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Brief Communications

New 2-(2-pyridyl)-substituted benzothiazoles with polyethylene glycol substituents*

E. S. Barskaya, V. V. Shorokhov, A. V. Rzheutsky, A. D. Khudyakov, I. V. Yudin, V. A. Tafeenko, N. V. Zyk, and E. K. Beloglazkina★

Lomonosov Moscow State University, Department of Chemistry,
Build. 3, 1 Leninskie Gory, 119991 Moscow, Russian Federation.
Fax: +7 (495) 939 4653. E-mail: bel@org.chem.msu.ru

An approach for the synthesis of new organic ligands combining in their structure pyridine, benzothiazole, and polyethylene glycol fragments was developed, proceeding from 6-hydroxy-2-(pyridin-2-yl)benzothiazole and mono- or ditosyl-substituted polyethylene glycols. The ligand 2-(2-{[2-(pyridin-2-yl)benzothiazol-6-yl]oxy}ethoxy)ethanol (L) in the reaction with $Cu(ClO_4)_2 \cdot 6\ H_2O$ and $CuCl_2 \cdot 2\ H_2O$ formed coordination compounds of the composition $L_2Cu(ClO_4)_2 \cdot 7\ H_2O$ and $LCuCl_2 \cdot 0.5\ H_2O$, respectively.

Key words: benzothiazoles, polyethylene glycols, organic ligands, copper(II) complexes.

Antioxidant enzymes superoxide dismutase (SOD) protect the body from highly toxic oxygen radicals, catalyzing the dismutation of the superoxide anion to oxygen and hydrogen peroxide.[1] Hence, SOD play an essential role in the antioxidant protection of cells exposed to oxygen.[2] Several forms of superoxide dismutases are known depending on the type of transition metal, a cofactor of the enzyme active center, including Cu/Zn-containing SOD. Copper ion is a cofactor of the active site, while zinc is necessary to stabilize the conformation.[3] As was shown, the removal of Zn from the active center somewhat decreases the disproportionation rate of the superoxide, but does not inactivate the enzyme.[4,5]

The cofactor directly involved in the catalytic cycle, the Cu^{II} ion, in copper-containing SOD has a square-pyramidal environment consisting of four histidine residues forming an equatorial plane and weakly bound water molecules. The mechanism of the enzyme action involves the replacement of the water molecule with a superoxide anion, while maintaining the coordination number of copper.[4]

Currently, a number of both mononuclear and heterobynuclear Cu and Zn complexes with SOD activity are known.[6—14] The most obvious analogs of SOD are Cu complexes with amino acids present in the active center of Cu/Zn-containing SOD. However, only a few examples of such analogs are known, since the synthesis of such complexes is a non-trivial problem: it is necessary not only to retain the position of the imidazole bridge, but also to synthesize polypeptide ligands with the necessary amino

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acid sequence. Thus, the activity of the Na[glygly-Cu-im-Zn-glygly],[10] Na[glyala-Cu-im-X-glyala] (X — Zn^{2+} or Ni^{2+})[11] complexes was investigated. There are also several examples of mononuclear complexes of the type Cu^{2+}(dipeptide)$(H_2O)_n$ (dipeptide is alaile, alathr, alatyr).[12—14]

An alternative approach is the synthesis of copper complexes with a coordination environment as close as possible to the environment of the Cu^{2+} ion in the active center of Cu/Zn-containing SOD. Most of the ligands used in this approach form chelate complexes with Cu^{2+} and Zn^{2+} ions (or Cu^{2+} and Ni^{2+}, which can replace zinc), the complexes can also contain bridging imidazole between two metal ions. Typical examples of ligands in such complexes are diethylenetriamine, pentamethyldiethylenetriamine, tri(2-aminoethyl)amine.[15—17] There are also known complexes with SOD activity containing an oxalate ion or ethylenediamine instead of the imidazole bridge.[18] Mononuclear copper complexes also can exhibit SOD activity. It was shown that the absence of the second metal ion and even the change in the coordination environment of the Cu^{2+} ion is not critical for the activity to be present. Thus, many complexes exhibiting a fairly high SOD activity are known, in which the ligands are substituted benzothiazoles,[19] imidazole derivatives,[20,21] curcumin,[22] β-cyclodextrin.[23] However, the complexes with hydrophobic ligands containing aromatic fragments (imidazole, benzothiazole, triazole) were found to exhibit the highest SOD activity.[24]

For many years, the research teams at the Chair of Organic Chemistry of the Department of Chemistry of the Lomonosov Moscow State University have studied approaches to the synthesis and biological activity of five-membered heterocycles and their derivatives.[25] Earlier,[26] our research group have synthesized a square-pyramidal complex $[Cu(pbt)_2(OH_2)](ClO_4)_2$ (pbt is 2-(2-pyridyl)benzothiazole) benzothiazole) structurally similar to the active center of copper-containing SOD with a basal plane occupied by the nitrogen atoms of two molecules of the bidentate organic ligand and a water molecule in the apical position. This complex demonstrated moderate SOD activity in the xanthine oxidase test, however, the low solubility of this compound in water and water-containing mixtures interfered with its detailed biological testing.

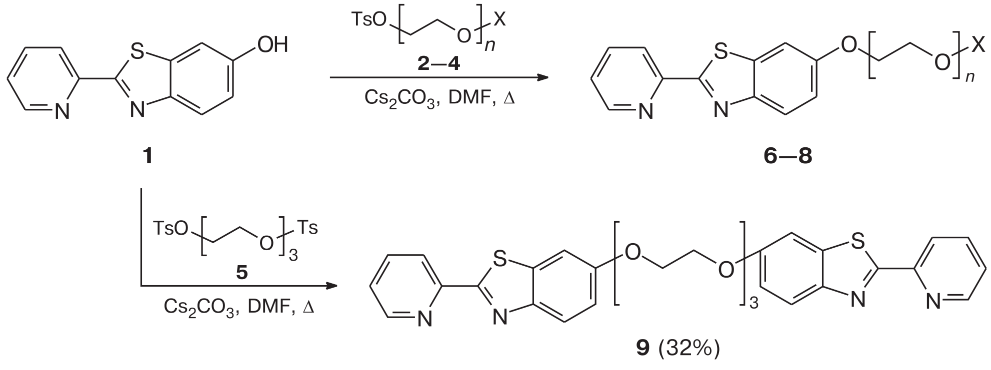
The purpose of the present work is to develop methods for the synthesis of new 2-(2-pyridyl)benzothiazole-derived ligands, which have hydrophilic polyethylene glycol fragments in their structure to increase water solubility, and to study them in the complexation with Cu^{II} salts.

Synthesis of organic ligands. The reaction of 6-hydroxy-2-(pyridin-2-yl)benzothiazole (**1**), synthesized as described earlier,[18] with the corresponding mono- and ditosylated polyethylene glycols **2**—**5** in the presence of cesium carbonate as a base gave polyethylene glycol-substituted benzothiazoles **6**—**9** (Scheme 1). The yields were 35—83%. The products were purified by column chromatography. The product yields were the highest when cesium carbonate was used as a base; running the reactions in the presence of K_2CO_3 led to an increase in the reaction time and resulted in the difficult-to-separate mixtures of products with insignificant amounts of the target compounds.

The obtained ligand **6** was studied in the complexation reactions with copper(II) chloride and perchlorate, which gave powdery precipitates of coordination compounds **10** and **11** in moderate isolated yields (Scheme 2). The complexes were characterized by elemental analysis, IR and UV spectroscopy.

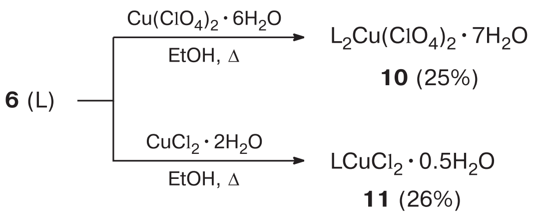
According to the elemental analysis and IR spectroscopy data, water molecules are present in the composition of the resulting complexes; the composition remains un-

Scheme 1



Compound	X	*n*	Product	Yield (%)
2	H	2	**6**	57
3	H	3	**7**	83
4	Me	4	**8**	16

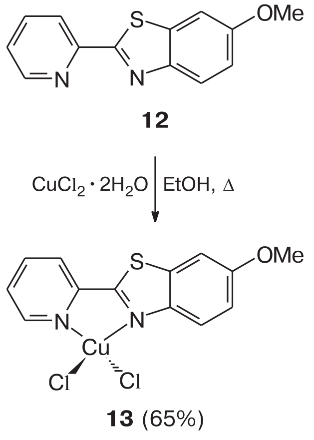
Scheme 2



changed upon prolonged drying of coordination compounds **10** and **11** *in vacuo*. According to the UV spectroscopy data (the presence of a broad weak absorption band in the region of ~650—880 nm corresponding to the metal d—d transition, as well as a strong metal-to-ligand charge transfer band in the region 330—340 nm)[27], the coordination environment geometry of the copper ion in complex **10** is similar to that for the previously obtained square-pyramidal coordination compound $[Cu(pbt)_2(OH_2)](ClO_4)_2$ (pbt is 2-(2-pyridyl)benzothiazole),[26] *i.e.*, corresponds to the geometry of the active center of the copper-containing SOD. Complex **11** has apparently a distorted tetrahedral coordination environment of copper ions, which is confirmed by electron spectroscopy data similar to those obtained for the model complex characterized by X-ray diffraction data (see below).

It was impossible to obtain crystals of complexes **10** and **11** suitable for X-ray diffraction studies, they crystallize as amorphous powders, possibly, due to the presence of a conformationally labile polyethylene glycol chain in the organic fragment. However, we reacted 6-methoxy-2-(2-pyridyl)benzothiazole **12** with copper(II) chloride dehydrate to obtain a simplified analog of coordination compound **11** (complex **13**), which has a methoxy substituent in the organic ligand (Scheme 3).

Scheme 3



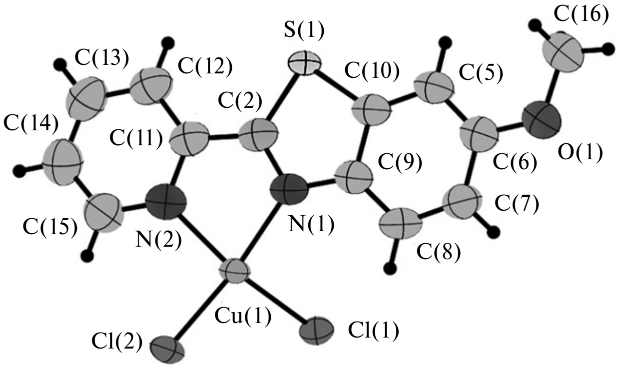


Fig. 1. Molecular structure of compound **13**.

In the molecule of compound **13** (Fig. 1), the copper atom is coordinated by two nitrogen atoms of the pyridine and the thiazole rings of the organic ligand and by two chloride anions, which form a distortion of the planar coordination environment typical of the Cu^{2+} cation. The analysis of the structure of Cu^{2+} coordination compounds similar to our (*i.e*, two chloride anions and two nitrogen atoms as ligands) and the structural data in the Cambridge Crystallographic Data Center database shows that the distortion of the planar structure can be avoided only for compounds in which a *trans*-arrangement of chloride anions is possible. Apparently, the source of the distortion is both the intramolecular interaction between the ligands and the intermolecular effects of the atoms of the neighboring molecules.

The aromatic system of the pyridylbenzimidazole ligand fragment is almost flat. The deviation of atoms from the mean square plane passed through the atoms of the pyridyl and benzimidizol fragments does not exceed 0.022 Å. The copper cation deviates from this plane by 0.15 Å, while the Cl(1) and Cl(2) anions deviate by 1.62 and 0.72 Å, respectively. The angle between the plane passed through the π-atoms and the plane passed through the copper cation and the chlorine anions is 46.2°.

A weak π—π-interaction occurs between the neighboring in stack molecules in the crystal structure of complex **13** (Fig. 2).

The distances between the mean square planes passed through the π-atoms of the neighboring in stack molecules alternate (see Fig. 2): 3.40 Å between the (*xyz*) and the $i = (1 - x, 1 - y, 1 - z)$ planes; 3.60 Å between the (*xyz*) and the $ii = (-x, 1 - y, 1 - z)$ planes.

The UV spectrum of coordination compound **13** is similar to the corresponding spectrum of complex **11**, which suggests a similar coordination environment of copper ions in these compounds.

All the ligands obtained, in particular compound **9**, are extremely poorly soluble in all the organic solvents tested. At the same time, both ligands **6**—**9** and coordination compounds **10** and **11** have a high solubility in water. For comparison: the solubility of unsubstituted 2-(2-pyridyl)benzothiazole in water at pH 7 is less than 1 mg/100 mL,

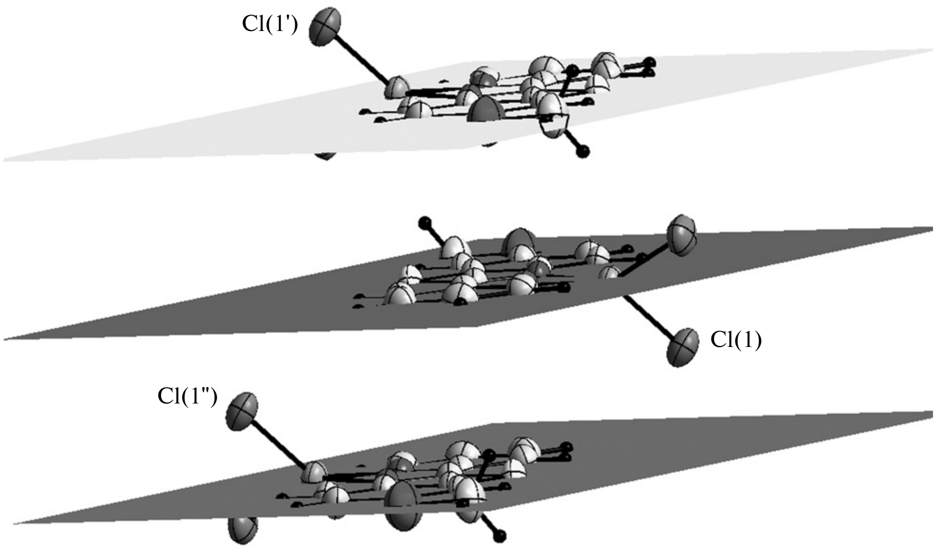


Fig. 2. Arrangement of the molecules of complex **13** in the crystal structure.

while the solubility of ligand **6** under the same conditions is ~30 mg/100 mL.

In conclusion, four new water-soluble polyethylene glycol-containing 2-(2-pyridyl)benzothiazole ligands were synthesized by alkylation of the corresponding benzothiazole hydroxy derivative with mono- and ditosylated polyethylene glycols in the presence of cesium carbonate and the possibility of obtaining copper(II) complexes with these compounds was demonstrated.

Experimental

The reaction progress and the compound purity were monitored by thin layer chromatography (TLC) on Silufol-UV254 silica gel precoated plates. Melting points were determined in a block with an open capillary and were not corrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance and Agilent 400-MR spectrometers (400 and 101 MHz, respectively). Chemical shifts are given in the δ scale relative to hexamethyldisiloxane as an internal standard. Electrospray ionization (ESI) high-resolution mass spectra (HRMS) were recorded on a Bruker microTOF II instrument. The measurements were performed in the positive ion mode (capillary voltage, 4500 V). Mass scanning range, *m*/*z* 50—3000 Da, external or internal calibration (Electrospray Calibration Solution, Fluka). Compounds were injected as solutions in acetonitrile, the flow rate was 3 μL min^{-1}. The nebulizer gas was nitrogen (4 L min^{-1}), the interface temperature was 180 °C. IR spectra were recorded on a TermoNicolet IR200 Fourier transform IR spectrometer (USA) with a resolution of 4 cm^{-1} in KBr pellets.

The X-ray diffraction study of a single crystal of compound **11** was carried out on a STOE StadiVari Pilatus 100K diffractometer, Cu-Kα radiation (1.54186 Å, from a GeniX3D Cu HF generator with a microfocus X-ray tube and a Xenocs FOX3D HF multilayer thin-film ellipsoidal monochromator (France). Data collection and processing of the recorded diffraction peaks were carried out using the X-Area 1.67 software package (STOE & Cie GmbH, Darmstadt, Germany, 2013). The intensities of reflections on the frames obtained from the 2D detector were scaled using the LANA program (incorporated in the X-Area package), which upon diffraction data processing minimizes the intensity differences of symmetrically equivalent reflections (multi-scan method). The structural data were deposited with the Cambridge Crystallographic Data Center (CCDC 1874574).

The structure was solved by the direct method implemented in the SHELXS-97 software package.[28] The positional and thermal parameters of nonhydrogen atoms were refined in the full-matrix anisotropic approximation. The positions of hydrogen atoms at heteroatoms (N, O) were determined from the Fourier syntheses and refined freely. The positions of hydrogen atoms at carbon atoms were calculated and refined in the isotropic approximation using a riding model. Graphic images of a molecule in the crystal were made using the DIAMOND program.[29]

Starting compoundя **1**, **2—5**, and **12** were synthesized according to the procedures described in the works.[18,30,31,32]

Synthesis of 6-hydroxy-2-(pyridin-2-yl)benzothiazole (1) (modified procedure). A 48% aqueous HBr (11 mL) was added to 6-methoxy-2-(2-pyridin-2-yl)benzothiazole (630 mg, 2.76 mmol). The mixture was refluxed for 24 h, diluted twice with water, and neutralized to pH 7. A grey precipitate formed was collected by filtration, dried in air, and recrystallized from ethanol to obtain compound **1** (573 mg, 96 %) as a white powder. M.p. 131—132 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$), δ: 9.96 (br.s, 1 H, OH); 8.67 (d, 1 H, Ar, *J* = 4.8 Hz); 8.23 (d, 1 H, Ar, *J* = 7.9 Hz); 7.98 (t, 1 H, Ar, *J* = 7.8 Hz); 7.88 (d, 1 H, Ar, *J* = 8.9 Hz); 7.52 (br.s, 1 H, Ar); 7.41 (s, 1 H, Ar); 7.00 (d, 1 H, Ar, *J* = 8.8 Hz). ^{13}C NMR (100 MHz, DMSO-d$_6$), δ: 165.63, 156.69, 151.15, 150.24, 147.80, 138.13, 137.55, 125.89, 124.47, 120.29, 116.79, 107.27. IR, ν/cm^{-1}: 3058 (OH), 1585 and 1509 (C=N). HRMS, *m*/*z*: calculated: 229.0430 [M + H]; $C_{12}H_8N_2OS$; found: 229.0430 [M + H].

Synthesis of polyethylene glycol-substituted benzothiazoles (general procedure). Monotosyl-substituted polyethylene glycol (1 equiv.) or ditosyl-substituted polyethylene glycol (0.5 equiv.) and cesium carbonate (1 equiv.) were added to 6-hydroxy-2-

(pyridin-2-yl)benzothiazole (**1**) (1 equiv.) dissolved in DMF (5 mL). The mixture was refluxed for 14 h (TLC monitoring), the solvent was evaporated at reduced pressure. Water (20 mL) was added to the mixture, which was extracted with ethyl acetate (3×30 mL). The organic phase was dried with anhydrous Na_2SO_4, the solvent was evaporated at reduced pressure on a rotary evaporator.

2-(2-{[2-(Pyridin-2-yl)benzo[*d*]thiazol-6-yl]oxy}ethoxy)ethanol (6). The reaction of 6-hydroxy-2-(pyridin-2-yl)benzothiazole **1** (319 mg, 1.399 mmol), 2-(2-hydroxyethoxy)ethyl tosylate **2** (363 mg, 1.399 mmol), and Cs_2CO_3 (456 mg, 1.399 mmol) gave compound **6** (263 mg, 57%) as a beige powder. M.p. 114—115 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 8.68 (d, 1 H, Ar, *J* = 4.2 Hz); 8.33 (d, 1 H, Ar, *J* = 7.9 Hz); 7.98 (d, 1 H, Ar, *J* = 9.0 Hz); 7.84 (t, 1 H, Ar, *J* = 7.7 Hz); 7.43 (s, 1 H, Ar); 7.37 (t, 1 H, Ar, *J* = 7.2 Hz); 7.15 (d, 1 H, Ar, *J* = 8.9 Hz); 4.25 (t, 2 H, OCH_2, *J* = 4.52 Hz); 3.94 (t, 2 H, OCH_2, *J* = 5.01 Hz); 3.77—3.82 (m, 2 H, OCH_2); 3.72 (t, 2 H, OCH_2, *J* = 4.65 Hz); 2.08 (br.s, 1 H, OH). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 167.07, 157.20, 151.46, 149.59, 149.01, 137.53, 137.02, 124.94, 124.19, 120.43, 116.42, 105.09, 72.66, 69.59, 68.01, 61.78. IR (KBr), ν/cm^{-1}: 1585 and 1515 (C=N), 1228 ($ArOCH_2$), 1134 and 827 ($CH_2CH_2OCH_2CH_2$), 1066 and 3376 (—OH). HRMS, *m/z*: calculated: 317.0954 [M + H]; $C_{16}H_{16}N_2O_3S$; found: 317.0958 [M + H].

2-[2-(2-{[2-(Pyridin-2-yl)benzo[*d*]thiazol-6-yl]oxy}ethoxy)ethoxy]ethanol (7). The reaction of 6-hydroxy-2-(pyridin-2-yl)benzothiazole (**1**) (234 mg, 1.026 mmol), 2-[(2-hydroxyethoxy)ethoxy]ethyl tosylate **3** (312 mg, 1.026 mmol), and Cs_2CO_3 (401 mg, 1.231 mmol) gave compound **7** (306 mg, 83%) as a beige powder. M.p. 103—104 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 8.67 (dd, 1 H, Ar, J_1 = 4.8 Hz, J_2 = 1.4 Hz); 8.32 (dd, 1 H, Ar, J_1 = 8.0 Hz, J_2 = 1.2 Hz); 7.96 (d, 1 H, Ar, *J* = 9.0 Hz); 7.84 (td, 1 H, Ar, J_1 = 7.7 Hz, J_2 = 1.8 Hz); 7.43 (d, 1 H, Ar, *J* = 2.5 Hz); 7.37 (m, 1 H, Ar); 7.15 (dd, 1 H, Ar, J_1 = 8.9 Hz, J_2 = 2.5 Hz); 4.24 (dd, 2 H, OCH_2, J_1 = 5.6 Hz, J_2 = 3.9 Hz); 3.89—3.96 (m, 2 H, OCH_2); 3.70—3.79 (m, 6 H, OCH_2); 3.61—3.67 (m, 2 H, OCH_2); 2.44 (br.s, 1 H, OH). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 166.99, 157.27, 151.50, 149.58, 148.99, 137.51, 136.98, 124.90, 124.15, 120.42, 116.48, 105.12, 72.53, 70.86, 70.36, 69.68, 68.00, 61.74. IR (KBr), ν/cm^{-1}: 3228 and 1072 (—OH), 1585 and 1515 (C=N), 1228 ($ArOCH_2$), 1135 and 1103 ($CH_2CH_2OCH_2CH_2$). HRMS, *m/z*: calculated: 361.1217 [M + H]; $C_{18}H_{20}N_2O_4S$; found: 361.1217 [M + H].

6-(2,5,8,11-Tetraoxatridecan-13-yloxy)-2-(pyridin-2-yl)benzo[*d*]thiazole (8). The reaction of 6-hydroxy-2-(pyridin-2-yl)benzothiazole (**1**) (400 mg, 1.754 mmol), 2,5,8,11-tetraoxatridecan-13-yl tosylate (**4**) (698 mg, 1.929 mmol), and Cs_2CO_3 (643 mg, 2.631 mmol) gave compound **8** (62 mg, 16%) as a beige powder. The product was purified by column chromatography in the system $CHCl_3$—EtOAc (2 : 1). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 8.65 (d, 1 H, Ar, *J* = 4.65 Hz); 8.29 (d, 1 H, Ar, *J* = 7.95 Hz); 7.95 (d, 1 H, Ar, *J* = 9.05 Hz); 7.81 (td, 1 H, Ar, J_1 = 7.70 Hz, J_2 = 1.47 Hz); 7.40 (d, 1 H, Ar, *J* = 2.45 Hz); 7.34 (t, 1 H, Ar, *J* = 5.01 Hz); 7.13 (dd, 1 H, Ar, J_1 = 8.93 Hz, J_2 = 2.45 Hz); 4.21 (t, 2 H, OCH_2, *J* = 4.89 Hz); 3.90 (t, 2 H, OCH_2, *J* = 4.65 Hz); 3.72—3.77 (m, 2 H, OCH_2); 3.61—3.72 (m, 8 H, OCH_2); 3.50—3.56 (m, 2 H, OCH_2); 3.34 (s, 3 H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 166.91, 155.18, 151.52, 149.58, 148.94, 137.51, 136.97, 124.88, 124.11, 120.40, 116.52, 105.09, 71.91, 70.87, 70.63 (2 C), 70.60, 70.51, 69.68, 68.09, 59.03. HRMS, *m/z*: calculated: 419.5220 [M + H]; $C_{21}H_{26}N_2O_5S$; found: 419.1634 [M + H].

1,2-Bis[2-{[2-(pyridin-2-yl)benzo[*d*]thiazol-6-yl]oxy}ethoxy]ethane (9). In contrast to the general procedure, in this case product **9** precipitated upon addition of water to the reaction mixture, the precipitate was collected by filtration and dried on a rotary evaporator. The reaction of 6-hydroxy-2-(pyridin-2-yl)benzothiazole (**1**) (400 mg, 1.754 mmol), [ethane-1,2-diylbis(oxy)]bis(ethane-2,1-diyl) bis(tosylate) (**5**) (402 mg, 0.877 mmol), and Cs_2CO_3 (572 mg, 1.754 mmol) gave compound **9** (159 mg, 32%) as a beige powder. M.p. 199—200 °C. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 8.68 (d, 2 H, Ar, *J* = 4.8 Hz); 8.24 (d, 2 H, Ar, *J* = 7.8 Hz); 7.99 (d, 2 H, Ar, *J* = 8.8 Hz); 7.94 (t, 2 H, Ar, *J* = 7.6 Hz); 7.70 (s, 2 H, Ar); 7.54 (t, 2 H, Ar, *J* = 6.5 Hz); 7.13 (d, 2 H, Ar, *J* = 9.1 Hz); 4.18 (t, 4 H, OCH_2, *J* = 5.1 Hz); 3.80 (t, 4 H, OCH_2, *J* = 4.2 Hz); 3.65 (m, 4 H, OCH_2). IR (KBr), ν/cm^{-1}: 1554 and 1513 (C=N), 1268 and 1213 ($ArOCH_2$), 1137 ($CH_2CH_2OCH_2CH_2$). HRMS, *m/z*: calculated: 571.1468 [M + H]; $C_{30}H_{26}N_4O_4S_2$; found: 571.1468 [M + H].

Coordination compound 2-(2-{[2-(pyridin-2-yl)benzothiazol-6-yl]oxy}ethoxy)ethanol with $Cu(ClO_4)_2 \cdot 6\ H_2O$ (10). 2-(2-{[2-(Pyridin-2-yl)benzothiazol-6-yl}oxy]ethoxy)ethanol **6** (0.05 g, 0.16 mmol) was dissolved in ethanol (10 mL), followed by the addition of $Cu(ClO_4)_2 \cdot 6\ H_2O$ (0.0293 g, 0. 08 mmol). Then the mixture was refluxed for 12 h. A precipitate formed upon cooling was collected by filtration and dried *in vacuo* (water-jet pump) to obtain compound **10** (0.0402 g, 25 %) as a green powder. M.p. 238—239 °C. UV (DMSO), λ_{max}/nm (ε): 336 (12700), 752 (67). IR (KBr), ν/cm^{-1}: 3461 (OH), 3332 (OH), 1459 (C=N), 1101 (ClO_4^-), 622 (Cu—C=N). Found (%): C, 37.03; H, 4.04; N, 5.53. $C_{32}H_{32}N_4O_{14}S_2CuCl_2 \cdot 7\ H_2O$. Calculated (%): C, 37.63; H, 4.54; N, 5.49.

Coordination compound 2-(2-{[2-(pyridin-2-yl)benzothiazol-6-yl]oxy}ethoxy)ethanol with $CuCl_2 \cdot 2\ H_2O$ (11). 2-(2-{[2-(Pyridin-2-yl)benzothiazol-6-yl]oxy}ethoxy)ethanol (**6**) (0.05 g, 0.16 mmol) was dissolved in ethanol (8 mL), followed by the addition of $CuCl_2 \cdot 2\ H_2O$ (0.0274 g, 0.16 mmol). Then the mixture was refluxed for 12 h. A precipitate formed upon cooling was collected by filtration and dried *in vacuo* (water-jet pump) to obtain compound **11** (0.0193 g, 26%) as a dark green powder. M.p. 207—208 °C. UV (DMSO), λ_{max}/nm (ε): 337 (23140), 745 (37). IR (KBr), ν/cm^{-1}: 3396 (OH), 1494 (C=N), 586 (Cu—C=N). Found (%): C, 41.74; H, 3.83; N, 6.27; S, 7.38. $C_{16}H_{16}N_2O_3SCl_2Cu \cdot 0.5\ H_2O$. Calculated (%): C, 41.79; H, 3.73; N, 6.09; S, 6.97.

Coordination compound 6-methoxy-2-(2-pyridyl)benzothiazole with $CuCl_2 \cdot 2\ H_2O$ (13) was obtained according to the proceduree for complex **11**. The reaction of 6-methoxy-2-(2-pyridyl)benzothiazole (**12**) (0.2 g, 0.83 mmol) with $CuCl_2 \cdot 2\ H_2O$ (0.141 g, 0.83 mmol) in ethanol (15 mL) gave compound **13** (0.2 g, 65%) as a green powder. Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether vapor into the solution of compound **13** in a mixture of CH_2Cl_2—EtOH (1 : 1). M.p. 279—280 °C. UV (DMSO), λ_{max}/nm (ε^3): 337 (19260), 752 (39). IR (KBr), ν/cm^{-1}: 3340 (OH), 1459 (C=N), 622 (Cu—N=C). Found (%): C, 39.45; H, 2.81; N, 6.77; S, 7.83. $C_{13}H_{10}N_2OSCl_2Cu \cdot H_2O$. Calculated (%): C, 39.55; H, 3.06; N, 7.10; S, 8.12.

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