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**SYNTHESIS AND IR SPEKTROSKOPIC STUDY OF HYDRAZONS OF
1-FERROCENYL BUTANEDIONE-1,3 AND THEIR COMPLEXES**

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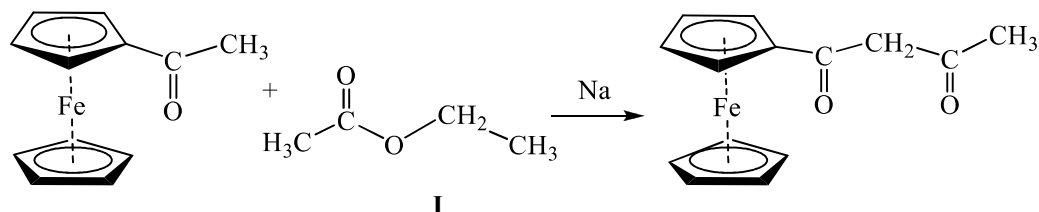
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We obtained β -diketone-1-ferrocenylbutanedione-1,3 by Kleisen condensation. Hydrazones of monocarboxylic acids 1-ferrocenylbutanedione-1,3 (H_2L) were synthesized by the interaction of carboxylic acid hydrazides with ferrocenoylacetone. On their basis, complexes with copper(II), zinc(II), and nickel(II) ions were obtained. The IR spectra of the synthesized compounds were studied. The research results showed that H_2L in solution exists in the form of a tautomeric mixture: hydrazone, α -hydroxyzine, and cyclic 5-hydroxypyrazoline forms. According to the results of IR spectra, 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: ferrocene, monoacetylferrocene, hydrazone, Claisen ester condensation, tautomerism, IR spectroscopy

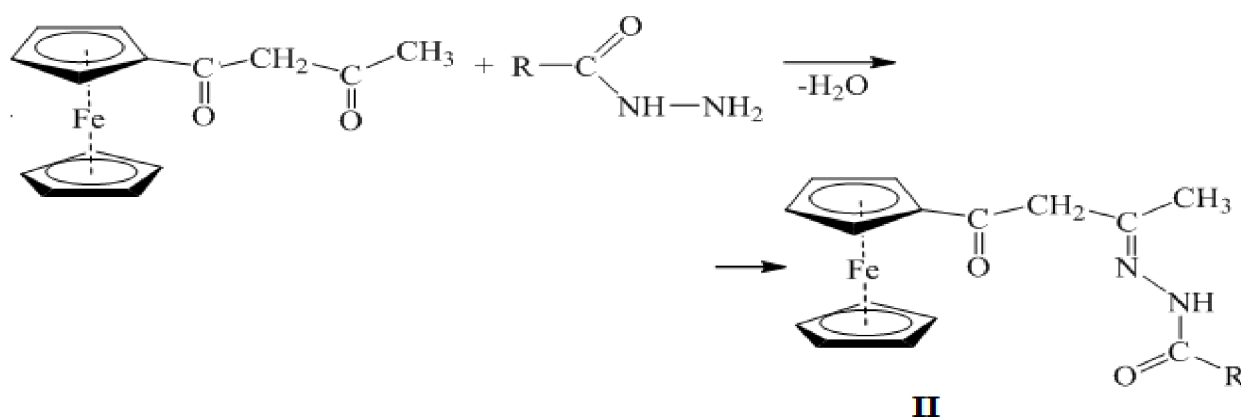
At present, a huge number of ferrocene-containing ligands are used in coordination chemistry [1], and complexes with 3d metals are widely used as biostimulants [2]. To a special extent, biological activity is inherent in hydrazone derivatives of ferrocene, which is due precisely to their chelating ability. In addition, they can be used as surfactants in soil remediation and as selective colorimetric and electrochemical chemosensors of agricultural interest. Numerous experiments have established that the use of molecular and intra-complex 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 and 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 [3].

At the first stage of the synthesis, we carried out the condensation reaction of mono-acetylferrocene with ethyl acetate [4, 5, 6, 7, 8]. The β -dicarbonyl derivative of ferrocene – 1-ferrocenylbutanedione-1,3 (I) was synthesized according to the following reaction scheme:



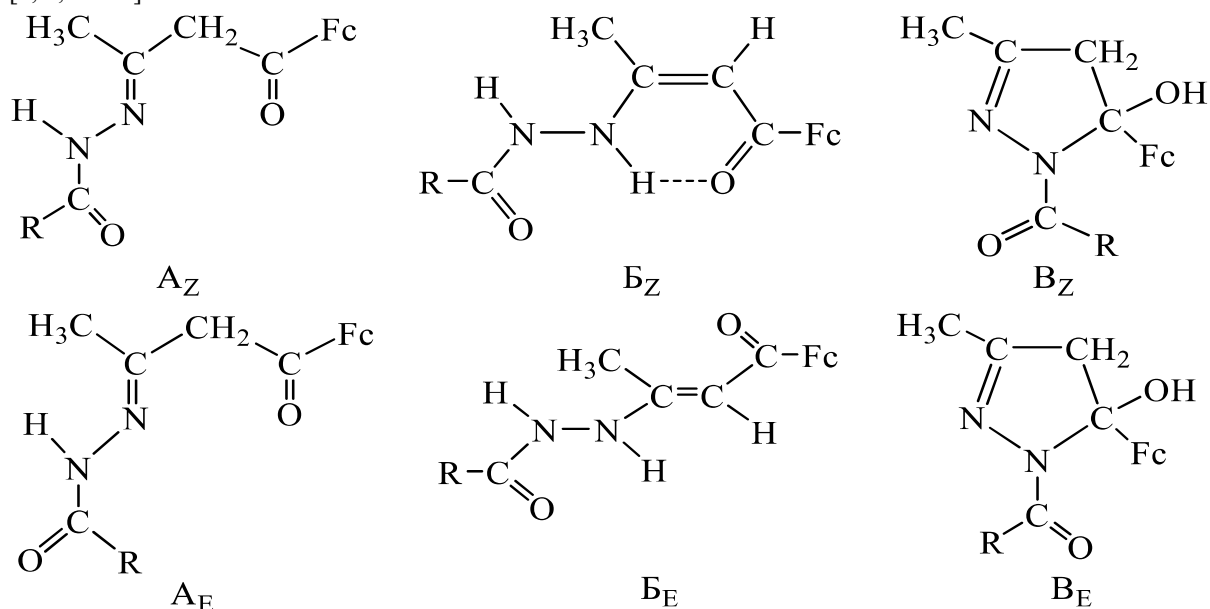
New ligands H_2L^1 - H_2L^5 , respectively, were synthesized by the interaction of alcoholic solutions of equimolar amounts of 1-ferrocenylbutanedione-1,3 with alcoholic solutions of acetylhydrazide, benzoylhydrazide, meta-nitrobenzoylhydrazide, hydrazides of 5-bromosalicylic and phenylacetic acids,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

Ligands H_2L^1 - H_2L^5 were synthesized according to the following reaction scheme:



X=O: R=CH₃ (H₂L¹), C₆H₅ (H₂L²), *m*-NO₂-C₆H₄ (H₂L³), *n*-NO₂-C₆H₄ (H₂L⁴), 2-OH-5-Br-C₆H₃ (H₂L⁵), C₆H₅CH₂ (H₂L⁶). X=S, R=NH₂, (H₂L⁷).

The presence of a hydrazone group in compound II suggests wide possibilities for tautomerism. For it, we can assume the possibility of the existence of at least three tautomeric forms: hydrazone (A), enhydrazine (B), and cyclic pyrazoline (C) forms. In addition, configurational isomerism should also be taken into account for them [3, 9, 10-16].



In the IR spectra of all type II ligands, characteristic absorption bands near 1040-1080, 1270-1300, 1535-1600, and 3190-3278 cm⁻¹, attributed to the vs and vas vibrations N-N, C-N, C=N and N-H bonds, respectively (Fig. 1, Table 1). In the short-wavelength region of the spectrum, two absorption bands are noted, which are characteristic of ferrocene-containing compounds, attributed to torsional vibrations of the cyclopentadienyl fragments of the ligands about the fivefold axis of the metallocene. Also characteristic are the absorption bands at 835-850 cm⁻¹ ν_{C=S} of the H₂L⁷ ligand with thiosemicarbazone fragments [16-20].

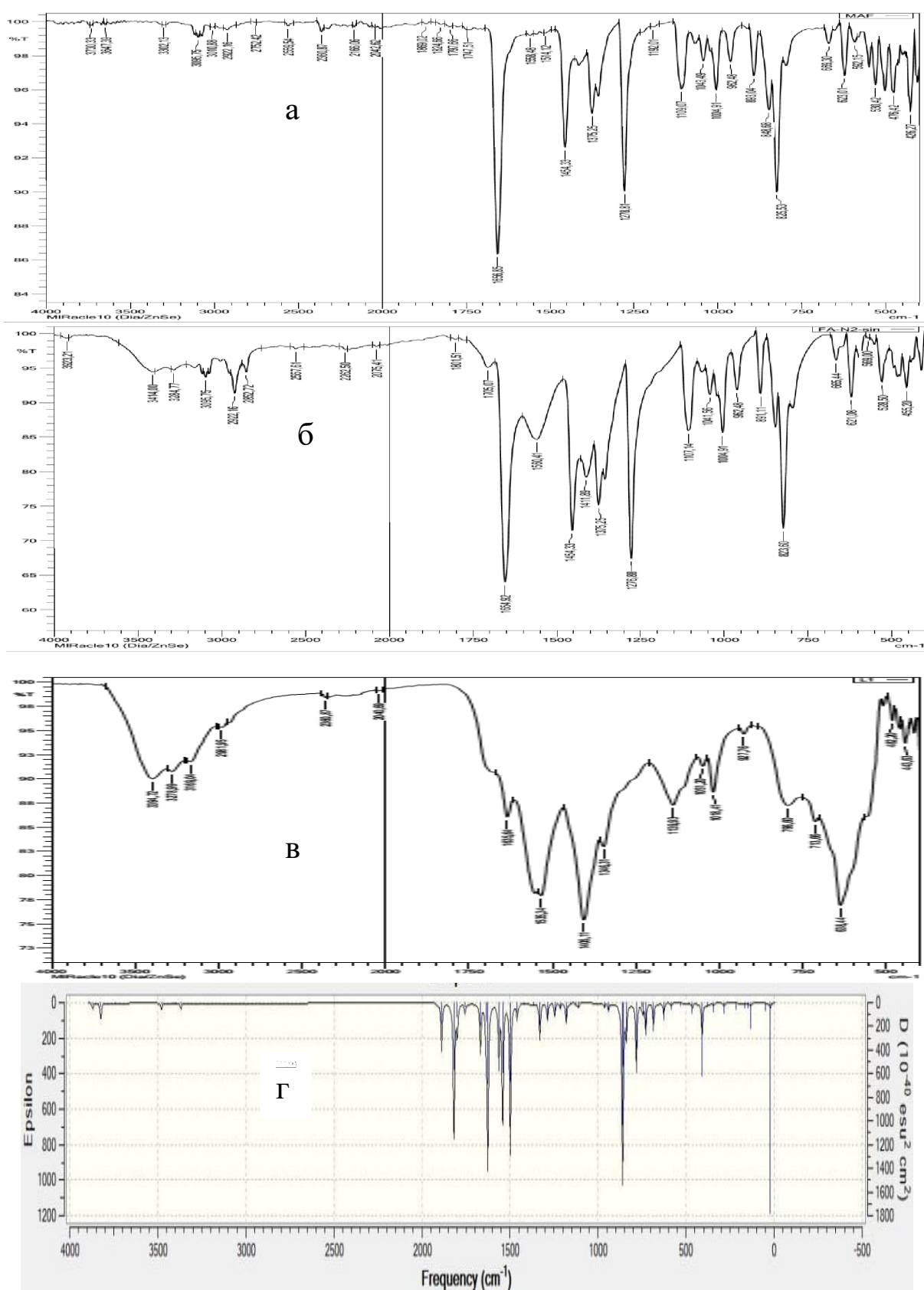


Fig.1. IR spectra of monoacetylferrocene (a), ferrocenoylacetone (b), H₂L³ ligand (c) and IR spectrum of H₂L³ ligand calculated using the AVOGADRO program (r).

The IR spectrum of H₂L⁴ shows absorption bands within 3230, 1540, and 1050 cm⁻¹, assigned to ν_s and ν_{as} vibrations of N-H, C=N, N-N bonds, respectively. The spectrum also contains high-intensity bands characteristic of ν_s and ν_{as} vibrations of NO₂ at 1535 cm⁻¹ and 1346 cm⁻¹.

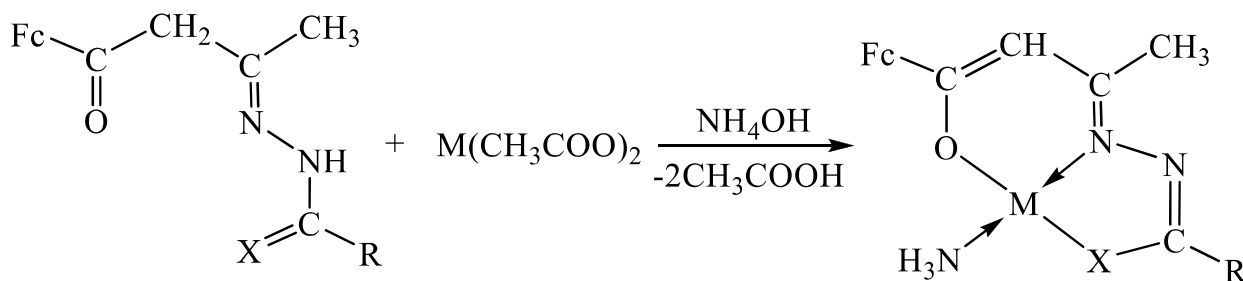
The IR spectrum of H₂L⁶ in a pressed KBr pellet showed that the intensities of the absorption band in the region of 3500 cm⁻¹ (ν_{O-H}). IR spectra leading characteristic bands within 480-505 cm⁻¹, corresponding to the rotation of cyclopentadienyl rings.

Table 1.
Assignment of stretching vibration frequencies (ν, cm⁻¹) in
IR spectra of ligands H₂L¹-H₂L⁵

Compound	NH ₂	N-H	C-H	C=O	C=N	NO ₂	C-N	N-N	C=S	Fe-Cp
H ₂ L ¹	-	3230	3030	1655	1535	-	1285	1065	-	480/500
H ₂ L ²	-	3190	3025	1680	1590	-	1295	1080	-	485/502
H ₂ L ³	-	3278	2981	1660	1545	1535/1346	1300	1051	-	482/503
H ₂ L ⁴	-	3230	2975	1665	1540	1538/1348	1295	1050	-	483/505
H ₂ L ⁵	-	3193	2972	1680	1540	-	1290	1040	-	485/502
H ₂ L ⁶	-	3233	2995	1665	1595	-	1270	1070	835	482/500
H ₂ L ⁷	3425	3275	2980	1662	1635	-	1300	1051	-	482/503

The IR spectra of all compounds synthesized by us, in addition to the main characteristic bands, have absorption bands of average intensity of about 480-505 cm⁻¹, corresponding to the rotation of cyclopentadienyl rings.

By mixing alcohol solutions of ligands of the H₂L type and an aqueous ammonia solution of M(CH₃COO)₂, (where M=Cu(II), Ni(II) and Zn(II)), in an equimolar ratio, CuL·NH₃ complex compounds were obtained:

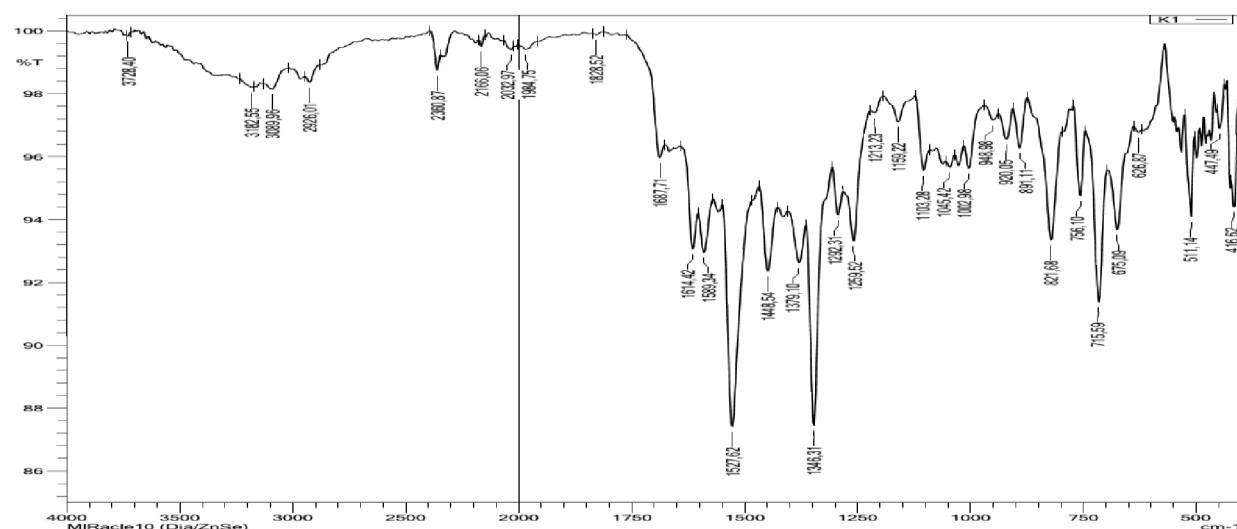


III

M = Cu(II), Ni(II) и Zn(II)

X=O: R=CH₃ (CuL¹·NH₃, NiL¹·NH₃, ZnL¹·NH₃), C₆H₅ (CuL²·NH₃, NiL²·NH₃, ZnL²·NH₃), *m*-NO₂-C₆H₄ (CuL³·NH₃, NiL³·NH₃, ZnL³·NH₃), *o*-NO₂-C₆H₄ (CuL⁴·NH₃, NiL⁴·NH₃, ZnL⁴·NH₃), 2-OH-5-Br-C₆H₃ (CuL⁵·NH₃, NiL⁵·NH₃, ZnL⁵·NH₃), C₆H₅CH₂ (CuL⁶·NH₃, NiL⁶·NH₃, ZnL⁶·NH₃); X=S, R=NH₂ (CuL⁷·NH₃, NiL⁷·NH₃, ZnL⁷·NH₃).

The formation of the complex is confirmed by clear analytical features in the IR spectrum (Table 2, Fig. 2). Judging by the results of the IR spectra of the complexes in the solid state, there are no characteristic absorption bands of the free ligand near 1655-1680 cm⁻¹, 3190-3278 cm⁻¹ (ν_{C=O}, ν_{N-H}). The IR spectra of the complexes show low-intensity absorption bands at 3375-3380, 3320-3330, 3240-3250, and 3150 cm⁻¹, which should be assigned to symmetric and antisymmetric stretching vibrations of the coordinated ammonia molecule.



Rice. 2. IR spectrum of a copper(II) complex compound $\text{CuL}^3\cdot\text{NH}_3$.

The IR spectra of the complexes show a number of bands of medium and strong intensity in the regions 1580-1585, 1530-1540, 1470-1480, 1420-1430, 1395-1400 cm^{-1} metal cycles.

Analysis of the IR spectrum of the $\text{CuL}^3\cdot\text{NH}_3$ complex showed that the spectrum contains bands at 416, 447, 675, 715, 766, 821, 1103, 1259, 1346, 1527, 1589, 1614, 1687, 3089, 3420 cm^{-1} . It should be noted that in the IR spectrum of the $\text{CuL}^3\cdot\text{NH}_3$ complex (Fig. 2), the vibrational frequency ($\nu_{\text{C=N}}$ 1614 cm^{-1}) compared to the spectrum of the free ligand ($\nu_{\text{C=N}}$ 1635 cm^{-1}) is shifted to low frequencies by 21 cm^{-1} , at the same time, the value of the C=N bond frequency increases by 5-10 cm^{-1} . This allows us to state that the ligand is coordinated to the metal through two amide and β -diketone oxygen atoms and azomethine nitrogen atom.

The identity of the IR spectra of copper(II) and nickel(II) compounds with the ligands of the same name indicates a similar structure of these complexes. According to the results of elemental analysis, the general formula $\text{NiL}\cdot\text{NH}_3$ was assigned to the complex compounds. The IR spectra of complex compounds differ from the IR spectra of free ligands in that there are no absorption bands in the region of 1660-1700 and 3400 cm^{-1} . This indicates the deprotonation of ligands during complexation.

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

Compound	NH ₂	C-H	C=N	N=C-C=N	N=C-O-	N-N	NO ₂	Fe-Cp
NiL ² ·NH ₃	3384	2935	1630	1586	1550	1086	-	480-500
NiL ³ ·NH ₃	3240	3035	1610	1595	1552	1092	1535/1340	481/503
NiL ⁴ ·NH ₃	3396	3050	1625	1600	1555	1045	1535/1340	482/504
CuL ⁴ ·NH ₃	3420	3089	1614	1589	1527	1103	1535/1346	483/500
CuL ² ·NH ₃	3423	3085	1600	1590	1535	1105	-	470/500
ZnL ¹ ·NH ₃	3440	3020	1615	1597	1548	1075	-	466/500
ZnL ² ·NH ₃	3410	2930	1650	1600	1540	1070	-	465/502
ZnL ⁴ ·NH ₃	3395	3035	1620	1592	1542	1088	1535/1340	465/503
ZnL ⁵ ·NH ₃	3405	3080	1610	1595	1525	1100	-	468/503

Zinc is also prone to complex formation, but due to the spherical symmetric d^{10} -configuration, the effect of stabilization by the ligand field has not been established for zinc complex compounds [18-20].

Comparing the IR spectra of $H_2L^1-H_2L^7$ and their complexes with metal acetates, we can say that the position of the stretching vibrations of the Fe-Cp bond remains unchanged, being located in the region of 465-505 cm^{-1} . The bands appearing in the IR spectra of the complexes at 3380-3420 cm^{-1} are assigned to ν_s and ν_{as} of the coordinated ammonia molecule. Hence, it can be concluded that the doubly deprotonated ligand residue is coordinated by the metal atom through two oxygen atoms and by the nitrogen atom of the hydrazone fragment. The fourth position in the planar square of the trans- N_2O_2 coordination site is occupied by the ammonia molecule. Practically planar five- and six-membered conjugated metallocycles are almost coplanar with each other.

Based on the results of elemental analysis, IR spectroscopy, and literature data, it can be assumed that the ligand in the complexes is bidentately coordinated to copper(II), zinc(II), and nickel(II) ions. The acetate anion of the starting salts acts as a deprotonating agent in ethanol solution, and the square planar structure **III** is assigned to the complexes.

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