii, V.N., et al., *Koord. Khim.*, 2004, vol. 30, no. 4, pp. 305–311.