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CONTENTS

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SYNTHESIS AND NMR SPECTROSCOPIC STUDY OF HYDRAZONE DERIVATIES OF FERROCENOYLACETONE AND THEIR COMPLEXES

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Annotatsiya: Klyayzen kondensatsiyasi orqali β-diketon – 1-ferrotsenilbutandion-1,3 olindi. Monokarbon kislota gidrazidlari va ferrotsenoilatsetonning o'zaro ta'sirlashuvi natijasida gidrazonlar (H_2L) va ular asosida oraliq metall ionlarining komplekslari sintez qilindi. Olingan birikmalar spektroskopik usullarda o'rganildi. Tadqiqotlar natijasiga ko'ra, H_2L eritmada gidrazon, α-oksiazin va halqali 5-oksipirazolin kabi tautomer shakllarida uchraydi. Spektroskopik tadqiqotlar natijalariga ko'ra kom-plekslar tekis-kvadrat tuzilishiga ega ekanligi va ularda ikki marta de-protonlangan ligand qoldig'i metall atomi bilan ikkita kislorod atomi hamda gidrazon fragmentining azot atomi orqali tridentat koordinatsion bog'langani hamda tekis kvadrat trans-N_2O_2-koordinatsion qurshovining to'rtinchi o'rnini ammiak molekulasi egallagani aniqlandi.

Kalit so'zlar: gidrazon, ferrotsenoilatseton, Klyayzenning murakkab efir kondensatlanishi, tautomeriya, YaMR spektroskopiya

Аннотация: Нами конденсацией Кляйзена получен β-дикетон – ферроценоилацетон. Синтезированы гидразоны монокарбоновых кислот (H_2L) взаимодействием гидразидов карбоновых кислот с ферроценоилацетоном. На их основе полу-чены комплексы с переходными металлами. Синтезированные соединения изучены спектроскопическими методами. Результаты исследований показали, что H_2L в растворе существует в виде таутомерной смеси: гидразонной, енгидразинной и циклической 5-оксипиразолиновой формах. По результатам спектроскопических исследований комплексам приписано плоско-квадратное строение, где дважды депротонированный остаток лиганда тридентатно координирован атомом металла через два атома кислорода и атом азота гид-разонного фрагмента. Четвертое место в плоском квадрате транс-N_2O_2-коор-динационного узла занимает молекула аммиака.

Ключевые слова: гидразон, ферроценоилацетон, сложноэфирная конденсация Кляйзена, таутомерия, ЯМР спектроскопия

Abstract: We obtained β-diketone – ferrocenoylacetone by Kleisen condensation. Hydrazones of monocarboxylic acids (H_2L) were synthesized by the interaction of hydrazides of carboxylic acids with ferrocenoylacetone. On their basis, complexes with transition metals were obtained. The synthesized compounds were studied by spectroscopic methods. The research results showed that H_2L in solution exists in the form of a tautomeric mixture: hydrazine, enhydrazine and cyclic 5-hydroxypy-razoline forms. According to the results of spectroscopic studies, the complexes were assigned a planar-square structure and in them the doubly deprotonated ligand residue is coordinated by a metal atom through two oxygen atoms and a nitrogen atom of the hydrazone fragment. The fourth place in the flat square of the trans-N_2O_2-coordination site is occupied by the ammonia molecule.

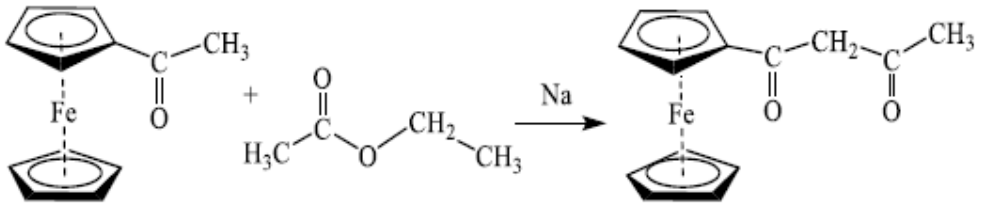
Keywords: hydrazone, ferrocenoylacetone, Claisen ester condensation, tautomerism, NMR spectroscopy

Introduction: Ferrocene is a unique compound in terms of chemical and thermal stability, as well as the possibility of direct application in various organic reactions. This is due to its "sandwich" structure, which is a three-dimensional aromatic system.

Literature review: Thus, many ferrosene-containing compounds are widely studied as new materials [1] and used in coordination chemistry [2]. Currently, a huge number of studies are being carried out to study the biological activity of ferrocene derivatives [3]. A special degree of biological activity is inherent in hydrazone derivatives of ferrocene, which is due precisely to their chelating ability. Numerous experiments have established that the use of molecular and intracomplex compounds based on ferrocene-containing derivatives of trace elements, such as copper, nickel and zinc, leads to an improvement in the germination of plant seeds. It is a potent pesticide and has a beneficial effect on the growth and development of plants. It has been established that the stimulating properties of complex compounds depend on the nature of the metal, methods of coordination of ligands, as well as the chemical composition and geometric structure of the complexes.

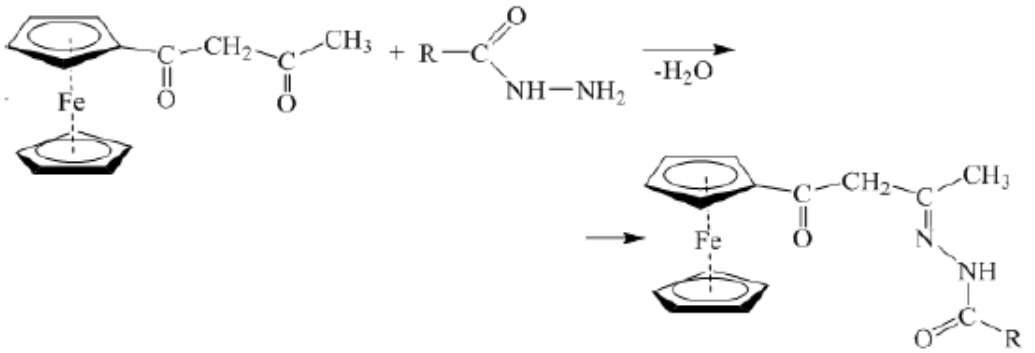
Research Methodology: To expand the range of tridentate chelating ligand systems containing ferrocene fragments; we have synthesized new ligands HL^1- HL^6.

At the first stage of the synthesis, we performed the Claisen ester condensation of monoacetylferrocene with ethyl acetate [4, 5, 6, 7, 8]. The β-dicarbonyl derivative of ferrocene, 1-ferrocenylbutanedione-1,3 (**I**) (ferrocenoylacetone), was synthesized according to the following reaction scheme:



I

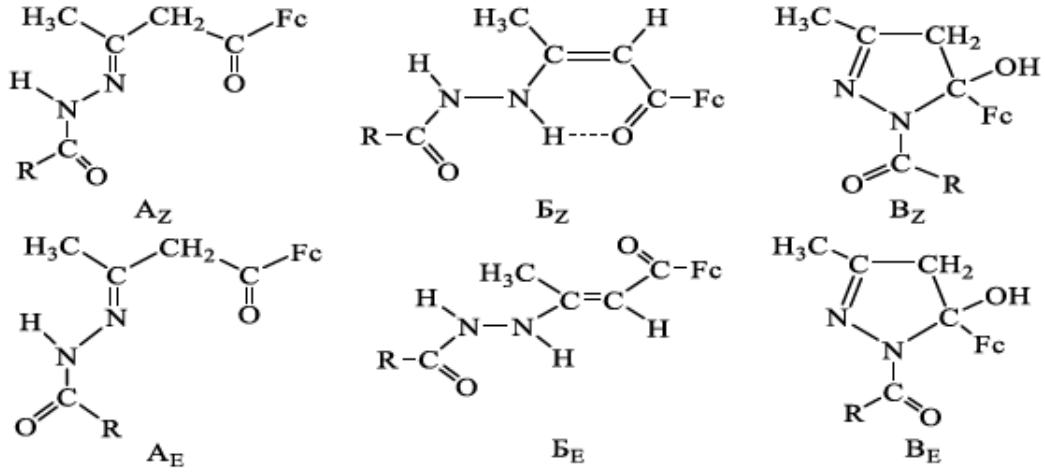
New ligands H_2L^1 - H_2L^6, respectively, were synthesized by the interaction of alcoholic solutions of equimolar amounts of 1-ferrocenylbutanedione-1,3 with alcoholic solutions of acetylhydrazide, benzoylhydrazide, *para*- and *meta*-nitrobenzoylhydrazides, and hydrazides of 5-bromosalicylic and phenylacetic acids, respectively.



II

R=CH_3 (H_2L^1), C_6H_5 (H_2L^2), *м*-NO_2-C_6H_4 (H_2L^3)), *п*-NO_2-C_6H_4 (H_2L^4), 2-OH-5-Br-C_6H_3 (H_2L^5), $C_6H_5CH_2$ (H_2L^6).

The presence of a hydrazone group in compound **II** suggests wide possibilities for tautomerism. It can be assumed that at least three tautomeric forms can exist for it: hydrazone (A), enhydrazine (B), and cyclic pyrazoline (C) forms. In addition, configurational isomerism should also be taken into account for them [3, 9].



Analysis and results: The composition and structure of the obtained ligands were studied by elemental analysis and spectroscopic methods.

Table 1.

Yields, melting points, and results of elemental analysis of ferrocenoylacetone condensation products with monocarboxylic acid hydrazides (H_2L^1- H_2L^6)

Com-pound	Output,%	$T_{пл.}$°C	Gross-formula	Found/Computed, %			
				C	H	N	Fe
H_2L^1	49	167-169	$C_{16}H_{18}N_2O_2Fe$	58,31/58,89	5,37/5,52	8,65/8,58	17,22/17,17
H_2L^2	43	150-152	$C_{21}H_{20}N_2O_2Fe$	64,76/64,95	5,18/5,16	7,19/7,22	14,66/14,43
H_2L^3	65	153-155	$C_{21}H_{19}N_3O_4Fe$	58,1/58,2	4,4/4,39	9,59/9,7	12,73/12,93
H_2L^4	49	157-158	$C_{21}H_{19}N_3O_4Fe$	58,1/58,2	4,4/4,39	9,59/9,7	12,73/12,93
H_2L^5	52	131-133	$C_{21}H_{19}N_2O_3BrFe$	51,99/52,17	4,12/3,93	5,62/5,8	11,12/11,6
H_2L^6	54	179	$C_{22}H_{22}N_2O_2Fe$	65,99/65,67	5,42/5,47	6,95/6,96	13,98/13,93

We recorded the ^{1}H NMR spectra of the H_2L^1-H_2L^6 ligands in solutions (Table 1). For example, in the ^{1}H NMR spectrum of a solution of the compound H_2L^2 in DMSO-d_6+CCl_4 taken after preparation and reflecting the structure of the substance in the solid state, a set of signals corresponding to the hydrazone structure is observed. In this case, the proportion of hydrazone increases when DMSO-d_6+CCl_4 is used as a solvent compared to other solvents. The ^{1}H NMR spectrum of the H_2L^2 ligand contains a set of singlet signals at δ 2,67; 4,602 and 11,45 ppm, assigned by us to the protons of the methyl, methylene group and N–H amide bond. The low field position of the last signal indicates configuration B, where the formation of a chelate hydrogen bond between the N–H group and the carbonyl group is possible. The position of the signals and their intensity are consistent with the hydrazone structure of A. Thus, for the H_2L^2 compound, it is 80% in this case. Proton signals of cyclopeantadienyl rings were registered at δ 4,23; 4,27 and 4,87 ppm The spectrum shows a set of multiple signals centered at δ 7,10; 7,76 and 8,05 ppm, with a total intensity of 5H, assigned by us to the protons of the aromatic ring. The H_2L^2 ligand is also in the hydrazone – 5-hydroxypyrazoline equilibrium. In the ^{13}C NMR spectrum of the ligand, the signal of the carbon atom in the position of the 5-hydroxypyrazoline ring lies at δ 94,90 ppm and has a singlet form.

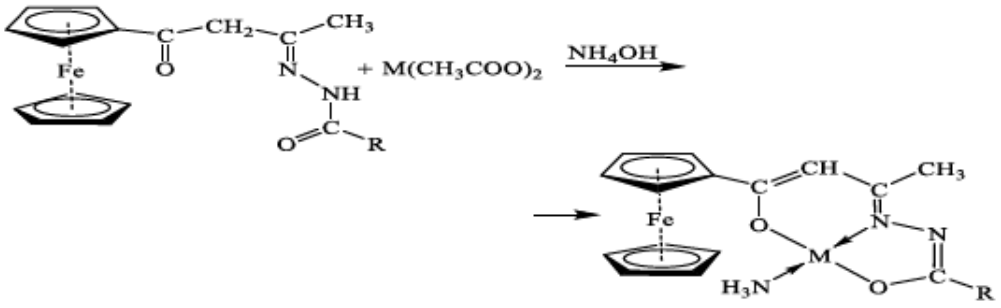
Table 2.

^{1}H NMR parameters of H_2L^1-H_2L^6 ligands in solution DMCO-d_6+CCl_4 (δ, м.д.)

Compound	CH_2	CH_3	C_6H_5	Fc

H_2L^1	3,58;	2,05	–	4,99; 4,55; 4,18
H_2L^2	4,602	2,67	7,10; 7,76; 8,05	4,23; 4,27; 4,87
H_2L^3	2,12	2,83	7,45; 7,55; 7,96	4,95; 4,57; 4,31
H_2L^4	3,30	2,58	7,35; 7,56; 8,02	4,78; 4,31; 4.10
H_2L^5	3,56; 3,75	2,40	7,50; 7,95	4,68; 4,38; 4,22
H_2L^6	3,02	2,12	–	4,99; 4,55; 4,26
H_2L^7	2,12	2,83	7,46; 7,57; 7,95	4,45; 4,57; 4,31

By mixing alcoholic solutions of ligands of the H_2L type and an aqueous ammonia solution of $M(CH_3COO)_2$, in an equimolar ratio, complex compounds of the composition $ML{\cdot}NH_3$ were obtained. The results of elemental analysis and consideration of the spectra allowed us to propose the following mononuclear structure for these complexes **III**:



III

M=Cu(II), Ni(II) and Zn(II)

R=CH_3 ($ML^1{\cdot}NH_3$), C_6H_5 ($ML^2{\cdot}NH_3$), *м*-NO_2-C_6H_4 ($ML^3{\cdot}NH_3$), *o*-NO_2-C_6H_4 ($ML^4{\cdot}NH_3$), 2-OH-5-Br-C_6H_3 ($ML^5{\cdot}NH_3$), $C_6H_5CH_2$ ($ML^6{\cdot}NH_3$).

The diamagnetic properties and good solubility of the synthesized nickel (II) and zinc (II) complex compounds based on the H_2L^1-H_2L^6 ligands in solvents such as chloroform, DMSO, and DMFA allowed us to study them by ^1H NMR spectroscopy. The data of ^1H NMR spectra and their diamagnetism indicate a planar-square structure of the resulting complexes in solution. It should be noted that the ^1H NMR spectra of the synthesized complexes differ strongly from the spectra of the corresponding starting ligands. Consider, as an example, the ^1H NMR spectrum of the $ZnL^3{\cdot}NH_3$ complex (Fig. 1). Singlet signal at δ 2, 31 ppm refers to three protons of the CH_3 group. The signal from the (5H) protons of the unsubstituted cyclopentadiene ligand was recorded as a multiple signal at δ 4, 07-4, 41 ppm. The proton signals of the substituted cyclopentadiene ring are shifted downfield. Showing chemical shifts of 4, 49 (2H, *o*-C_5H_4) and 4,27 (2H, *m*- C_5H_4) ppm. In the region of weak fields, the multiple signals at 7, 68; 7,78 and 7,87 with a total intensity of four protons are due to the protons of the phenyl ring of the *m*-nitrobenzhydrazide fragment. The introduction of a strong electron-withdrawing NO_2-group in the $ZnL^3{\cdot}NH_3$ complex causes a downfield shift of the proton signals in the spectrum, which was to be expected. A broadened low-intensity signal from the protons of the coordinated ammonia molecule is recorded in the ^1H NMR spectrum at δ 12 ppm. The results of the study of ^1H NMR spectra allow

us to conclude that the obtained complex com-pounds of structure **III** have a flat-square structure. This conclusion follows from consideration of the ^{13}C NMR spectrum (Fig. 2). The ^{13}C NMR spectrum of the $ZnL^3 \cdot NH_3$ complex showed signals at δ 39,524; 68,669; 69,672; 70,195; 81,299; 96,48; 118,554; 121,859; 130,397; 193,020 ppm.

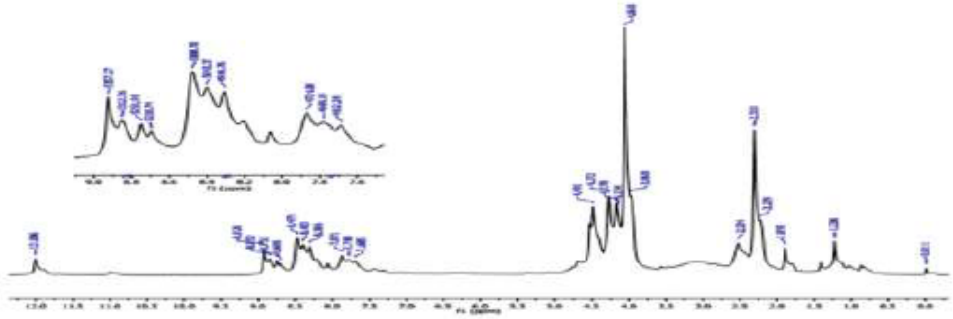


Fig. 1. ^1H NMR spectrum of the $ZnL^3 \cdot NH_3$ complex in DMSO-d_6+CCl_4 solution.

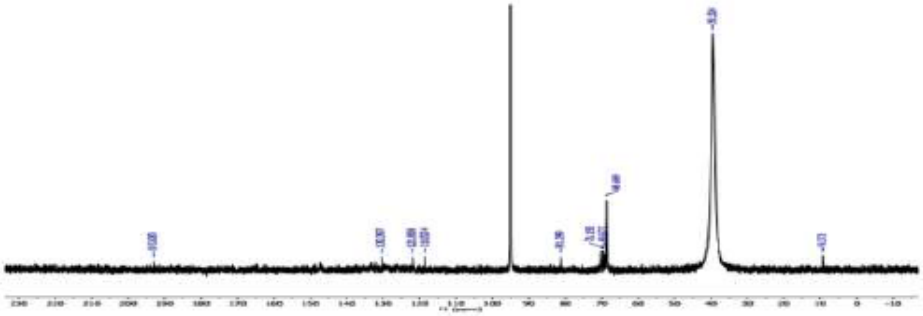


Fig. 2. ^{13}C NMR spectrum of the $ZnL^3 \cdot NH_3$ complex in DMSO-d_6+CCl_4 solution.

In the ^1H NMR spectrum of the $NiL^5 \cdot NH_3$ complex, in contrast to the data known in the literature, the signals of protons containing Br-, OH-substituents in the benzene ring of the aroylhydrazide fragment appear somewhat differently. The parameters of the ^1H NMR spectra of solutions in deuterated DMSO-d_6+CCl_4 complexes of nickel (II) are given in Table 2. The proton signals of the end groups in the $NiL^5 \cdot NH_3$ complex are shifted to strong fields compared to the proton signals in the $NiL^2 \cdot NH_3$ complex, which is due to the introduction of electron donor groups in the benzene nucleus. Multiple signals centered at δ 7, 22 and 7,64 ppm with a total intensity of five protons due to the protons of the phenyl ring of the hydrazide residue. The isolated nickel (II) complex compounds turned out to be diamagnetic in solutions of various solvents as well. The results of the study of ^1H NMR spectra and diamagnetism allow us to conclude that the synthesized nickel (II) complex compounds of structure III have a square-planar structure. The proton signals of the end groups in the $NiL^5 \cdot NH_3$ complex are shifted to strong fields compared to the proton signals in the $NiL^2 \cdot NH_3$ complex, which is due to the introduction of electron donor groups in the benzene nucleus. Multiple signals centered at δ 7, 22 and 7, 64 ppm with a total intensity of five protons due to the protons of the phenyl ring of the hydrazide residue. The isolated nickel (II) complex compounds turned out to be diamagnetic in solutions of various solvents as well. The results of the study of ^1H NMR spectra and diamagnetism allow us to conclude that the synthesized nickel (II) complex compounds of structure **III** have a

square-planar structure. As an example, consider the ^1H NMR spectrum of the complex compound $NiL^2 \cdot NH_3$. The ^1H NMR spectrum of the $NiL^2 \cdot NH_3$ complex compound in a DMSO-d_6+CCl_4 solution shows multiple signals centered at δ 7,31; 8,064 and 8,068 ppm due to the protons of the aromatic nucleus. The type of signals is somewhat complicated due to their overlap. The signal from the protons of the coordinated ammonia molecule was recorded at δ 10,2 ppm. and has a slightly lower integral intensity. In our opinion, this is explained by the partial replacement of the ammonia molecule by the donor solvent molecule. The ^1H NMR spectrum of $NiL^4 \cdot NH_3$ differs slightly from that of $NiL^2 \cdot NH_3$. The signal from the proton of the vinyl part resonates at δ 5,52. The signals from protons of aromatic substituents are more complex due to the presence of bromine in the benzene core of the molecule and appear at δ 7,87; 8,41; 8,75; 8,85 ppm A weak signal from the protons of the coordinated ammonia molecule was detected at δ 10 ppm. The slightly up field shift of the signal from the vinyl proton should be explained by the formation of d-π-type dative bonds between the d-electrons of nickel(II) and the π-orbital of the conjugated system of five- and six-membered metallocycles.

Table 3.

Parameters of the ^1H NMR spectrum of nickel(II) complexes in solution DMSO-d_6+CCl_4 (δ, ppm)

Compound	-CH=	CH_3-C=N	C_6H_5	Fc
$NiL^2 \cdot NH_3$	5,18	2,27	7,31; 8,064; 8,068	4,04; 4,45; 4,87
$NiL^3 \cdot NH_3$	5,48	2,51	7,12; 7,32; 7,64	4,12; 4,41; 4,69
$NiL^4 \cdot NH_3$	5,52	1,90	7,87; 8,41; 8,75; 8,85	4,20; 4,41; 4,57

Conclusion: Thus, because of the ^1H and ^{13}C NMR spectroscopic studies, it was found that the ligands predominantly exist in the hydrazone form. Upon complex formation, the doubly deprotonated ligand residue is tridentately coordinated in a square planar form to develop five- and six-membered metallocycles. The effect of the nature of substituents on the aromatic ring of the benzhydrazide fragment on the electronic structure of the complexes was established by ^1H and ^{13}C NMR spectroscopy for nickel(II) and zinc(II) complexes.

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