Brief Communications

Synthesis and structures of iron(III) complexes based on azo derivatives of 5-oxo- and 5-thioxopyrazole

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New potentially tridentate ligands, *viz.*, 3-methyl-1-phenyl-4-(quinolin-8-ylhydrazono)pyrazol-5(1*H*)-one and 3-methyl-1-phenyl-4-(quinolin-8-ylhydrazono)pyrazole-5(1*H*)-thione (LH), and their complexes with Fe^{III} were synthesized. The structures of the ligands and metal chelates (FeL_2A; A = ClO_4 or $FeCl_4$) were studied by ^1H NMR spectroscopy and magnetochemistry. The FeL_2A complex (A = $FeCl_4$) was investigated by X-ray diffraction. These low-spin complexes have pseudooctahedral structures with the N_4X_2 ligand environment (X = O or S).

Key words: nitrile hydratase, azo compounds, iron(III) chelates, X-ray diffraction analysis, NMR spectroscopy, magnetochemistry.

Iron(III) chelates in a nitrogen chalcogen ligand environment can serve as models of the active center of nitrile hydratase.[1—3]

Earlier,[4—6] we have synthesized and studied enamines of type **1** and iron(III) chelates of type **2**, which reproduce certain spectroscopic and structural parameters of nitrile hydratase. As part of our continuing studies, we synthesized new tridentate ligands of type **3** and iron chelates **4** based on these ligands.

Ligand **3a** was synthesized by the reaction of 3-methyl-1-phenylpyrazol-5-one with a quinolin-8-diazonium salt using a modified procedure described earlier[7—9] (Scheme 1). Like 4-arylazo derivatives of pyrazolone,[9] compound **3a** reacts with $POCl_3$ to give a 5-chloro-substituted product **5**. The reaction of the latter with Na_2S affords 3-methyl-1-phenyl-4-(quinolin-8-ylhydrazono)pyrazole-5(1*H*)-thione (**3b**) (see Scheme 1). Taking into account the results of studies of enamines **1** by X-ray diffraction analysis and ^1H NMR spectroscopy[10] and by analogy with the data published in the literature,[11—13] we

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† Deceased.

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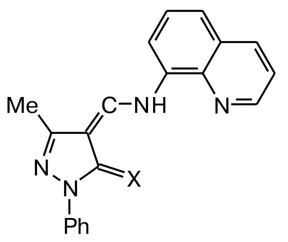
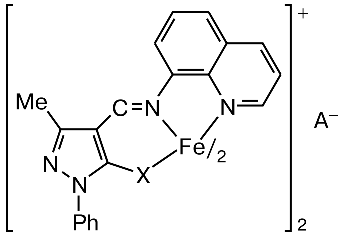
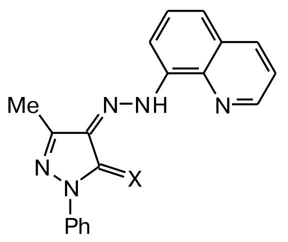


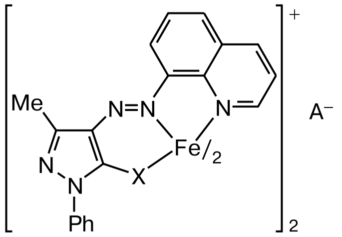
1a—c



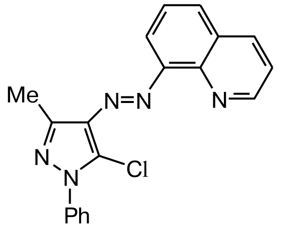
2a—f



3a,b



4a—d



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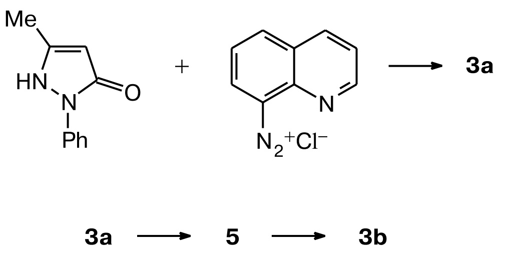
	1a, 3a	**1b, 3b**	**1c**	**2a, 4a**	**2b, 4b**	**2c, 4c**	**2d, 4d**	**2e**	**2f**
X	O	S	Se	O	O	S	S	Se	Se
A	—	—	—	$FeCl_4$	ClO_4	$FeCl_4$	ClO_4	$FeCl_4$	ClO_4

assigned the oxo- and thioxohydrazone structures to ligands **3**.

Scheme 1



Iron(III) complexes **4a—d** were synthesized by the direct reaction of compound **3a,b** (1 equiv.) with $Fe(ClO_4)_3 \cdot nH_2O$ or $FeCl_3 \cdot 6H_2O$ (1 equiv.) in EtOH. Complexes **4a,c** were satisfactorily characterized by elemental analysis data.

According to the results of X-ray diffraction analysis, the iron atom in the cation of complex **4c** (Fig. 1) is in an N_4S_2-type pseudooctahedral environment with the *cis* arrangement of the sulfur atoms (S(1)—Fe—S(1′), 94.36(4)°). Complex **4c** contains $FeCl_4^-$ as the anion. The ligands coordinated to the iron ion are in the orthogonal orientation with respect to each other (the dihedral angle is 90.1°). The principal geometric parameters of the ligands are virtually identical. The six-membered and five-membered metallocycles adopt the chair and envelope conformations with the metal atoms deviating from the planes of the rings by 0.49 and 0.34 Å, respectively. The folding angles of the five- and six-membered rings are 13° and 24°, respectively. The presence of two five-membered metallocycles, which are sterically more hindered than six-membered rings, leads to only slight distortions of the octahedral symmetry of the coordination polyhedron (the corresponding bond angles deviate from 90° within 7.5°). The structure of metal chelate **4c** is similar to that of complex **2c** studied by us earlier.[4,5] For example, the Fe—S distances in **4c** (2.207(1) and 2.209(1) Å) are only slightly shortened compared to those in **2c** (2.227(2) and 2.230(2) Å).[4,5] The $Fe—N_{azo}$ bond length in **4c** (1.939(3) Å (1.946(3) Å)) is smaller, on the average, by 0.03 Å than that in metal chelate **2c** (Y = CH), whereas the $Fe—N_{qin}$ distance (2.012(3) Å (2.021(3) Å)) is, on the contrary, larger, on the average, by 0.015 Å.

Taking into account that iron(III) chelates with the NO-ligand environment are generally high-spin or belong to compounds exhibiting the spin-equilibrium behavior,[3,14,15] the magnetic moment of complex **4b** in the solid state (μ_{eff} = 1.98 μ_B) is unexpectedly low. The state with S = 1/2 of the iron(III) ion in the cation is typical of sulfur-containing derivatives of **4d** (μ_{eff} = 2.17 μ_B). The unusually high effective magnetic moments of compounds **4a** and **4c** (μ_{eff} = 6.17 and 6.20 μ_B, respectively) are attributed to the combined contribution of the low-spin Fe^{III} cation (S = 1/2) and the high-spin Fe^{III} anion $FeCl_4$ (S = 5/2). The effective magnetic moments of complexes **4b,d** measured in $CDCl_3$ and DMSO solutions by the Evans method[16] are 2.16 μ_B ($CDCl_3$) and 2.36 μ_B (DMSO) for **4b** and 2.16 μ_B ($CDCl_3$) and 2.17 μ_B (DMSO) for **4d**. The fact that the magnetic moments of metal chelates

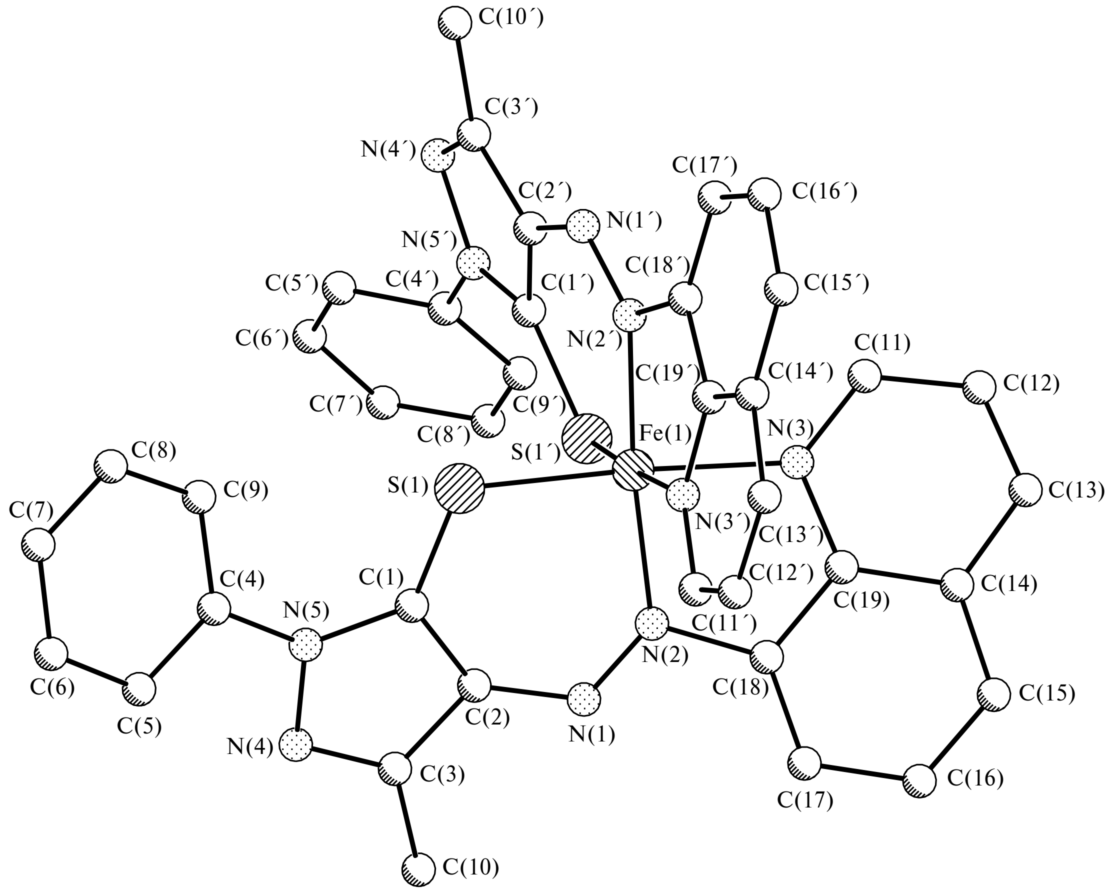


Fig. 1. Overall view of cation **4c**.

4b,d determined in the crystalline state are similar to those measured in solutions indicates that these complexes retain the magnetic properties and, apparently, their structures in solutions.

Experimental

The ^{1}H NMR spectra were recorded on a Varian UNITY-300 spectrometer (300 MHz) in $CDCl_3$. The magnetic moments of the complexes in the crystalline state at 299 K were measured on an instrument designed at the Rostov State University[17] using the Faraday method. The effective magnetic moments were calculated by the formula $\mu_{eff} = (8\lambda_m T)^{1/2}$, where λ_m is the molar magnetic susceptibility taking into account the Pascal magnetic corrections. The magnetic moments in $CDCl_3$ and DMSO solutions were determined using the Evans method[16] on a Varian UNITY-300 spectrometer. 8-Aminoquinoline (Aldrich) and 3-methyl-1-phenylpyrazol-5-one (Lankaster) were used. Since compounds **4b,d** contain the perchlorate anion and are potentially explosive, they were not analyzed.

X-ray diffraction study of complex **4c.** Crystals are triclinic, at 110 K: a = 12.200(1), b = 12.253(1), c = 16.613(2) Å, α = 75.510(2)°, β = 70.576(2)°, γ = 65.461(2)°, V = 2112.2(4) Å^3, d_{calc} = 1.615 g cm^{-1}, space group $P\bar{1}$, Z = 2. The intensities of 19968 reflections were measured on an automated Smart 1000 CCD diffractometer at 110 K (Mo-Kα radiation, graphite monochromator, ω scanning technique, $2\theta_{max}$ = 56°), and 10176 observed reflections (R_{int} = 0.0421) were used in calculations. The structure was solved by direct methods and refined by the full-matrix least-squares method based on F^2 with anisotropic and isotropic thermal parameters. The hydrogen atoms were revealed from difference electron density syntheses and refined using the riding model. The final reliability factors were as follows: wR_2 = 0.1243, GOOF = 0.971 (R_1 = 0.0564 for 5101 reflections with $I > 2\sigma(I)$). All calculations were carried out using the SHELXTL PLUS program package.

3-Methyl-1-phenyl-4-(quinolin-8-ylhydrazono)pyrazol-5(1*H*)-one (3a) was synthesized according to a procedure analogous to that described earlier.[7—9] 8-Aminoquinoline (0.72 g, 5 mmol) was dissolved in concentrated HCl (6 mL) and water (10 mL). The reaction solution was cooled to 0—5 °C and then a solution of $NaNO_2$ (0.42 g, 6 mmol) in water (2 mL) was added dropwise. The reaction mixture was kept at this temperature for 20 min. The resulting solution of the diazonium salt was added with thorough stirring to a solution of 3-methyl-1-phenylpyrazol-5-one (0.87 g, 5 mmol) in EtOH cooled with ice. After 30 min, the reaction mixture was neutralized with $NaHCO_3$ to pH 7—8. The precipitate that formed was filtered off and washed with water. The reaction product was recrystallized from toluene. The yield was 1 g (60%). Found (%): C, 69.35; H, 5.01; N, 21.21.

$C_{19}H_{15}N_5O$. Calculated (%): C, 69.29; H, 4.59; N, 21.26. ^{1}H NMR (DMSO-d$_6$), δ: 2.30 (s, 3 H, Me); 7.20—9.00 (m, 11 H, C_6H_5, C_9H_6N); 14.50 (s, 1 H, OH or NH).

(5-Chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(quinolin-8-yl)diazene (5) was prepared according to a procedure analogous to that describe earlier.[9] Compound **3a** (3.29 g, 0.01 mol) was added to $POCl_3$ (25 mL, 0.27 mmol) and the resulting mixture was refluxed for 12 h. Then the major portion of $POCl_3$ was distilled off *in vacuo*. The remaining portion was poured onto ice and kept for 12 h. The precipitate that formed was filtered off, washed with water, and recrystallized from a toluene—AcOH mixture. The yield was 2.61 g (75%). Found (%): C, 65.57; H, 4.19; N, 20.10. $C_{19}H_{14}ClN_5$. Calculated (%): C, 65.61; H, 4.06; N, 20.14. ^{1}H NMR (DMSO-d$_6$), δ: 2.70 (s, 3 H, Me); 7.40—9.20 (m, 11 H, C_6H_5, C_9H_6N).

3-Methyl-1-phenyl-4-(quinolin-8-ylhydrazono)pyrazole-5(1*H*)-thione (3b). Derivative **5** (3.48 g, 0.01 mol) was added to a suspension of $Na_2S \cdot 9H_2O$ (3.6 g, 0.015 mol) in DMSO (20 mL). The reaction mixture was stirred at 60 °C for 4 h, cooled to 20 °C, diluted with water (200 mL), and extracted with Et_2O. The aqueous layer was acidified with 10% HCl to pH 7. The precipitate that formed was filtered off and recrystallized from toluene. The yield was 1 g (29%). Found (%): C, 65.97; H, 4.30; N, 20.25. $C_{19}H_{15}N_5S$. Calculated (%): C, 66.07; H, 4.38; N, 20.27. ^{1}H NMR ($CDCl_3$), δ: 2.45 (s, 3 H, Me); 7.20—9.00 (m, 11 H, C_6H_5, C_9H_6N); 17.50 (s, 1 H, SH or NH).

Iron complexes 4 were prepared by heating an ethanolic solution of the corresponding azo derivative **3** (1 mmol) and $Fe(ClO_4)_3 \cdot nH_2O$ or $FeCl_3 \cdot 6H_2O$ (1 mmol) for 30—40 min. The precipitates that formed were filtered off, washed with EtOH, and recrystallized from toluene or a CH_2Cl_2—Et_2O mixture. The yields were 50—65%.

{Bis[3-methyl-1-phenyl-4-(quinolin-8-yldiazenyl)-5-pyrazolato]iron(III)} tetrachloroferrate (4a). The yield was 0.591 g (65%). Found (%): C, 49.97; H, 3.30; N, 15.20. $C_{38}H_{28}Cl_4N_{10}O_2Fe_2$. Calculated (%): C, 50.14; H, 3.10; N, 15.39. $\mu_{eff} = 6.17\ \mu_B$.

{Bis[3-methyl-1-phenyl-4-(quinolin-8-yldiazenyl)-5-pyrazolato]iron(III)} perchlorate (4b). The yield was 0.44 g (55%), $\mu_{eff} = 1.98\ \mu_B$ (solid), 2.36 μ_B (DMSO-d$_6$), 2.16 μ_B ($CDCl_3$).

{Bis[3-methyl-1-phenyl-4-(quinolin-8-yldiazenyl)-5-pyrazolethiolato]iron(III)} tetrachloroferrate (4c). The yield was 0.57 g (60%). Found (%): C, 48.27; H, 2.70; N, 15.25. $C_{38}H_{28}Cl_4N_{10}S_2Fe_2$. Calculated (%): C, 48.43; H, 2.99; N, 14.86. $\mu_{eff} = 6.20\ \mu_B$.

{Bis[3-methyl-1-phenyl-4-(quinolin-8-yldiazenyl)-5-pyrazolethiolato]iron(III)} perchlorate (4d). The yield was 0.406 g (50%). $\mu_{eff} = 2.17\ \mu_B$ (solid), 2.16 μ_B ($CDCl_3$), 2.17 μ_B (DMSO-d$_6$).

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