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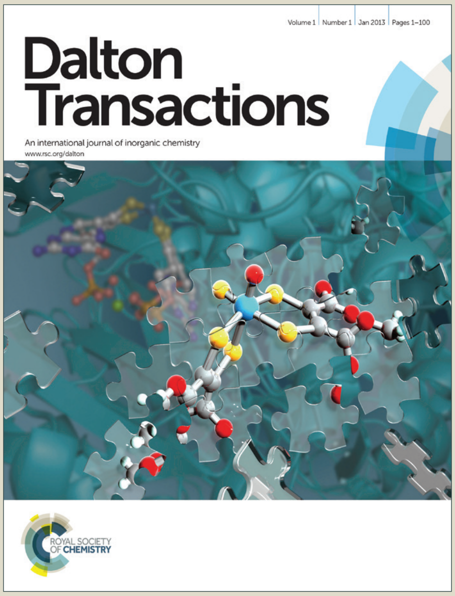

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Crystal Structures of Benzoxazolyl-Copper(III, II, I) Complexes and Cu(II)-Mediated Aryl Carbon-Hydrogen Bromination

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Copper complexes have been frequently invoked in many Cu-mediated carbon-hydrogen halogenation reactions. We fortunately obtained three different valents benzoxazolyl-copper complexes along with the aryl carbon-hydrogen bromination in the self-assembly of ligands with $CuBr_2$, which have been characterized by X-ray single crystal diffraction successfully. The results indicate that **1** consists of di-brominated p-benzoxazolylphenylamine (**L**) and the relevant unusual high valent copper(III) complexes with tetrahedral geometries, **2** is also the first polymeric catenulate di-brominated benzoxazolyl-copper(I) complex and **3** is the mono-brominated benzoxazolyl-copper(II) complex. We speculate the proposed mechanisms for the formation of these complexes and the bromination of aryl carbon-hydrogen based on these crystal structures.

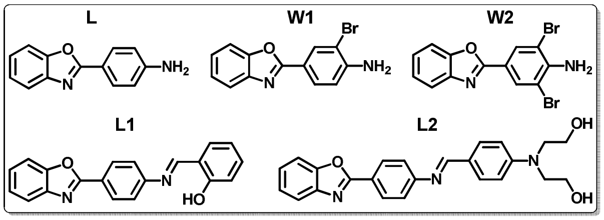
Introduction

In recent years, the earth-abundant copper salts have been used as succedaneums of noble metals such as palladium to mediate and catalyze carbon-hydrogen functionalization reactions for constructing the formation of carbon-carbon and carbon-heteroatom bonds.[1-6] In recent Cu-mediated/ catalyzed carbon-hydrogen activation reactions, researchers speculated some proposed reaction mechanisms for the formation of carbon-carbon and carbon-heteroatom bonds.[3,7-11] Among these mechanisms, the species of unusually high valent Cu (III) are frequently suggested as an essential and key intermediate that can urge the transformations of carbon-hydrogen bond.[1,3,5,9,11,] The Cu (I) and Cu (II) is the most common oxidation states, while the Cu (III) are scarce in inorganic and coordination chemistry.

Since Burton *et al* reported the first crystallo-graphically characterized copper(III) complex, $[Cu^{III}(CF_3)_2(SC(S)NEt_2)]$ in 1989,[12,13] a few copper(III) complexes have been structurally well-defined by rapid-injection nuclear magnetic resonance (RI-NMR) spectroscopy, X-ray crystallography, X-ray absorption spectroscopy (XAS) and et al successively.[1,5,10] Most Cu (III) complexes show square-planar or tetrahedral geometries, in agreement with a d^8 electronic configuration. Thus the strategy of using anionic tetradentate ligands to force square-planar geometry has been widely used for stabilizing Cu (III) complexes.[14,15] Similarly, porphyrins and corrole derivatives have also been used to stabilize copper in high oxidation state.[5,16,17]

Although the formation of Cu (III) species has been frequently suggested in recent Cu-mediated/catalyzed carbon-hydrogen functionalization reactions, owing to the rather reactive nature of Cu (III) species, they all cannot provide the direct evidence to support their hypothesis.[18] Furthermore, to the best of our knowledge, no structurally well-defined copper (III) complexes with tetrahedral geometries have been reported in the literature.[1,3,4,7-11,17-19]

In the self-assembly of benzoxazolyl ligands with $CuBr_2$ in room temperature, we obtained three different valent benzoxazolyl-copper complexes based on the mono-/di-brominated ligand **L** that have been characterized by X-ray single crystal diffraction analysis. Herein, we present the unprecedental example of benzoxazolyl-copper(III) complex **1** with tetrahedral geometries for the first time. At the same time, **2** also exhibits an unusual polemeric benzoxazolyl-copper(I) chain. The structures also indicate that the Schiff base **L1** and **L2** were decomposed into **L** under the weak acidity of Lewis Cu^{2+}. In addition, we speculate the proposed mechanism of Cu(II)-mediated direct aryl carbon hydrogen halogenation according to the crystal structures of **1**-**3**. The molecular structures of ligands **L**, **L1**, **L2** and the brominated products **W1**, **W2** are shown in Scheme 1.



Scheme 1 The molecular structures of ligand **L**, **L1**, **L2** and the brominated products **W1**, **W2**.

Results and discussion

Three copper complexes with different oxidation states are stable under atmospheric conditions and their molecular structures were determined based on X-ray single crystal diffraction analyses. The crystallographic data of **1**-**3** are summarized in Table 1, the selected bond lengths and angles data and the geometrical parameters of the hydrogen bonds are tabulated in Table S1-S2, ESI†), respectively.

Table 1 Crystallographic data for **1-3**.

	1	**2**	**3**
empirical formula	$C_{26}H_{16}Br_7CuN_4O_2$	$C_{13}H_8Br_3CuN_2O$	$C_{26}H_{18}Br_4CuN_4O_2$
formula weight	1039.34	511.48	801.62
crystal system	Monoclinic	Monoclinic	Triclinic
space group	P 21/c	P n	P -1
a [Å]	7.402(5)	4.043(5)	7.974(5)
b [Å]	21.994(5)	14.545(5)	9.060(5)
c [Å]	19.692(5)	12.082(5)	9.663(5)
α [°]	90.000(5)	90.000(5)	81.395(5)
β [°]	100.110(5)	95.877(5)	73.778(5)
γ [°]	90.000(5)	90.000(5)	83.536(5)
V [Å^3]	3156(2)	706.8(10)	660.9(6)
Z	4	2	1
T [K]	296(2)	296(2)	296(2)
D_{calcd}[g ·cm^{-3}]	2.187	2.403	2.014
μ [mm^{-1}]	9.586	10.019	6.905
ϑ range [°]	1.85-25.00	2.20-24.98	2.21-25.00
total no. data	22266	4840	4738
no.unique data	5555	2349	2309
no. params	361	178	169
R_1	0.0476	0.0232	0.0618
wR_2	0.1558	0.0490	0.1850
GOF	1.048	0.991	1.034

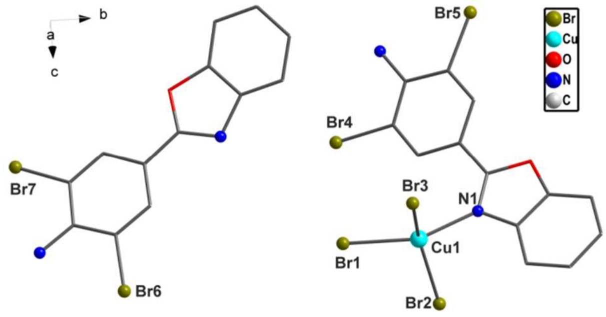


Fig. 1 Molecular structure of **1**. All hydrogen atoms are omitted for clarity.

Structure of Benzoxazolyl-Copper(III) Complexes (1). The crystal structure of complex **1** is illustrated in Fig. 1. Black complex **1** crystalizes in a monoclinic system and space group P21/c and the asymmetric unit consists of two kinds of compounds: the dibromine substituted *p*-benzoxazolyl-phenylamine (**W2**) and its copper complex (**W2**-**CuBr$_3$**). The bromine atoms substitute the *o*-positions of phenylamine. In addition, the copper atom is four-coordinated and displays a seriously distorted tetrahedral geometry supplied by three bromine atoms (Cu1-Br1 2.3397(15) Å, Cu1-Br2 2.3707(19) Å, Cu1-Br3 2.4202 Å, Br1-Cu1-Br2 96.91(6) °, Br1-Cu1-Br3 96.17(7) °, Br2-Cu1-Br3 146.41(7) °) and one nitrogen atom from benzoxazole group (Cu1-N1 1.997(6) Å, N1-Cu1-Br1 151.3(2)°, N1-Cu1-Br2 92.05(19)°, N1-Cu1-Br3 91.1(2)°). These bond lengths and angles around copper center are analogous to that of other copper complex systems.[33-37] The existence of the neutral **W2** compounds and the three bromine atoms in **1** clearly indicates that the copper center is in high-valent +3 oxidation states. Thus, **1** presents the first unusual high-valent copper(III) complex with tetrahedral geometry. [1,3,4,7-11,17-19]

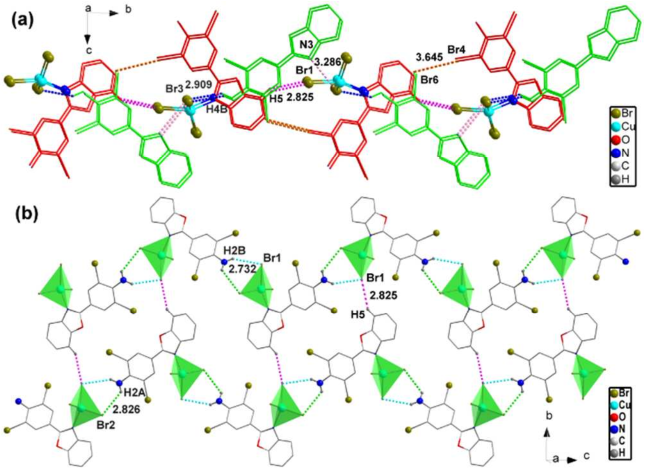


Fig. 2 (a) The two dimensional layer structure of **1**, (b) the two dimensional layer structure of **1**, The colorized dotted lines represent the weak interactions and hydrogen atoms not participating in hydrogen bonds are omitted for clarity.

As shown in Fig. 2b (ESI†), the bromine atoms of the **W2-CuBr$_3$** complex molecules form hydrogen bond interactions with hydrogen atoms (H2B···Br1 2.732(1) Å, H2A···Br2 2.8252 Å, H5···Br1 2.825(1) Å), yielding an infinite two dimensional layer supramolecular structures in the solid state. The resulting layers and **W2** molecules are packed together to generate a multilayer band structure by intermolecular weak interactions between them, including H4B···Br3 2.909(1) Å, Br4···Br6 3.645 Å, Br3···N3 3.286 Å (Fig. 2a, ESI†), which indicate that the **W2** ligand is in favour of the crystallization process of **1**. Fig. S1 (ESI†) exhibits the three dimensional latticed structure of **1** along the [100] direction.

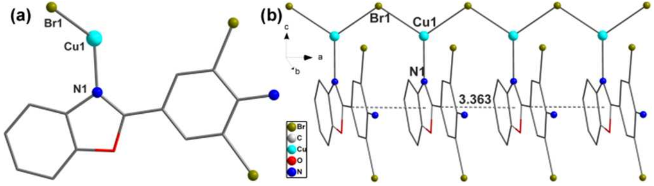


Fig. 3 (a) The molecular structure of unit of **2**. (b) The one dimensional polymeric chain of **2** formed by multiple Br-Cu-Br bonds and π···π interactions. All hydrogen atoms are omitted for clarity.

Structure of Benzoxazolyl-Copper(I) Complexes (2). X-ray single crystal diffraction analysis reveals that **2** crystallizes in the monoclinic system with space group P n and the crystal structure of unit is depicted in Fig. 3a. Fig. 3b shows that **2** features one dimensional polymeric chains formed by multiple Br-Cu-Br bonds (Br1-Cu1 2.411(2) Å, Br1-Cu1$^{\#2}$ 2.392(2) Å) and π···π interactions (*d* = 3.363 Å). In the structure of **2**, the copper center is three-coordinated by two Br atoms and one N atom from the benzoxazolyl group in a planar trigonal geometry, and the Br atoms are also coordinated with two copper atoms, respectively (Fig. 3b). To the best of our knowledge, **2** is the first three-coordinated copper bromine coordination polymer with Cu^{I}-Br-Cu^{I} structural motif that has been structurally characterized.[20-25] These one dimensional polymeric chains are further linked to form three dimensional supramolecular network architecture by multiple N-H···Br (H2B···Br1 3.045(3) Å, H2A···Br3 2.888(1) Å), C-H···O (H3···O1 2.771(3) Å), Br···Br (Br2···Br3 3.497(4) Å) interactions, as shown in

Fig. S2 (ESI†). It is no doubt for these existing intramolecular hydrogen bonds to contribute significantly to the alignment of the molecules in the crystalline state.

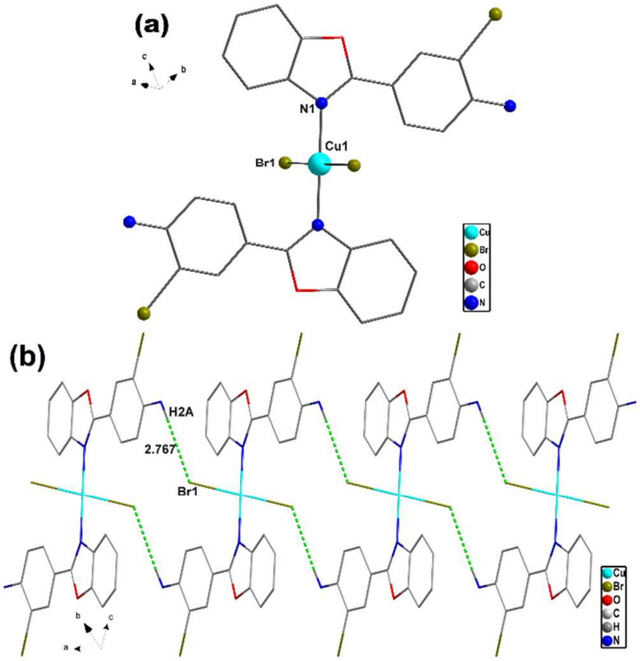
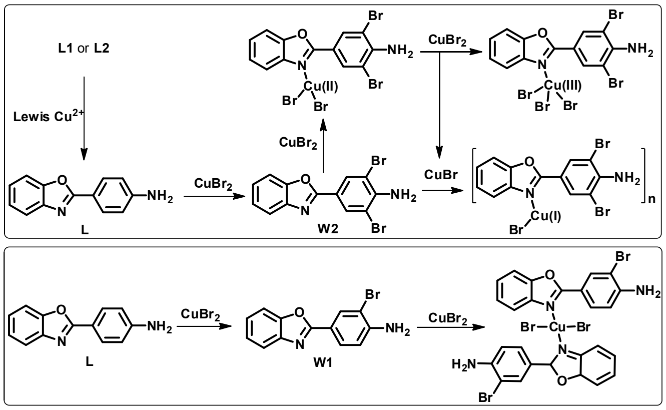


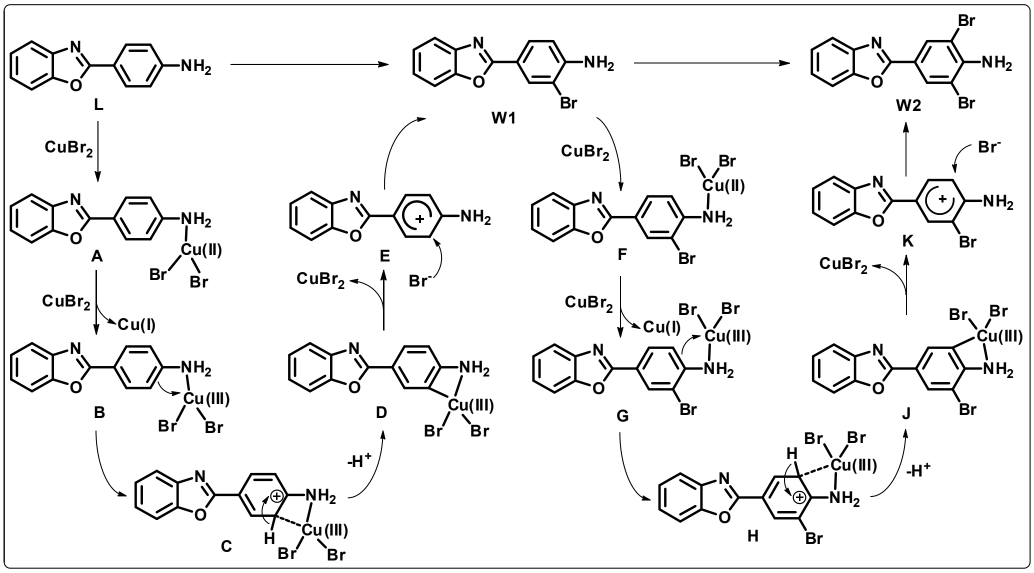
Fig. 4 (a) Molecular structure of **3**. (b) The one dimensional chain structure of **3** formed by multiple N-H···Br interactions. The colorized dotted lines represent the weak interactions and hydrogen atoms not participating in hydrogen bonds are omitted for clarity. All hydrogen atoms are omitted for clarity.

Structure of Benzoxazolyl-Copper(II) Complexes (3). Fig. 4a exhibits the molecular structure of complex **3**. X-ray single crystal diffraction analysis demonstrates that complex **3** crystalizes in a triclinic system, space group *P*-1. Different from complex **1** and **2**, complex **3** performs a symmetric unit that consists of one independent Cu atom, two coordinated bromine groups and two mono-bromine substituted p-benzoxazolylphenylamines (**W1**). Obviously, the copper center is four-coordinated in square-planar geometry and the equatorial positions of copper center are occupied by two nitrogen atoms from two benzoxazolyl groups and two bromine atoms. The distance between copper center and nitrogen atoms is 1.983(7) Å and the Cu-Br bond length is 2.4266(15) Å. The angles of N-Cu-Br are 90.1(2)° and 89.9(2)°, respectively. Fig. 4b (ESI†) displays the one dimensional band structure of **3** formed by the N-H···Br (H···Br 2.767(2) Å) hydrogen bonds.



Scheme 2 Proposed mechanisms for synthesis of benzoxzolyl-copper complexes.

Formation of Benzoxazolyl-Copper Complexes. The above results clearly demonstrate that the Schiff base ligands **L1** and **L2** decomposed into ligand **L** under the weak acidity of Lewis Cu(II). And then, ligand **L** firstly transforms into new ligand **W1** or **W2** through the carbon-hydrogen bromination of aniline, which can be proved by the above crystal structures. The resulting ligand **W2** coordinates with CuBr$_2$ to produce the intermediate **W2-CuBr$_2$**. The Cu(II) ion acts as an oxidant to oxidize the intermediate **W2-CuBr$_2$** into complex **W2-CuBr$_3$**, and itself is reduced into Cu(I) ion. Finally, the complex **W2-CuBr$_3$** crystallizes with ligand **W$_2$** to produce **1**. On the other hand, the resulting CuBr coordinates with ligand **W$_2$** to produce polymeric **2**. The direct coordination between the mono-brominated **W1** with **CuBr$_2$** produces complex **3**, which may restrict the further bromination of **W1** and the oxidation of copper(II) complex. The stepwise formation of these benzoxazolyl-copper complexes are shown in Scheme 2.



Scheme 3 Proposed mechanisms for the Cu-mediated carbon-hydrogen bromination of aniline.

Bromination Mechanism of Aryl Carbon Hydrogen. On the basis of the above depicted works and the related literatures[3,5,11,17,18,26-29], we speculated and proposed a 2Cu(II) →Cu(III) + Cu(I) mechanism for the bromination reactions, as shown in Scheme 3. Namely, coordination of Cu(II) with amino group in **L** generates the Cu(II) intermediate **A**. Intermediate **A** transfers to the high valent Cu(III) intermediate **B** under the oxidation of $CuBr_2$, and the $CuBr_2$ simultaneously translates into CuBr.[5,11,18,26] Here, the above mentioned complex **1** and **2** can provide the direct evidence to support the existence of Cu(III) and Cu(I) in the system. And then, nucleophilic attack of the phenyl ring to highly valent Cu(III) center in the intermediate **B** produces the Cu(III) intermediate **D** via intermediate **C** through a dearomatization and rearomatization process.[3,18] Finally, the reductive elimination of intermediate **D** generates the intermediate **E** and the nucleophilic attack of the bromine ions to active intermediate **E** delivers the mono-brominated product **W1**. At this point, **L** transfers to **W1** through the above the transformation of intermediates. Then, **W1** gets into the next same catalytic cycle process to produce the di-brominated product **W2** through the transformation of intermediates **F**, **G**, **H**, **J** and **K**. The existences of mono-/ di-brominated product **W1** or **W2** in the complexes effectively prove that the above proposed mechanisms of carbon-hydrogen bromination of aniline are reasonable.

Table 2 The Mulliken charge distribution of N atoms in different ligands

Ligands	**L**	**W1**	**W2**
q_{N1}	-0.555	-0.574	-0.595
q_{N2}	-0.730	-0.721	-0.707

q_{N1}: the Mulliken charge of N atom in benzoxazolyl group, q_{N2}: the Mulliken charge of N atom in amino group.

We calculated the Mulliken charge distribution of nitrogen atoms in different ligands by using the density functional theory at B3LYP/6-31G(d) level based on their molecular conformation in the crystal structures, and the results are shown in Table 2 and Fig. S3-S4 (ESI†).[30-31] The Mulliken charge of N atom in amino group is more negative than that in benzoxazaolyl group, which illustrates that the amino group is easier to coordinate with Cu(II) ion than benzoxazaolyl group. With the increasing of bromine in ligand **L**, the Mulliken charge of N atom in amino group decreases and however the Mulliken charge of N atom in benzoxazolyl group increases. At the same time, the existence of two bromines atoms enhances the steric hindrance, which also effectively restrains the further coordination between copper ions and amino group. These discussions indicate that the nitrogen atoms in benzoxazaolyl group are inclined to coordinate with copper ions. In addition, there not exists the nucleophilic attack of the phenyl ring to Cu(III) center in the product **W2-CuBr₃** in the formation of benzoxazolyl-copper(III) complexes, which may be caused by the existence of bromine atoms. The explanation can be generalized in two aspects: the bromine atoms act as electron-withdrawing groups to reduce the electronegativity of phenyl group and the bromine atoms also increase the steric hindrance of phenyl group, which eliminate the possibility of the nucleophilic attack of the phenyl ring.

Conclusions

In summary, we have reported for the first time the crystal structures of a series of stable benzoxazolyl-copper complexes with three different oxidation valent states (+3, +2 and +1). To the best of our knowledge, **1** presents the unprecedented high-valent benzoxazolyl-copper(III) complex with tetrahedral geometry, **2** is also the first example of benzoxazolyl-copper(I) complex that contains polymeric Cu^{I}-Br-Cu^{I} structural chain and **3** is mono-brominated benzoxazolyl-copper(II) complex. According to these crystal structures, we speculate the possible bromination process of aryl carbon-hydrogen and the formation of these benzoxazolyl-copper complexes.

Experimental

Materials and methods. All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. Theoretical calculations were carried out using Gaussian 03W package of programs based on their molecular conformation in the crystal structure.

Crystal Structure Determination. The X-ray diffraction measurements were performed on a Bruker SMART CCD area detector using graphite monochromated MoK radiation (λ = 0.71069 Å) at 298 (2) K. Intensity data were collected in the variable ω-scan mode. The structures were solved by direct methods and difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. Calculations were performed with SHELXTL-97 program package. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC: 1020489, 1020490, 1038362.

Synthetic procedures. The ligands were prepared according to the synthetic routes shown in Scheme S1 (ESI†) and our previous work [32]. Complexes **1**-**3** were prepared by a similar procedure. The methanol solution (20 mL) of $CuBr_2$ (0.447 g, 2 mmol) were added into the solution of ligands (**L1**: 0.314 g, 1 mmol, **L2**: 0.401 g, 1 mmol and **L**: 0.210 g, 1 mmol) in dichloromethane (10 mL) and the product was obtained by slow interlayer diffusion at room temperature, respectively. We single out the stable and regular single crystals of **1**-**3** under microscope and the crystals are characterized by single crystal X-ray diffraction analyses. Result: **1**, black block crystal, 0.075 g, yield 9.85%, **2**, light yellow needle crystal, 0.067 g, yield 7.9%, **3**, black block crystal, 0.09 g, yield 13.3%.

Acknowledgements

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Notes and references

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† Electronic Supplementary Information (ESI) available: Crystallographic information files (CIF), the selected bond lengths and angles data, the geometrical parameters of the hydrogen bonds, the multi-dimensional supramolecular structures of crystal structures and the Mulliken charge distribution of atoms, experimental section and computational details. CCDC 1020489, 1020490, 1038362. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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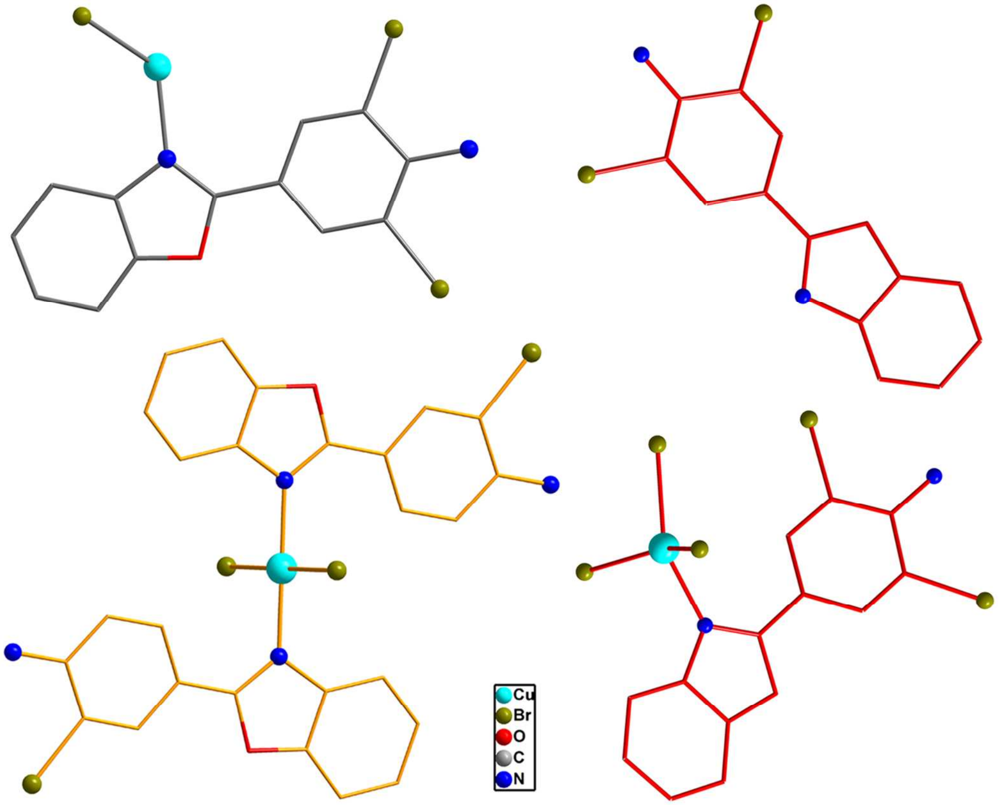

We report three new copper complexes with different oxidation states based on phenylbenzoxazole system.
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