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ARYL AND 1,3-DIOXOINDANYL DERIVATIVES OF AZOLES AND AZINES (REVIEW)*

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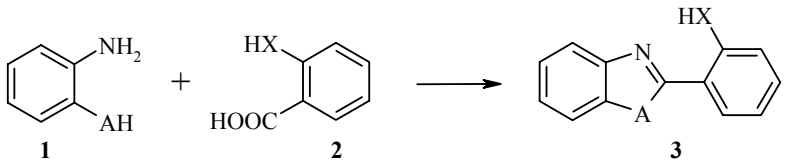
Data on the synthesis, tautomerism, complexing characteristics, and luminescence of 2-(2′-amino-, hydroxy-, hydrochalcogenophenyl)azoles, azines, and hetarylindanediones are reviewed.

Keywords: 2-(2′-amino-, hydroxy-, mercapto-, tosylaminophenyl)azoles, azines, hetarylindanediones, luminescence, metal complexes, synthesis, tautomerism.

This review is devoted to the recent chemistry of five- and six-membered nitrogen-containing heterocycles containing 2-amino-, 2-hydroxy-, and 2-hydrochalcogenophenyl and indanedione (thione) fragments. These compounds are of fundamental importance during the investigation of fundamental problems in the chemistry of heterocyclic compounds – synthesis, tautomerism in heteroaromatic systems [1-4], their complexing characteristics [5], and their valuable properties [6-8].

1. SYNTHESIS

The general method for the synthesis of five-membered nitrogen-containing heterocycles is based on the condensation of the respective phenols **1** with of benzoic acid derivatives **2**, leading to compounds **3** [9-11].



1 **2** **3**

A = NH, O, S; X = N, O

The 2-(2′-tosylaminophenyl)benzazoles **5** were obtained in the reaction of 2-(2′-aminophenyl)benzazoles **3** with *p*-toluenesulfonyl chloride **4** [12, 13].

* In memory of V. P. Litvinov

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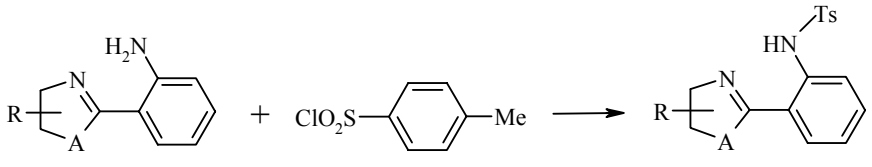
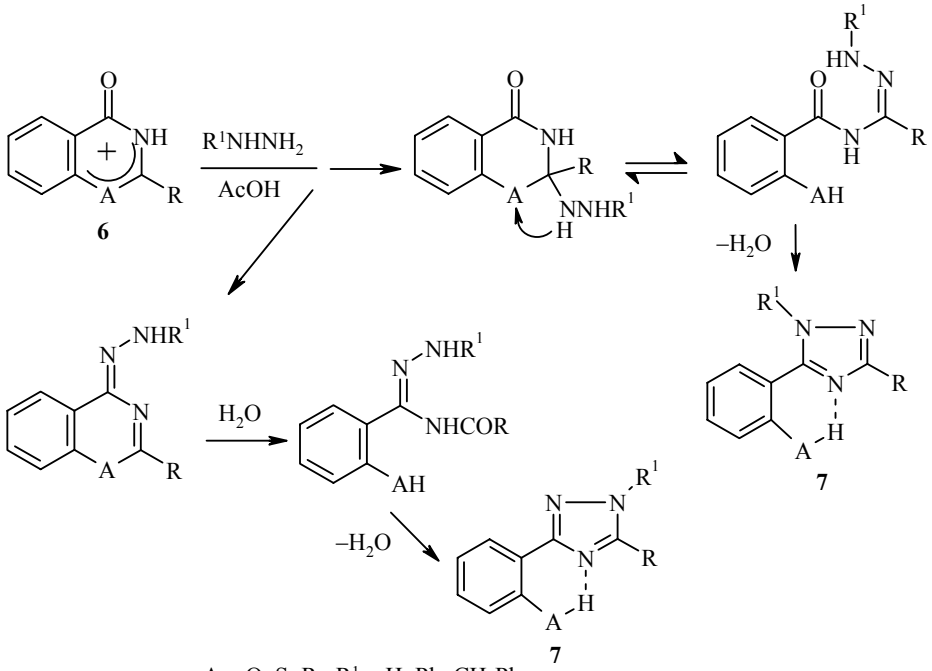


3 **4** **5**

R = H, 4,5-CH=CH–CH=CH–

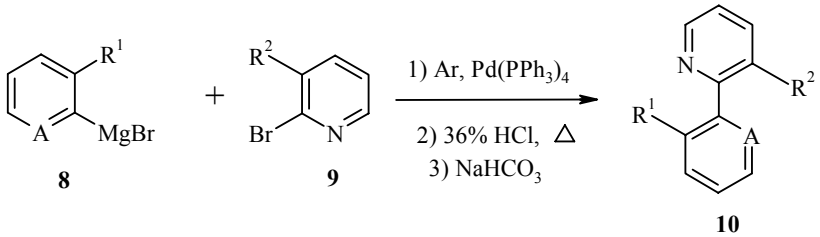
As shown in [14-20], recyclization of benzoxazinium and benzothiazonium salts **6** by the action of hydrazine leads to *o*-hydroxy- and *o*-mercaptophenyl-1H-1,2,4-triazoles **7**.



6 **7** **7**

A = O, S; R, R^1 = H, Ph, CH_2Ph

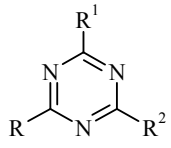
The mono- and dihydroxy derivatives of pyridine **10** can be obtained by using Grignard reagents **8** and derivatives **9** [21-23].



8 **9** **10**

8, **9** R^1, R^2 = H, OMe; A = CH, N; **10** R^1, R^2 = H, OH

Using the method for the production of compound **7**, the authors of [17, 19, 24-26] developed a preparative method for the production of 2-amino-, methylamino-4-(*o*-hydroxyaryl)-, and alkylthiotriazines **11**. Recyclization of *o*-hydroxyphenylbenzoxazinonium perchlorate leads to the 4,6-di-*o*-hydroxyphenyl analogs [27, 28]. Substituted imidazo[1,5-*a*]pyridines (imidazoles, isoquinolines) **13** were obtained as a result of catalytic oxidation of the derivatives **12** [29].



R = H, Me, Et, Pr, OMe, *o*-C_6H_4OH; R^1 = SMe, NH_2, NHMe, *o*-C_6H_4OH; R^2 = NMe_2, OMe, *o*-C_6H_4OH

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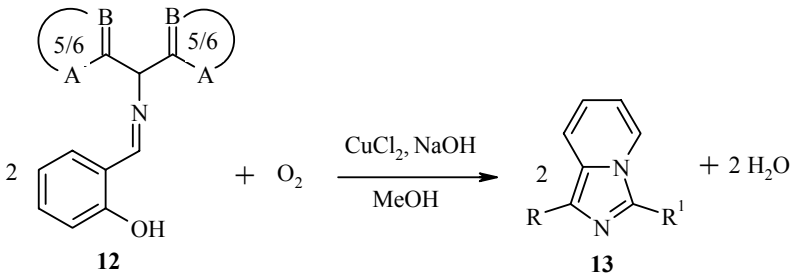
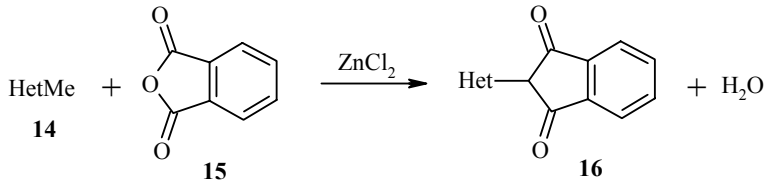


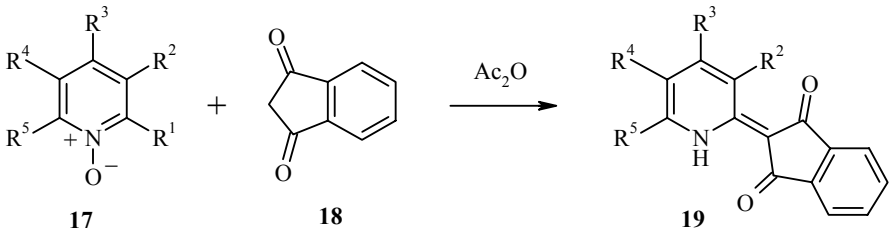
12 A = N, B = CH, N; **13** R = pyridyl, imidazolyl, R^1 = *o*-C_6H_4OH

The 2-(2′-hetaryl)-1,3-indanediones **16** were synthesized by fusing the 2-methyl derivatives of benzimidazole, benzothiazole, and perimidine **14** with phthalic anhydride **15** [30-34].



14 **15** **16**

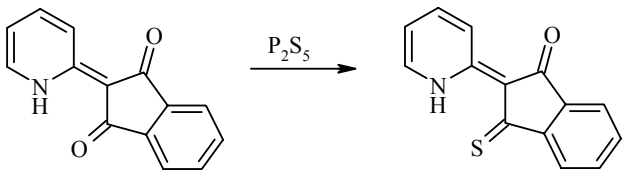
A more convenient method for the synthesis of 2-(2′-pyridyl)-1,3-indanediones **19** was developed by reacting the N-oxides of pyridine derivatives **17** with indanedione **18** in acetic anhydride [34].



17 **18** **19**

a $R^1 = R^2 = R^3 = R^4 = R^5$ = H; **b** $R^1 = R^3 = R^4 = R^5$ = H, R^2 = Me; **c** $R^1 = R^2 = R^4 = R^5$ = H, R^3 = Me; **d** $R^1 = R^2 = R^3 = R^5$ = H, R^4 = Me; **e** $R^1 = R^2 = R^3 = R^4$ = H, R^5 = Me

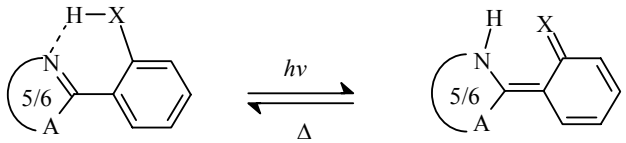
The reaction of 2-(2′ pyridyl)-1,3-indanedione (**19**) with P_2S_5 leads to the monothio-substituted product (**20**) [35].



19 **20**

2. TAUTOMERISM AND THE H-BOND

For five- and six-membered nitrogen-containing heterocycles containing 2-amino(hydroxy-, mercapto-, tosylamino)phenyl substituents the formation of two tautomeric forms is possible [1-3, 36-58].

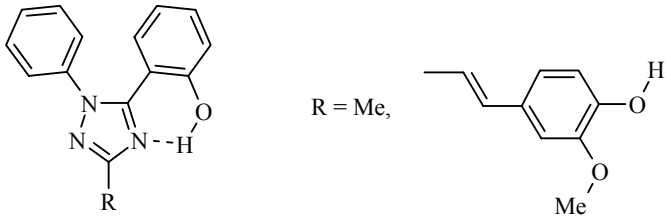


3, **5**, **10** **3'**, **5'**, **10'**

A = CH, NH, O, S; X = NH, OH, NTs

The effect of various solvents on the displacement of the tautomeric equilibrium and the stabilization of the tautomeric forms was studied. Thus, for 2-(2'-hydroxyphenyl)benzimidazole it was shown that the enolic forms **3**, **5**, and **10** are formed exclusively in nonpolar and low-polarity solvents. In protic and polar solvents the keto form is stabilized [41, 59]. The presence of the amine and enol forms in the case of 2-(2'-tosylaminophenyl)benzimidazole [60] and 3-(3'-methoxy-2'-hydroxyphenyl)benzimidazole [61] was proved by X-ray crystallographic analysis.

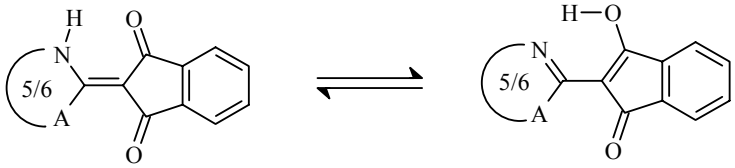
In [62, 63] the effect of intermolecular contacts on the strength of the O–H···N bond in crystals of the hydroxy derivatives of azoles and azines was examined in detail in so far as the strength of the H-bonds is determined by the nature of the proton donor and acceptor and also by the presence of intermolecular hydrogen bonds. Thus, the characteristics of the O–H···N interactions in the molecule of **21**, in which the nitrogen atom is in the triazole heterocycle, were studied in the investigations in [62, 63].



21

The energy of the intramolecular O─H···N bond in these systems as a function of the angle of rotation of the hydroxyl substituent and the effect of the concurrent intermolecular interactions on its strength were assessed on the basis of X-ray diffraction [62, 63].

In contrast to the 2-(2'-hydroxyphenyl)benzazoles and azines, the diketone form is stabilized in the 2-(2-hetaryl)indan-1,3-diones **16** and **19** [34, 64].

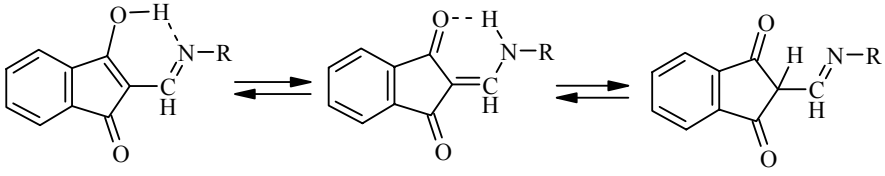


16, **19** **16', 19'**

A = CH, NR, S; R = Me, Bu, Oct

This tautomeric form is confirmed by the data from IR and ^{1}H and ^{13}C NMR spectroscopy, X-ray crystallographic analysis [35, 64], and quantum-chemical calculations by the nonempirical RHF SCF method in the 6-31 G** basis set [65]. Investigation of compound **19** by IR and ^{1}H NMR spectroscopy showed that the solution (in $CDCl_3$) contains the NH form [64].

The 2-N-aryl- and 2-N-alkylaminomethylene derivatives of indane-1,3-dione **22**, which are acyclic analogs of hetarylindanediones, can exist in three tautomeric forms [66, 67].



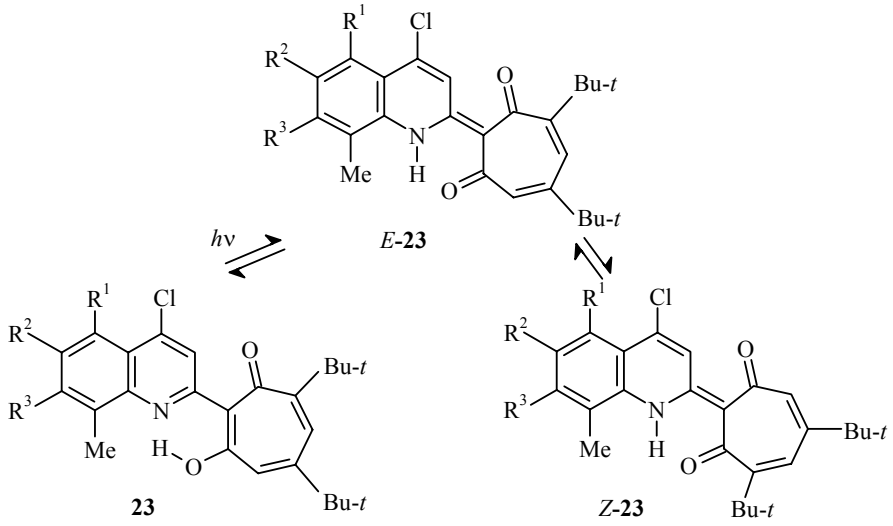
22a **22b** **22c**

R = Alk, Ar

It was demonstrated that compounds **22** exist exclusively in the ketoenamine form **22b** in solution, irrespective of the external conditions (the temperature of the solution, the nature of the solvent) and structural factors [66, 67].

Like their benzazole analogs 2-(2′-hydroxyaryl)pyridines exist predominantly in the enolic form [4]. The presence of an intramolecular hydrogen bond between the proton of the hydroxyl group and the nitrogen atom of the pyridine was detected by NMR spectroscopy and X-ray crystallography, and the dependence of its characteristics on the structural features of the pyridines **10** (A = CH, R^2 = OH) was investigated [22, 68-71].

An O–H···N intramolecular hydrogen bond was also found in the case of quinoline-2-yl-β-tropolones **23**. The photolysis of solutions of **23** in hexane is accompanied by proton phototransfer O–H···N → O···H–N followed by disrotatory electrocyclic rearrangement [72, 73].



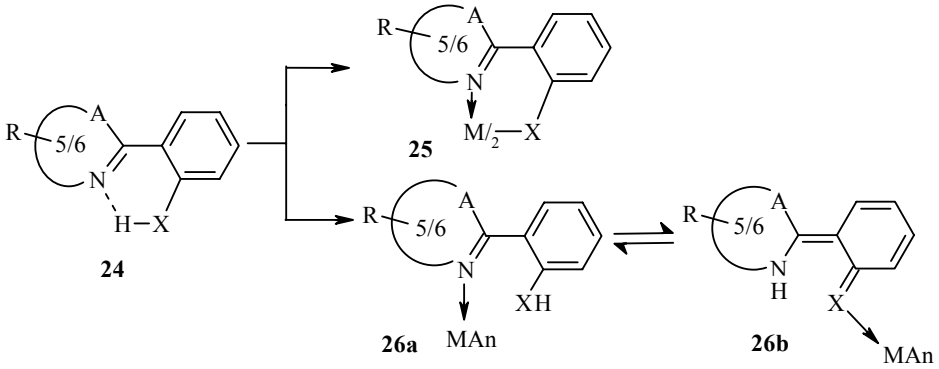
E-**23** **23** *Z*-**23**

a $R^1 = R^2 = R^3$ = H, **b** $R^1 = R^2$ = H, R^3 =Me, **c** $R^1 = R^3$ = H, R^2 =Me,
d $R^1 = NO_2$, R^2 = H, R^3 = Me, **e** $R^1 = NO_2$, R^2 = Me, R^3 = H

The authors of [72, 73] showed that the position of the tautomeric equilibrium depends on the nature of the substituent in the quinoline fragment. Thus, a donating substituent stabilizes the diketone form *E*-**23** while an accepting substituent stabilizes the enolic tautomeric form **23**.

3. METAL COMPLEX COMPOUNDS

2-Tosylamino(hydroxy)phenylazoles(azines) and their derivatives **24** form two types of metal complexes in reaction with metal salts, i.e., intramolecular coordination compounds (chelates) **25** and molecular adducts **26** [3, 5, 15, 74, 75].

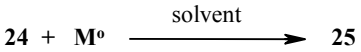


A = NTs, O, S; X = NTs, O, S; R = H, Alk, annulated benzene fragment, annulated naphthalene fragment; An = $MeCOO^-$, Cl^-, NO_3; M = d- metals

Chelate compounds **25** with the acetates of Zn(II), Pd(II) [74, 76], Ni(II), Cd(II) [77], Cu(II), and Co(II) [12, 78] were obtained from 2-(2'-toslyaminophenyl)benzazoles **5**. According to elemental analysis and IR spectroscopy, they have the composition ML_2 and chelate structures [74, 76-78].

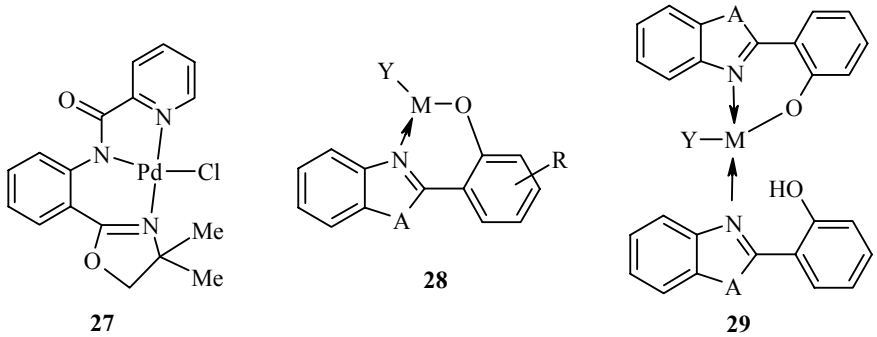
The luminescence-spectral characteristics of the intramolecular coordination compounds of Zn(II) and Cd(II) with 2-(2′-tosylaminophenyl)benzoxazole were obtained. In solutions in methanol and toluene and even in the solid phase both complexes contain the ligand in the keto and enol forms in equilibrium [74].

The chelates of metals with 2-(2′-tosylamino)oxazole were synthesized both by the usual method (by reaction of the ligand and the metal acetate) and by an electrochemical method involving anodic dissolution of the metals in a zero degree of oxidation [5, 75]. The structure of the Co(II) complex was proved by X-ray crystallographic analysis [78].



The complex **27** with a nonstandard 2-aminophenyl-substituted oxazoline was synthesized and structurally identified [79].

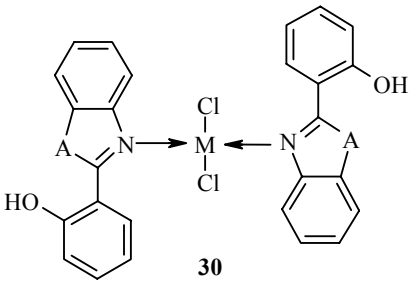
For 2-(2′-hydroxyphenyl)benzazole it was established that not only complexes **25** and **26** but also the complexes **28** and **29** retaining the anions are formed [77, 80-85].



28 R = NH_2, *t*-Bu, OMe, Br; Y = MeCOO, M = Cu, Ni, Co, Cd, Zn;
29 A = NR, O, S; R = H, Alk; Y = NO_3, M = Ni, Cd

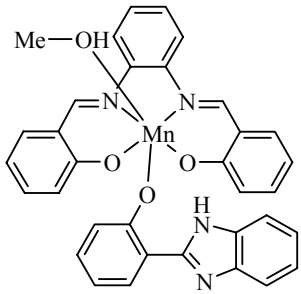
In the structurally characterized molecular complex of 2-(2′-hydroxyphenyl)benzazole **30** with N-coordination of the metal the enolic tautomeric form of the ligand is retained [3, 86].

The complex **31**, in which the deprotonated 2-hydroxyphenylbenzimidazole ligand performs a monodentate function and not the usual chelate function, as in the case of **25**, was synthesized [87, 88].



30

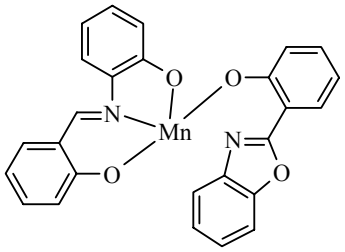
A = NH, O; M = Pd, Pt



31

The two modes of coordination of the ligands mentioned for complexes **25** and **31** are also characteristic of the benzoxazole complex **32** [89].

An extremely unexpected coordination of the ligand system is observed in the complex **33**. According to data from X-ray crystallographic analysis, the enolic form of the ligand is retained during coordination of 2-(2′-hydroxyphenyl)benzimidazole with Mo, and the metal substitutes the hydrogen atom at the endocyclic nitrogen atom and not the exocyclic phenolic proton [3].



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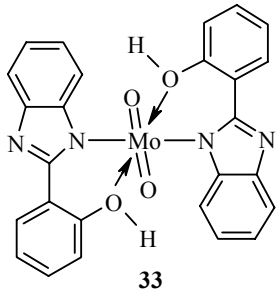
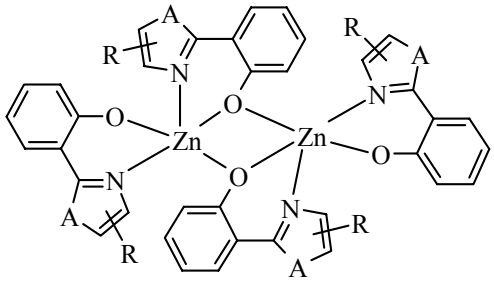


33

A complex with the composition Fe(OPBT)Cl [OPBT is the (2-hydroxyphenyl)benzothiazole residue] was obtained in the reaction of $FeCl_3$ with 2-(2′-hydroxyphenyl)benzothiazole. It was shown that an intramolecular coordination compound of type **25** is a monomer and has a distorted tetragonal or rhombic structure. In the case of coordination with $Fe(ClO_4)_3 \cdot 9H_2O$ a complex with the composition $[Fe(OPBT)_2]_2O$, the stable form of which is a dimer with an oxo bridging group, is formed [90].

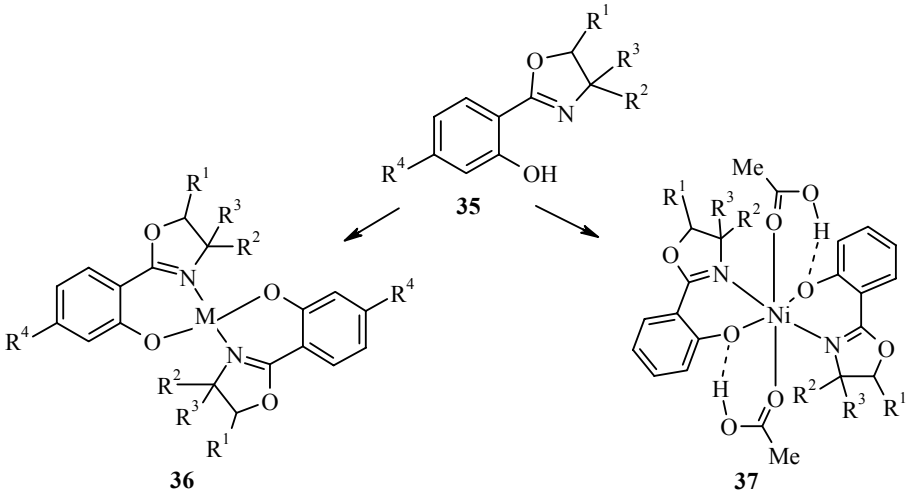
The complexes of metals with 2-(2′-hydroxyphenyl)oxazole and their functional derivatives were synthesized and studied [89, 91-94]. In the case of *o*-hydroxyphenyloxazole it was shown that the Zn complex can exist in the dimeric form **34** and also as a 2D-coordinated polymer [95].



34

A = O, S; R = H, 4,5-$(CH{=}CH)_2$

The chelates **36** and **37** were synthesized on the basis of the derivatives of 2-hydroxyphenyloxazolines **35** and were structurally identified [96, 97].

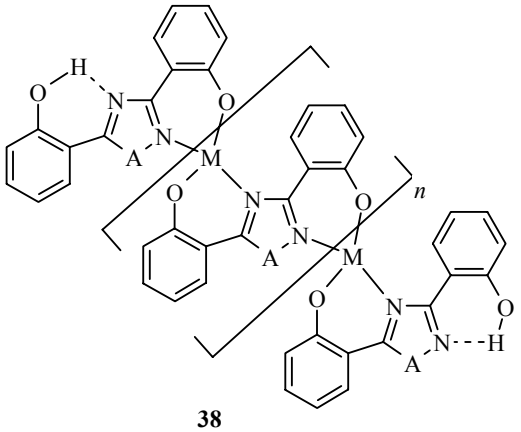


35

36 **37**

R^1 = H, Ph, R^2 = H, Ph, Me, R^3 = Me, R^4 = H, Bu-*t*; M = Zn, Ni, Co, Cu, Mn

A series of polymeric chelate compounds **38** were obtained (98-101). Thus, a polymeric complex $LH(ML)_nM{\cdot}LH$ (n = 1, 2, … ∞) is formed in the case of the coordination of transition metals with di-(*o*-hydroxyphenyl)-1,2,4-oxadiazole and -1,2,4-triazole [100].

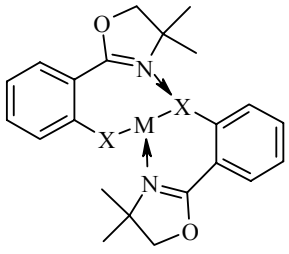


38

A = O, NH, NPh; M = Cu, Co, Ni

2-(2′-Hydroxyphenyl)pyridine and its functional derivatives form structurally identified chelates with Zn, Co, Cu [102, 103], Ni, Cd, Cr, Mn [103-108], and Pd [105].

Only a few complexes based on the analogous 2-phenylthio [109], phenylseleno [110], and phenyltelluro [111] derivatives **39** are known.

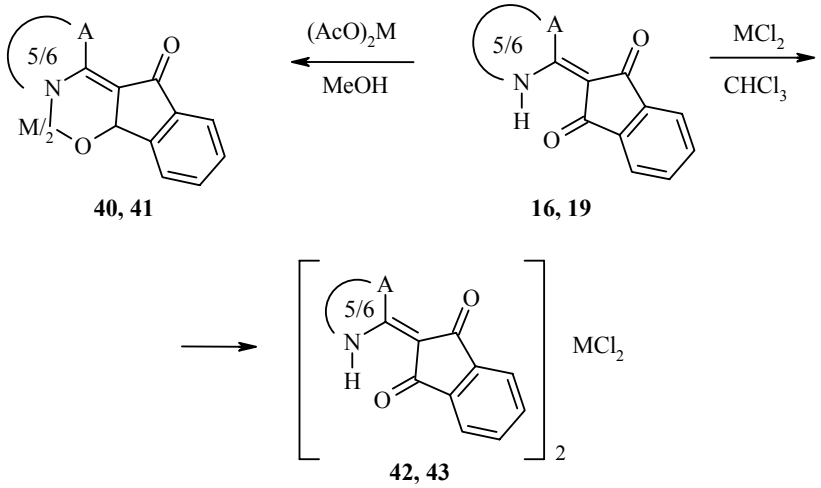


39

X = S, Se, Te; M = Zn, Cd

Depending on the conditions of synthesis [5, 75] and on the metal salts employed, the ligands **16** and **19**, like **24**, form two types of complexes: Chelates **40** and **41** (composition ML_2) and molecular complexes **42** and **43** $[(HL)_2 \cdot MCl_2]$.

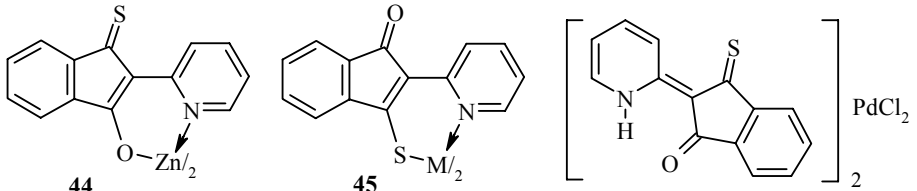
The IR spectra of the complexes make it possible to assume that both types of coordination compounds are formed [34, 64].



40, **41** M = Zn, Ni, Co, Cu, Cd, Pd; **42**, **43** M = Zn, Pd;
40–**43** A = CH, NR, S; R = Me, Bu, C_8H_{17}

Direct evidence for the formation of chelate structures **40** and **41** was obtained on the basis of the data from X-ray crystallographic analysis of the zinc complex of 2-(2-pyridyl)indane-1,3-dione **41** (A = CH, M = Zn) [64].

It was shown that, according to the principle of hard and soft acids and bases [3, 112, 113], the presence of the two coordination centers (the hard oxygen atom and the soft sulfur atom) in the ligating molecule **20** favors a different method of metal bonding. Thus, a hard acid (the Zn cation) is coordinated at the hard oxygen atom in **44**, whereas soft (Hg^{2+} and Pd^{2+}) and intermediate (Ni^{2+}) acids are linked to the sulfur in **45** and **46**, as demonstrated by the data from IR and EXAFS spectroscopy and also by quantum-chemical calculations [34].



44 **45** **46**

M = Ni, Hg, Pd

4. LUMINESCENT CHARACTERISTICS

Investigation of the luminescent characteristics of organic and coordination compounds is one of the central problems of modern chemistry [6, 7].

Thus, the authors of [13, 114] studied the fluorescence with an anomalously large Stokes shift emitted during the transfer of a proton from the nitrogen of the tosylamino group to the nitrogen of the azole fragment in compound **5**.

There are data on the hypsochromic shift of the absorption bands of the long-wave maximum [74, 114], due probably to decrease in the strength of the intramolecular hydrogen bond in the tosylamino derivatives **5**. This effect is explained by increase in the distance between the nitrogen atoms –N···H–N in comparison with the –N···H–O distances and also by the difference in the strength of the electron-donating characteristics of the hydroxy and tosylamino groups that determine the ease of intramolecular proton transfer.

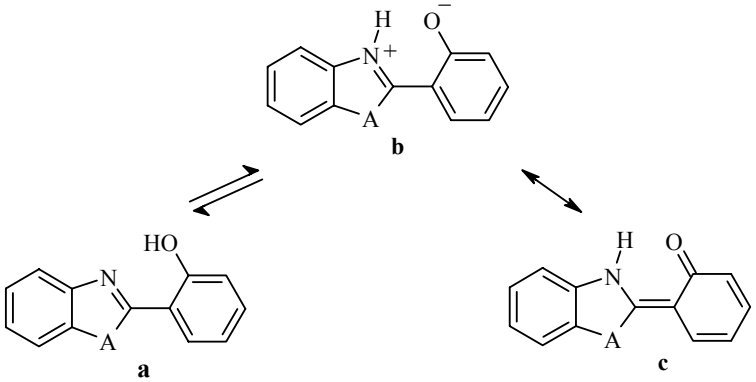
The absorption and fluorescence spectra of 2-(2′-aminophenyl)benzothiazole **3** (A = S) were investigated in various solvents and at various concentrations [115].

The UV and fluorescence spectra and also the low pK_a value are determined by the intramolecular hydrogen bond in the singlet ground state. The very small fluorescence quantum yield with a small Stokes shift in nonpolar solvents indicates the absence of fluorescence in the phototautomer. This is proved by the increase of the quantum yield in protic solvents [115].

Derivatives of benzazoles absorb in the region of 300-400 nm and fluoresce strongly in solutions (T = 293 K) in the region of 320-450 nm. The fluorescence is characterized by a normal Stokes shift and by the presence of several bands for vibrational structure. Vibrational analysis of the quasi-line luminescence spectra shows that the same vibrations exhibit activity in the $T_1 \rightarrow S_0$ transition (to which phosphorescence is attributed) as in the $S_1 \rightarrow S_0$ transition determining the fluorescence [114].

A characteristic feature of 2-(2′-hydroxyphenyl)benzazoles is the presence of fluorescence in the UV region (370-380 nm) with an anomalously large Stokes shift (10 000 cm^{-1}) in solutions in polar and nonpolar solvents and in the crystalline state. A bathochromic shift of the emission in the visible region is observed in the series of NH, O, and S benzazoles **3** [114].

It was established that the fluorescent form for the crystalline state and for the solutions [114] is not the keto structure **c** but exclusively the bipolar structure **b** with the hydrogen covalently bonded to the nitrogen atom.

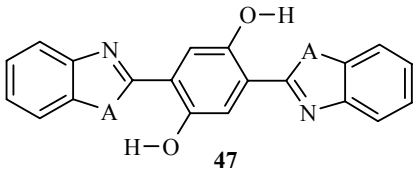


The photoinduced proton transfer processes of 2-(3′-hydroxy-2′-pyridyl)benzimidazole in acetonitrile, ethanol, and water were examined [116].

The absorption, fluorescence, and excitation spectra of 2-(2′-hydroxyphenyl)benzoxazole were investigated in various solvents, and the nature of the fluorescence and phosphorescence bands was established [115, 117-119]. The weak UV fluorescence (λ_{max} = 370 nm) was attributed to the enolic form **a**, whereas the fluorescence in the visible region (λ_{max} = 440 nm) is emitted by the bipolar structure **b**. The fluorescence with anomalous Stokes shift was attributed to structures with a hydrogen atom covalently bonded with the nitrogen atom [in a polar solvent λ_{max} = 490 nm (**b**), in a nonpolar solvent λ_{max} = 520 nm (**c**)] [120, 121].

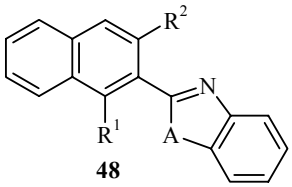
It should be noted that with "doubling" of the molecule in the benzimidazoles **47** an extremely strong bathochromic shift of the luminescence spectra in relation to the spectra of the initial molecules (by 160, 110, and 270 nm for X = S, O, and NH respectively) is observed [120].

The electronic and emission spectra of 2-[1′(2′)-hydroxy-2′(3′)-naphthyl]benzazoles **48** were investigated at various temperatures and in solvents with various polarity [122].



47

A = NH, O, S



48

R^1, R^2 = H, OH; A = NH, O

The mechanism of reversible proton transfer in the ground state for 2-(2′-hydroxyphenyl)benzothiazole was studied by fast absorption and two-stage laser excitation [9, 123, 124]. The obtained data indicate that two long-lived phototautomers exist in the ground state.

Most of the chelate compounds of Zn(II) with 2-(2'-hydroxyphenyl)benzazoles (azoles, azines) can be used as OLEDs (organic light-emitting diodes), lasers, transistors, and fluorescent sensors. The chelate compounds can have various molecular structures, both monomeric and polymeric [7, 125, 126].

Zinc 2-(2′-hydroxyphenyl)benzothiazolate is one of the best luminescent materials used in OLEDs. The structure of the complex **34** (A = S) was proved by X-ray crystallographic analysis. The molecule is dimeric and has pentacoordinated geometry [127].

In the absorption spectra of the dimer in methanol at 298 K there is a strong band at λ = 337 nm. The complex has good luminescence, emission (404 nm), and quantum yield (0.28).

The luminescent characteristics of the trinuclear chelate compound of Zn with 2-(2′-hydroxyphenyl)-5-phenyl-1,3-oxazole **49** were investigated [126].

It was shown that the system can exist as two trimeric polymorphous and monomeric structures with different sublimation temperatures. The oligomer produced at 340°C is used as an OLED.

Chelate compounds of Al(III) (**50**) and Be(II) (**51**) based on oxadiazoles, which can be used as OLEDs, have been described [127].

In conclusion of this review we call attention to the fact that the presented data extend the concepts of contemporary chemistry of heterocyclic [128] and coordination [6, 129] compounds together with their use for practical purposes.

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