



Синтез И Спектроскопическое Исследование Комплексных Соединений Переходных Металлов Гидразонными Производными Ферроцена

Annotation:

Synthesized series of new complexes based on derivatives of ferrocene with hydrazide mono-, dicarboxylic acids. Methods elemental analysis, IR and PMR spectroscopic methods established the composition and structure of the obtained complexes.

Keywords:

Ligand, derivatives of ferrocene, condensation reaction, hydrazides of carboxylic acids, complex.

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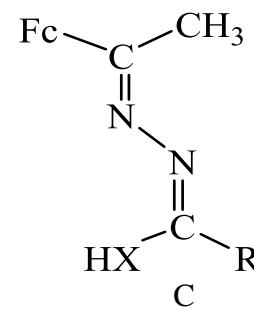
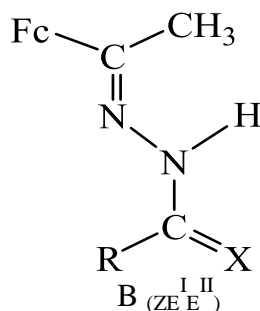
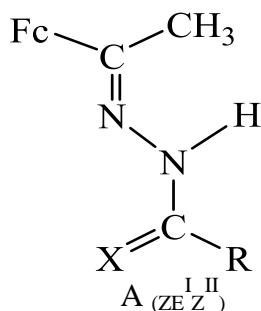
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Ferrocene derivatives are of constant theoretical and practical interest due to their ability to easy reversible oxidation, the manifestation of second-order nonlinear optical properties, as well as catalytic and biological activity. The latter is especially characteristic of hydrazone derivatives of ferrocene, which is due to their chelating ability [1–3]. Transition metal complexes with hydrazones of carboxylic acids are convenient models for studying the factors affecting the nature of the magnetic exchange interaction between paramagnetic transition metal ions [4, 5].

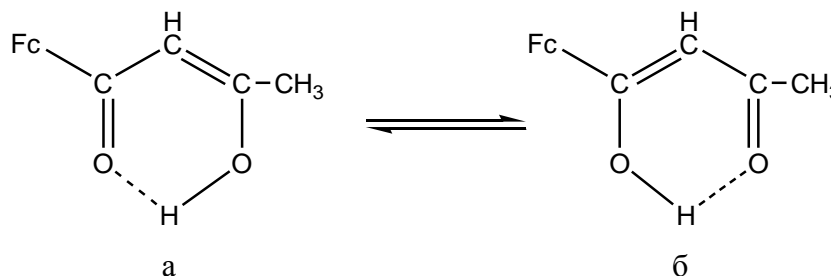
We synthesized new ligands by Claisen condensation of monoacetylferrocene with carboxylic acid hydrazides. It has been established that these compounds mainly exist in the form of two potential configurations $ZE^I Z^II$ (A), $ZE^I E^II$ (B) of the hydrazone form and react in the process of complex formation in the form of α -hydroxyazine form (C) [6-8].



$R=CH_3$, $X=O$: $R=CH_3$ (HL¹), 3-NO₂-C₆H₄ (HL²), C₆H₅-CH₂ (HL³); $R^3=NH_2$, $X=S$ (HL⁴).



In crystals of β -dicarbonyl derivatives of ferrocene, there is an intramolecular hydrogen bond. In an acetoacetyl substituent, four carbon atoms are coplanar with two oxygen atoms. The lengths of the C-C and C=O bonds differ significantly from the bond lengths in other 1,3-diketones (C-C 1.522 Å and C=O 1.217 Å), the existence of which has been proven in the keto form. This determines the possibility of enolization and the formation of two tautomeric forms [9-12]:



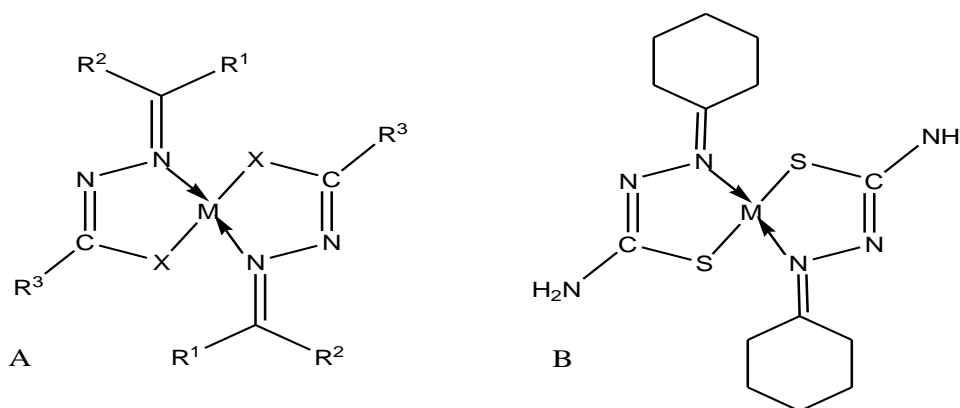
In the ferrocenylacetone molecule, the carbonyl group, located at a greater distance from the donor ferrocenyl group, is more stable; therefore, the tautomeric form (b) is more probable. The length of the intramolecular hydrogen bond is 2.462 Å.

Table 1. Yields, melting points and results of elemental analysis of ligands

HL	Yield %	T _{m.p.} ⁰ C	Gross formula	Found/Computed, %			
				C	H	N	Fe
HL ₁	35	168-170	C ₁₄ H ₁₆ N ₂ OFe	59,01/59,18	5,37/5,68	10,23/9,86	19,22/19,65
HL ₂	43	102-104	C ₁₉ H ₁₇ N ₃ O ₃ Fe	58,46/58,33	4,31/4,38	10,95/10,74	14,01/14,28
HL ₃	57	155-157	C ₂₀ H ₂₀ N ₂ OFe	66.31/66.68	5,25/5,60	8,07/7,78	15,37/15,50
HL ₄	49	151-153	C ₁₃ H ₁₅ N ₃ SFe	51,49/51,84	5,14/5,02	14,23/13,95	18.62/18,54

On the basis of these ligands, complex compounds of transition metals have been synthesized, the composition and structure of which have been established by elemental analysis, IR and NMR ¹H spectroscopy [13-16].

According to the data of elemental analysis and IR spectroscopy, the structures of the synthesized complexes are similar to previously established structures of similar complexes. Complexes of the composition ML₂.



I



Type A connections: $R^1=CH_3$, $R^2=Fc$, $X=O$, $R^3=CH_3$, $Ni(NiL^2_2)$, $Co(CoL^2_2)$, $R^3=C_6H_5-CH_2$, $X=O$, $M=Zn(ZnL^3_2)$, $R^3=NH_2$, $X=S$: $M=Ni(NiL^4_2)$, $Co(CoL^4_2)$.

Judging by the results of IR spectra, in the solid state, complex compounds of unsymmetrical monocarbonyl compounds have structure (I) of type A; there are no characteristic absorption bands of free ligands around $1660-1700\text{ cm}^{-1}$, 3225 cm^{-1} ($\gamma\text{ C=O}$, $\gamma\text{ N-H}$), in the spectrum of complexes with the HL^4 ligand, at $835-850\text{ cm}^{-1}$ ($\gamma\text{ C=S}$). This indicates the enolization and deprotonation of the ligands during complexation. The IR spectra of the complexes are characterized by absorption bands at cm^{-1} ($\gamma\text{ N=C-C=N}$) and $1610-1630\text{ cm}^{-1}$ ($\gamma\text{ C=N}$): the latter is shifted to the low-frequency region by $10-15\text{ cm}^{-1}$ compared to with an absorption band of free ligands (Table 1, Fig. 1). A single band at $1535-1540\text{ cm}^{-1}$ corresponds to stretching vibrations of the $N=C-O^-$ system. The band of weak intensity at $1040-1050\text{ cm}^{-1}$ in the IR spectra of the complexes belongs to $\gamma\text{ N-H}$, which is shifted by $10-20\text{ cm}^{-1}$ to the high-frequency region compared to the spectra of the ligands. In contrast to complexes with derivatives of acyl- and aroylhydrazones, the IR spectrum of complexes with thiosemicarbazones shows absorption bands of medium intensity in the region of $3420-3140\text{ cm}^{-1}$, which should be attributed to the γ_S and γ_{AS} NH_2 -groups of the thiosemicarboside fragment. The isolated complexes of nickel(II) and zinc(II) turned out to be diamagnetic in solutions of various solvents. Diamagnetism and the results of analysis of the NMR 1H spectra of nickel(II) complexes indicate their square planar structure [17-22].

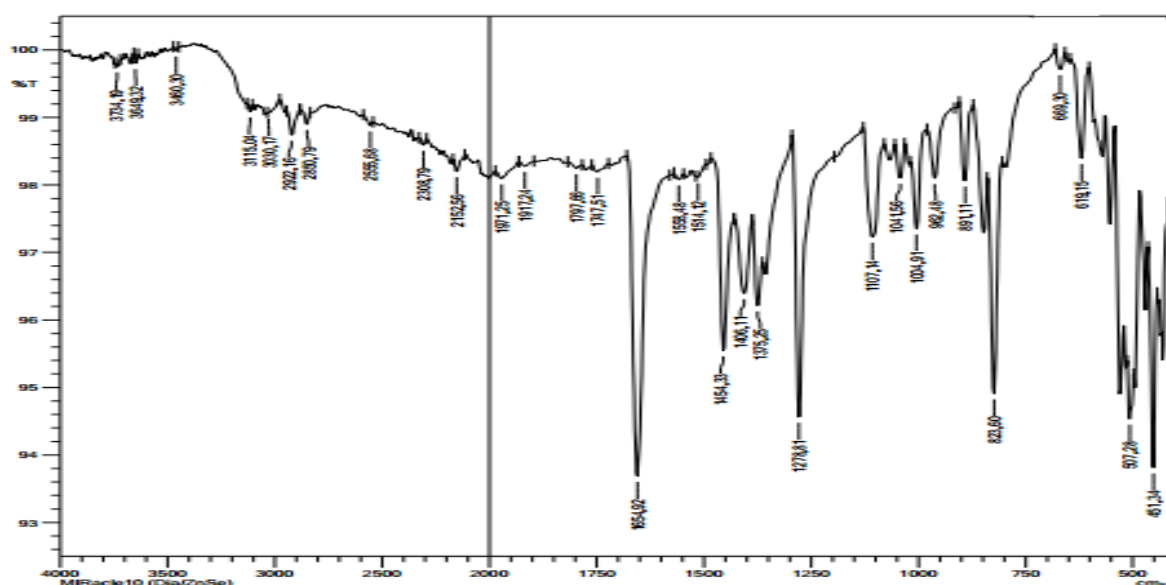


Fig. 1. IR spectra of ligand HL^2 .

Table 2. Assignment of stretching vibration frequencies (ν , cm^{-1}) in IR spectra of nickel(II) and zinc(II) complexes of structure (I)

Compound	NH_2	C-H	C=N	N=C-C=N	N=C-O ⁻	N-N	NO_2	Fe-Cp
NiL^2_2	-	3020	1600	1586	1550	1086	1535/1346	470-500
CoL^2_2	-	3035	1610	1595	1555	1092	1535/1340	465/503
ZnL^3_2	-	3050	1650	1600	1555	1045	-	465/504
NiL^4_2	3420	3085	1600	1590	1535	1105	-	470/500
CoL^4_2	3423	3085	1600	1590	1535	1105	-	470/500

In the PMR spectrum of the complex NiL^4_2 , (HL^4 -thiosemicarbazone of acetylferrocene) in a solution of $DMSO-d_6$, no paramagnetic broadening of the signals is observed.



It is known that the ferrocene fragment in all compounds of heterometallic complexes is diamagnetic. The signals from the protons of the Fc cyclopentadienyl rings in the NiL^4_2 complex do not change in character and intensity compared to the spectrum of the HL^4 ligand (Fig. 2)

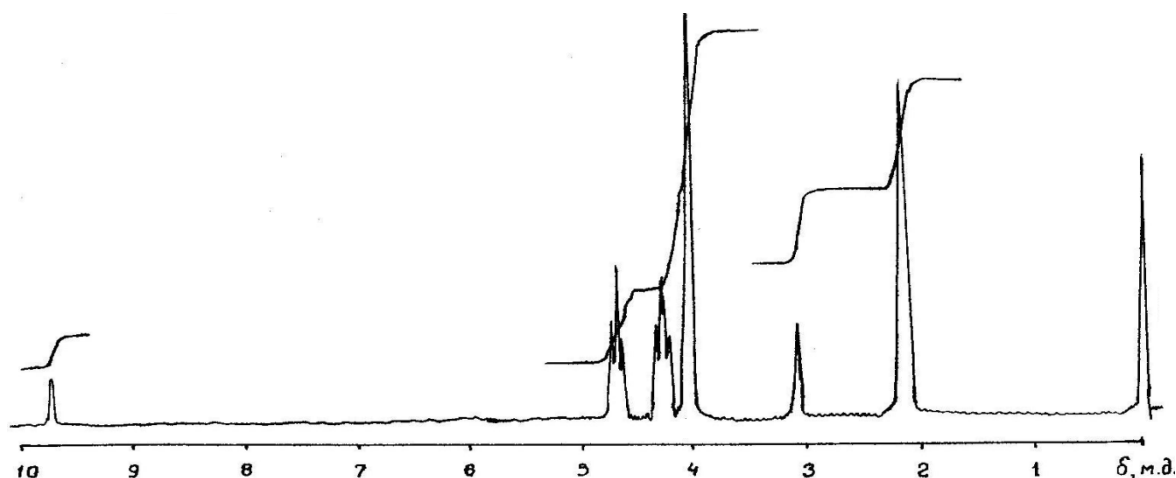


Fig. 2. NMR 1H spectrum of HL^4 ligand, thiosemicarbazone acetylferrocene, in $DMSO-d_6$ solution.

It should be noted the shift to the strong field of the singlet signal of the CH_3 group in the PMR spectrum of the complex (δ 1.65 ppm), which, in our opinion, is associated with the formation of a $d-\pi$ -type dative bond. During chelation due to structural distortions, paramagnetism of the ferrocene fragment sometimes appears. Such an anomalous magnetic property of ferrocene is explained by the deviation of cyclopentadienyl rings from coplanarity, which is due to the transformation of the molecular orbitals of ferrocene and the transition of the Fe^{2+} ion to a high-spin state with a total spin of $S=2$. However, in the case of zinc(II) complexes with ferrocene derivatives of acylhydrazones, we did not observe such paramagnetic anomalies.

The use of the synthesized complex compounds on slightly saline and wilt soils in the Bukhara region reduces the degree of Fusarium wilt disease, accelerates the growth and development of cotton, reduces the vegetation process, and is also proposed as a drug to increase the yield and quality of raw cotton fiber.

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