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The first tris(imidazolylbenzothiazole) copper(II) complex

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The new copper(II) complex $[Cu(IBT)_3](ClO_4)_2$ [where IBT = 2-(1*H*-imidazol-2-yl)-1,3-benzothiazole] has been synthesized and characterized by single crystal X-ray crystallography, showing a slightly distorted octahedral coordination geometry, in which two nitrogen atoms of each IBT molecule coordinate the copper ion.

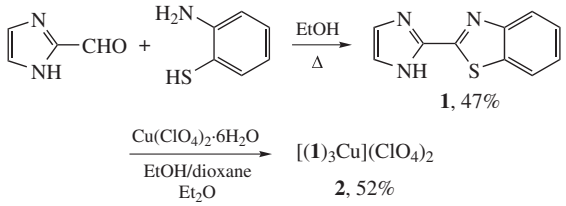
The heterocyclic ligands benzothiazole and its derivatives display a wide range of biological activities.[1] Importantly, the combinations of pharmaceutical agents with metal ions can further improve their biological activity and decrease their toxicity.[2,3] Hence, the synthesis and study of the metal complexes of benzothiazole or its derivatives are of great importance.

A limited number of copper complexes with bidentate 2-hetarylbenzothiazole ligands have been structurally characterized by X-ray diffraction. All these data refer to the complexes of 2-(2′-pyridyl)benzothiazole (PBT). Usually, the complexation of PBT with copper halides leads to tetrahedral mono-PBT complexes with additional halide ligands, whereas a change to hydrated BF_4 or PF_6 salts resulted in the isolation of square-pyramidal complexes, which contain two PBT ligand frames and one water in the coordination sphere. Thus, the reactions of PBT with $CuBr_2$ and $ZnCl_2$ in acetonitrile produce complexes $Cu(PBT)Br_2$ and $Zn(PBT)Cl_2$, respectively; both of the complexes have distorted tetrahedral coordination environments,[4] which are often observed in other complexes of copper(II) halides with 2-pyridyl-substituted heterocyclic ligands.[5] When $Cu(PBT)Br_2$ is dissolved in DMF, complex $Cu(PBT)Br_2(DMF)$ with the distorted tetrahedral coordination environment of Cu^{II} is formed.[4] The same complex was obtained by the reaction of copper(II) chloride with PBT in DMF solution.[6] The ternary complex $[Cu(PBT)(Gly)(H_2O)]ClO_4$ (Gly = glycinate) with a slightly distorted coordination geometry was described;[1(d)] this complex showed good antibacterial activities as compared with those of free PBT and $Cu(ClO_4)_2$. Ligation with PBT and $CoCl_2·H_2O$ or $Cu(BF_4)_2·H_2O$ resulted in the formation of the six-coordinate octahedral Co^{II} complex *cis*-$[Co(PBT)_2Cl_2]$ or the five-coordinate Cu^{II} complex $[Cu(PBT)_2(OH_2)](BF_4)_2$, respectively.[7] Earlier, we found that copper(II) perchlorate reacts with PBT[8] to give the similar square-pyramidal complex $[Cu(PBT)_2(OH_2)](ClO_4)_2$ with the basal plane occupied only by the nitrogen atoms of two molecules of bidentate nitrogen donor organic ligands, and the apical site occupied by the oxygen atom of a water molecule. Note that the coordination environment of the copper ion in this complex is analogous to that found for the active site of copper-containing superoxide dismutases (SOD).[9,10]

It is well established that different low-molecular-weight complexes of copper can be studied as SOD mimics,[11] and the complex $[Cu(PBT)_2(OH_2)](ClO_4)_2$ demonstrated a reasonable SOD-like activity in xantine/xantine oxidase-NBT assay tests. The above complex, as well as other model copper(II) complexes with polydentate N-ligands, not truly reflect the copper bonding in the SOD active site since none of nitrogen atoms ligating the copper atom is from an imidazole group, in contrast to the fact that the copper atom in Cu/Zn-SOD is coordinated by four imidazole residues and one aqua ligand. We supposed that the replacement of a pyridyl moiety in the ligand by the imidazole fragment should not greatly affect the type of the formed coordination compound, and the synthesis of copper complexes containing imidazole groups can be useful in elucidating the relationship between the structure and properties of coordination compounds.

In this context, we synthesized new bidentate ligand 2-(1*H*-imidazol-2-yl)-1,3-benzothiazole (IBT) **1**[†] by the condensation of 2-aminothiophenol with 1*H*-imidazole-2-carbaldehyde and studied its complexation with copper(II) perchlorate. However, the reaction of $Cu(ClO_4)_2·6H_2O$ with ligand **1** surprisingly did not led to a square-pyramidal bis(ligand) complex; complex **2** with a quite different composition and structure was formed (Scheme 1).

Complex **2** was characterized by single crystal X-ray analysis[‡] (see Figure 1 and Online Supplementary Materials). The central copper ion is ligated by six nitrogen atoms from three IBT ligands and adopts a slightly elongated octahedral geometry due



Scheme 1

† *2-(1*H*-Imidazol-2-yl)-1,3-benzothiazole* **1**. A solution of 2-aminothiophenol (0.6 ml, 5 mmol), 1*H*-imidazole-2-carbaldehyde (0.48 g, 5 mmol) and a drop of glacial acetic acid in 15 ml of EtOH was refluxed with stirring for 1.5 h. The precipitate formed after cooling was filtered off and dried in air giving 0.49 g (47%) of compound **1** as a black solid. ^{1}H NMR (DMSO-d_6) δ: 13.5 (s, 1H, NH), 8.15 (d, 1H, *J* 7.4 Hz), 8.02 (d, 1H, *J* 8.2 Hz), 7.65 (t, 1H, *J* 8.2 Hz), 7.47 (t, 1H, *J* 8.2 Hz), 7.42 (s, 1H), 7.18 (s, 1H). ^{13}C NMR (DMSO-d_6) δ: 153.97, 139.85, 134.37, 129.80, 126.97, 126.95, 126.10, 123.33, 122.52. IR (ν/cm^{-1}): 1575. Found (%): C, 59.92; H, 3.71; N, 20.79; S, 15.68. Calc. for $C_{10}H_7N_3S$ (%): C, 59.68; H, 3.51; N, 20.88; S, 15.93.

*Tris[2-(1*H*-imidazol-2-yl)-1,3-benzothiazole]copper(II) diperchlorate* **2**. To a solution of compound **1** (15 mg, 0.075 mmol) in 1 ml of dioxane, a solution of $Cu(ClO_4)_2·6H_2O$ (13.8 mg, 0.037 mmol) in 1 ml of EtOH was added. After 1 h, the resulting solution was exposed to diethyl ether vapor for a week. The green crystals formed were filtered off and dried in air. Yield, 11.2 mg (52%), mp > 250 °C. Found (%): C, 41.19; H, 2.60; N, 14.41; S, 11.02. Calc. for $C_{30}H_{21}Cl_2CuN_9O_8S_3$ (%): C, 41.60; H, 2.44; N, 14.55; S, 11.10.

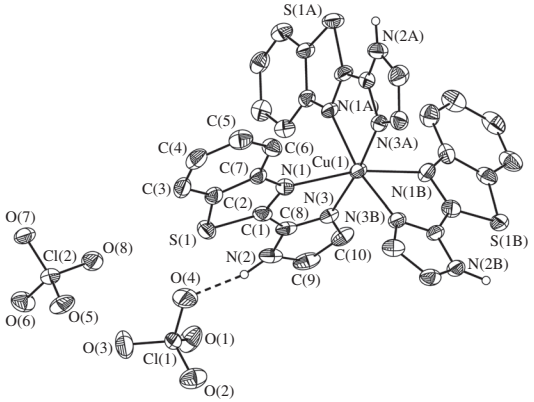


Figure 1 General view of complex **2** in the representation of atoms *via* thermal ellipsoids at a 50% probability level. Hydrogen atoms, except those of NH groups and some labels of carbon atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–N(3A) 1.976(4), Cu(1)–N(3B) 2.025(4), Cu(1)–N(1A) 2.150(4), Cu(1)–N(1B) 2.387(4), Cu(1)–N(1) 2.391(4); N(3A)–Cu(1)–N(3) 172.74(16), N(3A)–Cu(1)–N(3B) 91.49(14), N(3)–Cu(1)–N(3B) 93.06(15), N(3A)–Cu(1)–N(1A) 80.91(15), N(3)–Cu(1)–N(1A) 95.42(15), N(3B)–Cu(1)–N(1A) 168.31(15), N(1)–Cu–N(1B) 164.80(13). Hydrogen bonds (Å and °): N(2A)–H(2NA)···O(5)#1 [*d*(D–H) 0.86, *d*(H···A) 2.59, *d*(D···A) 3.176(5), ∠DHA 126]; N(2A)–H(2NA)···O(8)#1 [*d*(D–H) 0.86, *d*(H···A) 2.00, *d*(D···A) 2.851(6), ∠DHA 170]; N(2)–H(2N)···O(4)#2 [*d*(D–H) 0.94, *d*(H···A) 1.87, *d*(D···A) 2.782(6), ∠DHA 163]; N(2B)–H(2NB)···O(7)#3 [*d*(D–H) 0.95, *d*(H···A) 1.99, *d*(D···A) 2.888(5), ∠DHA 157]. Symmetry transformations used to generate equivalent atoms: (#1) $x - 1/2, -y + 1/2, -z$; (#2) x, y, z; (#3) $x + 1/2, -y + 1/2, -z$.

to the Jahn–Teller effect,[12,13] which is commonly observed in Cu^{II} complexes. Two of the longest Cu–N(benzothiazole) bonds with apical ligands, namely, Cu–N(1) and Cu–N(1B) (both 2.39 Å), are in the *trans* position to each other, while the shortest bond Cu–N(1A) [2.150(4) Å] is opposite to the Cu–N(3B)(imidazole) bond. The Cu–N(imidazole) bond lengths are 1.976(4)–2.025(4) Å; the Cu–N(benzothiazole) bond lengths are 2.150(4)–2.391(4) Å. The lengths of Cu–N bonds are typical of copper(II) complexes containing imidazole[14,15] and pyridine[16,17] groups. The coordination angles reflect the strong distortion, which is most likely the result of the small bite angle of the IBT ligand. The analogous metal–ligand bond lengths and ligand–metal–ligand bond angles are almost identical for all of the IBT ligand frames bound to the copper.

Hydrogen bonding is very important in consolidating the crystal structures of complex **2**. The uncoordinated nitrogen atoms of each imidazole group of IBT donate a medium strength hydrogen bond to one of the perchlorate anion oxygen atoms [*d*(D···A) 2.782(6)–2.851(6) Å] (Figure 1). These hydrogen bonds demonstrate the very strong tendency of the uncoordinated nitrogen atom of the ligated imidazole to form a hydrogen bond with a proton acceptor group; this behavior is commonly observed in the active sites of metalloenzymes, playing a very important role in catalytic processes.[18–20] Infinite layers along the crystallographic *ab* plane are formed in the crystal due to hydrogen bonds between the cations and anions.

In conclusion, the use of imidazole-substituted benzothiazole ligand instead of structurally similar 2-(2′-pyridyl)benzothiazole one yielded an entirely different copper complex containing three 2-(imidazole-2-yl)benzothiazole moieties, which is the first example of copper(II) complexes with imidazole-containing benzothiazole ligands and tris(ligand) octahedral complexes of 2-(2′-hetaryl)-1,3-benzothiazole. Thus, small changes in the structure of an organic ligand can lead to dramatic changes in the structure of the formed complex and the metal ion environment.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.03.025.

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‡ *Crystal data for* **2**: green crystal, $C_{30}H_{21}Cl_2CuN_9O_8S_3$ (M = 866.18), orthorhombic, space group $P2_12_12_1$, at 120(2) K: a = 13.0454(14), b = = 14.3302(14) and c = 18.4226(18) Å, V = 3444.0(6) Å^3, Z = 4, d_{calc} = = 1.671 g cm^{-3}, μ = 1.037 mm^{-1}. Bruker Smart Apex II CCD diffractometer, 27616 reflections collected, 9131 observed reflections with $I > 2\sigma(I)$, final R = 0.0584, wR_2 = 0.0983, 6191 unique reflections with $F^2 \geqslant 2\sigma(I)$, S = 1.040.

CCDC 1015811 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.