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Synthesis and spectroscopic study of complex compounds of some 3D metals with the condensation product of 1-ferrocenylbutanedione-1,3 and succinic acid dihydrozide

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ABSTRACT

We obtained by Claisen condensation β-diketone-1-ferrocenylbutanedione-1,3. The dicarboxylic acid dihydrazone of 1-ferrocenylbutanedione-1,3 (H_4L) was synthesized by reacting succinic acid dihydrazide with ferrocenylacetone in a ratio of 2:1. Based on them, homobinuclear complex compounds with copper (II), zinc(II)and nickel(II) ions were obtained. The IR-, UV- and NMR spectra of the synthesized organic compounds were studied. The results of the studies showed that the H_4L ligand in solution exists as a tautomeric mixture: diketone (A), keto-enol (B) and in dienol(C) forms. According to the results of spectroscopic studies, the complexes were assigned a square planar structure, where the four times deprotonated ligand residue is coordinated by each metal atom through two oxygen atoms and a 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. Planar five- and six-membered metal cycles of synthesizers are practically coplanar with each other.

Selection and peer-review under responsibility of the scientific committee of the Fourth International Conference on Recent Advances in Materials and Manufacturing 2022.

1. Introduction

The chemistry of ferrocene continues to develop rapidly around the world. The wide scope of ferrocene derivatives depends on their properties. Of great importance is the production of ferrocene derivatives of chemo- and biosensors, redox-active DNA markers, redox labels, “smart glasses”, “smart watches”, structural materials for magnetic and random access memory, materials with liquid crystal properties, turnstiles, molecular magnets, solar batteries, in medicine: anticancer, antimicrobial and antianemic agents, electrochemical glucometers, liquid crystal indicators, etc. At presentferrocene-containing complex compounds are often included in the composition of materials used in photonics and nonlinear optics, they are used as ligands in the creation chemosensors are being studied as molecular tweezers, rotors, shuttles, brakes, etc. [1,2,3,4,5,6,7].

1.1. Methodical part

1.1.1. Materials and research methods

Synthesis of succinic acid dihydrazoneferrocenylacetone. To 0.365 g of a suspension of succinic acid dihydrazide in 20 ml of ethanol (0.0025 mol) was added 1.35 g (0.005 mol) of ferrocenylacetone in 20 ml of ethanol. After three hours of heating the solution with a reflux condenserleft for 3 days. The precipitate that formed was separated, washed with ethanol, and dried. Received - 0.78 g (48%) H_4L, brown crystals. Found, %: C 58.95, H 5.11, O 9.48, N 8.42, Fe 17.49. Calculated for $C_{32}H_{34}N_4O_4Fe_2$, %: C 59.07, H 5.23, O 9.84, N 8.61, Fe 17.23.

To determine the composition and structure of the obtained ligand in the solid state, we used the data of elemental analysis, IR spectroscopy [8,9,10,11].

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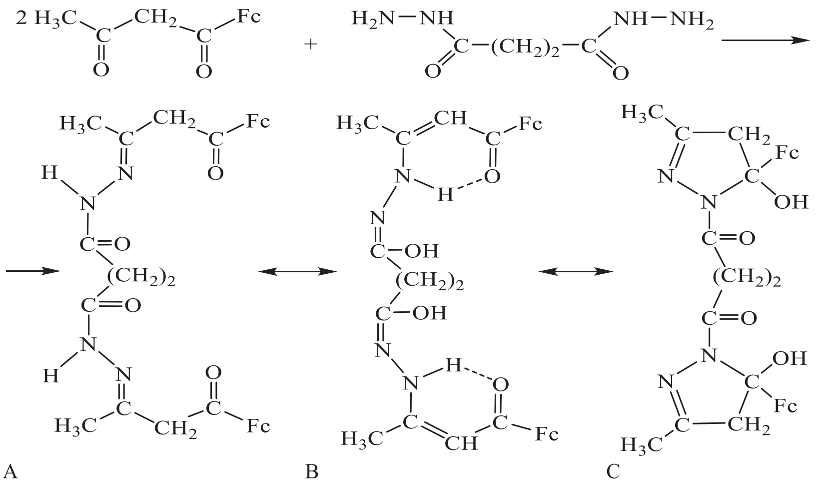
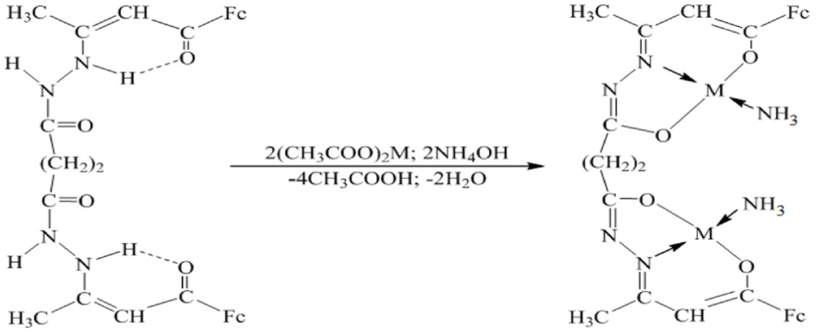


Synthesis $\boldsymbol{Cu_2L{\cdot}2NH_3}$**.** With constant stirring to 1.3 g (0.002 mol) of a hot solution of the H_4L ligand in 50 ml of absolute ethyl alcohol was added 2 g (0.004 mol) of copper(II) acetate in 20 ml of concentrated ammonia solution. A week later, the dark brown precipitate was filtered off and washed several times with distilled water and ethyl alcohol, then dried in air. The yield of the copper(II) complex was 0.86 g (53%).

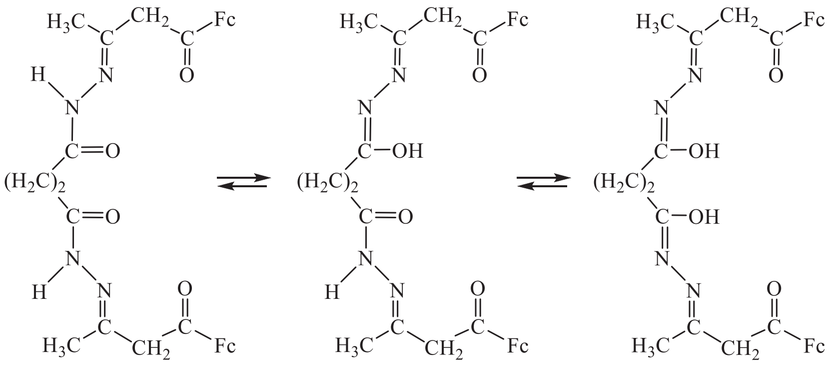


Ni(II) and Zn(II) complexes were synthesized in the same way. The resulting complexes are slightly soluble in chloroform, toluene, polar organic solvents and insoluble in water and acetone. It should be noted that ligands such as H4L are characterized by the formation of homo- and heterobinuclear complexes. We have synthesized homobinuclear complexes.

2. Results and discussions

For the synthesis of the ligandferrocenylacetone, succinic acid dihydrazide of the "chemically pure" qualification were used as starting reagents. The following salts of the "pure for analysis" qualification were used as starting reagents for the synthesis of complex compounds: nickel(II), copper(II) and zinc(II) acetates. Elemental analysis for macro- and microelements of the synthesized ligand and complex compounds was carried out by the atomic absorption method on an ISP MC NexION 2000 instrument (Perkin Elmer USA).IR absorption spectra were recorded on an IR Tracer-100 IR spectrophotometer (Shimadzu, Japan, 2017) in the region of 400–4000 cm^{-1} in the form of KBr tablets with a diameter of 7 mm and a resolution of 4 cm^{-1}, sensitivity signal / noise ratio - 60,000:1; scanning speed - 20 spectra per second. The measurements were carried out in the laboratory of the Scientific Research Institute of Bioorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan.^{1}H NMR spectra of 5–10% solutions of ligands and complexes were recorded on a JNM-ECZ400R spectrometer (Jeol, Japan) at an operating frequency of 400 MHz and recorded on a Bruker spectrometer DPX-300 (300.13 MHz).1H NMR spectra of 5–10% solutions of ligands and complexes were recorded on a JNM-ECZ400R spectrometer (Jeol, Japan) at an operating frequency of 400 MHz and recorded on a Bruker spectrometer DPX-300 (300.13 MHz). The ^{13}C NMR spectra were recorded on a device and a Bruker DPX-300 (75 MHz) for saturated solutions in the pulsed mode with a Fourier transform under conditions of monoresonance and noise decoupling from rotons. Tetramethylsilane (TMS) and hexamethyldisilane (HMDS), solvents: deuterated dimethylsulfoxide (DMSO d_6) were used as an internal reference. The measurements were carried out in the laboratory of the Scientific Research Institute of Chemistry of Plant Substances of the Academy of Sciences of the Republic of Uzbekistan. Electronic absorption spectra were recorded on a UV-1900 spectrophotometer (Shimadzu, Japan) in the wavelength range from 190 to 1000 nm, cuvette length 10 mm, solvent - absolute ethyl alcohol, sample concentration 10^{-5}mol/l.The measurements were carried out in the laboratory of the Scientific Research Institute of Chemistry and Polymer Physics of the Academy of Sciences of the Republic of Uzbekistan.

Literature data show that, depending on the nature of the solvent, dicarboxylic acid dihydrazone can enter into complex formation reaction in diketo (A), keto-enol (B), or dienol form (C). And they react in the form of α-hydroxyazinenol.



In the IR spectrum of the H_4L ligand (Fig. 1), valence and valence-strain vibrations of cyclopentadienyl rings of ferrocene are noted at 491 and 502 cm^{-1}. The intense absorption band in the mid-frequency region at 1654 cm^{-1} corresponds to the stretching vibrations $\nu_{(C=O)}$. In the region of high frequencies, about 3190–3250 cm^{-1}, a broad absorption band is attributed by us to the

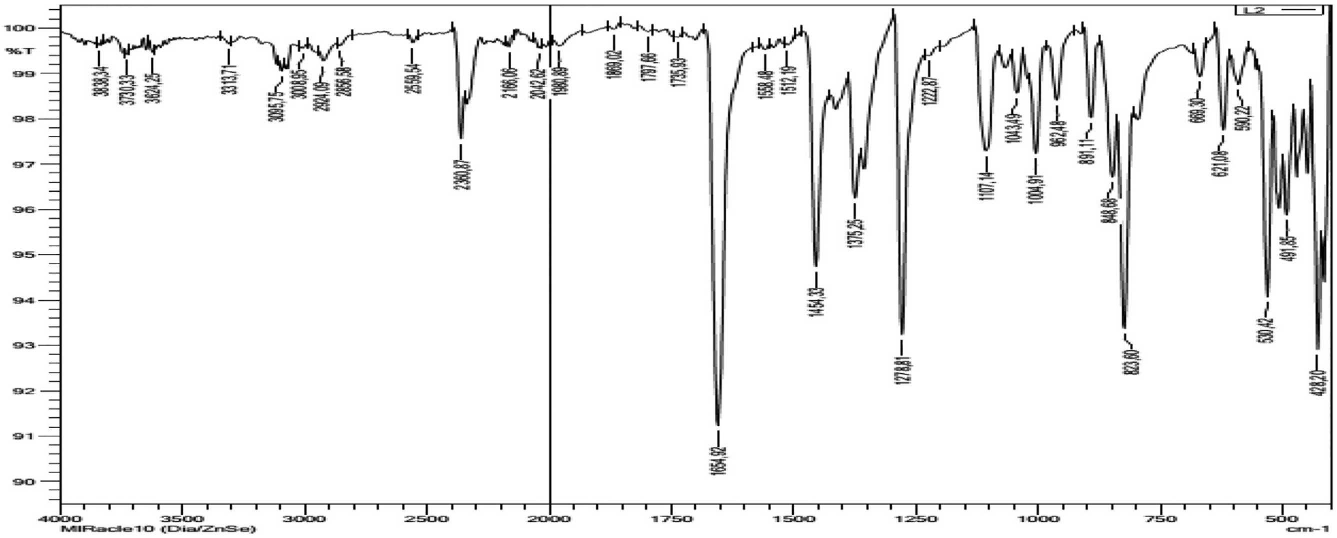


Fig. 1. IR spectrum of H_4L ligand.

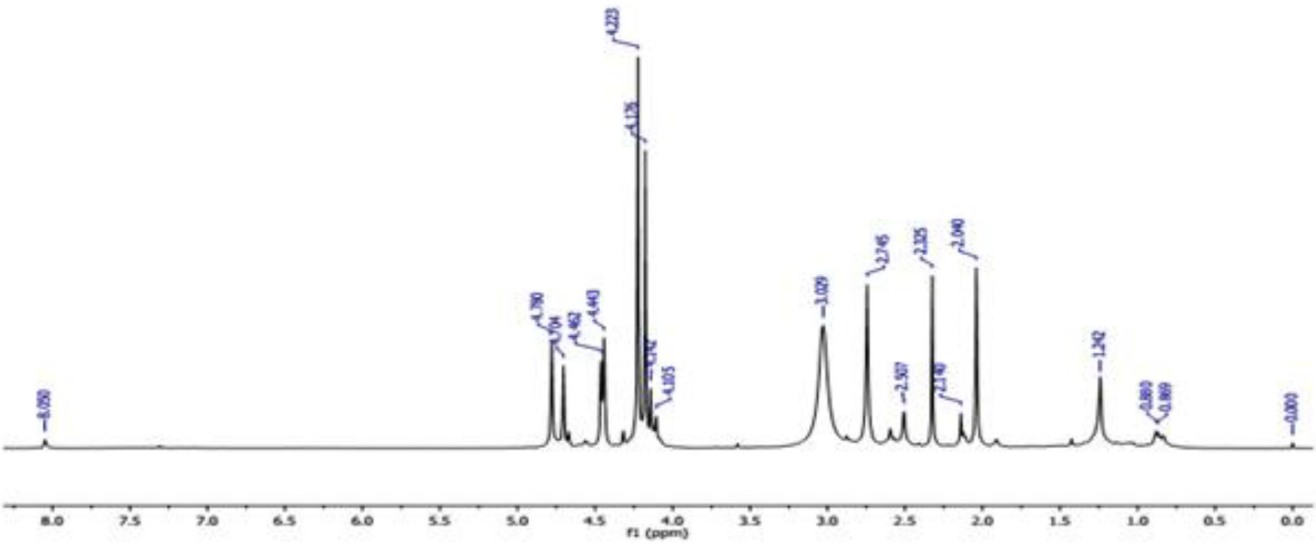


Fig. 2. ^1H NMR spectrum of H_4L ligand in DMSO d_6 + CCl_4 solution.

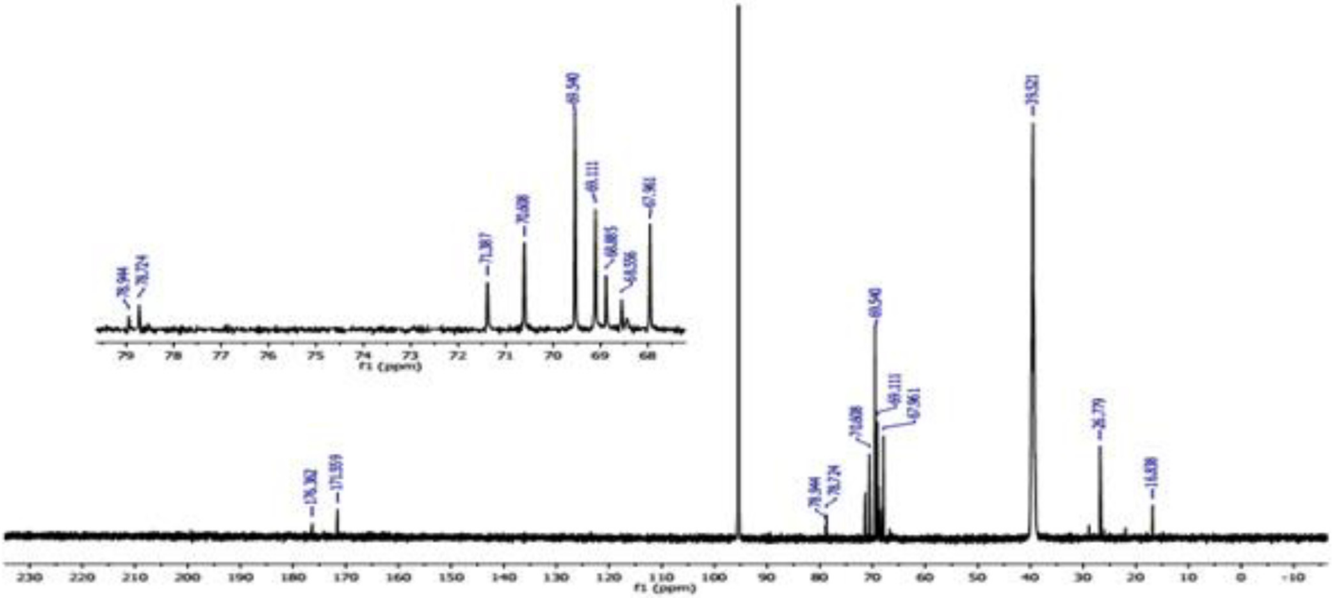


Fig. 3. ^{13}C NMR spectrum of H_4L ligand in DMSO d_6 + CCl_4 solution.

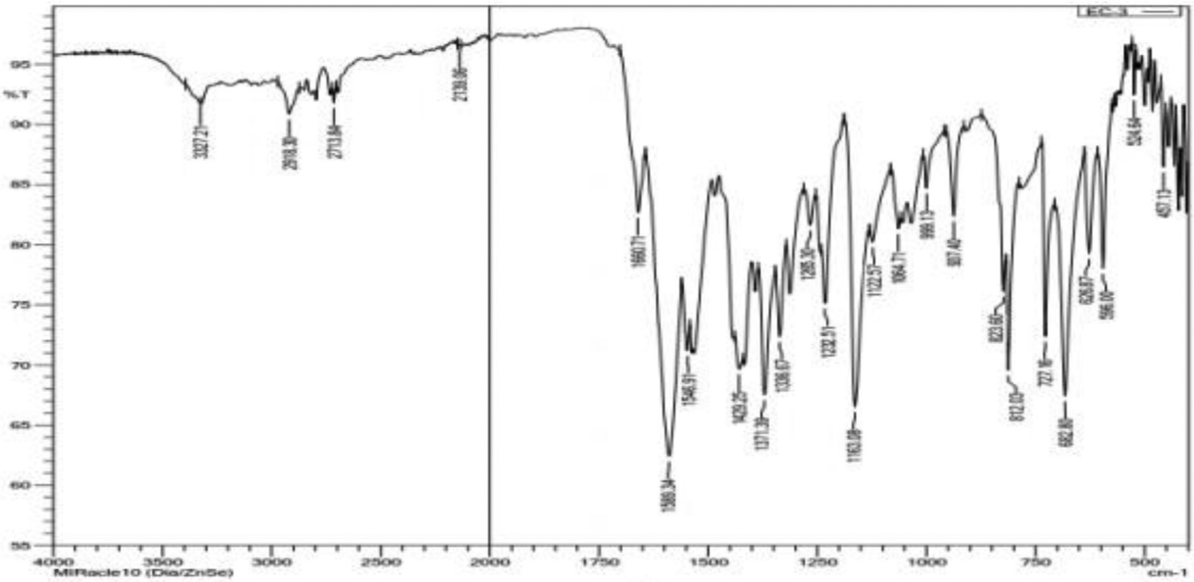


Fig. 4. IR spectrum of the $Cu_2L{\cdot}2NH_3$ complex.

stretching vibrations of the $\nu_{(O-H)}$ and $\nu_{(N-H)}$ bonds. According to the data of elemental analysis and IR spectroscopy, H_4L confirms that the ligand in the solid state is mainly in the rectilinear diketo form with an intramolecular hydrogen bond [12,13].

The ^{1}H NMR spectrum of the H_4L ligand in a DMSO d_6 + CCl_4 solution also indicates the retention of the rectilinear diketo form (A) (Fig. 2).

In the strong field region at δ 2.75 ppm signals from two bridging –$(CH_2)_2$– groups of the ligand bound to C = O amide substituents were noted with an intensity of four protons. Unequal proton signals of the two cyclopentadienyl rings were recorded at δ 4.46 (2H), 4.78 (2H), and 4.70 (5H) ppm. The proton signals of two methyl groups (6H) in the spectrum were recorded in the high field region at δ 1.24 ppm. like an intense singlet. And the protons of the N–H (2H) groups resonate in the region of weak fields in the form of singlet signals at δ 10.01. Thus, we attributed the weakest signal to the proton of the hydrazone group. After 4–5 min, a second set of signals appears, related to the form (B). The change in the H_4L spectra stops after a few days and an equilibrium is established between stereoisomers A and B and the cyclic form (C).

The diketone form of the H_4L ligand is confirmed by the ^{13}C NMR spectrum (Fig. 3). In the ^{13}C NMR spectrum of the H_4L ligand, signals were found at δ δ 16,83 (CH_3); 39,52; (CH_2); 67,96 ($C^{2,5}$ Fc); 69,54 ($C^{3,4}$ Fc); 70,60 (5C Fc); 78,72 (5C Fc); 171,56 (C = O); 176,36 (C = N) ppm. Low intensity signal at δ 171,56 ppm refers to the carbon atom of the C = O group.

The complexing ability of the H_4L ligand is due to the presence in the compound of several donor centers connected by a system of conjugated bonds, and, in addition, a mobile hydrogen atom. The interaction of an alcoholic solution of the H_4L ligand with aqueous

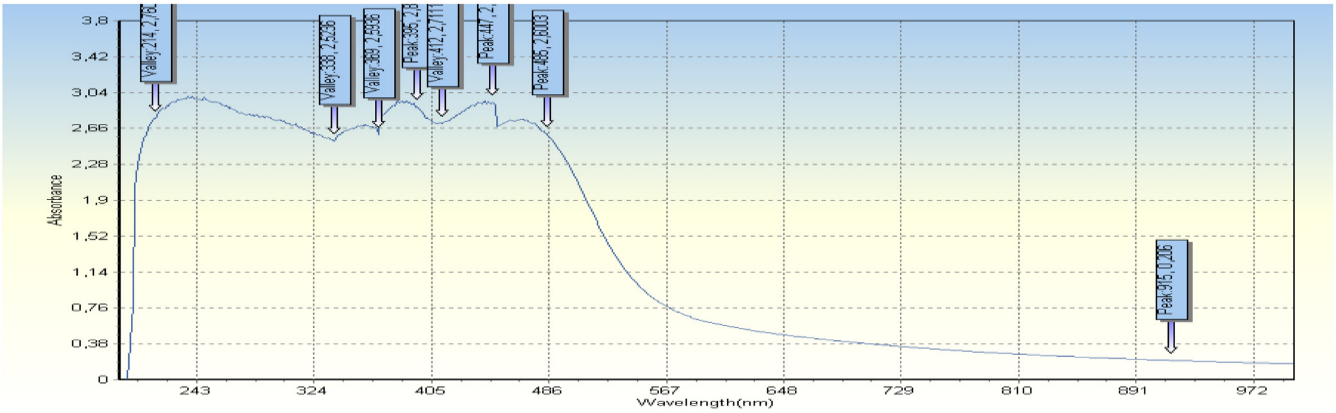


Fig. 5. UV spectrum of H_4L ligand in ethanol.

Table 1
Obtained and calculated optical characteristics of MAF, FA, H_4L ligand and their complexes based on the data of electronic absorption spectra (solvent-absolute ethanol, concentration 10^{-5} M).

Compound	λ^{abs}_{max}, nm	λ^{abs}_{onset}, nm	E^{opt}_{g}, эV	ε, l·mol^{-1}·sm^{-1}
MAF	256, 369, 450, 480, 536	729	1,7	3,016; 2,65; 2,94; 3,1; 3,27
FA	248, 357, 372, 417, 459	891	1,39	3,06; 2,72; 2,55; 1,798; 1,92
H_4L	214, 338, 369, 395, 412, 447, 485	730	1,69	2,76; 2,53; 2,6; 2,8; 2,71; 2,74; 2,6
$Cu_2L{\cdot}2NH_3$	225; 246; 346	650	1,91	2,96; 3,51; 2,99
$Ni_2L{\cdot}2NH_3$	213; 229; 352	650	1,91	3,07; 3,44; 2,84
$Zn_2L{\cdot}2NH_3$	221; 273	570	2,17	2,60; 1,84
$E^{opt}_{g} = 1240/\lambda^{abs}_{onset}$				

ammonia solutions of Ni(II), Cu(II) and Zn(II) acetates in a molar ratio of 1:2 gives complex compounds. Based on the results of elemental analysis of the complexes, the general formula $M_2L{\cdot}2NH_3$ was proposed.

Our use of elemental analysis and IR spectroscopy data composition and structure of the synthesized ligand in solid state, and the structure in solution was studied by ^1H NMR spectroscopy.

IR spectra of homobinuclear complexes of copper(II), nickel(II), and zinc(II) were recorded in the range of 400–4000 cm^{-1}. A comparative analysis of the IR spectra of the H_4L ligand and its complexes showed that, that after coordinating the ligand to the metal atom in the spectrum of complex compounds, there are no absorption bands of N–H valence vibrations and carbonyl groups hydrazone fragments. Stretching vibrations of the M—N and M—O bonds registered at 456 and 525 cm^{-1}. In this case, the C = N stretching vibrations are shifted to the high-frequency region by 20 cm^{-1} compared to the spectrum of the free ligand. This fact indicates the coordination of the hydrazone with the participation of the azomethine nitrogen atom in the coordination. After coordination of donor atoms with metal ions, the electron density is redistributed and a pseudoaromatic bond system appears in five- and six-membered metal rings. As an example on Fig. 4 shows the IR spectrum of the $Cu_2L{\cdot}2NH_3$ complex.

To reveal the optical properties of the synthesized compounds, the electronic absorption spectra of all ferrocene derivatives obtained in the work in ethanol were recorded. The positions of the absorption maxima were determined from the electronic absorption spectra (λ^{abs}_{max}) and the value of the start of absorption (λ^{abs}_{onset}) and also the value of the molar extinction coefficient (ε) and calculated on the basis of the beginning of the absorption of the value of the band gap (E^{opt}_{g}) (Tabl. 1) [14,15,16].

The electronic absorption spectrum of the H_4L ligand in the UV region has an absorption band of maxima at 214, 338, 369, and 395 nm (Fig. 5). At 412, 447, and 485 nm, in the visible region of the ligand spectrum, an absorption band is fixed, which correspond to π–π*transitions occurring in cyclopentadienyl rings (Table 1) [17].

It can be seen from the spectrum of the H_4L ligand that the band of this transition in a solution of absolute ethanol is subject to the bathochemical effect.

3. Conclusion

According to the results of spectroscopic studies, the complexes were assigned a square planar structure, where the four times deprotonated ligand residue is coordinated by each metal atom through two oxygen atoms and a 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. Planar five- and six-membered metal cycles of synthesizers are practically coplanar with each other.

Based on the acquired values of the red boundary of the absorption region, the values of E^{opt}_{g} calculated by us show, that the compounds studied in this work can be attributed to narrow-gap semiconductors, for which the band gap is smaller or about 2 eV.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Sulaymonova Zilola Abduraxmonovna reports article pub-

lishing charges was provided by Bukhara State University. Sulaymonova Zilola Abduraxmonovna reports a relationship with Bukhara State University that includes: employment, non-financial support, and speaking and lecture fees.

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