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Synthesis of Complexes Based On Monocarbonyl Ferrocene Derivatives with Carbonic Acid Hydrases

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Abstract: *A series of new complexes based on monocarbonyl derivatives of ferrocene with hydrazides of mono- and dicarboxylic acids has been synthesized. The composition and structure of the obtained complexes were established by the methods of elemental analysis, IR and YaMR^{1}H spectroscopy.*

Keywords: ligand, ferrocene derivatives, condensation reaction, carboxylic acid hydrazides, complex.

Introduction

The unremitting interest in the chemistry of complex compounds of transition metals with ligands based on acyl- and thioacylhydrazones of mono- and dicarbonyl compounds is due to their extremely important theoretical and practical importance.

Acyl- and thioacylhydrazones, bis-5-hydroxypyrazolines of mono-, α- and β-dicarbonyl compounds can exist in various tautomeric forms depending on the nature of functional substituents and have the ability to form metal chelates of various structures.

Physicochemical studies of the fine structure of metal complexes with hydrazones are of independent interest for the development of theoretical concepts of coordination and inorganic chemistry, since the synthetic capabilities of these compounds allow purposefully changing the ligand environment in the complexes, obtaining compounds with predetermined physicochemical, stereochemical, electronic and magnetic properties.

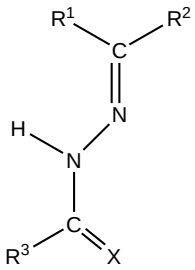
The practical importance of these compounds is emphasized by the special role of hydrazone complexes in the composition of antitumor, antiviral, antibacterial, anticarcinogenic and carcinoprotective gents. It should be noted that complexes of this class are promising objects for fixing atmospheric nitrogen, direct dissolution of metals in non-aqueous solvents, stabilization of polymers, and production of new types of combustion regulators and catalysts.

The possibility of synthesis based on new ligands along with mononuclear, binuclear complexes with paramagnetic ions predetermine the emergence of new areas of use of these compounds, exhibiting exchange interactions between the paramagnetic centers of metal chelates through bridging units [1,2].

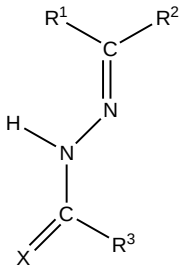
Ferrocene derivatives are, first of all, attracting attention due to the wide spectrum of their biological activity. Biological activity is especially characteristic of hydrazone derivatives of ferrocene, which is due to their chelating ability.

Exprimental part

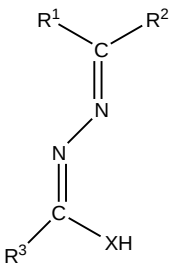
We have synthesized new ligands by condensation of claisenmonoacetylferrocene with carboxylic acid hydrazides. It was found that these compounds predominantly exist in the form of two potential configurations ZE^{I}Z^{II} (A), ZE^{I}E^{II} (B) of the hydrazone form and, in the course of complexation, react in the form of the α-hydroxyazine form (C) [3].



A$_{(ZE^1Z^1)}$



B$_{(ZE^1E^{11})}$



C

R^1=CH_3 R^2 =Fc, X=O: R^3=CH_3 (HL_1), 3-NO_2-C_6H_4 (HL_2), C_6H_5-CH_2 (HL_3); R^3=NH_2, X=S (HL_4).

Table 1

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Yields, Melting Points and Elemental Analysis Results of Ligands

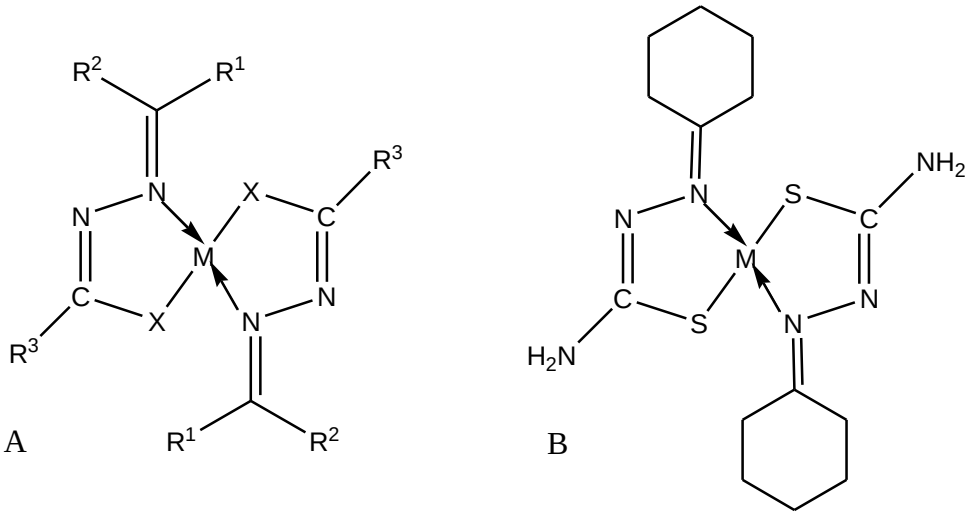
HL	HL Exit %	$T_{melt.0C}$	Empirical formula	Found / Calculated,%			
				C	H	N	Fe
HL^1	35	168-170	$C_{14}H_{16}N_2OFe$	59,01/59,18	5,37/5,68	10,23/9,86	19,22/19,65
HL^2	43	102-104	$C_{19}H_{17}N_3O_3Fe$	58,46/58,33	4,31/4,38	10,95/10,74	14,01/14,28
HL^3	57	155-157	$C_{20}H_{20}N_2OFe$	66.31/66.68	5,25/5,60	8,07/7,78	15,37/15,50
HL^4	49	151-153	$C_{13}H_{15}N_3SFe$	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 were synthesized, the composition and structure of which were determined by the methods of elemental analysis, IR, and YaMR^{1}Hspectroscopy [4].

Result and discussion

Elemental analysis and IR spectroscopy showed the presence of similarity in the structure of the synthesized complexes with the previously established structures of similar complexes [5].

Complexes of composition ML_2 were synthesized by the interaction of alcohol solutions of metal acetates and HL-type ligands.



Type A compounds: $R^1 = CH_3$, R^2 = Fc, X = O, R^3 = 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 asymmetric monocarbonyl compounds have a structure (I) of type A, there are no characteristic absorption bands of free ligands at about 1660-1700 cm^{-1}, 3225 cm^{-1} (γ C = O, γ NH), and in the spectrum of complexes with ligand HL^4 - at 835-850 cm^{-1} (γ C = S). This indicates the enolization and deprotonation of the ligands in the course of complexation.

The IR spectra of the complexes are characterized by absorption bands at 1590-1605 cm^{-1} (γ N = CC = N) and 1610-1630 cm^{-1} (γ C = N): the latter is shifted in the low-frequency region by 10-15 cm^{-1}compared to with an absorption band of free ligands (Table 1, Fig. 1). A single band at 1535-1540 cm^{-1} corresponds to stretching vibrations of the N = C-O- system.

The band of weak intensity at 1040-1050 cm^{-1} in the IR spectra of the complexes belongs to γN-H, which is shifted by 10-20 cm^{-1} towards high frequencies in comparison with the spectra of 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 cm^{-1}, which should be attributed to the S and γ_{AS} NH_2 groups of the thiosemicarbazide fragment.

The isolated complexes of nickel(II) and zinc(II) turned out to be diamagnetic in a solution of various solvents. Diamagnetism and the results of the analysis of the YaMR^{1}H spectra of nickel(II) complexes indicate their planar-square structure.

Table 2

Assignment of stretching vibration frequencies (ν, cm^{-1}) in the IR spectra of nickel(II), cobalt(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

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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_2[3]	-	3050	1650	1600	1555	1045	-	465/504
NiL_2[4]	3420	3085	1600	1590	1535	1105	-	470/500
CoL_2[4]	3423	3085	1600	1590	1535	1105	-	470/500

In the YaMR[1]H spectrum of the NiL_2 complex, (HL^4-thiosemicarbazone acetylferrocene) in a DMSO-d_6 solution, no paramagnetic broadening of signals is observed (Table 3, Fig. 2).

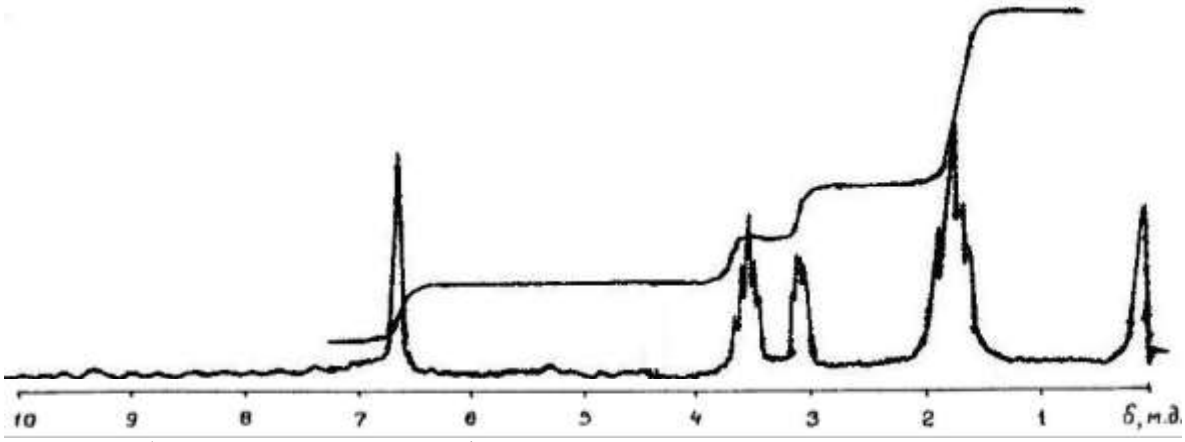

Fig. 2. YaMR[1]H spectrum of complex NiL_2[4]

It is known that the ferrocene fragment in all compounds of heterometallic complexes is diamagnetic. Signals from the protons of the cyclopentadienyl rings Fc in the NiL_2[4]complex do not change in character and intensity compared to the spectrum of the HL^4 ligand (Fig. 3).

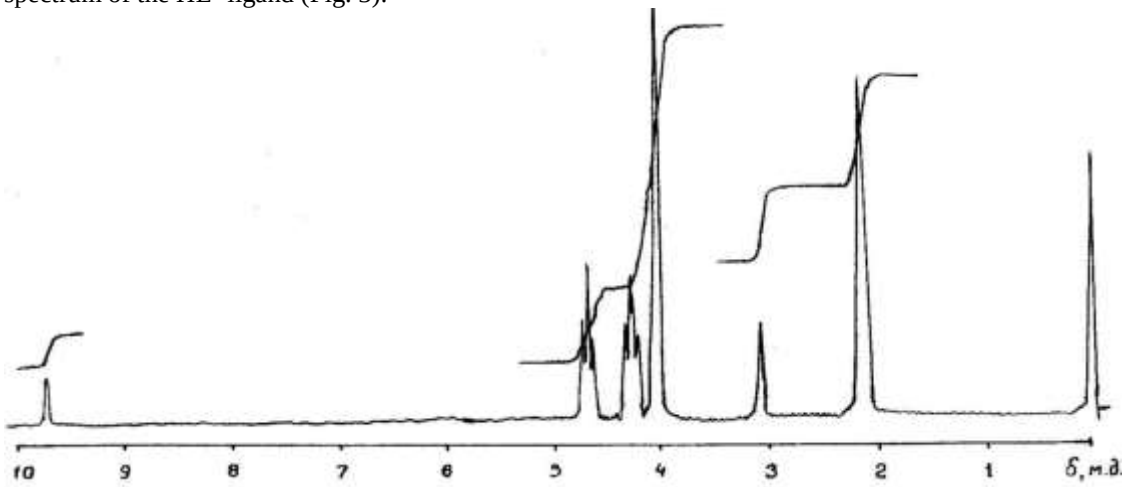

Fig. 3.YaMR [1]Hspectrum of the HL^4 ligand - thiosemicarbazoneacetylferrocene in DMSO-d_6 solution.

It should be noted that the strong-field shift of the singlet signal of the CH3 group in the PMR spectrum of the complex (δ 1.65 ppm) is noted, which, in our opinion, is associated with the formation of a d-π-type dative bond. During chelation due to structural distortions, paramagnetism of the ferrocene fragment sometimes appears. This anomalous magnetic property of ferrocene is explained by the deviation of the cyclopentadienyl rings from coplanarity, which is caused by the transformation of molecular orbitals of ferrocene and the transition of the – Fe^{2+}ion to a high-spin state with a total spin S = 2. However, in the case of zinc(II) complexes with ferrocene derivatives of acylhydrazones, we did not observe such paramagnetic anomalies.

Table-3

Parameters of the YaMR[1]H spectra of nickel (II) and zinc (II) complexes (LXYI) in a DMSO-d_6 solution ((δ, ppm)

Compound	R	R	R
ZnL_2[2 a)]	2,21/2,35[б)]	4,10/4,18; 4,83/5,03	7,4; 7.94; 8,14; 8,43
NiL_2[4]	1,65	4,11; 4,30; 4,76	6,18

Notes: a) - The YaMR[1]H spectrum was recorded in a solution of deuteratedtrifluoroacetic acid.
b) Signals of syn-anti isomers from substituents R^1 and $R^2$of the ketone fragment of the tetrahedrally distorted zinc(II) complex.

Conclusion

The use of 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 growing season, and is also proposed as a drug to increase the yield and quality of raw cotton fiber.

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