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NOVEL REAGENT FOR SYNTHESIS OF MIXED LIGAND CHELATES

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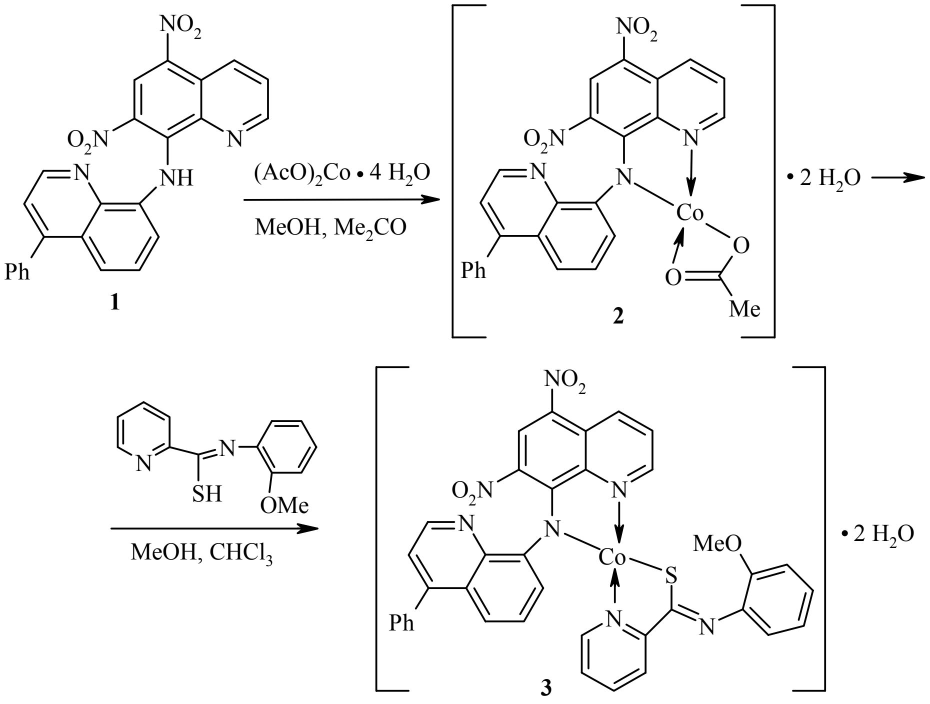
Of special interest, from the standpoint of similarity to natural enzymes, are metal chelates in which the metal experiences different ligand environments. These are "mixed ligand chelates" (containing unequal pairs of ligands) of general formula $L^1–M–L^2$, the synthesis of which under conventional conditions for coordination chemistry, namely reaction of the starting ligands with metal salts in suitable solvents, does not yield a positive result. Generally under these conditions, a mixture of chelates is formed of composition $L^1–M–L^1$ and $L^2–M–L^2$, the separation of which is a rather difficult experimental problem.



During a study of processes of complex formation by organic compounds with intramolecular charge transfer ("self-complexes"), from a self-complex of the dinitroquinoline series **1** with transition metal acetates (described in [1]) we obtained a complex compound of Co(II) as its monoacetate **2**. Examples of such a structure for some monoacetate complexes are known in the literature [2, 3].

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Based on this convenient reagent, complex **2**, we developed a method for synthesis of mixed ligand chelates with a specified structure. For example, by reaction of this complex with a sulfur-containing ligand N-(*o*-methoxyphenyl)-2-thiocarboxamidopyridine, we obtained a mixed metal chelate of cobalt **3**, the molecules of which are characterized by the presence of two types of chelate units with N,S and N,N coordination.

[N-(4-Phenylquinolin-8-yl)-5,7-dinitroquinoline-8-aminato]cobalt(II) Acetate (2) was obtained by boiling a mixture prepared from a methanol solution of cobalt(II) acetate tetrahydrate (0.028 g, 0.144 mmol) and an acetone solution of self-complex **1** (0.085 g, 0.19 mmol). Red-brown powder, stable in air. Yield 0.05 g (52%); mp 262-264°C (decomp.). UV spectrum (MeCN), λ_{max}, nm (ε): 311 (inflection), 353 (12100), 462 (15629), 526 (13613). Found, %: C 53.75; H 2.91; N 11.77. $C_{26}H_{17}CoN_5O_6\cdot 2H_2O$. Calculated, %: C 53.19; H 3.59; N 11.86.

[N-(4-Phenylquinolin-8-yl)-5,7-dinitroquinoline-8-aminato][(2-methoxyphenylimino)(pyridin-2-yl)methylthionato]cobalt(II) (3) was obtained by boiling a mixture prepared from a methanol/chloroform solution of complex **2** (0.04 g, 0.074 mmol) and a methanol solution of N-(*o*-methoxyphenyl)-2-thiocarboxamidopyridine (0.016 g, 0.074 mmol). Dark-red crystals. Yield 0.038 g (67%); mp 238-240°C. UV spectrum (MeCN), λ_{max}, nm (ε): 268 (33195), 349 (12643), 506 (14537). Found, %: C 57.27; H 3.47; N 11.70. $C_{37}H_{25}CoN_7O_5S\cdot 2H_2O$. Calculated, %: C 57.37; H 3.77; N 12.26.

The UV spectra were recorded on a Helios α spectrophotometer (Unicam, UK), concentration of solutions 10^{-3} to 10^{-4} mol/l, resolution 2 nm, spectral range 200-800 nm, cuvet thickness 0.1 cm. The spectra, obtained in digital form, were processed using the program *Origin*. Since chelates **2** and **3** are paramagnetic, their NMR spectra could not be obtained.

Using the proposed reagent **2** for synthesis of mixed ligand chelates will make it possible to solve problems of targeted synthesis of chelates with specified ligand environments, with a view toward designing catalytic systems operating on the basis of principles found in nature.

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