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# Novel Mixed Complexes of Copper(II) and Ethylenediamine: Synthesis, Crystal Structure, and Catalytic Activity in the Cross-Coupling Reaction of 1-Phenyl-5*H*-tetrazole-5-thiol and Iodobenzene

L. V. Myznikov<sup>a</sup>\*, A. I. Fisher<sup>b</sup>, U. N. Dmitrieva<sup>a</sup>, T. V. Artamonova<sup>a</sup>, and Yu. E. Zevatskii<sup>a,c</sup>

<sup>a</sup> St. Petersburg State University of Industrial Technologies and Design, ul. Bol'shaya Morskaya 18, St. Petersburg, 191186 Russia \*e-mail: myznikov lv@mail.ru

<sup>b</sup> St. Petersburg State Technological Institute (Technical University), St. Petersburg, Russia

<sup>c</sup> V.I. Ulyanov (Lenin) St. Petersburg State Electrotechnical University "LETI," St. Petersburg, Russia

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**Abstract**—Two earlier unknown complexes,  $[Cu(en)_2(Hptt)]Br$  (Hptt = 1-phenyl-1*H*-terazole-5-thiol, en = ethylenediamine) and *trans*- $[Cu(en)_2(H_2O)Br]Br$ , have been synthesized and characterized using X-ray diffraction analysis. In  $[Cu(en)_2(Hptt)]Br$  complex, the copper cation is bonded with the N<sup>4</sup> atom of tetrazole ring. Catalytic activity of the obtained complexes in cross-coupling reaction of 1-phenyl-5*H*-tetrazole-5-thiol with iodobenzene is comparable to that of CuBr<sub>2</sub> in the presence of 2 eq. of ethylenediamine.

**Keywords:** copper, ethylenediamine, 1-phenyltetrazole-5-thiol, complex compound, X-ray diffraction analysis, catalysis

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Copper complex compounds, in particular, heteroligand copper complexes with ethylenediamine and various organic and inorganic ligands [1-3] are attractive due to easiness of synthesis, catalytic activity, and practical applications in medicine, agriculture, microelectronics, and industry. The major factor providing the diversity of such complexes is the use of polyfunctional ligands with several sites forming the coordination bonds. The formed complexes structure is determined by the synthesis conditions. Tetrazole-5-thiols substituted at position 1 can form complex compounds involving nitrogen and sulfur coordination sites; they have been widely used in the synthesis of biologically active substances and functional materials [4]. In most cases, these compounds contain the metal-heteroatom coordination bonds involving sulfur atoms or simultaneously sulfur and nitrogen atoms [4, 5], the coordination exclusively with nitrogen is much less common [6].

Isolation of the mentioned complexes, their characterization, and investigation of their catalytic

activity may aid in optimizing the conditions of coppercatalyzed cross-coupling reactions of 1-substituted tetrazole-5-thiols with aryl iodides, because such complex compounds are formed during the reaction.

Based on our earlier studies on cross-coupling of 1-substituted tetrazole-5-thiols with aryl iodides in the presence of copper compounds [7, 8], we carried out targeted synthesis of mixed copper and ethylenediamine complexes at 85°C in the presence of copper(II) bromide in anhydrous DMF and in the presence of water.

The crystals of  $[Cu(en)_2(Hptt)]Br$  complex (Hptt = 1-phenyl-1*H*-tetrazole-5-thiol, en = ethylenediamine) **1** were obtained by slow evaporation of a solution of copper(II) bromide, ethylenediamine, K<sub>2</sub>CO<sub>3</sub>, and 1-phenyl-1*H*-tetrazole-5-thiol in anhydrous DMF at 85°C under vacuum. In presence of traces of water 1-phenyl-1*H*-tetrazole-5-thiol did not included in the inner sphere and octahedral  $[Cu(en)_2(H_2O)Br]Br_2$  complex was formed. Complexes **1** and **2** were air-stable non-hygroscopic crystalline substances, soluble in DMF.

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Parameter	1	2	Parameter	1	2
Formula	$C_{11}H_{21}BrCuN_8S$	C <sub>4</sub> H <sub>18</sub> Br <sub>2</sub> CuN <sub>4</sub> O	F(000)	1784	708
Μ	440.87	361.58	$\mu(CuK_{\alpha}), mm^{-1}$	5.832	10.288
Crystal system	Orthorhombic	Monoclinic	$\theta_{max}$ , deg	72.49	67.48
Space group	Pbca	$P2_{1}/n$	$h_{\rm max}/h_{\rm min}$	12/-10	7/—7
<i>a</i> , Å	9.9140(2)	6.4405(4)	$k_{\rm max}/k_{\rm min}$	17/-17	18/18
<i>b</i> , Å	14.2959(2)	15.4060(9)	$l_{\rm max}/l_{\rm min}$	29/26	14/9
<i>c</i> , Å	23.8361(6)	12.0440(7)	Number of independent Reflections	3345	2121
β, deg	90	98.003(6)	Number of reflections with $F_0^2 > 2\sigma(F_0^2)$	3085	2043
<i>V</i> , Å <sup>3</sup>	3378.26(12)	1183.39(11)	Number of refined parameters	199	118
<i>Т</i> , К	100(2)	100(2)	$R_1/wR_2 [F_0^2 > 2\sigma(F_0^2)]$	0.0210/0.0533	0.0436/0.1175
Ζ	8	4	$GOOF/F^2$	1.066	1.066
$d_{\text{calc}}, \text{g/cm}^3$	1.734	2.030	$\Delta \rho_{\rm max}, e/{\rm \AA}^3$	0.355	0.960
Color and appearance	Blue prisms	Blue prisms	$\Delta \rho_{\rm min}, e/{\rm \AA}^{-3}$	-0.371	-0.747
Crystal size, mm <sup>3</sup>	0.23×0.17×0.12	0.24×0.18×0.10			

Table 1. Crystallographic data and refinement parameters of the structures of compounds 1 and 2

The solubility of complex **2** was significantly higher. The absorption band of v(M-N) vibrations was observed at 536 and 526 cm<sup>-1</sup> in the IR spectra of complexes **1** and **2**, respectively.

The structure of compounds 1 and 2 was determined using single-crystal X-ray diffraction analysis. Compounds 1 and 2 exhibited orthorhombic and monoclinic crystal systems, respectively (Table 1). All asymmetric structural units contained a complex cation and a  $Br^-$  anion.



**Fig. 1.** General view of a molecule of compound **1** in a crystal. Nonhydrogen atoms are represented by thermal ellipsoids (50% probability), H atoms are represented by spheres with random radius; dashed line represents intramolecular hydrogen bond.

In the complex cation of compound 1,  $Cu^{2+}$  is coordinated with two ethylenediamine (en) molecules and one 1-phenyl-1*H*-tetrazole-5-thiol (Hptt<sup>-</sup>) anion in the square pyramid geometry (Fig. 1). The Cu–Nen distances are in the range of 2.016–2.032 Å range, the



Fig. 2. Molecular packing of compound 1 in a crystal. Hbonds are shown with dashed lines. Hydrogen atoms are not shown.



**Fig. 3.** General view of a molecule of compound **2** in a crystal. Nonhydrogen atoms are represented by thermal ellipsoids (50% probability), H atoms are represented by spheres with random radius.

Cu–N(Hptt) distance is equal to 2.306 Å. The intramolecular N–H···S hydrogen bond is formed by one of the coordinated en molecules and a Hptt<sup>–</sup> anion (N–S 3.315 Å).

The structure of complex 1 is stabilized by intermolecular N–H··· $\pi$  interactions between the NH group of the en-ligand and the benzene ring of the Hptt-anion of the neighbor complex cation (H–Cg 2.557 Å, Cg being the centroid of carbon atoms of the benzene ring); that leads to the formation of linear chain along the *b* axis (Fig. 2).

The complex cation of compound **2** consists of  $Cu^{2+}$ ion coordinated with two en molecules (as in compound **1**) an H<sub>2</sub>O molecule, and Br<sup>-</sup> anion, in octahedral geometry (Fig. 3) [9]. The Cu–N(en) distances are in the range of 1.999–2.036 Å, whereas the Cu–O and Cu–Br distances are severely longer (2.718 and 2.948 Å, respectively). Tetragonal Jahn–





Fig. 4. Molecular packing of compound 2 in a crystal. Hbonds are shown with dashed lines. Hydrogen atoms are not shown.

Teller distortion affect the octahedral geometry. The complex cations of compound **2** are bound with one another and with  $Br^-$  anions via the N–HO, O–HBr<sup>-</sup>, and N–HBr hydrogen bonds (N–O 3.169, O–Br 3.328–3.289, and N–Br 3.421–3.461 Å) (Fig. 4). The neighboring layers in the crystal structures of compounds **1** and **2** are bound via weak Van der Waals interactions.

The catalytic activity of obtained complexes was investigated using the cross-coupling of 1-phenyl-5*H*-tetrazole-5-thiol with iodobenzene as the test reaction, (Scheme 1) in comparison with  $CuBr_2$  in the presence of 2 eq. of ethylenediamine. The data on the catalytic activity are given in Table 2.

According to the data in Table 2, yield of the reaction products after 1.5 h of heating in the presence of complex 2 were significantly higher than in the case of complex 1; probably due to higher solubility of complex 2 in the reaction medium. Catalytic activity of

**Table 2.** Yields of product of cross-coupling of 1-phenyl-5*H*-tetrazole-5-thiol with iodobenzene after 1.5 h at 85°C

Catalyst	Yield, %	
Complex 1	35	
Complex 2	61	
CuBr <sub>2</sub> -2NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	39	
CuBr <sub>2</sub> -2NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> -H <sub>2</sub> O	55	
$CuBr_2\!\!-\!\!2NH_2CH_2CH_2NH_2\!\!-\!\!10H_2O$	59	
CuBr <sub>2</sub> -2NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	43 <sup>a</sup>	

<sup>a</sup> The reaction was carried out in DMF–H<sub>2</sub>O, 8 : 2 mixture.

complex 1 was comparable to that of the  $CuBr_2$ -2NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> system. The addition of water to the CuBr<sub>2</sub>-2NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> system likely enhances the solubility of copper complex compounds in the reaction medium, and the product yield was comparable to that obtained with the preliminarily prepared complex **2**. Further increase in the water amount in the reaction medium decreased the solubility of starting substances and reduced the yield of the reaction product.

In summary, complex compounds of 1-substituted tetrazole-5-thiols with the copper-heteroatom coordination exclusively at the nitrogen atom were formed under conditions of copper-catalyzed cross-coupling reaction. 1-Substituted tetrazole-5-thiol fragment of the formed complexes could be easily substituted with water molecule.

## EXPERIMENTAL

The IR spectra were registered using a Shimadzu FTIR-8400S spectrometer. Elemental analysis was performed using a LECO CHNS-932 device. X-ray diffraction data were collected with an Agilent Technologies Supernova Atlas diffractometer at 100 K using microfocused monochromatic  $CuK_{\alpha}$ -radiation. The structures were solved via the direct method and refined under anisotropic approximation for nonhydrogen atoms and under isotropic approximation for hydrogen atoms, using the full-matrix least squares method implemented in SHELXL-97 routine [10] included in OLEX2 software package [11]. H atoms at the C atoms were localized at the calculated positions and refined via the *rider* model,  $U_{iso}(H) = 1.2U_{eq}(N)$ and N–H 0.90 Å for NH<sub>2</sub> groups,  $U_{iso}(H) = 1.2U_{eq}(C)$ and C-H 0.97 Å for CH<sub>2</sub> groups,  $U_{iso}(H) = 1.2U_{eq}(C)$ and C-H 0.93 Å for CH groups. H atoms of H<sub>2</sub>O molecules were localized using differential Fourier series without refinement. The unit cell parameters were determined and the intensities of diffraction reflections were measured using CrysAlisPro software package [12]. The absorption was accounted for empirically using SCALE3 ABSPACK algorithm. Crystallographic data and refinement parameters of structures of compounds 1 and 2 were deposited at the Cambridge Crystallographic Data Center (CCDC 1022459 and 1022460, respectively).

[Cu(en)<sub>2</sub>(Hptt)]Br complex (1). 1.25 g (56 mmol) of CuBr<sub>2</sub>, 0.67 g (112 mmol) of ethylenediamine, and 1.54 g (112 mmol) of  $K_2CO_3$  were added to a solution

of 1 g (56 mmol) of 1-phenyl-1*H*-tetrazole-5-thiol in 150 mL of DMF. The mixture was heated to 85°C, slowly evaporated under vacuum until the onset of crystallization, and slowly cooled to room temperature under atmospheric pressure. The precipitate was filtered off and dried. IR spectrum (KBr), v, cm<sup>-1</sup>: 3321, 3294, 3219, 3164, 3108, 3090, 3077 (N–H), 2969. 2953, 2941, 2883 (C–H), 1595 (C=N), 1584, 1560, 1494, 1455, 1383, 1356, 1292, 1273, 1219, 1101, 1093, 1059 (N–N), 1043, 1014, 989, 919, 776, 721, 696, 687, 571, 536 (Cu–N). Found: %: C 30.13; H 4.99; N 25.33. C<sub>11</sub>H<sub>21</sub>BrCuN<sub>8</sub>S. Calculated, %: C 29.97; H 4.80; N 25.42. 30.13; H 4.99; N 25.33.

[Cu(en)<sub>2</sub>(H<sub>2</sub>O)Br]Br complex (2) was obtained similarly from 1.25 g (56 mmol) of CuBr<sub>2</sub>, 0.67 g (112 mmol) of ethylenediamine, 1.54 g (112 mmol) of K<sub>2</sub>CO<sub>3</sub>, 150 mL of DMF, and 1 mL of H<sub>2</sub>O. IR spectrum (KBr), v, cm<sup>-1</sup>: 3321, 3294, 3219, 3164, 3108, 3090, 3077 (N–H), 2969. 2953, 2941, 2883 (C–H), 1595 (C=N), 1584, 1560, 1494, 1455, 1383, 1356, 1292, 1273, 1219, 1101, 1093, 1059 (N–N), 1043, 1014, 989, 919, 776, 721, 696, 687, 571, 536 (Cu–N). Found %: C 13.17; H 5.15; N 15.64. C<sub>4</sub>H<sub>18</sub>Br<sub>2</sub>CuN<sub>4</sub>O. Calculated, %: C 13.29; H 5.02; N 15.50.

**Cross-coupling in the presence of complexes 1** and 2. 20 mol% of the complex compound was added to a solution of 1.0 g (5.6 mmol) of 1-phenyl-1*H*tetrazole-5-thiol, 1.1 g (5.6 mmol) of iodobenzene, and 0.77 g (5.6 mmol) of dry  $K_2CO_3$  in 15 mL of anhydrous DMF. The reaction mixture was stirred for 1.5 h at 85°C, cooled to 20°C, and poured into 50 mL of water. The precipitate was filtered off and purified using column chromatography (eluent: EtOAc–hexane, 2 : 8).

Cross-coupling in the presence of CuBr<sub>2</sub> and ethylenediamine. 0.25 g (11.2 mmol) of CuBr<sub>2</sub> and 0.134 g (22.4 mmol) of ethylenediamine were added to a solution of 1.00 g (5.6 mmol) of 1-phenyl-1*H*tetrazole-5-thiol, 1.14 g (5.6 mmol) of iodobenzene, and 0.77 g of dry K<sub>2</sub>CO<sub>3</sub> (5.6 mmol) in 15 mL of anhydrous DMF. The reaction mixture was stirred for 1.5 h at 85°C, cooled to 20°C, and poured into 50 mL of water. The precipitate was filtered off and purified using column chromatography (eluent: EtOAc–hexane, 2 : 8).

Cross-coupling in the presence of water was carried out similarly.

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