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Investigación

Non-Traditional Coordination in the Complexes of 2-[2'-hydroxy(2'-*N*-tosylamino)phenyl] and 2-[2'-hydroxyazomethine)]-1-alkylbenzimidazoles

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Abstract. In this paper the formation of molecular complexes (adducts) on the basis of benzimidazole derivatives is reported. The way of localization of the coordination bond in the synthesized compounds is also suggested. The synthesis of the adducts $(LH)_m \cdot MCl_n$ (m = 1, 2; n = 2, 4) is carried out by the interaction of typical chelating ligands 2-hydroxy-(*N*-tosylamino)phenylbenzazoles or hydroxyazomethines of 1-alkyl-2-aminobenzimidazole (LH) with copper, zinc, palladium, tin and titanium chlorides (MCl_n). The IR, UV and luminescence studies show that non-traditional coordinations of the ligands take place in the synthesized complexes. It is suggested that the ligands exist in the complexes, probably, in the quinonoid tautomeric form, connected to the metal atom through the nitrogen atom of pyridinic type and/or oxygen atom of phenolic fragment of the ligand systems. It is concluded that, in addition to well-known standard metal chelates, the adducts with completely conserved ligand system (LH) could be also formed on the basis of the typical chelating ligands above mentioned.

Key words: Non-traditional coordination, adducts, transition metal complexes.

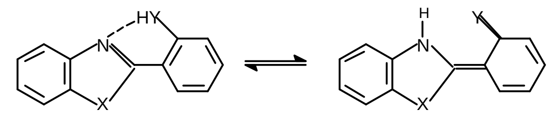
Resumen. Se reporta la formación de complejos moleculares (aductos) a partir de derivados del benzimidazol como ligantes. En particular, se presenta la síntesis de los complejos moleculares $(LH)_m \cdot MCl_n$ (m = 1, 2; n = 2, 4) por interacción de los ligandos quelatos típicos (2-hidroxi-(*N*-tosilamino) fenilbenzazolas o hidroxiazometína de 1-alquil-2-aminobenzimidazol (LH)) con cloruros de cobre, zinc, paladio, estaño y titanio (MCl_n). Los resultados de los estudios espectroscópicos (IR y UV) y de luminescencia muestran la presencia de coordinaciones no tradicionales de los ligandos en los complejos sintetizados. Se comenta, adicionalmente, sobre la posibilidad de que los ligantes existan en los complejos en la forma tautomérica quinonoide, unidos al átomo metálico a través del átomo de nitrógeno de tipo piridínico y/o del átomo de oxígeno del fragmento fenólico de los sistemas de ligandos de estudio. Se concluye, finalmente que, además de los bien conocidos quelatos metálicos estándares, pueden también formarse aductos con sistemas de ligandos (LH) totalmente conservados a partir de los ligandos quelantes típicos mencionados anteriormente.

Introduction

Chelate-forming nitrogen-containing ligands have an important role in modern coordination chemistry [1]. The main features of the ligand systems such as **1-3** are the presence of acidic HY-groups, which take part in the formation of an inner-molecular hydrogen bond [2], and the existence of the prototropic tautomery [3] (for example, **1a** ⇔ **1b**).

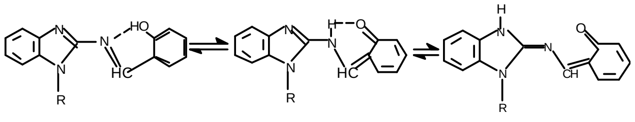
At present, it is accepted that only "standard" metal chelates, formed as a result of substitution of the proton of the HY-group by the metal, could be obtained for these and other chelating ligands. However, other ("non-standard") ways of metal connection can take place in such compounds which were generalized in recent review [4]. In the adducts formed as a result of a "non-standard" coordination, the neutral azomethinic molecules participate as ligands. A metal (in the form, for example, of $MHal_n$) can be coordinated through oxygen or nitrogen atom (or simultaneously with both ones) of one or more ligand molecules [4]. A conserved hydrogen atom can also occupy different position in the formed adducts: it can be connected with oxygen or/and nitrogen by covalent or donor-acceptor bond.

According to reported data, on the basis of the 2-(2'-hydroxy, tosylamino)phenyl derivatives **1** (HL^1) and the azomethines **2** (HL^2) and **3** (HL^3) of benzimidazole, the metal chelates of the types **4** [5], **5** [6a], and **6** [6b] are formed.

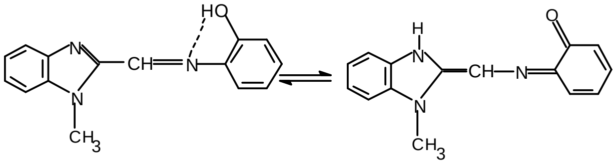


1a 1b

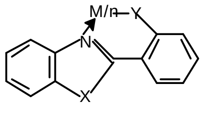
X = NR, O; Y = NTs, O; R = Alk



2a R=CH3, C8H11 2b 2c



3a 3b



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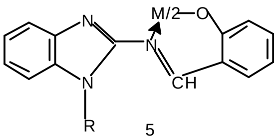

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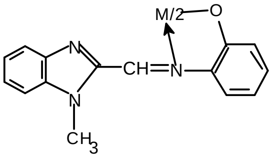

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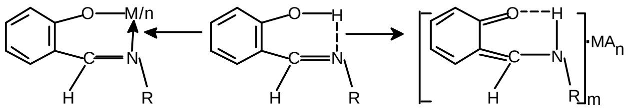
It has also been shown [7-10] that, on the basis of the aromatic azomethines **7**, both the traditionally coordinated chelate structures **8** and the molecular adducts **9** could be obtained.



8 7 9

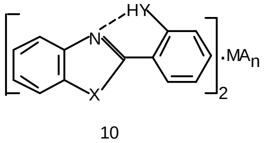
A = OCOMe, NO_3 ; R = Alk, Ar, Het; n = 2, 3

A = Hal, NO_3 , NCY (Y = O, S, Se); m,n = 1-4

The objective of the present paper is to obtain molecular complexes (adducts) on the basis of above mentioned typical chelating ligands - benzimidazole derivatives **1-3** and to establish the way of localization of the coordination bond in the synthesized compounds.

Results and discussion

The synthesis of the chelates of the types **4-6**, **8** and the adducts **9** is generally carried out by an adequate choice of metal salts and solvents [10, 11]. We have used this way to obtain the adducts of metal halides with benzimidazole ligands **1-3** (HL^1, HL^2, HL^3). The adducts of copper and zinc dichlorides were obtained by the interaction of the ligand systems with MCl_2 (M = Cu, Zn) in absolute metanol, while the adducts of tin and titanium were obtained with MCl_4 (M = Sn, Ti) in dry benzene. The adducts of palladium dichloride have been prepared by a ligand-exchange reaction of the benzonitrile complex $PdCl_2(PhCN)_2$ and the examined ligands in benzene solutions. Unlike these adducts, the chelate complexes of the same ligand systems have been obtained starting from metal acetates in methanol. The elemental analysis data (Table 1) testify that all the described adducts have structures with a completely conserved ligand system LH, which could be represented by the formulae **10-12**.



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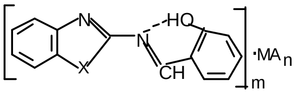
n=2, 4



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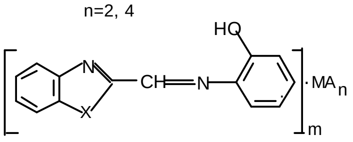
m=1, 2; n=2, 4



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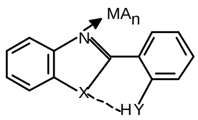
m=1, 2; n=2, 4

Taking into account the tautomeric equilibrium **1a** ⇔ **1b** and the presence of inner-molecular H-bond in these molecules, it is possible to suggest [10, 11-13] the existence of the structures **13-15** for the adducts of the ligand **1**.



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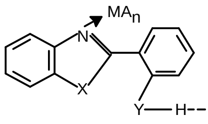

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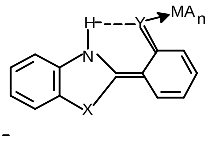

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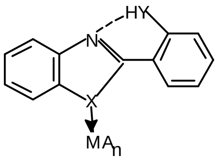
Moreover, it is also possible the participation of oxygen atoms of the oxazol fragments **16**, **17** in the coordination:



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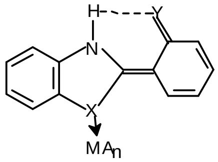


17

We have observed a wide band in the region of 3200-3400 cm^{-1} in the IR-spectra of adducts of the type **10**, which could be related to an H-bond; the bands 1590-1640 cm^{-1} could be attributed to valence oscillations of heteroarene systems. This result can be connected with the formation of the structure of the type **13**. At the same time, it does not exclude the formation of complexes having the structure **15**: the appearance of absorption bands in the region of 1600-1640 cm^{-1} could be related not only with coordinated benzazole fragments, but also with the decreased frequency of a quinonoid group [10, 13]. There is a low probability of existence of the structures **16** and **17**, since, although a connection of metals with oxygen atom of the oxazole derivatives is theoretically possible [14], this way of coordination of the oxazole cycle has not been proven yet by X-ray diffraction.

The main differences correspond to the structures **13-15**, in which the coordinative interaction leads to the stabilization of benzenoid or quinonoid tautomeric forms of the ligands (compare the reported structural data [7-10, 13] of the adducts of *o*-oxyazomethines and β-aminoketones with the Lewis acids).

In order to specify the structure of the adducts of the type **10** and to determine the influence of complex formation on the electronic and structural properties of the ligand systems of the type **1**, we have made a spectral-luminescence study of *o*-oxyphenylbenzimidazole (1, X = NH, Y = O) and its complex with $ZnCl_2$ (compound 3, Table 1). The chelates of zinc and cadmium (compounds **20** and **21**, Table 1) have also been studied in order to compare their properties with those of the complex **3**.

Table 1. Analytical data of the benzazole ligands **1-3** and their complexes.

No	Lig.	X	Y	Comp. HL · MA_n	Color	M.P., °C	% (f/ca)*					Formula
		(R)					C	H	N	M	Cl	
1	I	O	O	$2HL^1 \cdot PdCl_2$	Brown	287	49.84	3.00	4.73	16.98	11.03	$C_{26}H_{20}N_2O_5PdCl_2$
							50.55	3.24	4.53	17.27	11.49	
2	I	O	O	$2HL^1 \cdot SnCl_4$	White	>350	44.62	2.44	4.60	17.26	20.58	$C_{26}H_{18}N_2O4SnCl4$
							45.70	2.63	4.10	17.38	20.79	
3	I	NH	O	$2HL^1 \cdot ZnCl_2$	White	>250	55.96	3.39	10.50	12.50	12.21	$C_{26}H_{18}N_4O_2ZnCl_2$
							56.27	3.25	10.10	11.79	12.81	
4	I	NH	O	$2HL^1 \cdot PdCl_2$	Yellow	>280	52.80	3.12	9.70	18.15	10.30	$C_{26}H_{18}N_4O_2PdCl_2$
							52.52	3.04	9.40	17.91	11.92	
5	I	O	NTs	$2HL^1 \cdot PdCl_2$	Yellow	>300	55.57	4.20	6.30	10.62	7.16	$C_{46}H_{40}N_6O_4S_2PdCl_2$
							56.21	4.07	8.55	10.87	7.23	
6	2	CH_3		$HL^2 \cdot C_6H_6$	Yellow	173-174	69.20	7.30	16.80		10.50	$C_{15}H_{13}N_3O$
							71.70	5.18	16.73		11.12	
7	2	CH_3		$2HL^2 \cdot ZnCl_2$	Yellow	285	56.03	3.97	13.20	11.20	10.50	$C_{30}H_{26}N_6O_2ZnCl_2$
							56.39	4.07	13.16	10.24	11.12	
8	2	CH_3		$HL^2 \cdot CuCl_2$	Brown	297dec.	46.44	3.56	11.50	17.80	17.97	$C_{15}H_{13}N_3OCuCl_2$
							46.69	3.37	10.89	16.96	18.42	
9	2	CH_3		$2HL^2 \cdot SnCl4$	Yellow	250dec.	47.56	3.24	11.25	15.01	18.34	$C_{30}H_{26}N_6O_2SnCl_4$
							47.20	3.41	11.01	15.56	18.62	
10	2	CH_3		$HL^2 \cdot TiCl4$	Red	350dec.	40.36	2.79	10.10	10.06	31.89	$C_{15}H_{13}N_3OTiCl_4$
							40.82	2.95	9.52	10.86	32.21	
11	2	C_8H_{17}		HL^2	Yellow	71-72	76.00	7.45	12.15			$C_{22}H_{27}N_3O$
							75.64	7.73	12.03			
12	2	C_8H_{17}		$2HL^2 \cdot ZnCl_2$	White	175-176	62.70	5.90	11.50	7.00	8.17	$C_{44}H_{54}N_6O_2ZnCl_2$
							63.28	6.47	10.07	7.84	8.51	
13	2	C_8H_{17}		$2HL^2 \cdot PdCl_2$	Yellow	266-267	60.61	6.91	10.10	12.50	8.90	$C_{44}H_{54}N_6O_2PdCl_2$
							60.29	6.17	9.59	12.20	8.11	
14	3	–		HL_3	Yellow	183-184	69.31	7.20	16.73			$C_{15}H_{13}N_3O$
							70.29	5.18	16.72			
15	3	–		$2HL^3 \cdot CuCl_2$	Brown	244	56.01	4.25	13.42	10.00	11.84	$C_{30}H_{26}N_6O_2CuCl_2$
							56.56	4.08	13.19	9.98	11.15	
16	3	–		$HL^3 \cdot ZnCl_2$	Orange	365dec.	45.86	4.56	11.29	5.84	18.23	$C_{15}H_{13}N_3O\ ZnCl_2$
							46.46	3.36	10.89	5.92	18.33	
17	3	–		$2HL^3 \cdot PdCl_2$	Green	300	57.52	4.60	11.76	14.86	10.10	$C_{36}H_{32}N_6O_2PdCl_2$
							57.01	4.22	11.09	14.08	9.37	
18	3	–		$2HL^3 \cdot SnCl4$	Red	230dec.	49.35	3.26	11.52	15.01	18.84	$C_{30}H_{26}N_6O_2SnCl_4$
							47.20	3.41	11.01	15.56	18.62	
19	3	–		$HL^3 \cdot TiCl_4$	Brown	240dec.	41.13	3.01	10.10	11.86	32.02	$C_{15}H_{13}N_3OTiCl_4$
							40.82	2.95	9.53	10.86	32.21	
20	1	O	NTs	ZnL^1_2	White	>336	60.40	3.64	7.17	8.50		$C_{40}H_{30}N_4O_6S_2Zn$
							60.64	3.79	7.07	8.26		
21	1	O	NTs	$CdL^1_2 \cdot H_2O$	Pink	>250	54.62	3.48	6.80	12.40		$C_{40}H_{32}N_4O_7S_2Cd$
							56.04	3.73	6.54	13.12		
22	2	R = CH_3		$ZnL^2 \cdot CH_3CO_2$	Yellow	>280	54.12	5.45	10.88	17.42		$C_{17}H_{13}N_3O_3Zn$
							54.78	3.49	11.28	17.56		

* f: found, ca: calculated.

The absorption, fluorescence and fluorescence-excitation electronic spectra of oxyphenylbenzoxazole (1, X = Y = O) in different solvents were studied in [15, 16]. A weak fluorescence (λ_{max} 370 nm) is related to benzenoid form of the molecule; a fluorescence in the visible region (λ_{max} 440 nm) corresponds, according to the opinion of the authors of [15, 16], to the intermediate "anionic" form; a long-wave fluorescence is related to those structures in which a hydrogen atom is transferred and connected covalently with the nitrogen atom (quinonoid form 1b (X = Y = O); in a polar solvent λ_{max} 490 nm, in a non-polar solvent λ_{max} 520 nm). The quinonoid form of **1b** molecules is also possible, when a proton transfer from the nitrogen atom of tosylaminogroup to the nitrogen atom of the heterocycle takes place in the molecules of [2-(2'-tosylaminophenyl)]benzoxazole (X = O, Y = *N*Ts) [17].

The spectral-luminescence characteristics of 2-(o-oxyphenyl)benz-imidazole (1, X = NH, Y = O) obtained in the present research are practically coinciding for the solid phase, and also for the metanol and etanol solutions. It testifies about the π,π*-character of the electronic transfers, which is typical for plane non-polar molecules. The correlation of emission and absorption spectra suggests the existence of free molecules of 2-(o-oxyphenyl)benzimidazole, principally in the benzenoid tautomeric form.

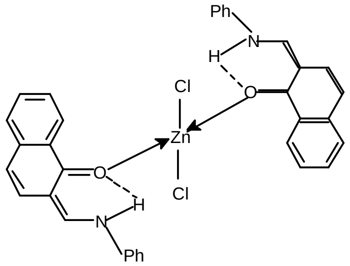
The spectral study of the adducts of [2-(2'-hydroxyphenyl)]benzimidazole with zinc chloride (compound **3**, Table 1) in a toluene solution suggests the existence of both the benzenoid and quinonoid forms of the ligand [15]. This study consists of a comparison of the absorption spectra of the free ligand and of its complex, and also a comparison of the fluorescence-excitation and absorption spectra. When fluorescence is excited in the long-wave emission band (λ_{max} 520 nm), the band l = 380 nm appears in the absorption spectra; this band is absent in the electronic absorption spectra. This fact testifies about the existence in the complex molecule 10 (X = NH, Y = O, M = Zn, n = 2) of the second ligand form (probably, the quinonoid).

Such a spectral behavior is also observed for 2-(2'-tosylaminophenil)benzimidazole 1 (X = NH, Y = NTs) and its complex with zinc dichloride. These results permit to propose the existence of the structure 15, which is similar to 9, in the case of the discussed adducts. The latter structure is confirmed by X-ray diffraction for the *Schiff* base of 2-hydroxynaphthoic aldehyde and aniline with $ZnCl_2$ 18[9].

The ligands of the type 2 behave similarly in the reactions of adduct formation.

Taking into account the data of [10, 11, 13] and the high donor activity of the N-atom of pyridine type of benzimidazole cycle [3], the adducts of the type **11** can have one of the following structures with an entirely conserved ligand system.

According to the literature data [5], a strong inner-molecular bond (ν(OH) = 2800-2500 cm^{-1}) exists in the ligand system 2. There is a delocalization of the electrons through six-member quasiaromatic cycle of H-bond here. Such a situation, evidently, leads to the structure **2a** and to a small content of the possible quinonoid tautomer **2b** in the ligand in its basic state.



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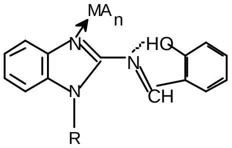

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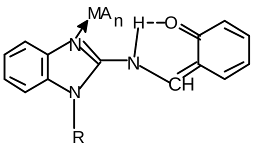

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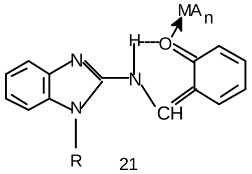

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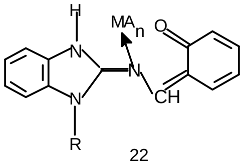

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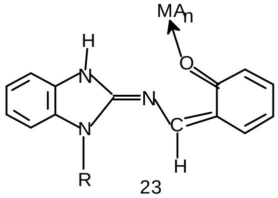


23

However, infrared spectra show that the proposition of the quinonoid form **2b** increases in the type 2 molecular complexes. This is indicated by the appearence of intense absorption bands in the regions of 1650-1675 cm^{-1} (1617 cm^{-1} in the ligand) and 3200-3300 cm^{-1} (these bands are related to the absorption of ν(N-H), participating in the formation of the H-bond).

In order to determine the influence of the coordination of MCl_n on the electronic-tautomeric properties of salicylal-1-methyl-2-aminobenzimidazole 2 (R = CH_3), the electronic absorption and fluorescence spectra of the ligand 2 and its molecular and chelate complexes with Zn^{2+} (compounds **6** and **7**, Table 1) have been obtained and compared. An absorption band with a maximum at λ_1 380 nm and a broad shoulder (bs) at λ_2 330 nm is observed in the electronic absorption spectra of the studied ligand in toluene. A well-defined band with the maximum at λ_1 375 nm and the bs at λ_2 333 nm is observed for methanol solution.

The electronic spectra of the adduct of the ligand 2 (R = CH_3) with zinc chloride (compound **7**, Table 1) in toluene and methanol practically coincide with the absorption bands of the ligand. The fluorescence spectrum of this compound in toluene has a maximum in λ 520 nm and the corresponding maxima at λ_2 350 nm and the peak at λ_1 380 nm (bs) in the excitation spectra, which are in agreement with the corresponding absorption spectra. The band at λ_1 380 nm could be related with the absorption of the quinonoid structure, while the band at λ_2 350 nm could be attributed to the benzenoid one. On the basis of the ratio of optical densities observed in the absorption spectra, it is possible to suppose that the quinonoid form of molecule **2** predominates in the toluene solution (~ 60:40%). In the luminescence spectrum of the adduct $2HL^2 \cdot ZnCl_2$ (compound 7, Table 1), dissolved in methanol, an emission band is observed with a maximum at λ 470 nm and a bs at λ 520 nm, as well as a corresponding maximum at λ 360 nm in the excitation spectra.

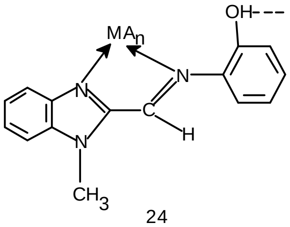
In the electronic absorption spectrum of zinc chelate (compound **22**, Table 1), a well defined absorption band is observed with a maximum in the region of λ_2 330-350 nm and a longer wave band in the region of λ_1 370 nm (which could be attributed to quinonoid form of complex). A maximum at λ 420 nm and a bs at λ 490 nm are observed in the emission spectrum, as well as the corresponding maximum at λ 330 nm in the excitation spectrum. The long wave emission band could be related to the deactivation of the quinonoid structure of molecules of inner-complex compounds; however, its contribution is very small as compared to that of the quinonoid structure (< 5%).

The band at λ_2 287 nm predominates in the absorption spectra of the solution of this complex (the compound **22**, Table 1) in methanol; an absorption of small intensity with a maximum at λ_1 350 nm is also observed. However, the band λ_1 could not be attributed to the suggested quinonoid structure of the complex.

Conclusions

On the basis of the spectral-luminescence study, it is possible to propose that salicylal-1-methyl-2-aminobenzimidazole **2** (R = CH_3) has a benzenoid structure **2a** in its basic state. As a result of the complex formation, the part of the quinonoid form **2b** increases, specially in the case of the adducts of the type 11. However, it is difficult to select the right structure among the formulae **19**-**23**: up to now, it has not been possible to obtain the necessary X-ray diffraction data as a consequence of the unsuccessful attempts to obtain monocrystals of the adducts **11** (compounds **7-10**, **12**, **13**, Table 1).

A comparative study of IR spectra of the azomethine **3** (compound **14**, Table 1) and its complexes in the regions of 1500-1700 cm^{-o} (valence oscillations of the C = N bond and the azole cycle) and 2800-3500 cm^{-1} {ν(OH)} shows that IR spectral behavior of valence oscillations of the bond C = N of the azomethines 2 with six-member cycle of the hydrogen bond and that of the azomethine 3 with five-member H-cycle is different in the processes of complex formation. An increase of ν(C = N) is observed for the complexes of azomethines **2** with metal halides, while in the case of complexes of the azomethine **3** this frequency decreases. It is then possible to suggest that a structure **24**, containing a X_nMN_2 metal-cycle fragment, exists in the adducts of the ligands of the type **3**.



24

The observed frequency 1590-1600 cm^{-1} is probably a result of the frequency decrease of valence oscillations of the azomethinic bond and of the frequency increase of the azole cycle. In the spectra of the molecular complexes with the ligand **3** a wide band is observed in the 3200-3300 cm^{-1} region, which can be attributed to the oscillations of the molecularly-connected OH-group of the phenolic fragment.

The reported data testify that, on the basis of the typical chelate-forming ligands 2[2’-hydroxy(2’-*N*-tosylamino)phenyl]- and 2-hydroxyazomethines of the benzazole series, both standard metal chelates and adducts could be obtained. The completely conserved ligand systems (LH) (evidently, coordinated in the quinonoid tautomeric forms) are present in the adducts of these ligands.

Experimental part

The elemental analyses have been carried out in the equipment Perkin-Elmer Model 2400 II. The electronic absorption spectra have been registered in spectrophotometer SPECORD M-40. Purified toluene and methanol have been used as solvents. The concentration of the solutions was 10^{-3}-10^{-5} mol/L; quartz cells with 10 mm thickness were used. The luminescence spectra and luminescence-excitation spectra were registered in the equipment “FOTOLUM” (made in the Russian Academy of Medical Sciences). In the case of the solid phase spectra, the powders of the compounds were located between two parallel plane quartz sheets.

Synthesis of the ligands. 2-(2’-hydroxyphenyl)benzimidazole **1** (X = NH, Y = O) and 2-(2’-hydroxyphenyl)benzoxazole **1** (X = Y = O) (Aldrich) have been recristallized from ethanol to be used as ligands.

2-(2’-Tosylaminophenyl)benzimidazole **1** (X = NH, Y = NTs) and 2-(2’-tosylaminophenyl)-benzoxazole **1** (X = O, Y = NTs) have been synthesized according to the methods described in [12, 18].

The azomethines **2** and **3** have been obtained by the methods reported in [3-5].

Synthesis of the metal complexes. The adducts of tin and titanium tetrahalides have been obtained by mixing the solutions of the ligands **1**, **2**, **3** in absolute benzene and the metal halides in the molar ratio 2:1 at room temperature. In the case of $ZnCl_2$ and $CdCl_2$, their methanol solutions have been used.

Example. To synthesize the complex 10, 0.190 g (0.001 mol) of $TiCl_4$ in 10 mL of absolute benzene was added to the solution of HL^2 (0.502 g, 0.002 mol) of salicylal-1-methyl-2-aminobenzimidazole in 50 mL of absolute benzene in a dry box with air atmosphere at room temperature. After two hours the solid was filtered, washed 3 times using 5 mL of absolute benzene and dried in vacuum.

The adducts of $PdCl_2$ have been synthesized by ligand-exchange reaction between the benzonitrile complex of palladium dichloride $PdCl_2(C_6H_5CN)_2$ and the corresponding ligand in absolute benzene at room temperature.

Example. To synthesize the complex **1**, a solution of 0.383 g (0.001 mol) of a benzonitrile complex of palladium dichloride in 20 mL of absolute benzene was added with agitation to the solution of 2-(2'-hydroxyphenyl)benzoxazole (HL^1) (0.422 g, 0.002 mol) in 50 mL of absolute benzene at room temperature. After 2 hours the solid was filtered, washed 3 times using 5 mL of absolute benzene and dried in vacuum.

The zinc, cadmium, and palladium chelates of the ligands 1,2,3 have been obtained by boiling methanol solutions of the ligands and the acetates of the corresponding metals in the molar ratio "metal-ligand" 2:1 (palladium acetate was dissolved in methanol).

Example. To obtain the compound **20**, a solution of 0.219 g (0.001 mol) of the zinc acetate dihydrate in 10 mL of methanol was added with agitation to the solution of 2-(2-tosylaminophenyl)benzoxazole (HL^1, X = O, Y = NTs) (0.278 g, 0.002 mol) in 50 mL of methanol. This mixture was heated in a water bath during 1 hour. The formed solid was filtered, washed 3 times using 5 mL of methanol and dried in vacuum.

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