

Synthesis AzoCompounds and Study Properties

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Abstract : *In this paper we Isolated in a crystalline state and studied by a set of methods for analyzing complex-Metal compounds with azo-derivatives of benzo [4,5] imidazo [1,2-c] quinazoline carboxylic acids.*

Keywords: azo- dyes, electronic spectroscopy, theoretical treatments

1. Introduction

Azo dyes constitute more than 50% in the range of all industrial dyes. Their role lies in the universality of application in various fields, such as, for example, Dyeing of textile fibers or coloring of plastics. In addition, the azo compounds. Successfully used in biomedical research and in organic synthesis [1]. The interaction of the azo group with the conjugate system of bonds of the rest of the molecule and Donor-acceptor substituents underlies the theory of chromaticity [2]. Specific Properties of azo dyes are due to the following factors: azo-hydrazone tautomerism; electronic and spatial structure; the existence of several coordination centers, providing formation of polydentate bonds with metal cations and materials; Ability to form ionic forms in solutions. The introduction of metal cations into the azo dye composition leads to a change in their color Gamma and strength characteristics [3]. The formation of metal chelate cycles alters Spatial and electronic structure of organic molecules, which determines the color Properties of the dye. The effectiveness of the dye often correlates with the ability of organic Molecules to complex formation with metal cations. In this regard, it seems It is very interesting to study their spectral characteristics, spatial structure, and Processes of complex formation.

Benzo [4,5] imidazo [1,2-c] quinazoline carboxylic acid derivatives contain three rings, two of which are nitrogen-containing. They include as a benzo imidazole fragment, which has basic properties, and pyrimidine of to various tautomeric transformations. With a heterocyclic azo-compound. The purpose of this work was the synthesis of complex-Metal compounds with two azo-derivatives of benzo-[4,5] imidazo [1,2-c] quinazoline carboxylic acids (H_2L_1 and H_2L_2), as well as the study of their structure and properties. Previously [4] A combination of spectral and quantum chemical me-We have shown that organic ligand- In the gas phase and in solutions, there exist in the form of a non-Of CH azo-tautomers, which are two conjugate systems. The presented research is included in the work cycle Authors, devoted to the study of the structure and properties of heterocyclic azo-compounds and metal complexes On their basis [5-14].

2. Experimental Part

Electronic absorption spectra of ethanol solutions of organic molecules in the pH range From 2 to 9, and also when titrated with metal salts were recorded on a Varian Cary

spectrophotometer 50 Scan in the wavelength range 200-750 nm in cuvettes with a width of 1 cm. Concentrations were selected Individually for each connection. The deprotonation constants of organic molecules are determined by were measured spectrophotometrically according to the procedure described in [15]. Composition of complexes and constant their formation in solutions was determined by the saturation method [16, 17]. Statistical processing The results obtained were carried out according to the procedure described in [18] for the confidence probability 95%. The pH changes were carried out on a potentiometer EV-74 at 21-23 ° C. The IR absorption spectra were recorded on a SPECORD 75 IR instrument in the 4000- 400 cm^{-1} in suspension in baseline oil and in solutions in $CHCl_3$. Assignment of characteristic bands Absorption was carried out using literature data [19].

During the dyeing of polyamide fibers, the samples were treated with a detergent at Temperature 60 ° C for 10 minutes, washed with water and placed in a 3% aqueous solution of dye-And kept at a temperature of 40 ° C for 20 minutes. In the event that the dissolution was Incomplete, a suspension of the dye in water was used. Then, 100% acetic acid was added from Calculation of 1 g per 1 liter of solution, kept for another 25 minutes, after which the solution was slowly adjusted to Boiling and boiled for 40 minutes. The colored fibers were removed from the dye bath and Washed with water four times, gradually lowering the water temperature to 40 ° C. The fibers were dried and tested for durability to dry friction and washing. Synthesis of metal complexes was carried out according to the following procedure. To 10 ml of a solution of organic Ligand in acetone ($C 10^{-3} mol / L$) was added with stirring 10 ml of an aqueous solution of a metal salt ($C 10^{-3} mol / L$). The solutions obtained were heated in a water bath before evaporation of 50% of the solvent. Precipitation of complex compounds was maintained in the mother liquor for 24 hours, after which Was separated from the solution by filtration, washed with a small amount of acetone and dried in Desiccator above KOH to constant mass. On the individuality and single-phase products were judged with Using visual crystal-optical analysis. The results of chemical analysis and gross-Formulas of complex compounds are given in Table. 1.

Table 1: Results of chemical analysis and gross formulas of isolated compounds

Compound / Gross formula	Mg/mol	Content (found / calculated)%				
		C	H	N	M	Cl
$\text{Cu}_2(\text{L}^1)\text{Cl}_2 \cdot 6\text{H}_2\text{O} / \text{Cu}_2\text{C}_{21}\text{H}_{25}\text{N}_7\text{O}_{10}\text{Cl}_2$ (1)	733.47	34.71/34.39	4.08/3.44	12.88/13.37	16.84/17.33	9.45/9.67
$\text{Cu}(\text{L}^2) \cdot 6\text{H}_2\text{O} \cdot 2\text{acet}^* / \text{CuC}_{26}\text{H}_{34}\text{N}_6\text{O}_{12}$ (2)	686.13	45.56/45.51	5.61/4.99	11.45/12.25	9.00/9.26	
$\text{Cd}(\text{L}^2) \cdot 6\text{H}_2\text{O} \cdot 2\text{acet}^* / \text{CdC}_{26}\text{H}_{34}\text{N}_6\text{O}_{12}$ (3)	735.00	42.73/42.49	5.08/4.66	10.82/11.43	15.11/15.29	
$\text{Mn}(\text{L}^2) \cdot 4\text{H}_2\text{O} \cdot 2\text{acet}^* / \text{MnC}_{26}\text{H}_{30}\text{N}_6\text{O}_{10}$ (4)	641.50	47.91/48.68	5.29/4.71	12.85/13.10	7.78/8.56	
$\text{Zn}(\text{L}^2) \cdot 6\text{H}_2\text{O} \cdot \text{acet}^* / \text{ZnC}_{23}\text{H}_{28}\text{N}_6\text{O}_{11}$ (5)	629.89	43.68/43.86	3.85/4.48	13.08/13.34	10.00/10.38	
$\text{Co}_2(\text{L}^2)\text{Cl}_2 \cdot 6\text{H}_2\text{O} \cdot 2\text{acet}^* / \text{Co}_2\text{C}_{26}\text{H}_{34}\text{N}_6\text{O}_{12}$ (6)	811.36	38.36/38.49	3.44/4.22	10.27/10.36	14.02/14.53	8.29/8.74

* acet - Acetone

3. Results and its Discussion

The electronic absorption spectra of ethanol solutions H_2L_1 and H_2L_2 are characterized by wide intense absorption bands in the orange-red part of the spectrum (401 nm, $\text{lg}\epsilon$ 3.95 for

H_2L_1 and 488 nm, $\text{lg}\epsilon$ 4.31 for H_2L_2), which in alkaline solutions undergo a small hypsochromic shift, decreasing in intensity (Figure 1).

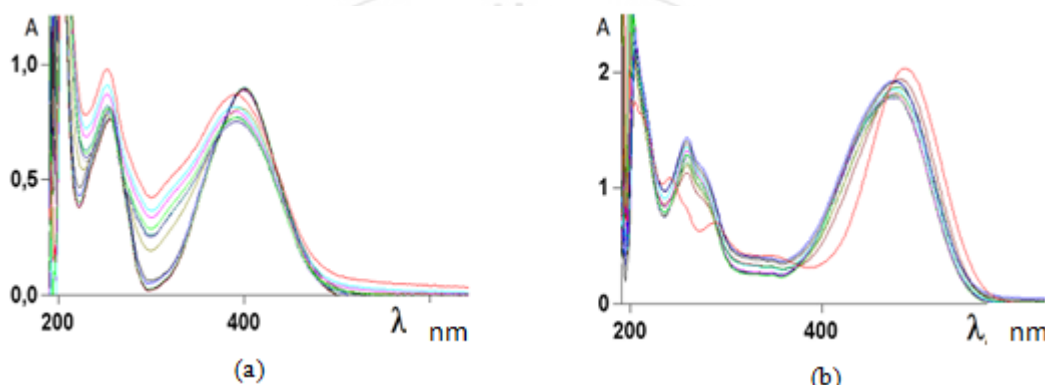
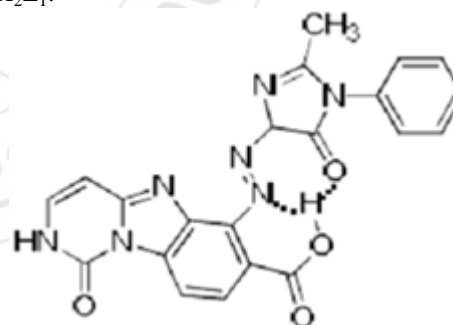


Figure 1: Electronic absorption spectra during titration of H_2L_1 (a) and H_2L_2 (b) solutions with sodium hydroxide solution

Changes in the spectra are not accompanied by the appearance of iso-bestic points, which complicates the interpretation of processes and the calculation of equilibrium constants. To determine the amount of hydrogen cations formed during dissociation of 1 mole of an organic molecule, potentiometric titration of water-ethanol; H_2L_1 . It was shown that, in the pH range from 6.7 to 12.2, the corresponding in-1 lost the pH when recording the electronic absorption spectra, on the titration curve of the observed. There is one jump in pH. The ratio $n(\text{H}_2\text{L}_1) : n(\text{NaOH})$ at the middle of the titration jump (at the point of equivalence) is 1: 1, which corresponds to dissociation of one proton of the carboxyl group. $\text{PKa1}(\text{H}_2\text{L}_1) = 9.8 \pm 0.2$. This value corresponds to low acidity of the carboxyl group, which can be explained by its participation in the formation of intramolecular hydrogen bonds. This conclusion does not contradict the results of quantum chemical calculations [4], according to which the position of the absorption bands in the electron-

Spectra corresponds to the following structure of the molecule H_2L_1 :



Addition of metal salt solutions to H_2L_1 solutions and H_2L_2 (Figure 2) leads to a bathochromic shift of the long-wave absorption band and the appearance in the spectra of isopiestic points, which indicates an equilibrium process of complex formation.

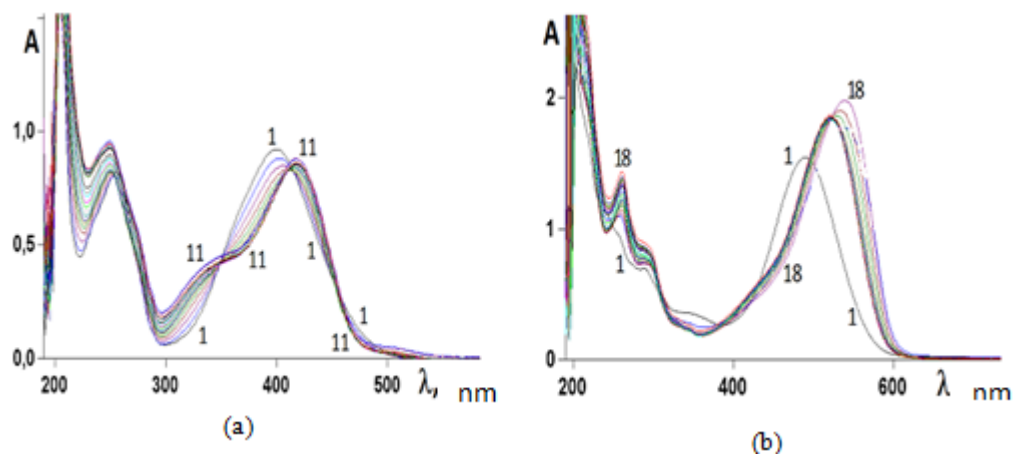


Figure 2: Electronic absorption spectra for titration of solutions of H₂L₁ (a) and H₂L₂ (b) with a solution of NiCl₂

Based on the results of spectrophotometric titration, saturation curves, on which the composition of complexes in solutions and the total production constant are calculated (Table 2).

Table 2: Composition of complexes (ML_n) and the values of their formation constants

Ligand	Metals	$\lambda_{\text{max}}(\text{nm})$	nBML _n	log B
H ₂ L ¹	Mn ⁺²	415	1	3.00±0.15
	Co ⁺²	418	1	3.17±0.21
	Ni ⁺²	420	1	3.55±0.08
	Cu ⁺²	403	1	3.62±0.13
	Zn ⁺²	412	1	3.24±0.11
	Fe ⁺³	404	1	3.11±0.14
H ₂ L ²	Mn ⁺²	524	1	2.65±0.24
	Co ⁺²	494	1	2.74±0.32
	Ni ⁺²	532	1	3.52±0.18
	Cu ⁺²	540	1	3.72±0.25
	Zn ⁺²	523	1	3.57±0.31
	Cr ⁺³	490	1	4.00±0.25
	Fe ⁺³	492	1	3.40±0.19
Ag ⁺	495	1	4.85±0.33	

Due to the fact that it was not possible to obtain single crystals of compounds, for the proposal schemes of their structure used spectral methods.

IR absorption spectra of uncoordinated H₂L₁ and H₂L₂ are characterized by several absorption bands in the region of stretching vibrations of carbonyl and carboxylic groups (Table 3). The medium intensity band is 1705 cm⁻¹, present in H₂L₁ and H₂L₂ and retaining its position in the transition to complex compounds, was attributed to vibrations of the carbonyl group of benzo [4,5] imidazo [1,2-c] quinazoline fragment of organo-molecules. A similar absorption band in the region of 1725-1690 cm⁻¹ is also present in the IR spectra of model compounds - derivatives of benzo imidazopyrimidinone [20]. The absorption coefficient of the average intensity of 1667 cm⁻¹ in H₂L₁ can be attributed to the vibrations of the carbonyl of the imidazolone moiety of the molecule, and the intense bands 1635 and 1640 cm⁻¹ in the spectra of H₂L₁ and H₂L₂, respectively, to the valence vibrations of C = O bonds of aromatic-carboxyl group bound by strong intramolecular hydrogen connections [21]. A wide absorption band with a maximum of 3310 cm⁻¹ in the IR spectrum of H₂L₂ causes the valence vibrations of the OH group of the 8-hydroxyquinoline fragment of the molecule, and its shift to the low-frequency region can be explained by the involvement in strong hydrogen-bonding.

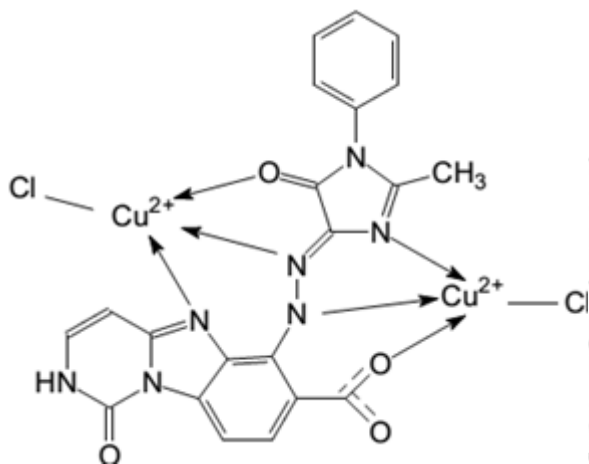
Table 3: Frequencies (cm⁻¹) of some absorption bands in IR spectra H₂L₁ and H₂L₂ and their metal complexes and their assignment

Compound	$\nu(\text{H}_2\text{O})$	$\nu(\text{OH})$	$\nu(\text{C}=\text{O})$ acetone	$\nu(\text{C}=\text{O})$ (NHCONH)	$\nu(\text{C}=\text{O})$ imidazo	$\nu(\text{C}=\text{O})$ (COOH)	$\nu^{\text{as}}(\text{COO}^-)$	$\nu^{\text{s}}(\text{COO}^-)$
H ₂ L ¹	-	-	-	1705cp	1667cp	1635c	-	-
1	3600-3400	-	-	1705cp	1655cp	-	1650c	1350c
H ₂ L ²	-	3310	-	1705cp	-	1640c	-	-
Na ₂ L ²	3600-3400	-	-	1705cp	-	-	1620c	1410c
2	3600-3400	-	1715cл	1705cp	-	-	1660c	1310c
3	3600-3400	-	1715cл	1705cp	-	-	1645c	1380c
4	3600-3400	-	1715cл	1705cp	-	-	1650c	1365c
5	3600-3400	-	1715cл	1705	-	-	1655c	1335c
6	3600-3400	-	1715cл	1705	-	-	1640c	1310c

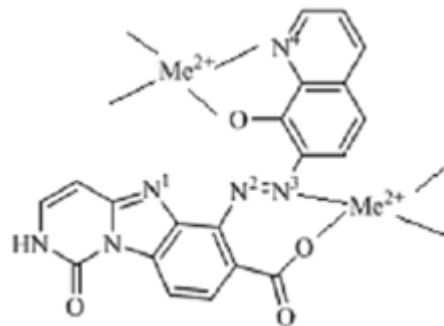
In the transition from uncoordinated H₂L₁ to its metal complex 1, in the IR spectrum the following changes occur. The 1705 cm⁻¹ band retains its position, which indicates to

the fact that the carbonyl group of benzo [4,5] imidazo [1,2-c] quinazoline fragment is not involved in coordination. The 1667 cm⁻¹ band of the imidazolone moiety is shifted in the

low-12 cm^{-1} , which can be explained by its participation in coordination. Appearance in IR spectrum of the complex compound of intense absorption bands at 1650 and 1350 cm^{-1} is associated with the ionization of the carboxylic group and the appearance of bands of antisymmetric and symmetric vibrations of the carboxyl anion involved in coordination with the cation metal. A wide absorption band in the 3600-3400 cm^{-1} region in the spectrum of the complex compound 1 refers to the vibrations of the crystallization molecules of water. Based on the metal: ligand ratio in the complex 1, equal to 2: 1, as well as the fact that, based on the results of qualitative analysis of chlorine anions are intrasphere character, it is possible to propose the following scheme of the structure of the complex compound:



In the IR absorption spectra of complex compounds 2-6, containing the organic ligand H₂L₂, as in the case of compound 1, absorption of 1705 cm^{-1} and the appearance of absorption bands $\gamma^s(\text{COO}^-)$ and $\gamma^{as}(\text{COO}^-)$ (Table 3). The shift of the band $\gamma^{as}(\text{COO}^-)$ into the high-frequency region and $\gamma^s(\text{COO}^-)$ into the low-frequency region with respect to the corresponding ("free" carboxylic anion), according to [19], can be explained by the filament of a carboxyl group in coordination with metal cations. The disappearance of the band absorption of the hydroxyl group 3310 cm^{-1} in the IR spectra of complex compounds is due to ionization of the hydroxyl group of the 8-hydroxyquinolylic fragment upon transition from H₂L₂ to its metal complexes, and a wide unresolved absorption band in the 3600-3400 cm^{-1} , we refer to the stretching vibrations of the crystallization water molecules. According to the results of the chemical analysis, H₂L₂ is included in the composition of coordination compounds in doubly deprotonation-bathroom-shape. The ratio of metal: ligand, equal to 1: 1 in the case of complex compounds 2-5, and a large number of electron-acceptor centers of organic molecules suggest the formation of polymeric structures in which the (L₂)²⁻ anion is bridged and realizes at once two metal-chelate cycles:



The compounds H₂L₁ and H₂L₂ have an extended conjugate system and a set of functional groups (carbonyl, carboxyl, hydroxyl, azo, heterocyclic nitrogen atoms) capable of initiating to interact with functional groups of natural and synthetic fibers. In connection with this, these organic molecules and their metal complexes can be considered as perspective dyes or pigments. For testing, a trial cotton, polyester and polyamide fibers. As test specimens H₂L₁, H₂L₂, Na₂L₂ sodium salt and complex 2 were taken. As shown by the experiment, cotton and polyester fibers were practically not stained with the selected under the given conditions. Polyamide fibers were stained with the compound H₂L₁ in golden-yellow color, and H₂L₂, its sodium salt and copper complex 2 - in bright-red color of different shades. Color fastness to dry friction and washing visually is estimated at the maximum score of 5. It should be noted that the dyeing process is accompanied by given by an almost complete transition of the dye from the solution to the fiber. This is a valuable property from the ecological point of view, as it prevents contamination of wastewater dyes.

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