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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 azogroup with the conjugate system of bonds of the rest of the molecule andDonor-acceptor substituents underlies the theory of chromaticity [2]. SpecificProperties of azo dyes are due to the following factors: azo-hydrazonetautomerism;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 colorGamma and strength characteristics [3]. The formation of metal chelate cycles altersSpatial and electronic structure of organic molecules, which determines the colorProperties of the dye. The effectiveness of the dye often correlates with the ability of organicMolecules to complex formation with metal cations. In this regard, it seemsIt is very interesting to study their spectral characteristics, spatial structure, andProcesses 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_1And 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 cycleAuthors, devoted to the study of the structure and properties of heterocyclic azo-compounds and metal complexesOn their basis [5-14].

2. Experimental Part

Electronic absorption spectra of ethanol solutions of organic molecules in the pH rangeFrom 2 to 9, and also when titrated with metal salts were recorded on a Varian Cary spectrophotometer50 Scan in the wavelength range 200-750 nm in cuvettes with a width of 1 cm. Concentrations were selectedIndividually for each connection. The deprotonation constants of organic molecules are determined bywere measured spectrophotometrically according to the procedure described in [15]. Composition of complexes and constantstheir formation in solutions was determined by the saturation method [16, 17]. Statistical processingThe results obtained were carried out according to the procedure described in [18] for the confidence probability95%.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 bandsAbsorption was carried out using literature data [19].

During the dyeing of polyamide fibers, the samples were treated with a detergent atTemperature 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 wasIncomplete, a suspension of the dye in water was used. Then, 100% acetic acid was added fromCalculation of 1 g per 1 liter of solution, kept for another 25 minutes, after which the solution was slowly adjusted toBoiling and boiled for 40 minutes. The colored fibers were removed from the dye bath andWashed 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 organicLigand 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 whichWas separated from the solution by filtration, washed with a small amount of acetone and dried inDesiccator above KOH to constant mass. On the individuality and single-phase products were judged withUsing visual crystal-optical analysis. The results of chemical analysis and gross-Formulas of complex compounds are given in Table. 1.

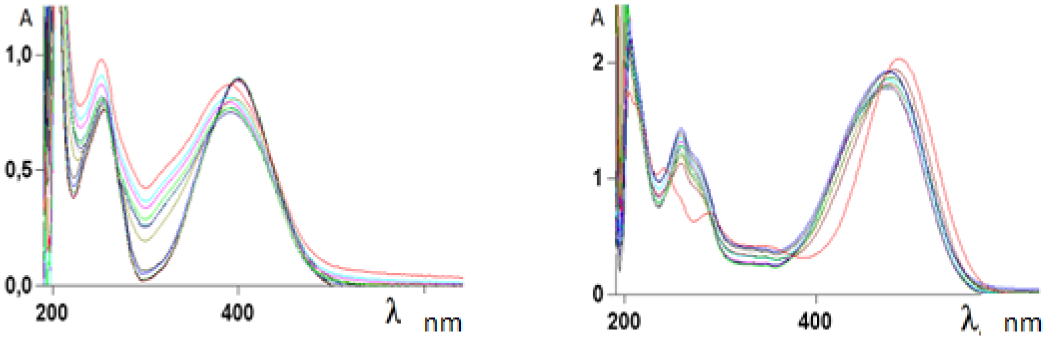
Table 1: Results of chemical analysis and gross formulas of isolated compounds

Compound / Gross formula	Mg/mol	Content (found / calculated)%				
		C	H	N	M	Cl
$Cu_2(L^1)Cl_2{\cdot}6H_2O$ / $Cu_2C_{21}H_{25}N_7O_{10}Cl_2$ **(1)**	733.47	34.71/34.39	4.08/3.44	12.88/13.37	16.84/17.33	9.45/9.67
$Cu(L^2){\cdot}6H_2O{\cdot}2acet^*$ / $CuC_{26}H_{34}N_6O_{12}$ **(2)**	686.13	45.56/45.51	5.61/4.99	11.45/12.25	9.00/9.26	
$Cd(L^2){\cdot}6H_2O{\cdot}2acet^*$ / $CdC_{26}H_{34}N_6O_{12}$ **(3)**	735.00	42.73/42.49	5.08/4.66	10.82/11.43	15.11/15.29	
$Mn(L^2){\cdot}4H_2O{\cdot}2acet^*$ / $MnC_{26}H_{30}N_6O_{10}$ **(4)**	641.50	47.91/48.68	5.29/4.71	12.85/13.10	7.78/8.56	
$Zn(L^2){\cdot}6H_2O{\cdot}acet^*$ / $ZnC_{23}H_{28}N_6O_{11}$ **(5)**	629.89	43.68/43.86	3.85/4.48	13.08/13.34	10.00/10.38	
$Co_2(L^2)Cl_2{\cdot}6H_2O{\cdot}2acet^*$ / $Co_2C_{26}H_{34}N_6O_{12}$ **(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

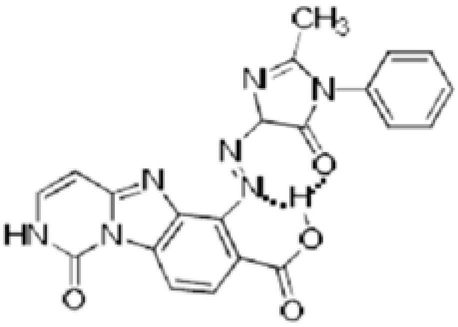
The electronic absorption spectra of ethanol solutions H_2L_1 and H_2L_2 are characterized byWide intense absorption bands in the orange-red part of the spectrum (401 nm,Lgε 3.95 for H_2L_1 and 488 nm, lgε 4.31 for H_2L_2), which in alkaline solutions undergoA small hypsochrome shift, decreasing in intensity (Figure 1).



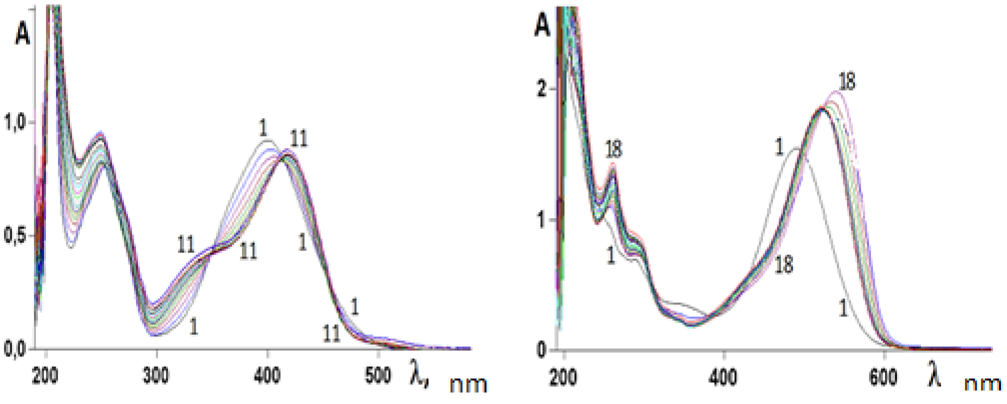
(a) (b)

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, whichComplicates the interpretation of processes and the calculation of equilibrium constants.To determine the amount of hydrogen cations formed during dissociation of 1Mole 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-I 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 (H_2L_1): n (NaOH) at the middle of the titration jump (at the pointEquivalence) is 1: 1, which corresponds to dissociationOne proton of the carboxyl group. PKa1 (H_2L_1) = 9.8 ± 0.2.This value corresponds to low acidity of the carboxylGroup, which can be explained by its participation in the formation ofIntramolecular hydrogen bonds. This conclusionDoes not contradict the results of quantum chemical calculations[4], according to which the position of the absorption bands in the electronSpectra corresponds to the following structure of the moleCokes 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 andThe appearance in the spectra of isopiestics points, which indicates an equilibrium processComplex formation



(a)

(b)

Figure 2: Electronic absorption spectra for titration of solutions of H_2L_1 (a) and H_2L_2 (b) with a solution of $NiCl_2$

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 (MLn) and the values of their formation constants

Ligand	Metals	$\lambda_{max (nm)}$	$nBML_n$	log B
H_2L^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_2L^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

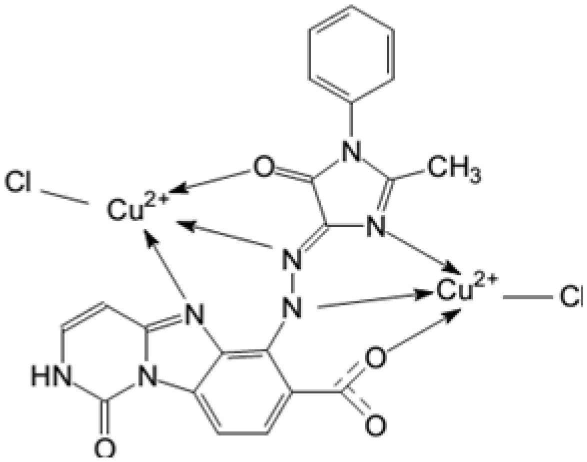
Due to the fact that it was not possible to obtain single crystals of compounds, for the proposalSchemes of their structure used spectral methods.

IR absorption spectra of uncoordinated H_2L_1 and H_2L_2 are characterized by severalAbsorption bands in the region of stretching vibrations of carbonyl and carboxylicGroups (Table 3). The medium intensity band is 1705 cm-1, present in H2L1 and H2L2 andRetaining its position in the transition to complex compounds, was attributed toVibrations 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 presentIn the IR spectra of model compounds - derivatives of benzo imidazopyrimidinone [20]. Polo-The absorption coefficient of the average intensity of 1667 cm-1 in H_2L_1 can be attributed to the vibrations of the carbo-Of the imidazolone moiety of the molecule, and the intense bands 1635 and 1640Cm^{-1} in the spectra of H_2L_1 and H_2L_2, respectively, to the valence vibrations of C = O bonds of aromatic-Carboxyl group bound by strong intramolecular hydrogenConnections [21]. A wide absorption band with a maximum of 3310 cm^{-1} in the IR spectrum of H_2L_2 causesThe 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-Binding.

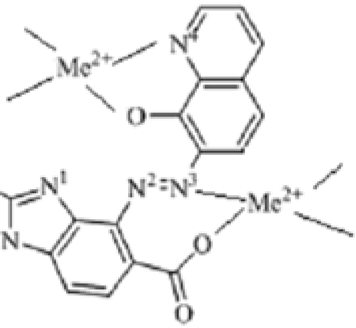
Table 3: Frequencies (cm^{-1}) of some absorption bands in IR spectraH_2L_1 and H_2L_2 and their metal complexes and their assignment

Compound	$\nu(H_2O)$	$\nu(OH)$	$\nu(C{=}O)$ acetone	$\nu(C{=}O)$ (NHCONH)	$\nu(C{=}O)$ imadazo	$\nu(C{=}O)$ (COOH)	$\nu^{as}(COO^-)$	$\nu^{s}(COO^-)$
H_2L^1	-	-	-	1705ср	1667ср	1635с	-	-
1	3600-3400	-	-	1705ср	1655ср	-	1650с	1350с
H_2L^2	-	3310	-	1705ср	-	1640с		
Na_2L^2	3600-3400	-	-	1705ср	-	-	1620с	1410с
2	3600-3400	-	1715сл	1705ср	-	-	1660с	1310с
3	3600-3400	-	1715сл	1705ср	-	-	1645с	1380с
4	3600-3400	-	1715сл	1705ср	-	-	1650с	1365с
5	3600-3400	-	1715сл	1705	-	-	1655с	1335с
6	3600-3400	-	1715сл	1705	-	-	1640с	1310с

In the transition from uncoordinated H2L1 to its metal complex 1, in the IR spectrumThe following changes occur. The 1705 cm^{-1} band retains its position, which indicatesTo the fact that the carbonyl group of benzo [4,5] imidazo [1,2-c] quinazoline fragment is not involvedCoordination. 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 IRSpectrum of the complexcompound 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 cationMetal. A wide absorption band in the 3600-3400 cm-1 region in the spectrum of the complexCompound 1 refers to the vibrations of the crystallization molecules of water. Based on the metal: ligand ratio in the complex1, equal to 2: 1, as well as the fact that, based onThe results of qualitative analysis of chlorine anions areIntrasphere character, it is possible to propose the followingScheme of the structure of the complex compound:



In the IR absorption spectra of complex compounds2-6, containing the organic ligand H2L2, As in the case of compound 1, Absorption of 1705 cm-1 and the appearance of absorption bandsas $\gamma^s(COO^-)$ and γ^{as} (COO^-) (Table 3). The shift of the band γ^{as} (COO^-)Into the high-frequency region and γ^s (COO^-) into the low-frequency region with respect to the corresponding("Free" carboxylic anion), according to [19], can be explained byThe filament of a carboxyl group in coordination with metal cations. The disappearance of the bandAbsorption of the hydroxyl group 3310 cm^{-1} in the IR spectra of complex compounds is due toIonization of the hydroxyl group of the 8-hydroxyquinolylic fragment upon transition from H_2L_2 toIts 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, H_2L_2 is included inThe composition of coordination compounds in doubly deprotonion-Bathroom-shape. The ratio of metal: ligand, equal to 1: 1 in the case ofOf complex compounds 2-5, and a large number of electron-The normal centers of organic molecules suggestThe formation of polymeric structures in which the (L_2) $_{2}$- anion isIt is bridged and realizes at once two metal-chelate cycles:



The compounds H_2L_1 and H_2L_2 have an extended conjugateSystem and a set of functional groups (carbonyl,Carboxyl, hydroxyl, azo, heterocyclic nitrogen atoms) capable of initiatingTo interact with functional groups of natural and synthetic fibers.In connection with this, these organic molecules and their metal complexes can be consideredAs perspective dyes or pigments. For testing, a trialCotton, polyester and polyamide fibers. As test specimensH_2L_1, H_2L_2, Na_2L_2 sodium salt and complex 2 were taken. As shown by the experiment,, cotton and polyester fibers were practically not stained with the selectedUnder the given conditions. Polyamide fibers were stained with the compound H_2L_1 inGolden-yellow color, and H_2L_2, its sodium salt and copper complex 2 - in bright-Red color of different shades. Color fastness to dry friction and washing visuallyIs estimated at the maximum score of 5. It should be noted that the dyeing process is accompanied byIs given by an almost complete transition of the dye from the solution to the fiber. This isValuable property from the ecological point of view, as it prevents contamination of wasteWater dyes.

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