

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

1Sulaymonova Zilola Abdurakhmanovna, 2Umarov Bako Bafaevich, 3Chorieva Sabina Akhmadalievna, 4Navruzova Mashhura Bakhtiarovna

1Senior Lecturer, Bukhara State University, Uzbekistan, Bukhara  
2Professor, Doctor of Chemistry, Bukhara State University, Uzbekistan, Bukhara  
3Student, Bukhara State University, Uzbekistan, Bukhara  
4Student, Bukhara State University, Uzbekistan, Bukhara  
E-mail: [sulaymonovaza75@mail.ru](mailto:sulaymonovaza75@mail.ru)

**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  $^{1}H$  NMR 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-,  $\alpha$ - and  $\beta$ -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.

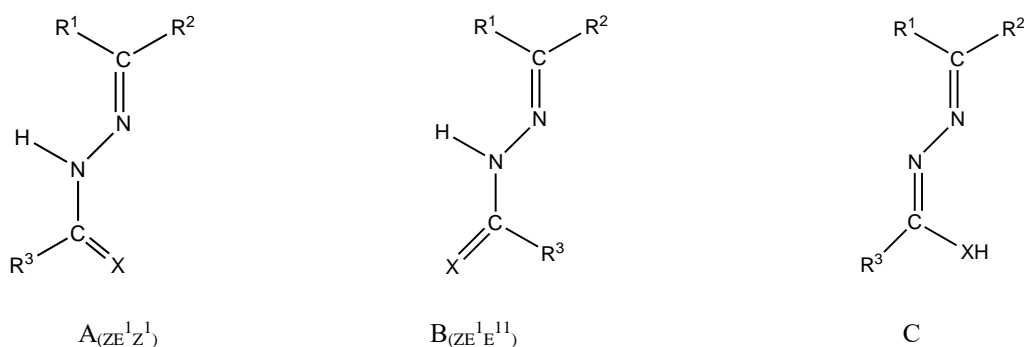
The practical importance of these compounds is emphasized by the special role of hydrazone complexes in the composition of antitumor, antiviral, antibacterial, anticarcinogenic and carcinoprotective agents. It should be noted that complexes of this class are promising objects for fixing atmospheric nitrogen, 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.

## Experimental 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  $\alpha$ -hydroxyazine form (C) [3].



$R^1=CH_3$ ,  $R^2=Fc$ ,  $X=O$ :  $R^3=CH_3$  (HL<sub>1</sub>), 3-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub> (HL<sub>2</sub>), C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub> (HL<sub>3</sub>);  $R^3=NH_2$ ,  $X=S$  (HL<sub>4</sub>).

## Yields, Melting Points and Elemental Analysis Results of Ligands

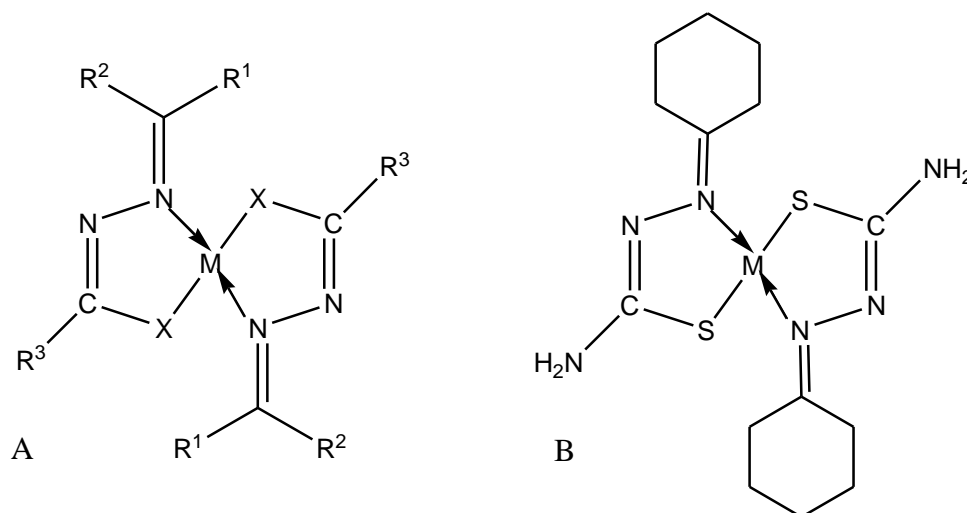
HL	HL Exit %	T <sub>melt.</sub> OC	Empirical formula	Found / Calculated,%			
				C	H	N	Fe
HL <sup>1</sup>	35	168-170	C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> OFe	59,01/59,18	5,37/5,68	10,23/9,86	19,22/19,65
HL <sup>2</sup>	43	102-104	C <sub>19</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> Fe	58,46/58,33	4,31/4,38	10,95/10,74	14,01/14,28
HL <sup>3</sup>	57	155-157	C <sub>20</sub> H <sub>20</sub> N <sub>2</sub> OFe	66.31/66.68	5,25/5,60	8,07/7,78	15,37/15,50
HL <sup>4</sup>	49	151-153	C <sub>13</sub> H <sub>15</sub> N <sub>3</sub> 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 were synthesized, the composition and structure of which were determined by the methods of elemental analysis, IR, and YaMR<sup>1</sup>H spectroscopy [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<sub>2</sub> were synthesized by the interaction of alcohol solutions of metal acetates and HL-type ligands.



Type A compounds: R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = Fc, X = O, R<sup>3</sup> = 3-Ni (NiL<sub>2</sub>), Co (CoL<sub>2</sub>), R<sup>3</sup> = C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>, X = O, M = Zn (ZnL<sub>3</sub>). R<sup>3</sup> = NH<sub>2</sub>, X = S: M = Ni (NiL<sub>4</sub>), Co (CoL<sub>4</sub>).

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<sup>-1</sup>, 3225 cm<sup>-1</sup> (γ C = O, γ NH), and in the spectrum of complexes with ligand HL<sup>4</sup> - at 835-850 cm<sup>-1</sup> (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<sup>-1</sup> (γ N = CC = N) and 1610-1630 cm<sup>-1</sup> (γ C = N): the latter is shifted in the low-frequency region by 10-15 cm<sup>-1</sup> compared to with an absorption band of free ligands (Table 1, Fig. 1). A single band at 1535-1540 cm<sup>-1</sup> corresponds to stretching vibrations of the N = C-O- system.

The band of weak intensity at 1040-1050 cm<sup>-1</sup> in the IR spectra of the complexes belongs to γN-H, which is shifted by 10-20 cm<sup>-1</sup> 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<sup>-1</sup>, which should be attributed to the S and γ<sub>AS</sub> NH<sub>2</sub> 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<sup>1</sup>H spectra of nickel(II) complexes indicate their planar-square structure.

**Table 2**  
Assignment of stretching vibration frequencies (ν, cm<sup>-1</sup>) in the IR spectra of nickel(II), cobalt(II) and zinc(II) complexes of structure (I)

Compound	NH <sub>2</sub>	C-H	C=N	N=C-C=N	N=C-O <sup>-</sup>	N-N	NO <sub>2</sub>	Fe-Cp
----------	-----------------	-----	-----	---------	--------------------	-----	-----------------	-------

NiL <sub>2</sub> <sup>2-</sup>	-	3020	1600	1586	1550	1086	1535/1346	470-500
CoL <sub>2</sub> <sup>2-</sup>	-	3035	1610	1595	1555	1092	1535/1340	465/503
ZnL <sub>2</sub> <sup>3-</sup>	-	3050	1650	1600	1555	1045	-	465/504
NiL <sub>2</sub> <sup>4-</sup>	3420	3085	1600	1590	1535	1105	-	470/500
CoL <sub>2</sub> <sup>4-</sup>	3423	3085	1600	1590	1535	1105	-	470/500

In the YaMR<sup>1</sup>H spectrum of the NiL<sub>2</sub> complex, (HL<sup>4-</sup>-thiosemicarbazone acetylferrocene) in a DMSO-d<sub>6</sub> solution, no paramagnetic broadening of signals is observed (Table 3, Fig. 2).

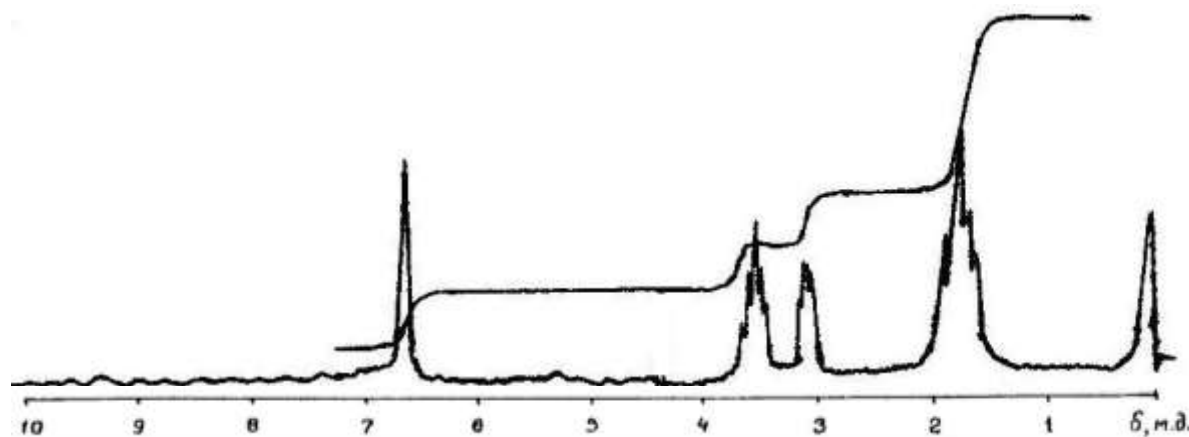


Fig. 2. YaMR<sup>1</sup>H spectrum of complex NiL<sub>2</sub><sup>4-</sup>

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<sub>2</sub><sup>4-</sup> complex do not change in character and intensity compared to the spectrum of the HL<sup>4-</sup> ligand (Fig. 3).

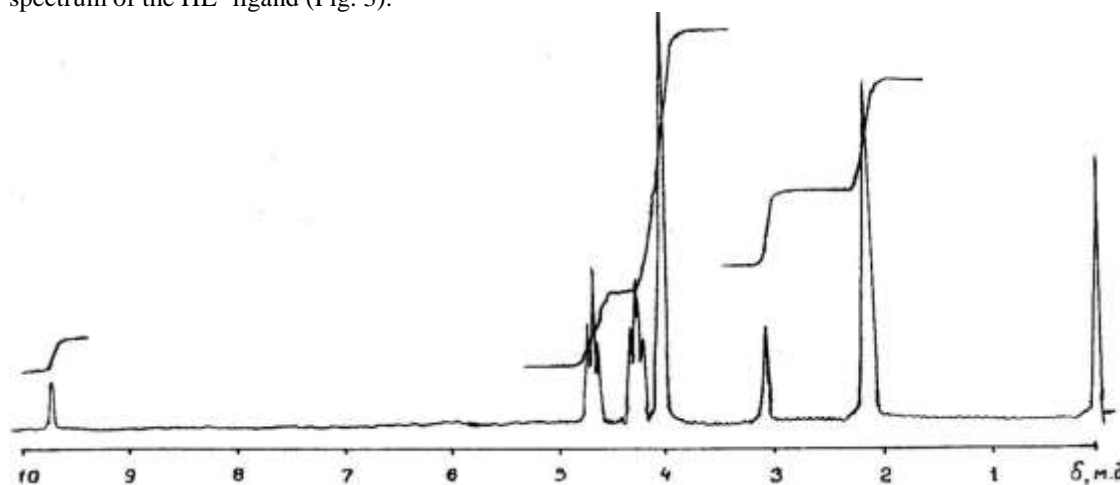


Fig. 3. YaMR<sup>1</sup>H spectrum of the HL<sup>4-</sup> ligand - thiosemicarbazoneacetylferrocene in DMSO-d<sub>6</sub> solution.

It should be noted that the strong-field shift of the singlet signal of the CH<sub>3</sub> group in the PMR spectrum of the complex ( $\delta$  1.65 ppm) is noted, 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. 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<sup>2+</sup> 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<sup>1</sup>H spectra of nickel (II) and zinc (II) complexes (LXYI) in a DMSO-d<sub>6</sub> solution (( $\delta$ , ppm)

Compound	R	R	R
ZnL <sub>2</sub> <sup>2 a)</sup>	2,21/2,35 <sup>b)</sup>	4,10/4,18; 4,83/5,03	7,4; 7,94; 8,14; 8,43
NiL <sub>2</sub> <sup>4</sup>	1,65	4,11; 4,30; 4,76	6,18

Notes: a) - The YaMR<sup>1</sup>H spectrum was recorded in a solution of deuterated trifluoroacetic acid.

b) Signals of syn-anti isomers from substituents R<sup>1</sup> and R<sup>2</sup> 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.

#### References

1. Kogan V.A., Zelentsov V.V., Larin G.M., Lukov V.V. Complexes of transition metals with hydrazones. Physical and chemical properties and structure - M.: Science. - 1990. - 112s.
2. Parpiev N.A., Yusupov V.G., Yakimovich S.I., Sharipov Kh.T. Acylhydrazones and their complexes with transition metals - Tashkent. - Fan. - 1988. - 161 p.
3. Tursunov M.A., Avezov K.G., Umarov B.B., Sevinchov N.G., Sulaymonova Z.A., Parpiev N.A. Tautomerism in the series of benzoylhydrazones of fatty aromatic ketoaldehydes // Materials of the Republican scientific and practical conference: "Current state and prospects of development of colloidal chemistry and nanochemistry in Uzbekistan" (to the 100th anniversary of the birth of Academician KS Akhmedov) Tashkent. 24-25 November 2014. S. 130-131.
4. Umarov B.B., Sulaymonova Z.A., Tillaeva D.M. Synthesis of ligands based on ferrocene derivatives with hydrazides of mono- and dicarboxylic acids. - Universum. - Moscow, 2020. - Issue: 3 (69). - P.19-21.
5. Umarov B.B., Kuchkarova R.R., Mardonov U.M., Alimov Y., Adizov N. Synthesis of copper(II) complexes with benzoylhydrazones 1- (2-tenoyl) -3,3,3-trifluoroacetone / Collection of abstracts of the international scientific and technical conference "ISTIQLOL" "Modern technology and technology of the mining and metallurgical industry and ways of their development." - Nav GGI. - September 23-25, 2004. - Navoi, pp. 134-135.
5. Ganiyev B. et al. Calculations of quantum chemical parameters of the compound of isocyanuric acid with semicarbazide // International Independent Scientific Journal. - 2020. - T. 2. - №. 16. - C. 3-9.
6. Tursunov M. A., Avezov K. G., Umarov B. B. Nickel (II) and Zinc (II) Complexes with Benzoylacetaldehyde Derivatives // Russian Journal of Coordination Chemistry. - 2019. - T. 45. - №. 7. - C. 484-488.
7. Umarov, B. B., Tursunov, M. A., & Minin, V. V. (2016). Kompleksy s proizvodnymi ketoal'degidov i ketoefirov.
8. Tursunov M. A. et al. <sup>1</sup>H NMR spectra and crystal structure of the nickel (II) complex with ethyl 5, 5-dimethyl-2, 4-dioxohexanoate aroylhydrazones // Russian Journal of Coordination Chemistry. - 2017. - T. 43. - №. 2. - C. 93-96.
9. Agrawal A., Sharma K. M., Prasad R. N. Synthesis and spectral studies of mixed ligand complexes of Co (II) with 5-nitrosalicylaldehyde and beta-diketones, hydroxyaryl aldehydes or ketones // Polish Journal of Chemistry. - 2007. - T. 81. - №. 12. - C. 2081-2087.
10. Umarov B. B. et al. SYNTHESIS AND CRYSTALLINE-STRUCTURE OF NICKEL (II) COMPLEX BASED ON PRODUCT OF 5, 5-DIMETHYL-2, 4-DIOXOHEXANIC ACID METHYL-ESTER CONDENSATION WITH BENZOHYDRAZIDE // KOORDINATSIONNAYA KHIMIYA. - 1992. - T. 18. - №. 9. - C. 980-984.
10. Umarov B. B. et al. Synthesis and crystal structure of nickel (II) complex based on 2-trifluoroacetylcycloalkanone benzoylhydrazones // Russian Journal of Coordination Chemistry. - 2014. - T. 40. - №. 7. - C. 473-476.
11. Conradie J. et al. Synthesis and characterisation of ferrocene-containing  $\beta$ -diketonato complexes of rhodium (I) and rhodium (III) // Inorganica Chimica Acta. - 2002. - T. 328. - №. 1. - C. 191-203.
12. Kuklin S. A. et al. Highly active iridium catalysts for alkane dehydrogenation. Synthesis and properties of iridium bis (phosphine) pincer complexes based on ferrocene and ruthenocene // Organometallics. - 2006. - T. 25. - №. 22. - C. 5466-5476.
13. Baryshnikova S. V. et al. Ferrocene-Containing Tin (IV) Complexes Based on o-Benzoquinone and o-Iminobenzoquinone Ligands. Synthesis, Molecular Structure, and Electrochemical Properties // Inorganic chemistry. - 2020. - T. 59. - №. 10. - C. 6774-6784.
14. Tursunov M. A., Umarov B. B., Avezov K. G. Copper (II) complexes with aroylhydrazones of ethyl ether 5, 5-dimethyl-2, 4-dioxohexanoic acid // Development of science and technology. Scientific and technical journal. - 2018. - №. 2. - C. 71-75.
15. Tursunov, M. A. (2019). Complexes of Some 3d Metals Based on Derivatives of Ketoaldehydes and Ketoesters, Their Structure and Properties: Autoref. diss.... PhD. BukhSU: Bukhara, 46.