STRUCTURE AND MAGNETIC PROPERTIES OF A NOVEL COMPLEX OF COPPER(II) CHLORIDE WITH 3-(HYDROXYIMINOMETHYL)-5-(2,5-DIMETHYLPHENYL)ISOXAZOLE

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A method is developed to prepare a complex of copper(II) chloride with 3-(hydroxyiminomethyl)-5-(2,5-dimethylphenyl)isoxazole (L) of the composition [Cu2L2(μ-Cl)2Cl2]. Its molecular and crystal structure is determined by single crystal X-ray diffraction. Examination of the curve μe(T) within the 2-300 K temperature range reveals the presence of antiferromagnetic interactions between unpaired electrons of copper(II).

Keywords: copper(II) complex, 3-(hydroxyiminomethyl)-5-(2,5-dimethylphenyl)isoxazole, crystal structure, effective magnetic moment.

INTRODUCTION

Isoxazole derivatives are efficiently used in targeted synthesis of diverse types of organic compounds, design of fused heterocyclic and steroid systems [1-3]. The isoxazole heterocycle is a part of many biomolecules: cytostatic agents, anticonvulsants, pesticides, and other biologically active compounds [4-7]. High synthetic potential of substituted isoxazoles and a wide spectrum of biological activity found for its derivatives stimulate continuing interest in the chemistry of isoxazoles and the preparation of new members of this class of compounds.

Complex formation of isoxazoles with metals received little attention. One of the pioneering works reported the reaction of M(II) perchlorates and tetrafluoroborates with non-substituted isoxazole (Iz) to yield complexes with the composition M[Iz6(BF4)2 (M = Mn(II), Fe(II), Co(II), Cd(II)), Fe[Iz6(ClO4)2, and Cu[Iz4(BF4)2] [8]. Spin crossover 1A1 ←→ 5T2 was found for the compound Fe[Iz6(ClO4)2. Studies on the preparation of complexes with non-substituted isoxazole were continued by the authors of the work [9]. The composition of complexes of iron(II) perchlorate and tetrafluoroborate with Iz was confirmed, and an iron(III) complex [Fe3O(OAc)6(Iz)6](ClO4)2 was prepared. Examination of magnetic properties revealed the occurrence of a two-step spin crossover in Fe[Iz6(BF4)2.

A series of works [10-12] and review [13] report the investigation of the complex formation of metals with substituted isoxazole derivatives. Thus, copper(II) compounds with 3,5-dimethylisoxazole [10] and 3-amino-5-methylisoxazole [11, 12], platinum(II) complexes with 5-methylisoxazole and cobalt(II) complexes with 3-amino-5-
methylisoxazole [13] were prepared and examined. X-ray crystallography studies revealed that non-substituted isoxazole as well as the studied substituted isoxazoles coordinated to metal in monodentate fashion by the nitrogen atom of the heterocycle.

In the literature, data on the complexation of metals with 3-(hydroxyiminomethyl)-5-(2,5-dimethylphenyl)isoxazole (L) are absent. It seemed expedient to begin the studies on the synthesis and investigation of metal complexes with this ligand.

The purpose of this work was the examination of the coordination potential of this ligand, synthesis of a new complex of copper(II) chloride with L, and its physicochemical analysis.

**EXPERIMENTAL**

CuCl₂·2H₂O (p) and acetone (p.a.) were used in the synthesis.

**Synthesis of L.** A mixture of 25 mmol (5.41 g) of 1-(2,5-dimethylphenyl)-3,4,4-trichloro-3-buten-1-one and 126 mmol (4.16 g) of NH₂OH were boiled for 15 h in 50 ml of methanol, then the reaction mixture was poured into ice-water mixture; the precipitate was collected by filtration, washed with water and recrystallized from chloroform. Yield 75%. Physicochemical characteristics of the product matched the published ones [14].

**Synthesis of [Cu₂L₂(μ-Cl)₂Cl₂].** A solution of 2 mmol (0.40 g) of L in 10 ml of acetone was added to a solution of 2 mmol of CuCl₂·2H₂O salt (0.34 g) in 20 ml of acetone. A light-green precipitate was formed in 1-2 min after the combination of the starting solutions. The solution with the precipitate was magnetically stirred for 0.5 h. The precipitate was collected by filtration, washed with acetone, and dried in a dessicator over magnesium perchlorate. Yield ~60%.

Analytical determination of C, H, N was carried out at the laboratory of microanalysis of NIOC SD RAS on a Carlo-Erba 1106 analyzer by the standard technique. Copper content was determined by EDTA titration after mineralization of samples by heating in a mixture of concentrated H₂SO₄ and HClO₄ (1:2). Found, %: C 41.6, H 3.9, N 8.3, Cu 18.0. For C₂₅H₂₅N₄O₄Cl₄Cu₂ calculated, %: C 41.1, H 3.5, N 8.0, Cu 18.1.

X-ray quality single crystals were obtained from the mother liquor by slow crystallization during one week. A crystal with dimensions of 0.14×0.13×0.12 mm was picked for the structural investigation.

**Instrumentation and methods.** A single crystal X-ray diffraction study of the complex was carried out by the standard technique on an automated four-circle Bruker-Nonius X8 Apex diffractometer equipped with a 2 D CCD detector at 150(2) K using graphite-monochromated molybdenum radiation (λ = 0.71073 Å). Reflection intensities were measured by φ-scanning of narrow (0.5°) frames. Empirical absorption correction was applied using SADABS. The structure was solved by the direct method and refined by full-matrix least squares in anisotropic approximation for non-hydrogen atoms using the SHELXTL program package [15]. Hydrogen atoms were refined in the rigid body approximation.

The structural data have been deposited to the Cambridge structural database, deposition number CCDC 741928. They are available free of charge at www.ccdc.cam.ac.uk/data_request/cif. Essential parameters of the structural experiment are given in Table 1; selected bond lengths and angles are given in Table 2.

A powder X-ray diffraction study was carried out on a PHILIPS-PW1700 diffractometer, CuKα radiation, Ni-filter, scintillation detector, step 0.015°, 2θ range 5-60°. The data were recorded at room temperature; silicon powder was used as the internal standard (a = 5.4309 Å).