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Synthesis and Properties of Some Metal Complexes Azo-Compounds

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Abstract: ***New complexes of some metalions with azo-compounds containing functionally substituted azo-derivatives of benzo-[4,5]-imidazo-[1,2-C]-pyrimidine carboxylic acids are isolated and characterized by a set physico-chemical methods. Aquantum-chemical calculations cycles were performed depending on the base of the conformity with the changes in experimental and calculated electronic absorption spectra while complexes formation.***

Keywords: azo- dyes, electronic spectroscopy, theoretical treatments

1. Introduction

Azo dyes make up more than50%of the range of industrial application (1).Their role is to versatility in a variety of areas, such as dyeing of textile fibers or plastics coloring. Additionally, azo compounds have been successfully used in biomedical research and in organic synthesis(1,2). Interaction with the conjugated system azo bonds in the rest of the molecule and the donor-acceptor substituent' sunder lying theory chrominance(3).This specific properties of azo dyes due to the: a) azo-hydrazone tautomerism; b) the electronic and spatial structure; c)the presence of several coordination centers providing educationpolydentateties with metal cations and materials; d)the ability to formionic species in solutions. The azo metal cations results in a change of color and strength characteristics like the resistance to physical impact, a certain bonding strength and other pictures(4,5). Education metal chelate cycles changes the spatial and electronic structure of organic molecules, which determines the color properties of the dye. Knowledge of regularities between the structure of metal dyes with their color characteristics, opens up the possibility of purposeful search for compounds with desired properties.In our work benzo pyrimidine carboxylic acids contain three fused rings, with two- nitrogen. It is composed as benzo imidazole moiety having basic properties and pyrimidine capable various tautomeric transformations, so they have to a certain extent, these combined properties(6).

2. Experiment

2.1 Physical Measurments and Analysis

Melting point of Gallen Kamp M.F.B. was used to measure melting points of all compounds. **IR absorption spectra** of the ligands in complexes(**1-4)**were recorded as Nujol mulls on a Specord_75 IR spectrophotometer within a frequency region of 400–4000 cm^{-1}.**Electronic absorption spectra** of ethanol solutions of compound in addition of NaOH and metal salt solutions were recorded on a Varian Cary 50Scan spectrophotometer within the wavelength region of 200–700 nm. To determine the composition of complexes in solutions, we used the saturation method. The formation constants of coordination compounds were calculated by a routine method. The protonation constants of the ligand were determined spectrophotometrically as described in. **Elemental analysis** of metals was carried out using the method of atomic emission spectrometry with inductively coupled plasma instrument on firm Varian 735-OES. Chemical analysis of nitrogen, carbon, hydrogen, chlorine and bromine micro method performed ,in the analytical laboratory Lomonosov Moscow State University on the unit CES-200.**Quantum-chemical simulation** were carried out by means of software Firefly 7.1.G on the supercomputer RCS "Chebyshev", and performed by the total electron ,(P.P.P. and PM_3) methods(7). Quantum-chemical modeling of the electronic structure of the different tautomers and conformers of neutral, anionic and protonated forms of organic molecules was performed by PM3, as well as in the approximation of the density functional theory using a three-parameter hybrid exchange functional Beke for the atoms of H, C, N, O use correlation-agreed valence three exponential basis set supplemented by diffuse functions (aug-cc-PVTZ) (8).

2.2 Synthesis of Metal Complexes

The ligand (azo derivatives benzo- [4,5] -imidazo -[1,2-C] pyrimidine carboxylic acid) prepared according to theliterature(9).Synthesis of four complexes carried out by mixing solutions in acetone and H_2L corresponding metal salt in a ratio of 1:1 for (Cu , Mn and Zn) and2:1 for Co in a neutral or alkaline media.

1) Added 10 ml of a solution of ligand (H_2L) in acetone (C 10^{-3} mol / L) was added to 10 ml of solution of a metal salts with stirring (C 10^{-3} mol / L). The resulting solution was heated on a water bath 50% solvent evaporation. Precipitation of complexes in the mother liquor was kept for a day, whereupon by separated, washed with a little acetone and dried in a desiccator.

2) Add 10 mlof ethanol solution of H_2L(C10^{-3}mol /L) was added with stirring to10ml of an ethanol solution of the metal salts ($MnCl_2$,$CoCl_2$,$ZnCl_2$, $CuCl_2$)(C10^{-3}mol /L) and heated on a steam bath for 2 hours. Followed by drop wise addition of (2 N) NaOH solution prior to crystallization. The mixture was placed in a hood and allowed to stand for1 day.

The resulting crystals were filtered through filter paper, washed with a small amount of ethanol and dried in a desiccator.

3. Result and Discussion

3.1 Physical Properties

Some physical properties and data of the (L)with their metal complexes are given in Table(1).

Table 1: Physical and analytical data for ligand and its metal commlexes.

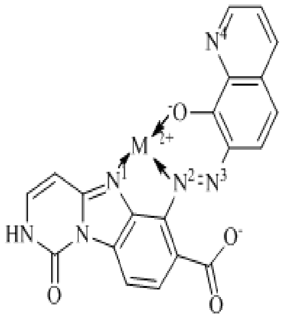
No.	Comp.	Color	Yield%	M.Wt g.mol^{-1}	Elemental analysis%found (calc.)					Proposed structure
					C	**H**	**N**	**M**	**Cl**	
1	$CuC_{26}H_{40}N_6O_7$.2Acet.	Brawn	80%	727.5	51.56 (52.78)	6.61 (7.14)	10.87 (11.54)	8.00 (8.73)	-	Oh
2	$MnC_{26}H_{40}N_6O_7$.2Acet	Brawn	73%	719	53.91 (53.40)	7.19 (7.23)	11.15 (11.68)	7.28 (7.64)	-	Oh
3	$ZnC_{26}H_{40}N_6O_7$.2Acet	Brawn	75%	729.4	51.68 (52.64)	6.92 (7.12)	11.08 (11.51)	8.00 (8.96)	-	Oh
4	$Co_2C_{26}H_{46}N_6O_{10}$.2Acet	Brawn	80%	907	41.85 (42.33)	6.04 (6.39)	9.30 (9.26)	12.62 (13.00)	8.29 (7.82)	Oh

Acet = acetone.

3.2 Inftred Spectra Studies$^{(10,11)}$

IR absorption spectra of free ligand H_2L show several absorption bands in the region of stretching vibrations of carbonyl and carboxyl groups (Table. 2). The coordination through the atomsN1, N2, N4leads tohypsochromic shift of the long-wave absorption bands in the spectra of model structures. Only coordination through the N3 atom causes the bathochromic shift of the ligand absorption bands. In the IR spectra of complexes absorption band of a carboxyl group disappears and new absorption band of anti-symmetrical and symmetrical vibrations of carboxylate anions exhibit, this indicate to ionization process of carboxyl group in complexes. The COO$^-$ vibrations are shifted to lower frequency in sodium salt. This can be explained by involving of a carboxyl group to coordination metal cations. , The absorption band of O-H stretching's in(L) disappears in spectra of complex compounds .This indicate its ionization and coordination with metals. So the most probable types of coordination may be appear as in the following shape 3 and 4 :

(1)



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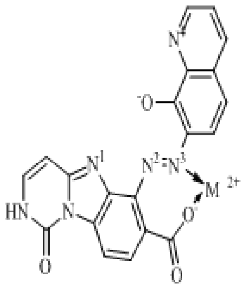

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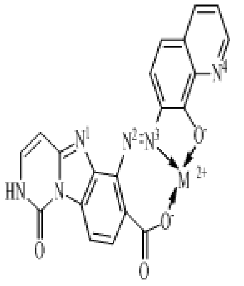
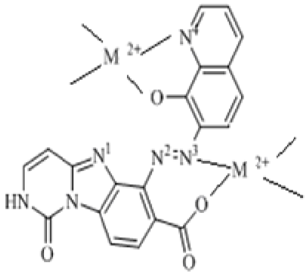


(4)



So the ligand behaves as tridentate or tetradentate in coordenation with metal ion.The disappearance of the bandsabsorption hydroxyl group 3310 cm^{-1} in IR spectra of the complex compounds related toionization hydroxyl-8-hydroxyquinol , wide absorption band at 3600-3400cm^{-1} refered to the stretching vibrations of molecules of coordinated water.

Table 2: The most diagnostic FTIR bands of the ligand and its metal complexes in (cm^{-1})

Comp.	ν (H_2O)	ν (OH)	ν(C=O) (acetone)	ν(C=O) (NHCONH)	ν(C=O) imadazol	ν(C=O) (COOH)	ν (C=N)	$ν_{asym.}$ (COO^-)	$ν_{sym.}$ (COO^-)
H_2L	-	3310	-	1705	-	1640	1616		
1	3600-3400	-	1715	1705	-	-	1613	1660	1310
2	3600-3400	-	1715	1705	-	-	1615	1650	1365
3	3600-3400	-	1715	1705	-	-	1616	1655	1335
4	3600-3400	-	1715	1705	-	-	1600	1640	1310

3.3 The Electronic Spectra

3.3.1 Electronic spectra of Ligand

Electronic absorption spectra of H_2Lethanol solutions characterized broad intense absorption bands at in the range (488 nm- 431 nmforH_2L),but in alkaline solutions undergo small hypsochromic shift with slightly decrease in intensity(fig. 1).

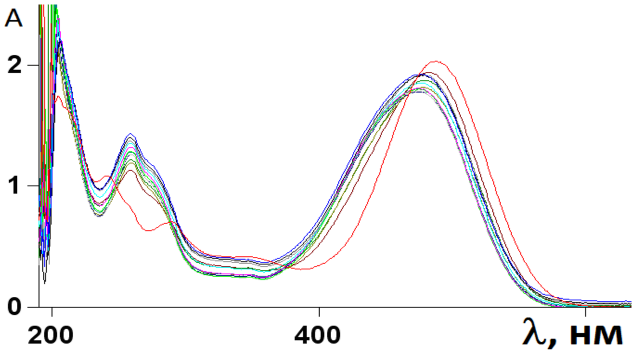


Figure 1: The electronic absorption spectrain the titrationsolution of H_2L with sodium hydroxide.

3.3.2. Electrionic Spectra of Complexes

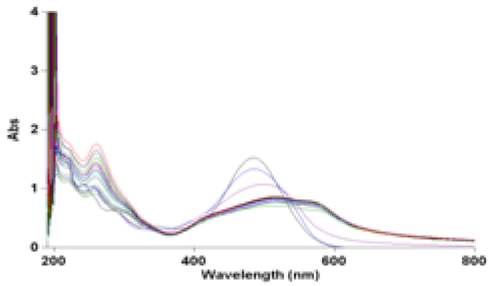


Figure 4: The electronic absorption spectra in the titration solution of H_2L and $CuCl_2$

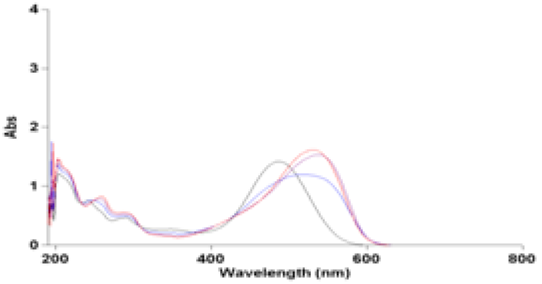


Figure 3: The electronic absorption spectra in the titration solution of H_2L and $CoCL_2$

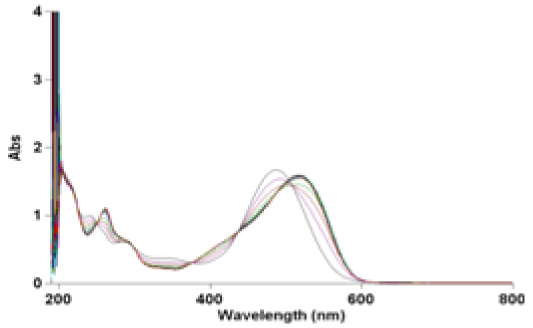


Figure 4: The electronic absorption spectra in the titration solution ofH_2L and $ZnCL_2$

According to the results of spectrophotometric titration curves constructed saturation, which are calculated composition of the complexes in solution and the overall formation constant(Table 3).

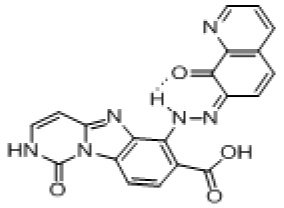
Table 3: Composition of (ML*n*) and stability of metal complexes

Compound	The metal cation	λmax, nm	n (in MLn)	logβ
H_2L	Cu^{+2}	540	1	3.72
	Mn^{+2}	524	1	2.65
	Co^{+2}	494	1	2.74
	Zn^{+2}	523	1	3.57

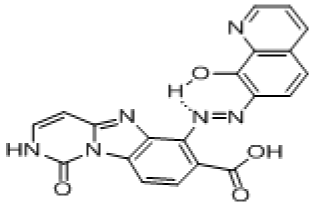
The constants of deprotonation of organic molecules is determined,spectrophotometrically by using the method that describein literature (12). The complex and constants formation in the solutions was determinedby using the method that describe in literature (13).

3.3 *Quantum chemical modeling of structure and properties ofH_2L.*

Molecule compounds H_2L potentially exist in different isomeric forms, in particular in the form of OH and hidrazo tautomera H_2L-1 tautomer H_2L-2:

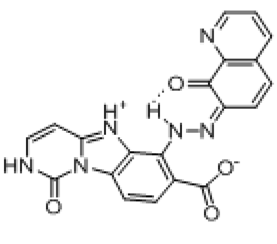


H_2L-1

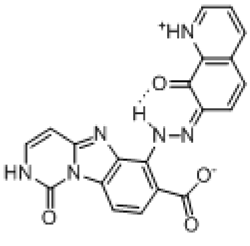


H_2L-2

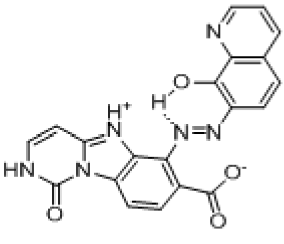
For each of tautomers not exclude the possibility of forming zwitter ionic forms, for example:



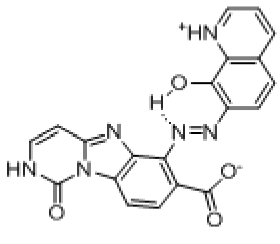
H_2L-1 zwitter 1



H_2L-1 zwitter 2



H_2L-2 zwitter 1



H_2L-2 zwitter 2

Additionally, for each different forms possible conformers distinguish different location relative to bonds C-N and N=N with the nitrogen atoms. Thus, as a rule, it is the most stable conformers for which the formation of intramolecular hydrogen bonds NO six-member rings. Calculated for the isomeric forms of the molecule H_2L by PM3 full energy of the molecules and their heat of formation and the relative energies are given in Table(4).

Table 4: Energies calculation of the isomeric forms of the molecule H_2L by PM3 method in kcal / mol

Isomer	E_{Total}	$E_{heat\ formation}$	$E_{binding}$
H_2L-1	-108376.3303	-2.6053	5,9
H_2L-1zw.1	-108330.5692	43.1573	51.6
H_2L-1zw.2	-108322.3506	51.3761	59,9
H_2L-2	-108382.2293	-8.5044	0
H_2L-2zw.1	-108334.4463	39.2800	47,8
H_2L-2zw2	-108323.9695	49.7571	58,3

The calculation results PM3 method indicate that the molecule H_2L each calculated form a single conjugated structure and has a planar structure except a carboxyl group which is rotated relative to the plane of the rest of the molecule (Fig. 5, 6).

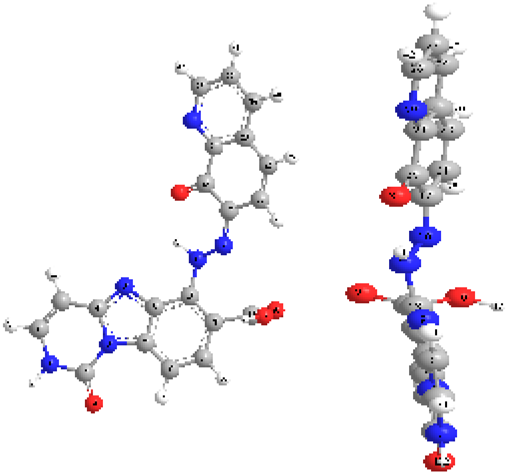


Figure 5: Optimization of structure H_2L-1according to thecalculation method PM3.

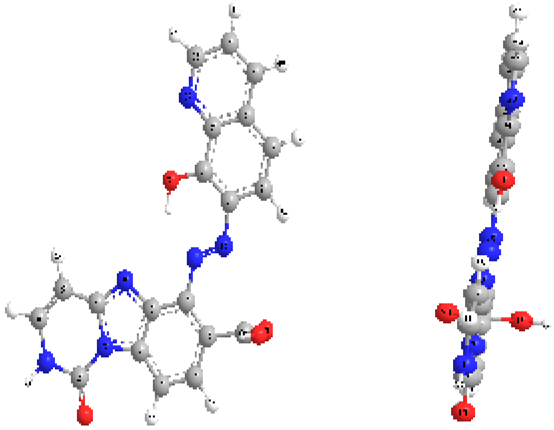


Figure 6: Optimization of structure H_2L-2 according to the calculation method PM3.

OH tautomer (H_2L-2) more stable than hidrazo tautomer (H_2L-1) (Table4). Zwitterionic forms significantly less stable than the neutral form. The difference in energy between the neutral and the corresponding zwitterionic forms of 45 - 60 kcal / mol, which allows further study of the molecular structure H_2L not consider the possibility of their existence.The calculations were performed for the neutral form and H_2L-1 H_2L-2 for a number of anionic forms:

Figure(7) H_2L-1 Zweter and anionic		**Figure(8) H_2L - 2 Zweter and anionic**	
H_2L-1 anionic 1		H_2L-2anionic1	
H_2L-1 anionic 2		H_2L-2anion2	

H_2L-1 neutral form		H_2L-2neutral	

In the (Table.5) shows the results of the calculation method of the P.P.P. for these forms of energy molecules H_2L atomization ΔH, energy π-bonds Eπ, solvation energies M and the wave -length λ_1 and corresponding strengths f. In addition, in Table. 5 shows the results of model calculations H_2L-1 'and H_2L-2' and anion H_2L-2'an2 in which no carboxyl group. The necessity of this approach stems from the fact that the calculation method in PM3 as shown in (Fig.5, 6), which are not carboxyl group is in conjugation with the rest of the molecule.

Table 5: Calculation of certain neutral and anionic forms of a molecule H_2Lmethod P.P.P. (energy in eV, 1 eV = 23.05 kcal / mole, the wavelengths in nm)

№	compound	*ΔH*	*Eπ*	*M*	λ_1	*(f)*
1	H_2L-1	214.679	50.914	9.952	541	1.157
2	H_2L-1an1	210.200	50.877	9.776	538	1.116
3	H_2L-1an2	212.321	52.710	11.992	594	1.422
4	H_2L-1nut.	207.844	52.674	11.820	593	1.412
5	H_2L-2	214.275	50.273	8.249	491	1.116
6	H_2L-2an1	209.791	50.231	8.044	488	1.105
7	H_2L-2an2	209.844	50.281	8.052	512	1.010
8	H_2L-2nut.	205.364	50.243	7.852	509	1.000
9	H_2L-1	197.634	45.437	7.997	521	1.209
10	H_2L-2	197.142	44.714	6.212	466	1.098
11	H_2L-2an2	192.700	44.710	6.008	488	0.979

From the results of the calculation of the energy characteristics of the tautomers (atomization energies ΔH, energy π-bonds Eπ, solvation coefficients M) shown in (Table 5), it follows that theH_2L-1hidrazotautomer is more stable compared with that of OH tautomer of H_2L-2. The difference in the energy of atomization is 0.404 eV. The difference in the solvation factor - 1.703 eV (1 eV = 23.05 kcal / mol). A similar difference is observed in the calculation of free COOH groups. This indicates a greater dimensional stability compared to H_2L-1, H_2L-2 isomer in the gas phase and in solution.As shown previously H_2L, ESP compound in ethanol solution is characterized by an intense absorption wavelength band in the wavelength region of 488 nm. In alkaline solutions, long-wavelength band is undergoing a small hypsochromic shift with a slight decrease in intensity.From the results shown in (Table.5), it follows that the deprotonation of the carboxyl group (go to H_2L-1an1 and H_2L-2an1) practically does not change the position of the DP-hypsochromic shift of 3nm. At the same time deprotonation NH or OH groups (and transition to H_2L-1an2 H_2L-2an2) leads to a marked bathochromic shift ESP (53 and 21 nm, respectively). The exception is based COOH leads to the expected hypsochromic shiftwave- length band associated with a decrease in the length of the conjugated chain. Given the small contribution found deprotonation of the carboxyl group to characterize the anionic form of the compound H_2L, use the model form H_2L-1 ', H_2L-2' and H_2L-2an2 'that and should be compared with experimental electronic absorption spectra. From the results shown in (Table. 5), it follows that with the experimental value of 488 nm wavelength band agreement between the calculated value for the hidrazotautomera H_2L-1 '(521 nm) and OH tautomer H_2L-2' (466 nm). This absorption band shape H_2L-2an2 '(488 nm) is relatively bathochromic band form H_2L-2' (466 nm) and relatively hypsochromic strip form H_2L-1 '(521 nm).In alkaline media the long-wavelength absorption band undergoes H_2L hypsochromic shift to 482 nm (Fig. 1). This fact can be explained by assuming that the compound in solution exists as a H_2L hidrazotautomera H_2L-1, which proceeds in alkaline media anion close in structure to the anion OH tautomer H_2L-2an2.Since the compound of H_2L not characterized by X-Ray crystallography, (Table. 6) shows calculated for H_2L-1 PM3 method interatomic distances, and (Table.7) display the chargesexit on atoms of molecules.

Table 6: The inter atomic distances in the molecule H_2L-1 according to the calculation method PM3 (Numbering of atoms is shown in Fig. 5).

Bond	Distances(A)	Bond	Distances (A)	Bond	Distances(A)
C(28)-H(42)	1.0966	C(25)-C(17)	1.4888	N(3)-C(4)	1.4365
C(27)-H(41)	1.0945	C(24)-C(25)	1.4874	C(2)-N(3)	1.4295
C(26)-H(40)	1.0961	N(29)-C(24)	1.3628	N(1)-C(2)	1.4221

C(22)-H(39)	1.0962	C(28)-N(29)	1.3436	C(6)-N(1)	1.4138
C(21)-H(38)	1.0984	C(27)-C(28)	1.4017	C(2)-O(14)	1.2223
O(19)-H(37)	0.9490	C(26)-C(27)	1.3841	C(13)-N(15)	1.4338
C(11)-H(36)	1.0972	C(8)-C(7)	1.4153	N(15)-N(16)	1.3402
C(10)-H(35)	1.0957	N(3)-C(7)	1.4221	N(16)-C(17)	1.3257
C(6)-H(34)	1.0979	C(10)-C(7)	1.3974	C(12)-C(18)	1.4948
C(5)-H(33)	1.0958	C(11)-C(10)	1.3823	C(18)-O(19)	1.3551
N(1)-H(32)	0.9949	C(12)-C(11)	1.4112	C(18)-O(20)	1.2104
C(24)-C(23)	1.4055	C(13)-C(12)	1.3976	C(25)-O(30)	1.2254
C(26)-C(23)	1.4043	C(8)-C(13)	1.4121	N(15)-H(31)	1.0172
C(22)-C(23)	1.4480	N(9)-C(8)	1.4190	C(5)-C(6)	1.3521
C(21)-C(22)	1.3445	C(4)-N(9)	1.3353		
C(17)-C(21)	1.4551	C(5)-C(4)	1.4414		

Table 7: The charges on the atoms of the molecule H_2L-1 according to thecalculation method PM3

SS	charge	atom	charge	atom	charge	atom	charge
N(1)	0.0993	C(12)	-0.1730	C(23)	-0.0242	H(34)	0.1310
C(2)	0.2170	C(13)	0.0330	C(24)	-0.1215	H(35)	0.1393
N(3)	0.1940	O(14)	-0.3655	C(25)	0.3671	H(36)	0.1144
C(4)	-0.0742	N(15)	0.1540	C(26)	-0.0803	H(37)	0.1980
C(5)	-0.1362	N(16)	-0.0240	C(27)	-0.1171	H(38)	0.1229
C(6)	-0.1218	C(17)	-0.2254	C(28)	-0.0872	H(39)	0.1125
C(7)	-0.1043	C(18)	0.4284	N(29)	-0.0019	H(40)	0.1142
C(8)	-0.1177	O(19)	-0.2696	O(30)	-0.3195	H(41)	0.1144
N(9)	-0.0743	O(20)	-0.3267	H(31)	0.1434	H(42)	0.1228
C(10)	-0.0866	C(21)	-0.0275	H(32)	0.1061		
C(11)	-0.0517	C(22)	-0.1302	H(33)	0.1485		

*The numbering of the atoms is shown in Fig. 5

3.3. The study of Ni complex formation in solutions

Addition of solutions of metal salts to solutions H_2L (Fig.9) causes a bathochromic shift of the absorption wavelength band and exhibit isobestic points.

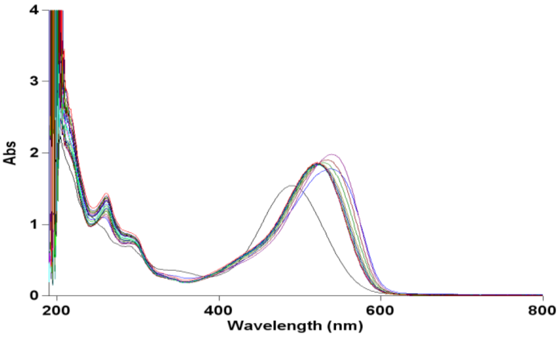
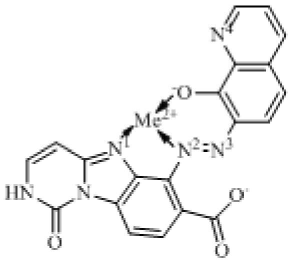


Figure 9: Changes in the bsorption spectra in the titrationsolution of H_2L and $NiCl_2$.

Such a change in the spectra observed in different ionization H_2L. To explain this phenomenon using the results of quantum-chemical calculations on the example of H_2L molecule is characterized by a number of donor centers capable of coordinated metal cations centers include four nitrogen atoms and two oxygen atoms. Knowing that the ligand is included in the composition in the form of the complex and based on the possibility of the formation of chelate bonds can provide the following modes of coordination:



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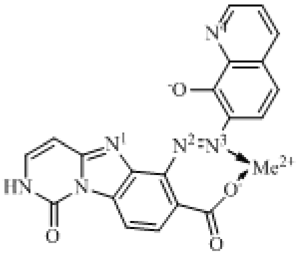
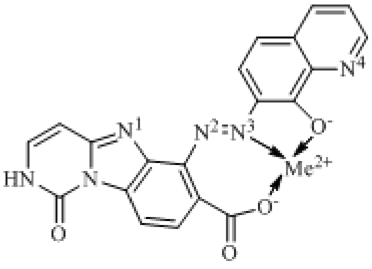
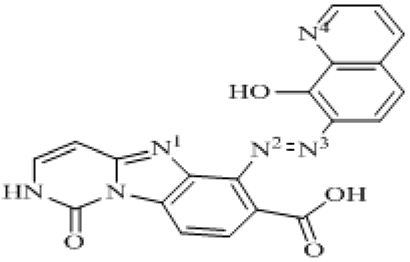


II

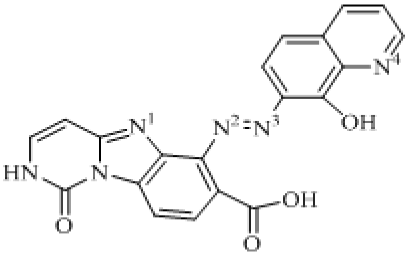


III

The proposed coordination methods I - III molecule H_2L stored in different conformations A and B .In the Table. 8 .shows the results of calculation of model compounds for the conformation of the molecule H_2L.Thus in accordance with the above findings of the compounds in models carboxyl groups and hidrazotautomera calculated model H_2L-1'A, instead H_2L-1A.



A conformation (H_2L-2A)



Conformation (H_2L-2B)

From Table.8(No.4) show that participate in the coordination atom N^1 results in a hypsochromic shift (486 nm) relative to the strip in a stable neutral molecule H_2L-1'A (521 nm). A similar pattern is observed when participating in coordination atom N^2 (514 nm), the atom N^4 (491 nm) and two atoms N^1 and N^2 (506 nm), where the band also shifted relative hypsochromic band 521 nm. And only coordinated with atom N^3 (Form H_2L-2an'AH $^+$) the band model form (558 nm)bathochromic shifted with respect to theposition band of the neutral form of the ligand (521 nm). This method involving coordination N^3 nitrogen atom and an oxygen atom of a carboxyl group in the shape 2previouslyshown .

Table 8: Calculation of some forms of a molecule model H_2L (without carboxyl group) by P.P.P. (energy in eV, 1 eV = 23.05 kcal / mole, the wavelengths in nm)

No	compound	ΔH	Eπ	M	λ1	(f)
1	H_2L-1’A	197.634	45.437	7.997	521	1.209
2	H_2L-2’A	197.142	44.714	6.212	466	1.098
3	H_2L-2an’A	192.700	44.710	6.008	488	0.979
4	H_2L-2an’A·H^+(N^1)	197.574	45.446	7.078	486	0.957
5	H_2L-2an’A·H^+(N^2)	197.267	45.136	6.864	514	0.966
6	H_2L-2an’A·$2H^+$(N^1, N^2)	202.129	45.862	7.932	506	0.959
7	H_2L-2an’A·H^+(N^3)	197.029	44.866	6.413	558	1.073
8	H_2L-2an’A·H^+(N^4)	197.376	45.219	6.728	491	0.882
9	H_2L-1’B	197.412	45.235	7.715	505	1.405
10	H_2L-2’B	196.949	44.522	6.125	454	1.459
11	H_2L-2an’B	192.511	44.521	5.947	472	1.352
12	H_2L-2an’B·H^+(N^3)	196.880	44.713	6.381	543	1.364

A similar pattern is observed for conformers in which the band designed to form H_2L-2an'B.H^+ (N^3) (543 nm) is also shifted relative bathochromic band neutral form of the ligand (521 nm). This method involving the coordination of the nitrogen atom N^3 and the two oxygen atoms shown previously in shape (3).Thus, the method of the P.P.P. shown that explain the behavior of the ESP H_2L compound by reacting with metal cations can suggest a role in the coordination of the nitrogen atom N^3 in accordance with the methods of shape 2 and 3.It is clear that these conclusions are tentative. To confirm their need X-ray study of coordination compounds. According to the results of spectrophotometric titration built saturation curves, which are designed composition of the complexes in solution and the overall formation constant (Table3).

3.3. The studying of the Properties of Color CuL Complex

ThecompoundsH$_2$Lextendedconjugated system and a set of functional groups (carbonyl, carboxyl, hydroxyl, azo group, heterocyclic nitrogen atoms) capable of reacting with the functional groups of natural and synthetic fibers. In this regard, H$_2$Landmetal complexes can be considered as dyes or pigments. Dyeing test was conducted cotton, polyester and polyamide fibers·The samples taken for testing, H_2L, complex compound Cu(L) dyeing was carried out according the method (15) where the samples treated with washing fiber at a temperature of60°C for 10min. and washed with waterin3%aqueousdye solution and heated at40°C for20min.then 100% acetic acid at the rate of 1 g per 1 liter of the solution was kept for another 25 min., finally the solution was boil for 40 min.Colored fibers from the dye bath, gradually lowering the water temperature to 40 °C. The filaments were dried and washing. The experiments showed that cotton and polyester fibers hardly stained with selected compounds at specified conditions. Bright red color of various shadow as shown in (Fig 10) of CuL polyamide fiber.

Figure 10: Polyamide fiber scolored of CuL .

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