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LETTERS
TO THE EDITOR

A New Ligand System Based on 7'-Hydroxy-3-methyl-8'-formyl-3,4-dihydro-2*H*-1,3-benzoxazine-2-spiro-2(*H*)-chromene Ferrocenoylhydrazone

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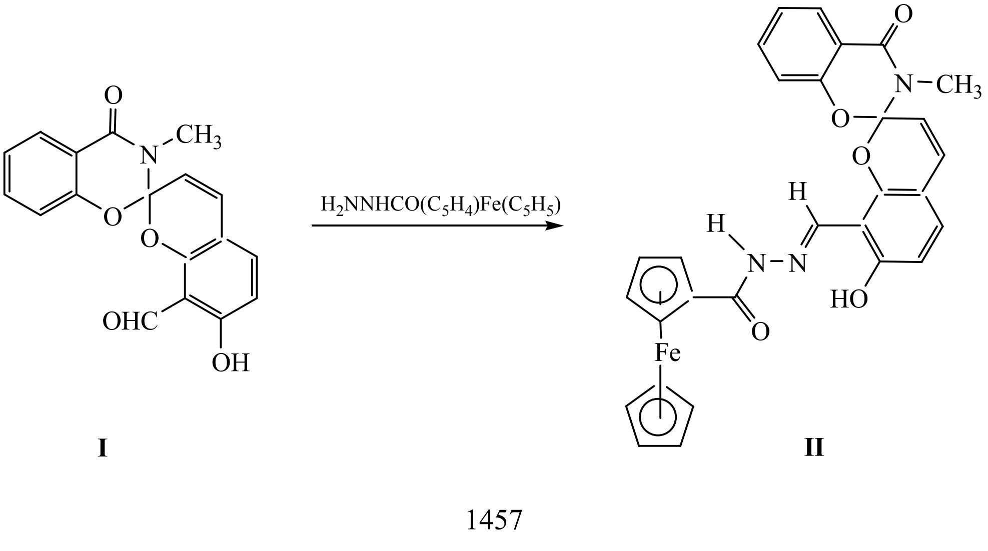
Spiropyrans are the class of organic photochromes [1–3] whose photochemical properties may be varied by introducing different substituents in the molecule, including the coordinatively active ones. The structural and chemical properties of the obtained derivatives suggest their potential photochemical activity and the ability to form the heteronuclear complexes containing coordination node with the predicted structure and parameters of the exchange interaction.

The object of our investigation is a hydrazone derived from a spiropyran of benzoxazine series containing formyl group in its 2(*H*)-chromene fragment. The metallocene structures, in particular ferrocene, are coordinatively and conformationally active and have specific redox properties [4–6]. Introducing a metallocene fragment into the spiropyran molecule provides an opportunity to further modifications of its physical and chemical properties. The variability of the valence states of the iron atom in ferrocene makes it possible to study the dependence of the spiropyran properties, primarily the photochemical ones, on the iron oxidation state. When the molecule contains two autonomous parts, the studying of the mixed-valence states and the relationship between the redox properties of these molecules and their potential photochemical activity is of interest. Thus, the use of the spiropyran derivatives as the active components is promising for the directed design of supramolecular systems whose photochemical and magnetic properties can be predicted.

Some hydrazones based on 7'-hydroxy-3-methyl-8'-formyl-3,4-dihydro-2*H*-1,3-benzoxazine-2-spiro-2(*H*)-



chromene **I** [7–9] and ferrocenecarboxylic acid hydrazide [10–18] have been formerly synthesized and studied. It was interesting to create a system containing both the photochemically active spiropyran fragment and the structurally active metallocene moiety for studying the possible mutual modification of the properties of these fragments in both the initial hydrazone and the transition metal complexes based on it. The reaction scheme of the hydrazone synthesis is shown above.

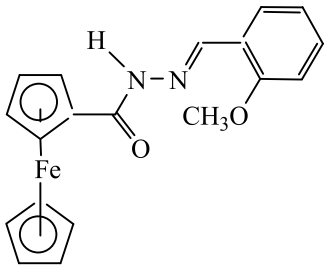
The composition and structure of compound **II** was established by the elemental analysis, IR, and ^{1}H NMR spectroscopy. In the shortwave region of the infrared spectrum of the ligand there are the absorption bands of the stretching vibrations of the N–H and O–H bonds. The spectrum contains also the absorption bands originating from the stretching vibrations of two carbonyl groups and azomethine moiety.

The obtained complex ligand reacts with zinc acetate. This ligand system is analogous to that of salicylaldehyde acylhydrazone, whose structural features suggest the formation of both mononuclear and binuclear metal complexes [19, 20]. By the elemental analysis data, the composition of the resulting complex corresponds to the metal–ligand ratio equal to 1:2, which indirectly indicates its mononuclear nature.

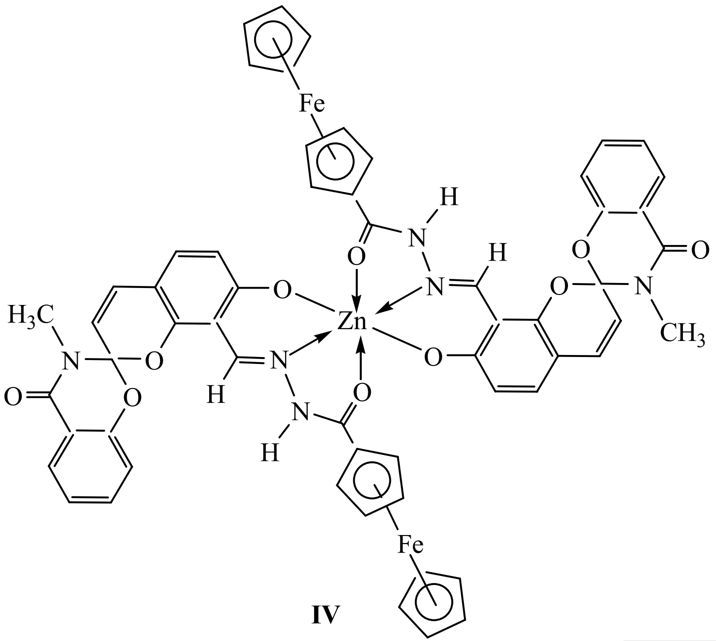
In the IR spectrum of the complex there are no absorption bands of stretching vibrations of the O–H bond. The absorption bands of imine and carbonyl groups are retained in the spectrum, but the latter is shifted to lower frequencies by 18 cm^{-1}. The C=N absorption band is also shifted to the lower frequencies by 20 cm^{-1}, which indicates the metal atom coordination.

In the ^{1}H NMR spectrum of the complex one of the proton signals in the strong field disappears, which is consistent with the hypothesis that the phenolic oxygen atom of the spiropyran molecule is substituted. The signals of azomethine and imine protons are shifted downfield by 0.2 and 0.7 ppm, respectively, which is also consistent with the participation of the azomethine group in the coordination.

For a more accurate assignment of the low-field signals in the ^{1}H NMR spectrum we obtained the model compound containing no hydroxy group, *ortho*-methoxybenzaldehyde ferrocenoylhydrazone **III**. In the ^{1}H NMR spectrum of this compound the imine proton signal is found at 11.00 ppm (compared to 11.30 ppm in the starting ligand).



III



IV

Based on the foregoing, the most probable is the structure **IV**. Taking into account the coordination of the nitrogen and oxygen atoms of the hydrazone group, it is presumable that the zinc atom has an octahedral environment. The above ligand forms complexes with other metals, in particular, with copper(II), nickel(II), iron(III), palladium(II), and others, whose properties will be discussed later.

Ferrocenecarboxylic acid. In a three-necked flask equipped with a mechanical stirrer 51 g of iodine (0.201 mol) and 46 g of acetylferrocene (0.202 mol) in

100 ml of pyridine were mixed for 90 min at room temperature. The mixture was then heated to 90°C and maintained at this temperature for another 90 min. The mixture was left for 12 h and then a solution of 25 g of NaOH (0.625 mol) in 1 l of water was added and the stirring was continued for 24 h. The mixture was filtered, the filtrate was acidified with concentrated HCl. The precipitate was filtered off, washed with water, and dried. Yield 48%, mp 200°C (toluene) (mp 210°C [21]).

Methyl ferrocenecarboxylate. To 5.02 g of ferrocenecarboxylic acid (0.09 mol) was added 14 ml of methanol and 0.05 ml of conc. H_2SO_4. The mixture was heated for 25 h and then filtered. The mother liquor was cooled and filtered. The precipitate was washed with water. Yield 87%, mp 60°C (methanol–water, 2:1) [22].

Ferrocenecarboxylic acid hydrazide. A mixture of 2 g (0.082 mol) of methyl ferrocenecarboxylate and 2.1 g (0.042 mol) of hydrazine hydrate (90%) was heated until complete dissolution and then for another 15 min. After cooling, the precipitate was filtered off, washed with water, and dried. Yield 50%, mp 170°C (toluene) [18].

7-Hydroxy-3-methyl-8'-formyl-3,4-dihydro-2*H*-1,3-benzoxazine-2-spiro-2(*H*)-chromene ferrocenoylhydrazone. To a solution of 10 mmol of spiropyran **I** [23] in 50 ml of ethanol was added a solution of 10 mmol of ferrocenecarboxylic acid hydrazide in 60 ml of ethanol. The mixture was refluxed for 15 min until the precipitate formation. The precipitate was filtered off while hot and washed twice with the boiling ethanol. Yield 52%, mp > 300°C (dioxane). IR spectrum (mineral oil), ν, cm^{-1}: 3234 (N–H), 1673 (C=O), 1664 (C=O), 1616 (C=N). ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.18 s (3H, NCH_3), 4.13 s (5H, C_5H_5), 4.35 s (2H, C_5H_4), 4.83 s (2H, s, C_5H_4), 6.05 d (1H, 3-H, *J* 9.67), 6.62 d (1H, 6'-H, *J* 8.42), 6.95 d (1H, 8-H, *J* 8.13), 7.05 d (1H, 4'-H, *J* 9.63), 7.22 m (2H, 6-H, 8-H), 7.51 t (1H, 7-H, *J* 7.22), 7.95 d (1H, 5'-H, *J* 7.10), 8.28 s (1H, CHO), 11.38 s (1H, NH), 12.43 s (1H, OH). Found, %: C 52.1, H 4.1; N 7.8; Fe 10.4. $C_{28}H_{23}FeN_3O_5$. Calculated, %: C 51.8, H 4.4; N 7.6; Fe 10.5.

7-Hydroxy-3-methyl-8'-formyl-3,4-dihydro-2*H*-1,3-benzoxazine-2-spiro-2(*H*)-chromene ferrocenoylhydrazone zinc(II) complex. To a solution of 0.01 mol 7-hydroxy-3-methyl-8'-formyl-3,4-dihydro-2*H*-1,3-benzoxazine-2-spiro-2(*H*)-chromene ferrocenoylhydrazone in 30 ml of ethanol was added a hot solution of 0.005 mol of zinc acetate in 10 ml of methanol. The mixture was refluxed for 30 min. The precipitate was filtered off, washed with 30 ml of boiling ethanol, and dried in a vacuum at 100°C. Yield 32%, mp > 300°C. IR spectrum (mineral oil), ν, cm^{-1}: 3219 (N–H), 1672 (C=O), 1642 (C=O), 1596 (C=N). ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.14 s (3H, NCH_3), 4.12 s (5H, C_5H_5), 4.46 s (2H, C_5H_4), 4.84 s (2H, C_5H_4), 5.90 d (1H, 3-H, *J* 9.34), 6.07 d (1H, 6-H, *J* 8.53), 6.95 d (1H, 8-H, *J* 10.91), 6.99 d (1H, 4'-H, *J* 9.39), 7.23 m (2H, 6-H, 8-H), 7.57 t (1H, 7-H, *J* 7.07), 7.99 d (1H, 5'-H, *J* 7.76), 8.43 s (1H, CHO), 12.11 s (lH, NH). Found, %: C 58.8, H 3.5; N 7.2; Fe 9.6; Zn 5.6. $C_{56}H_{44}Fe_2N_6O_{10}Zn$. Calculated, %: C 59.1, H 3.9; N 7.4; Fe 9.8; Zn 5.7.

***ortho*-Methoxybenzaldehyde ferrocenoylhydrazone.** To a solution of 10 mmol of *o*-methoxy-benzaldehyde in 30 ml of ethanol was added a solution of 10 mmol of ferrocenecarboxylic acid hydrazide in 60 ml of ethanol. The mixture was refluxed for 1 h until the precipitate formation. The precipitate was filtered off and washed twice with boiling ethanol. Yield 72%, mp > 300°C (DMF). IR spectrum (mineral oil), ν, cm^{-1}: 3210 (N–H), 1637 (C=O), 1601 (C=N). ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.90 s (3H, OCH_3), 4.17 s (5H, C_5H_5), 4.93 s (2H, C_5H_4), 5.07 s (2H, C_5H_4), 7.01 m (2H, C_6H_4), 7.33 d.d (1H, C_6H_4, ^3J 1.46, ^2J 7.11), 7.94 d (1H, ^2J 7.09), 8.72 s (1H, C=CH), 10.98 s (lH, NH). Found, %: C 62.8, H 4.9; N 7.8; Fe 15.8. $C_{19}H_{18}\cdot FeN_2O_2$. Calculated, %: C 63.0, H 5.0; N 7.7; Fe 15.5.

The IR spectra were recorded on a Varian Scimitar 1000 spectrometer in the region of 4000–400 cm^{-1} from mulls in mineral oil or fluorinated hydrocarbons. ^1H NMR spectra were obtained at 25°C on a Varian Unity 300 instrument (300 MHz) from DMSO-d_6 solutions relative to internal tetramethylsilane.

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