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COORDINATION PROPERTIES OF 1,3-BENZOTHIAZOLES. FORMATION OF A POLYMERIC COMPLEX WITH SQUARE-PLANAR COORDINATION AROUND THE COPPER(II) ION IN THE REACTION OF $CuCl_2 \cdot 6H_2O$ WITH 1,2-BIS[2-(1,3-BENZO-THIAZOL-2-YL)PHENYLTHIO]ETHANE

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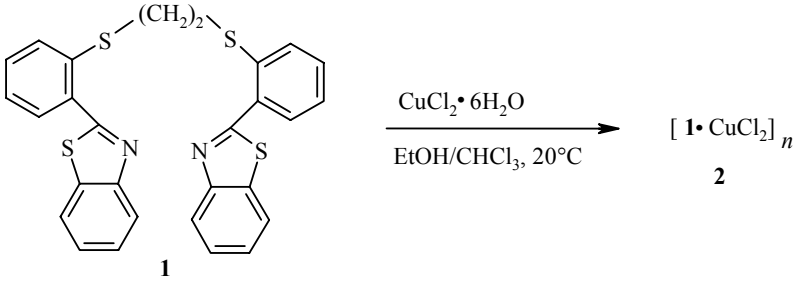
It is shown that a coordination polymer is formed by the reaction of 1,2-bis[2-(1,3-benzothiazol-2-yl)-phenylthio]ethane with copper(II) chloride in a mixture of ethanol and chloroform at room temperature. The structure of the polymer has been determined by X-ray crystallography. The copper atom in the coordination polymer has a square-planar ligand environment and is coordinated to the nitrogen atoms of the benzothiazole rings of two different molecules of ligand and two chloride anions.

Keywords: 1,3-benzothiazoles, coordination compounds, copper(II).

Metal-containing polymers are of interest as hybrid materials, combining such properties as huge differences in possible geometric and functional characteristics of the organic ligand, technologically valuable polymers, and electronic properties arising from the metal ion [1].There are some examples of the formation of polymeric complexes of copper(II) with square-planar coordination environments around the metal ion [2-4]. However participation of pyridine nitrogen atoms of the organic ligand in coordination of the metal is usual for such complex compounds. In a continuation of our investigation of the complex-forming properties of N_2S_2 ligands, containing sulfide donors and benzothiazole fragments [5, 6] we have studied the complexation reaction of 1,2-bis[2-(1,3-benzothiazol-2-yl)phenylthio]ethane **1** with copper(II) chloride hexahydrate.



1 **2**

* Dedicated to Academician of the Russian Academy of Sciences B. A. Trofimov on his 70th jubilee.

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We have previously established that when 1,3-bis[2-(1,3-benzothiazol-2-yl)phenylthio]propane reacted with copper chloride or perchlorate a complex compounds are formed, in which coordination is accomplished by four donor atoms of the diiminobis(sulfide) system [7].

In the present work we have established that the product of the reaction of 1,2-bis[[2-(1,3-benzothiazol-2-yl)phenylthio]ethane **1** with copper(II) chloride in an ethanol–chloroform mixture at room temperature is principally different coordination compound: the complex of polymeric structure **2**.

The structure of the coordination polymer **2** was determined by X-ray crystallography. The crystallographic data, details of the experiment, and the parameters of the refined structure are given in Tables 1 and 2, and the structure of the compound **2** is shown in Fig. 1. The copper atom in the complex has a square-planar

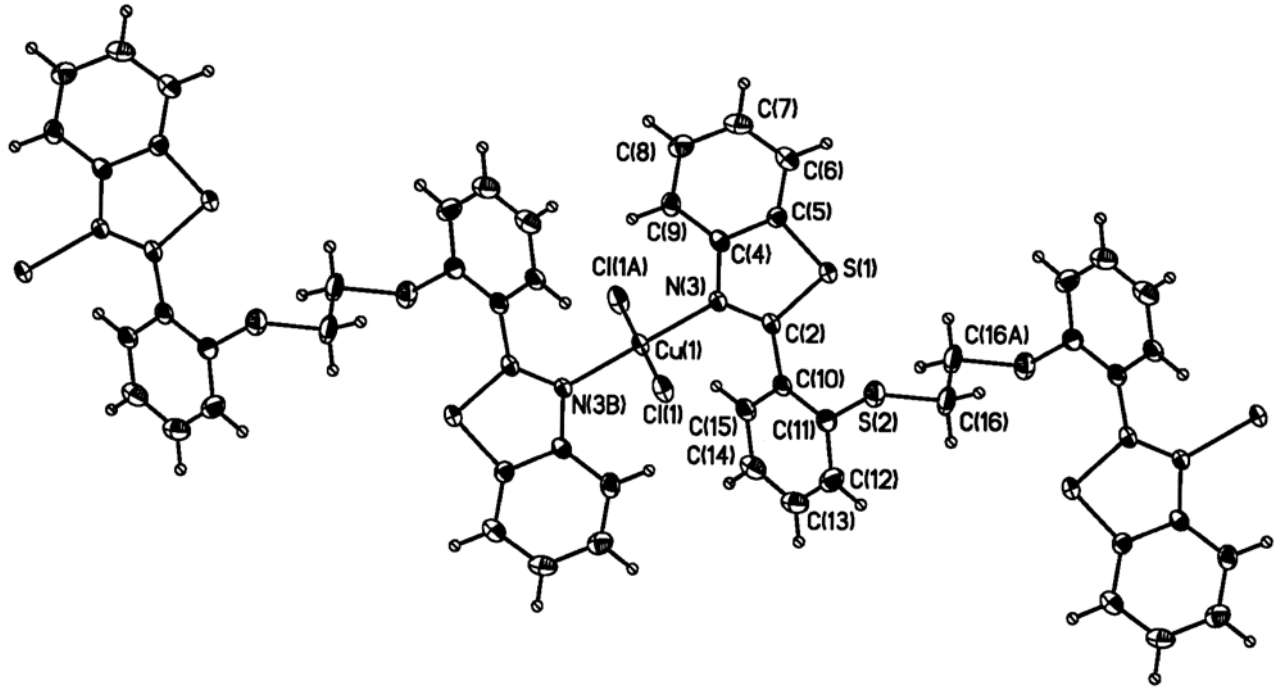

Fig. 1. The polymer chain fragment in the crystal of compound **2**.

ligand environment and is coordinated to nitrogen atoms of the benzothiazole ring of two different ligand molecules and two chloride anions. Endless chains are observed in the crystal, in which units of the ligand and $CuCl_2$ alternate, with the ligands take a special position [center of symmetry at the center of the C(16)–C(16A) bond, Fig.1] and the copper atom also takes a special position at a center of symmetry.

Table 1. Some Interatomic Distances (*l*) and Bond Angles (ω) in the Molecule of Compound **2**

Bond	*l*, Å	Angle	ω, deg
Cu(1)–N(3)	2.008(3)	N(3)–Cu(1)–N(3B)	180.00(14)
Cu(1)–Cl(1)	2.2501(8)	N(3)–Cu(1)–Cl(1A)	89.81(8)
S(1)–C(5)	1.731(3)	N(3)–Cu(1)–Cl(1)	90.19(8)
S(1)–C(2)	1.733(3)	Cl(1A)–Cu(1)–Cl(1)	180.00(5)
N(3)–C(2)	1.310(4)		
N(3)–C(4)	1.393(4)		

The data of the electronic spectra in the visible region for compound **2** (Experimental part) are in agreement with a square-planar structure of the complex [3] which permits the assumption that this geometry of the coordination environment of the copper(II) ion is retained in solution.

As far as we know, the reaction studied is the first example of the formation of a polymeric complex of copper(II) with a square-planar geometry of the coordination environment of the metal ion in the reaction with a ligand containing 1,3-benzothiazole donor units.

EXPERIMENTAL

Ligand **1** was prepared by a known method [7]. Electronnic spectra of DMF solutions were measured with a Specord M-40 (200-900 nm) in a quartz cuvette, thickness 0.1cm, at 20-22°C. Black-brown monocrystals of compound **2** were grown from a mixture of EtOH and $CHCl_3$ and a monocrystal was investigated using Bruker APEX II diffractometer (MoKα = 0.71073, graphite monochromator). Correction for absorbtion was introduced by using ω-scanning [8]. The mass of experimental data was treated using a complex of programs [9]. All of the later calculations were carried out using the SHELX97 complex of programs [10]. The crystal structure was determined by direct methods with subsequent refinement by full matrix least squares analysis with positional and thermal parameters in the anisotropic approximation for all non-hydrogen atoms.

Table 2. Crystallographic Characteristics, Details of the Experiment, and Characteristics of the Refined Structure of Compound **2.**

Empirical formula	$C_{28}H_{20}Cl_2CuN_2S_4$
Molecular mass	647.14
Temperature, K	100(2)
Wave length, Å	0.71073
Form of crystal	Black prisms
Crystal dimensions, mm	0.32 × 0.24 × 0.23
Crystal system	Monoclinic
Space group	*P*-21/*c*
Parameters of the unit cell	
a, Å	8.8381(14)
b, Å	10.8914(18)
c, Å	13.533(2)
β, deg	97.940(5)°
V, Å^3	1290.2(4)
Z	2
Calculated density, g·cm^{-3}	1.666
Coefficient of absorption, mm^{-1}	0.401
F(000)	658
Range of θ, grad	2.41–27.5
Range of reflection indexes	$-11 \le h \le 11$, $-140 \le k \le 13$, $-13 \le l \le 17$
Number of measured/independent reflections	6619 / 2965 (R_{int} = 0.0418)
Number of parameters refined	169
R-index on F^2	0.997
R-factors ($I > 2\sigma(I)$)	
R_1	0.0425
wR_2	0.1000
R-factors (all data)	
R_1	0.0684
wR_2	0.1122

Complex of 1,2-Bis[2-(1,3-benzothiazol-2-yl)phenylthio]ethane with Copper(II) Chloride (2). To a solution of ligand **1** (100 mg, 0.02 mmol) in $CHCl_3$ (1 ml) a solution $CuCl_2 \cdot 6H_2O$ (48.5 mg, 0.02 mmol) in EtOH (1 ml) was added slowly down the face of the container in order to form a two-phase system. The reaction mixture was tightly sealed and kept for 3 d until crystals formed. The residue was filtered off, washed with EtOH and dried in the air to give black-brown crystals of compound **2** (84 mg, 65%), mp >250°C. Electronic spectrum, λ_{max}, nm: 545, 600, 680. Found, %: C 51.31; H 2.84; N 4.21. $C_{28}H_{20}Cl_2CuN_2S_4$. Calculated, %: C 51.97; H 3.09; N 4.33.

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