

Metal complexes from aryl and hetarylazocompounds

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Dedicated to Professor M. Makosza on occasion of his 70th birthday

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Abstract

Significance of the phase transfer catalysis for the synthesis of less accessible aromatic and heterocyclic compounds is emphasized. A series of novel azo compounds containing pyrazole and quinoline fragments has been prepared and employed in the synthesis of 3d-metal coordination compounds with desired types of the coordination site.

Keywords: Phase transfer catalysis, azoligands, metal chelate complexes, synthesis, stereochemistry

Introduction

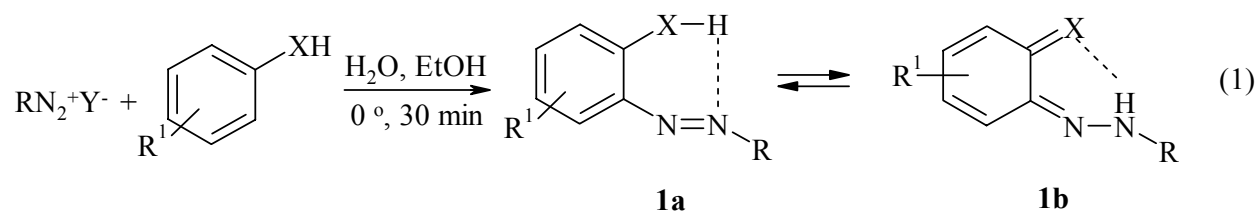
The formulation of the basic principles of phase transfer catalysis advanced by Mieczyslaw Makosza¹⁻³ dates back to the middle of sixties, and the method continues to be one of the powerful tools of the synthetic organic chemistry. In recent years phase transfer catalysis has assumed a new importance in organometallic⁴⁻⁶ and coordination metal chemistry^{7,8}, in particular as a useful approach to the preparation of ligands⁹⁻²⁹. While being employed mostly in the reactions of nucleophiles, the method may be applied also to the transformations occurring with the participation of electrophilic reactants in two- and triphase catalytic systems.^{5,7} An amply studied example of such type transformation is azo coupling reactions affording diverse less accessible aromatic and heterocyclic azo compounds in high (80-85%) yields^{5,30}. Many of these compounds serve as useful ligands in the synthesis of metal coordination compounds. This paper presents a concise review of the structural and preparative aspects of metal coordination compounds with azo-group containing aromatic and heterocyclic ligands.

Results and Discussion

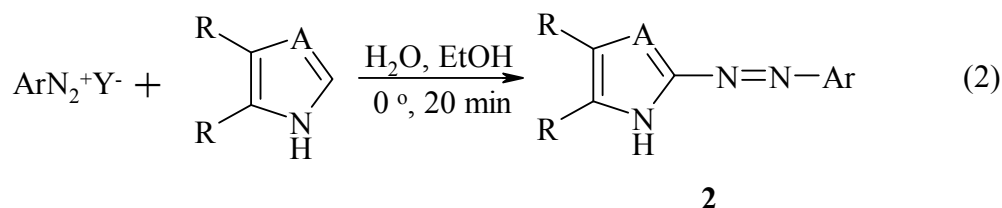
Metal coordination compounds with azo ligands

The chemistry of metal coordination compounds with azo ligands provides an illustrative example of the investigation into a number of key problems of the area, such as fitting the ligand to stereo- and electronic requirements of the metal center, stereo- and regioselective approach to the complexes with the targeted type of the coordination site, stabilization of a certain tautomeric form in the ligand etc.

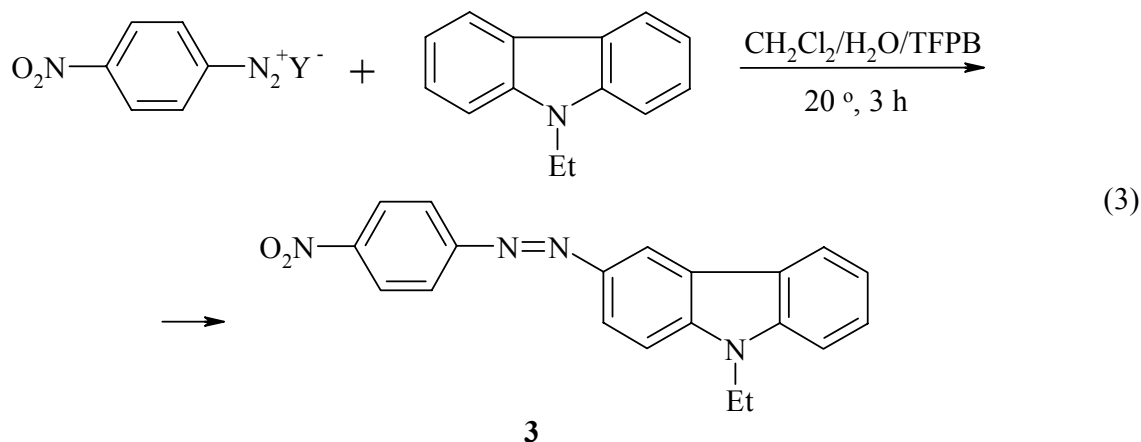
Synthesis of ligands. The reactions (1) and (2) represent two principal azo coupling processes employed for the synthesis of azo ligands of metal coordination compounds³¹⁻³⁴. As usual, these proceed smoothly in homogeneous water or water/alcohol media. A significant advancement of the method has been gained with the use of the CH₂Cl₂/H₂O two-phase system in the presence of catalytic amounts of 3,5-bis(trifluoromethyl)phenyl borate (TFPB) which allows regeneration *in situ* of the azo component of the reaction⁵. This modification of the reaction (1) is particularly convenient when applied to the diazonium salts obtained from nitroanilines characterized by low basicity and poor solubility in water. With carbazole, it gives rise to otherwise inaccessible azoheterocycle **3** (3).³⁵



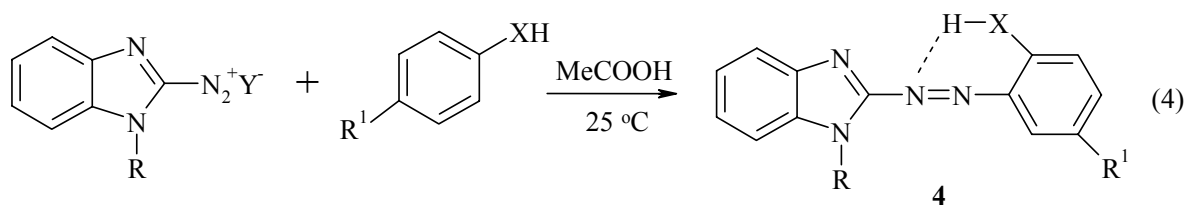
R = Ar, Het; R¹ = H, 5,6-benzo, Hal; X = O, NR²; Y = Hal, BF₄; R² = Alk, Ar



A = CR¹, N; R, R¹ = H, Alk, Ar

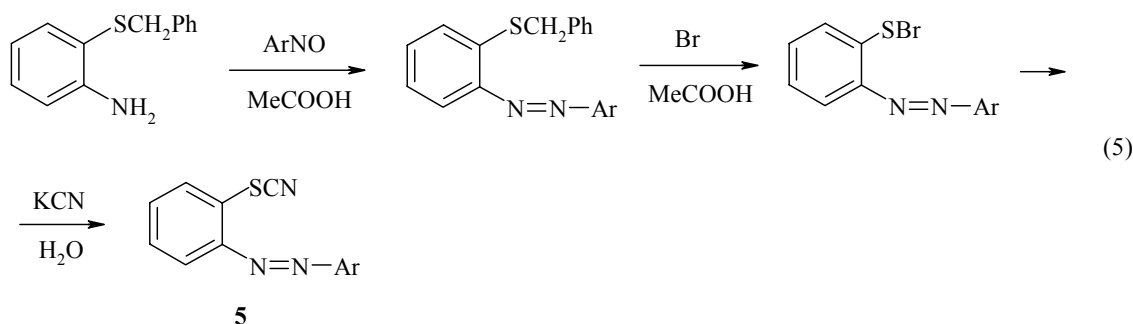


Not only aromatic, but also heterocyclic diazonium salts were used in the synthesis of azo ligands of metal coordination compounds. Thus, a series of azo compounds **4** was obtained based on the diazonium salts prepared from 2-amino-1-alkylbenzimidazoles (4).³⁶

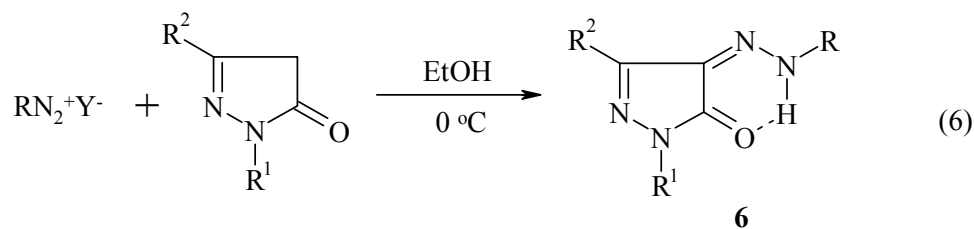


R = Me, n-Oct; R¹ = Me, OMe, C₄H₄; X = O, NAr; Y⁻ = Hal, BF₄

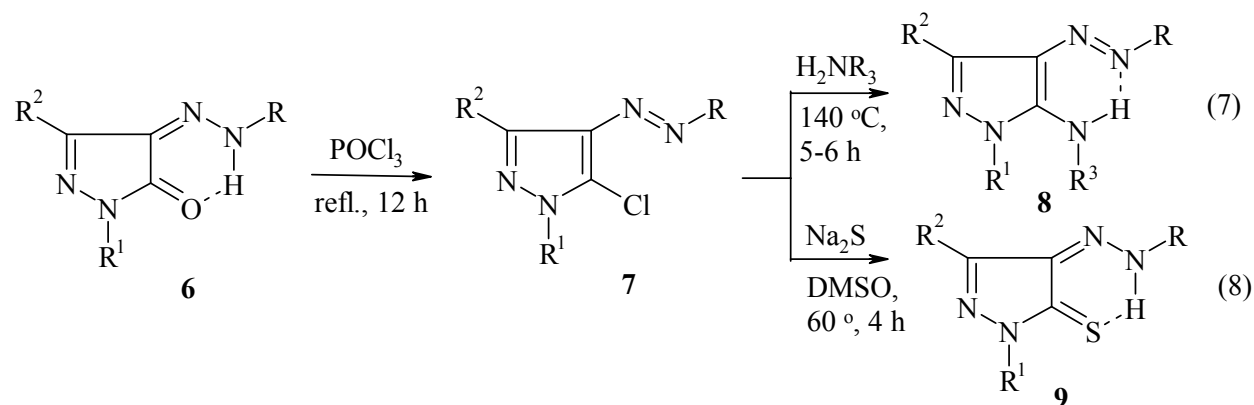
The azo compounds containing a mercapto group in the ring are rather unstable and are readily oxidized in the air. Therefore *o*-thiocyanateazobenzenes **5**^{37, 38} were used as their precursors in the synthesis (5) of the metal chelates with MN₂S₂ coordination sites.^{8, 38, 39}



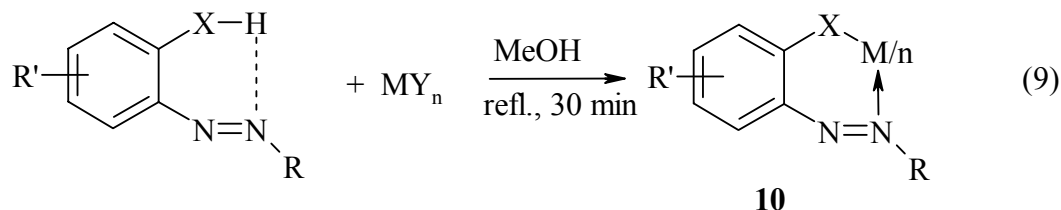
The azo coupling reaction (6) is a widely used method for the preparation of azo derivatives of azol-5-ones, e.g. 4-aryl(hetaryl)pyrazol-5-ones **6**.⁴⁰⁻⁴³ Through treatment of **6** with POCl₃ one can replace the carbonyl oxygen in **6** by a chloro substituent **7** which can be exchanged with a primary amine to form **8** (7)⁴¹ or with a sulfide to give in **9** (8)⁴³⁻⁴⁷.



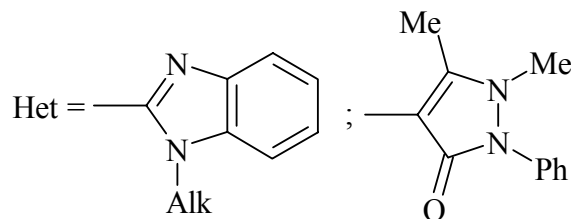
R = Ar, Het; R¹, R² = Alk, Ar



Metal chelate complexes. The bidentate aromatic **1** (R=Aryl)^{8, 48, 49} and heterocyclic **1** (R=1-alkylbenzimidazolyl)⁵⁰⁻⁵³ azo compounds readily form metal chelate complexes upon treatment with metal salts (preferably, acetates) in methanol or ethanol solution (9).

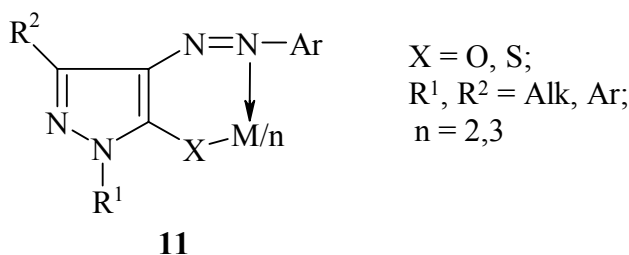


X = NAr, O; R = Ar, Het; R' = H, Alk, OAlk, cyclo-C₄H₄; Y = OAc, NO₃, Hal; M = 3d-metals

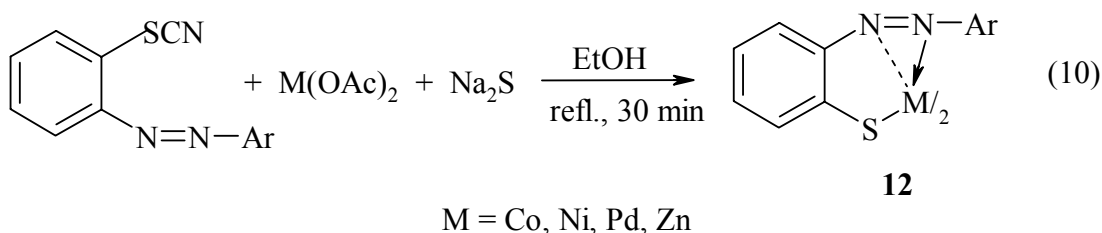


By this method a broad series of metal chelates **11** with azopyrazole ligands **6**, **8**, **9** has been prepared.^{40-43, 54, 55} Complexes **11** (X=S) were also obtained by coupling arylazopyrazolethiones **9** with metal nitrates in 75% dioxan/water solution under nitrogen atmosphere.^{44, 45} Preparation of

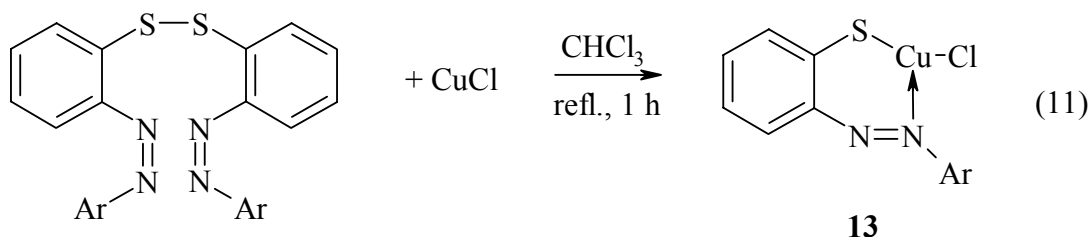
complexes **11** (X=O) may be performed based on zero-valence metals under conditions of the electrochemical gas phase or solid phase (mechanochemical) syntheses.^{8, 56-58}



The method of template synthesis was applied in the preparation of bis-(*o*-thioarylazobezolate) metal complexes **12** from *o*-thiocyanateazobenzenes **5**.^{8, 38, 39, 59}

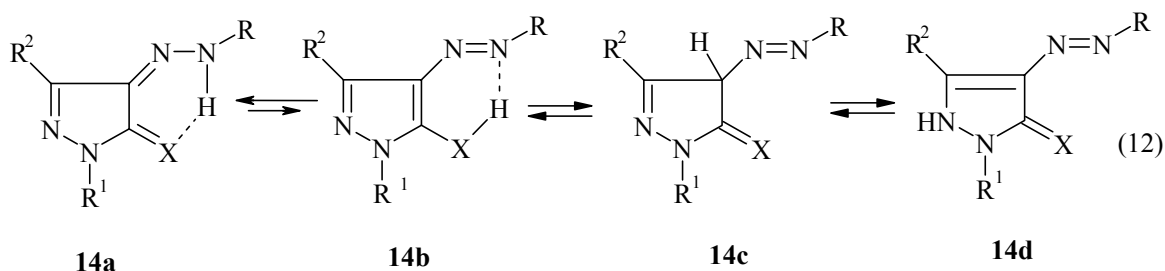


A monochelate Cu(II) complex **13** was obtained from by the redox reaction.⁵⁹

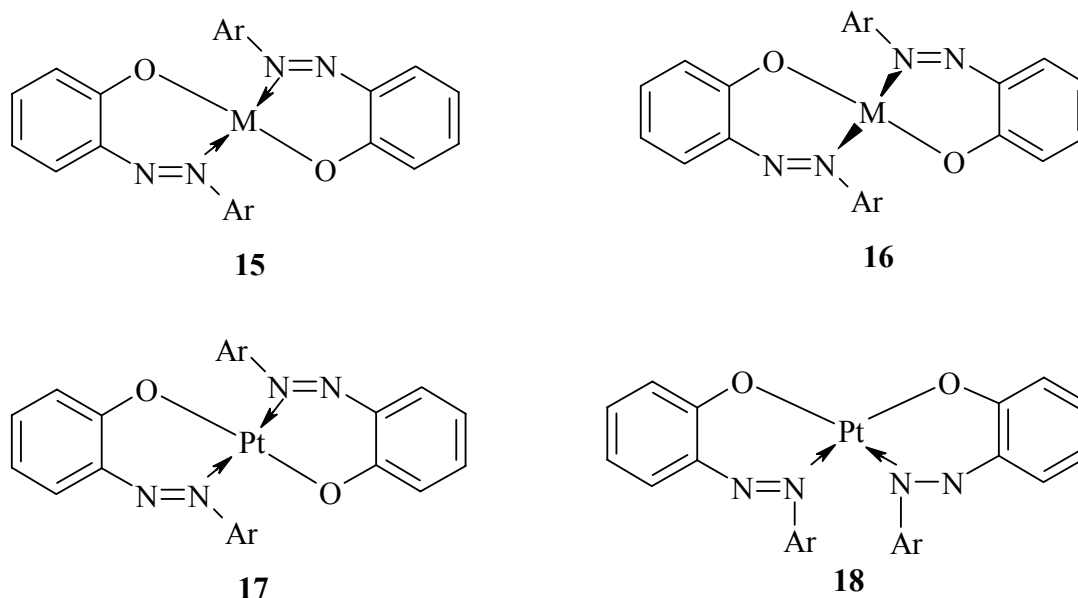


The structure of azo ligands and their metal complexes

Tautomerism. The azohydrazonic tautomerism is the characteristic property of azo compounds **1**, **6**, **8**, **9**.^{22, 31-34, 60, 61} For the *o*-amino- **1** (X=NR) and *o*-hydroxyderivatives **1** (X=O) the equilibrium (1) is shifted to the benzenoid azo forms^{32, 61}. In the case of azoazoles **14**, up to four prototropic isomers may be involved into the tautomeric equilibrium.^{22, 41, 42, 46, 60, 62, 63} As shown by NMR spectroscopy (solutions)^{22, 42, 61, 64} and X-ray structural determinations (solid phase),^{22, 60, 63, 65, 66} the hydrazone **14a** represents energy preferred isomeric forms of most of compounds **14**. For the imino derivatives **14** (X=NR³)⁴¹ the equilibrium (12) is shifted to the aminoazo forms **14b**.

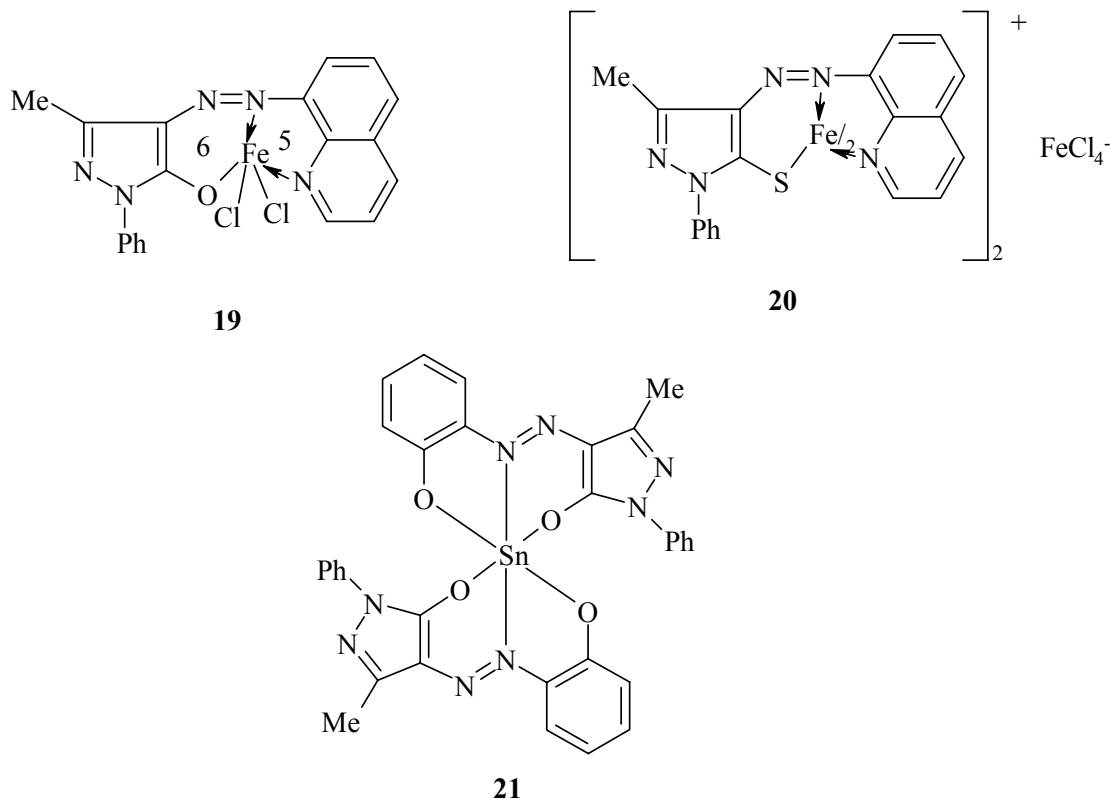


Stereochemistry of the metal chelates. Stereochemical configuration of a metal center in tetracoordinated metal chelate complexes of azo ligands is determined by the nature of the metal. As shown by X-ray studies, the *trans*-planar coordination sites are characteristic of the Ni(II), Cu(II) and Pd(II) complexes **15**, whereas similar Co(II) and Zn(II) complexes have the tetrahedral structure **16**.^{31, 67-69} Of special interest is the case of the Pt(II) metal chelate complex, for which two, *trans*-planar **17** (40-45%) and *cis*-planar **18** (4-6%) configurational isomers were obtained and isolated in a pure form.⁷⁰

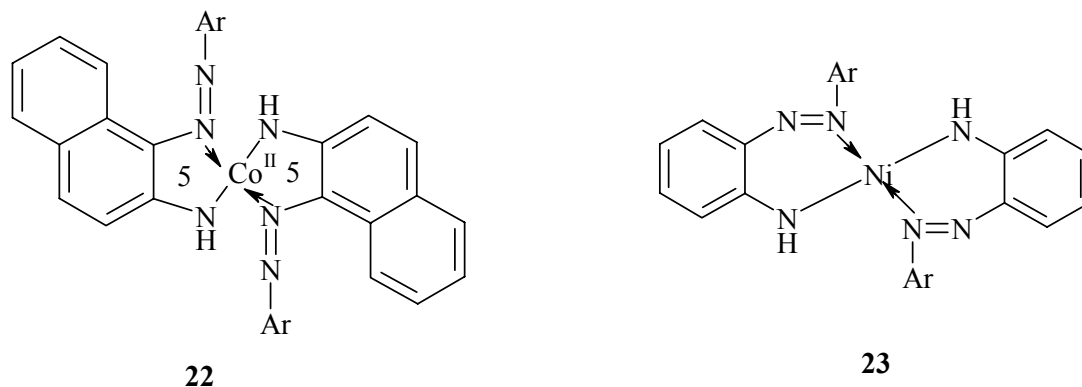


Annulation of a pyrazole fragment to the metal chelate ring results in the tetrahedral deformation of the coordination site in the Ni(II), Zn(II) complexes **11** (X=NAr, O).^{41, 42, 71} According to the X-ray diffraction data the complex **19** possesses pentacoordinated trigonal bipyramidal structure. The same structural effect was observed also for the azomethine analogues of **11**.^{8, 16, 17, 49} On the contrary, the sulfur complexes **11** (M=Ni, n=2, X=S) have a planar configuration of the coordination site.^{54, 71} The metal ions at higher oxidation numbers,

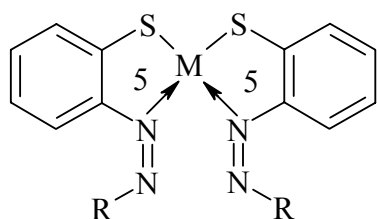
e.g. Co(III)⁴² and Ru(III)⁴⁷ can form octahedral complexes with bidentate azo ligands. The octahedral configuration of a metal center has been proven by X-ray determinations for the complexes **20**⁴³ and **21**⁷² with tridentate ligands, as well as [**11** · MeOH] (M = Ni, R¹ = Ph, R² = Me, Ar = *p*-*tert*-Bu-C₆H₄, n = 2).⁴²



Intrachelate isomerism. This type of bond-linkage isomerism^{19, 20} is characteristic of the metal chelate complexes containing several competitive donor centers in a coordination site. In the azo ligands **1**, **4**, **6**, **8**, **9** such a role may be played by each of the two nitrogens of an ambidental azo group.^{8, 20, 67} The possibility of the formation of the five-membered chelate ring due to donation of an electron pair by the nitrogen atom adjacent to the arene ring was considered as an explanation of the unexpected planarity of the coordination site of the Co(II) complex **22**.^{31, 73}

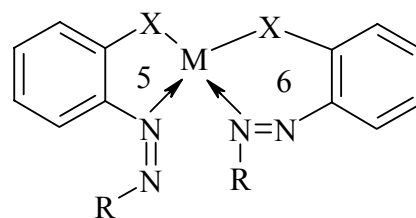


However, X-ray studies of the analogous Ni(II) complex as well as of its oxygen analogue witness the six-membered *trans*-planar structures **23**.⁶⁷ The first direct evidence of the inclusion of a metal center into the two five-membered rings formed by azo groups was obtained using X-ray determinations of the complexes **24a**⁷⁴⁻⁷⁷ and **24b**^{38, 39}. By varying the structure of the azo ligands (X and R in **25**), metal chelates **25a**⁷⁸ and **25b**⁷⁹ with both five- and six-membered ring within a molecule have been obtained and structurally characterized.



24a: M = Ni, Zn;
R = 4-MeC₆H₄-

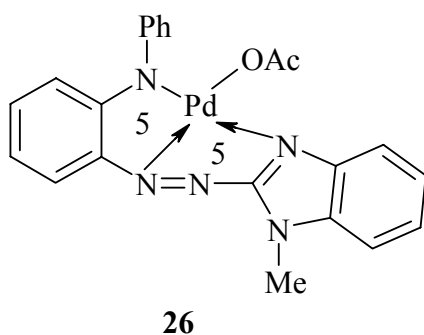
24b: M = Pd;
R = 2-MeC₆H₄-



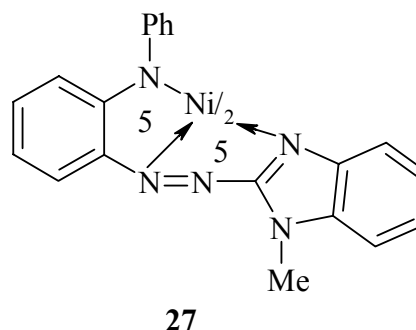
25a: M = Cu, X = NTs;
R = 4-MeC₆H₄-;
Ts = 4-MeC₆H₄SO₂-

25b: M = Pd, X = S,
R = 4-MeC₆H₄-

Examples of the similar type intrachelate isomers became known for the complexes **26**⁵² and **27**⁵³ with heterocyclic azo ligands.



26



27

Conclusions

The data above considered point to the possibilities of the significant variation of the structure and, therefore, properties of metal chelate complexes caused by diverse structural modifications of the azo-containing ligands. Less studied in this respect is the problem of the influence of strong electron-withdrawing and electron-releasing substituents in the aryl rings of the aromatic and heterocyclic azo compounds, which is essential for defining basicity and ligating abilities of the nitrogen centers in the azo groups. It is expected that the investigation into this problem may

be promoted by the further extension of the series of the relevant azo ligands and gaining deeper insight into the mechanism and preparative application of the azo coupling reactions under the phase transfer catalysis conditions.

Experimental Section

General Procedures. ^1H NMR spectra were registered on “Varian UNITY-300” spectrometer. Magnetic measurements were carried out on SQUID magnetometer “Quantum Design MPPSM-5 S” at 299 K.

4-[(E)-(2-Anilidonaphthyl-1)diazenyl]-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (**1**: X = NPh, R = 1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one-2-yl, R¹ = 5,6-benzo) was synthesized by coupling the diazonium salt derived from 4-amino-2,3-dimethyl-1-phenylpyrazol-5-one (solution in HCl) and N-phenyl-2-naphthylamine in ethanol. By addition of NaHCO₃ the pH of the solution was maintained at the level of 7-8 units. Dark red crystals were obtained after chromatographic purification (Al₂O₃, CHCl₃), mp 226-227 °C. Yield 85 %. Anal. Calcd. for C₂₇H₂₃N₅O, %: C, 74.81; H, 5.34; N, 16.16. Found, %: C, 74.69; H, 5.27; N 16.26. NMR ^1H (DMSO-d₆), δ (ppm): 2.74 (s, 3H, C-CH₃), 3.36 (s, 3H, N-CH₃), 7.09-7.80 (m, 15H, CH_{arom}), 12.09 (s, 1H, NH).

4-[(E)-(2-Hydroxy-1-naphthyl)diazenyl]-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (**1**: X = O, R = 1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one-2-yl, R¹ = 5,6-benzo) was obtained by the similar method using 2-hydroxynaphthalene as a substrate. Bright red crystals were obtained after recrystallization from methanol-chloroform mixture (2:1), mp 246-247 °C. Yield 82 %. Anal. Calcd. for C₂₁H₁₈N₄O₂, %: C, 70.38; H, 5.06; N, 15.63. Found, %: C, 70.11; H, 5.23; N, 15.75. NMR ^1H (DMSO-d₆), δ (ppm): 2.69 (s, 3H, C-CH₃), 3.34 (s, 3H, N-CH₃), 7.12-7.74 (m, 11H, CH_{arom}), 14.16 (s, 1H, OH).

(4Z)-3-Methyl-1-phenyl-1H-pyrazole-4,5-dione-4-(quinolin-8-ylhydrazone) (**6**: R = 8-Quin, R¹ = Ph, R² = Me) was obtained by analogous method according to scheme (6). Orange crystals (from toluene). Yield 85 %. Anal. Calcd. for C₁₉H₁₅N₅O, %: C, 69.29; H, 4.59; N, 21.26. Found, %: C, 69.35; H, 5.01; N, 21.21. NMR ^1H (DMSO-d₆), δ (ppm): 2.3 (s, 3H, CH₃); 7.2-9.0 (m, 5H, C₆H₅; 6H, C₉H₆N); 14.5 (s, 1H, NH).

(4Z)-3-Methyl-1-phenyl-5-thioxo-1,5-dihydro-4H-pyrazol-4-one quinolin-8-ylhydrazone (**9**: R = 8-Quin, R¹ = Ph, R² = Me) was synthesized according to scheme (8). Red crystals (from toluene). Yield 45 %. Anal. Calcd. for C₁₉H₁₅N₅S, %: C, 66.07; H, 4.38; N, 20.28. Found, %: C, 65.97; H, 4.30; N, 20.25. NMR ^1H (CDCl₃), δ (ppm): 2.45 (s, 3H, CH₃); 7.2-9.0 (m, 5H, C₆H₅; 6H, C₉H₆N); 17.5 (s, 1H NH).

Synthesis of the ML₂ metal complexes on the base of aromatic and heterocyclic compounds, as exemplified by scheme (9) was performed through interaction of ligands **1**, **6**, **8**, **9**

and metal acetates (M = Co, Ni, Cu, Zn) in 2:1 molar ratio in methanol under refluxing during 30 min. Palladium complexes **10** were obtained using methanol-acetone mixture as a solvent.

10a. (M = Pd; X = NPh; R = 1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one-2-yl, R¹ = 5,6-benzo). Dark violet crystals, mp > 320 °C. Anal. Calcd. for C₅₄H₄₄N₁₀O₂Pd, %: C, 61.43; H, 4.17; N, 13.65. Found, %: C, 61.52; H, 4.30; N, 14.35. NMR ¹H (DMSO-d₆), δ (ppm): 2.89 (s, 6H, 2 C-CH₃); 3.64 (s, 6H, 2 N-CH₃); 6.59-7.74 (m, 30H, CH_{arom}).

10b. (M = Pd; X = O; R = 1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one-2-yl, R¹ = 5,6-benzo). Red-brown crystals, m.p. > 320 °C. Anal. Calcd. for C₄₂H₃₄N₈O₄Pd, %: C, 66.76; H, 4.56; N, 14.41. Found, %: C, 66.59; H, 4.35; N, 14.25. NMR ¹H (DMSO-d₆), δ (ppm): 2.75 (s, 6H, 2 C-CH₃); 3.63 (s, 6H, 2 N-CH₃); 6.60-7.82 (m, 20H, CH_{arom}).

Metal coordination compounds **19**, **20** were synthesized by heating ethanol solutions of ligands **6** or **9** (R = 8-Quin, R¹ = Ph, R² = Me) and FeCl₃·6H₂O during 40 min.

(4Z)-3-Methyl-1-phenyl-5-thioxo-1,5-dihydro-4H-pyrazol-4-one quinolin-8-ylhydrazonedichloroiron(III) (19). Green-brown crystals (from toluene). Yield 65 %. Anal. Calcd. for C₁₉H₁₄Cl₂N₅OFe, %: C, 50.14; H, 3.10; N, 15.39. Found, %: C, 49.97; H, 3.30; N, 15.20. μ_{eff} = 6.17 MB. (X-ray⁸⁰).

({Bis[(4Z)-3-methyl-1-phenyl-5-thioxo-1,5-dihydro-4H-pyrazol-4-one quinolin-8-ylhydrazone]iron(III)}FeCl₄) (20). Brown crystals (from toluene). Anal. Calcd. for C₃₈H₂₈Cl₄N₁₀S₂Fe₂, %: C, 48.43; H, 3.00; N, 15.39. Found, %: C, 48.27; H, 2.70; N, 15.25. μ_{eff} = 6.20 MB.

Acknowledgments

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