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LETTERS TO THE EDITOR

Dedicated to V. F. Mironov on His 60th Anniversary

Ni(II) Complex of Bisthiophosphorylated Thiourea Prepared from the Betti Base

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Abstract—The interaction between bisthiophosphorylated thiourea with nickel(II) nitrate in the presence of potassium *tert*-butylate has afforded NiL_2 complex with square-planar configuration of the nickel(II) ion and the 1,3-*N,S*-coordination of the *trans*-positioned similar heteroatoms.

Keywords: thiophosphorylated thiourea, Betti base, nickel(II) complex

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The development of new types of multifunctional ligands is a actual problem of modern coordination chemistry, since it can potentially lead to the preparation of new catalysts of organic reactions as well as promising materials combining important properties like magnetization, electroconductivity, optical parameters, and photoreactivity [1–4]. Thiosphosphorylated thioureas have been recognized as efficient complex forming agent in the reactions with a number of *d*-elements. Owing to the presence of several competing nucleophilic sites in such molecules, the formed complexes can differ in the coordination polyhedron shape and the type of the ligands coordination [5–8].

We have recently prepared chiral thiophosphorylated thioureas by the reaction of thiophosphoryl isothiocyanate with racemic and enantiopure Betti base [9]. Unfortunately, the use of these compounds for the complexation is limited by their intramolecular cyclization due to the interaction of the naphthol hydroxy group with the thiocarbonyl group [9]. In view of that, we protected the naphthol group with another diethylthiophosphoryl group *via* the reaction of the starting thiourea with diethyl chlorophosphite followed by the treatment with elemental sulfur [10]. We aimed to prevent the cyclization processes and at the same time to introduce additional coordination site in the thiourea molecule. The tetradentate ligand (HL) prepared from the racemic thiourea was introduced in the complex formation reaction with nickel(II) nitrate in the presence of potassium *tert*-butylate. The crystallization from chloroform afforded violet crystals of the 1 : 1 solvate of the nickel complex of diphosphorylated thiourea NiL_2 with chloroform.

The complex was located at the center of symmetry in the crystal, and only half of the molecule was crystallographically independent (see figure). The nickel ion was in the square-planar surrounding, and the ligands exhibited the 1,3-*N,S*-coordination with *trans*-position of the same atoms. The chiral C^6 atoms were in the opposite orientation. The thiophosphoryl groups were not involved in the coordination. A peculiar feature of the complex was the π-stacking interactions of the naphthyl parts of the adjacent molecules in the crystal, the distance between the aromatic planes being 3.57 Å.

In summary, we prepared the square-planar complex of Ni(II) bisthiophosphorylated thiourea bearing a fragment of the Betti base as the ligands (Scheme 1).

1-[(2-Diethylthiophosphatoxynaphth-1-yl)phenylmethyl]-3-(*O*,*O*'-diethylthiophosphoryl)thiourea HL was prepared as described in our previous paper [10].