

## In situ Synthesis, Crystal Structure, XPS and Fluorescent Property of a Novel Two-Dimensional Binuclear Copper(I) Tetrazole Complex

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Received October 2, 2012, Accepted October 23, 2012

**Key Words :** Binuclear Cu<sup>I</sup> complex, Tetrazole compound, Crystal structure, Fluorescent property, XPS

Since pioneering work done by Sharpless *et al.*,<sup>1-7</sup> there has been a tremendous research interest focused on the exploration of *in situ* tetrazole organic ligand synthesis through [2+3] cycloaddition reactions between organic cyano compounds and NaN<sub>3</sub> in the presence of Lewis acid catalyst such as Zn<sup>2+</sup> ions.<sup>8-11</sup> As a result, there is much research concentrated on the crystallographic characterization of such intermediates containing metal ion and exploration of their applications in nonlinear optical, fluorescent (or phosphorescent), ferroelectric, and chiral properties.<sup>8-11</sup>

To the best of our knowledge, most of the metal tetrazole compounds reported by literature are zinc, cadmium and manganese complexes *etc.*, only a few copper tetrazole complexes from Demko-Sharpless [2+3] cycloaddition reaction were reported.<sup>3,4</sup> Moreover, in most of reported copper tetrazole complexes, the central copper atoms often adopt either four or five or six coordination modes, three coordination modes of copper complexes have not been reported before. Fortunately, when we perform pure inorganic complex bis-(4-cyanopyridine)copper(II) azide replacing the organic cyano group and NaN<sub>3</sub> during Sharpless's tetrazole synthesis, we got a novel two-dimensional copper(I) tetrazole complex with a rare irregular trigonal planar coordination mode of Cu(I). To our surprised, different from other copper(I) tetrazole complexes,<sup>3,12-14</sup> there exist a interesting Cu-Cu metal (3.258 Å) bonds in the crystal structure of title compound. Moreover, the Cu-Cu metal bond distance is obviously shorter than that of Gao (3.421 Å)<sup>15</sup> and Dan li<sup>16</sup> (3.484-3.592 Å) *et al.*'s work. Herein we report the synthesis, crystal structure, XPS and luminescent property of these intermediates.

### Experimental

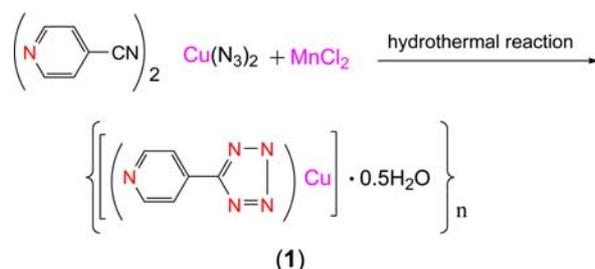
As shown in Scheme 1, a heavy walled Pyrex tube containing a mixture of Cu(4-cyanopyridine)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub> (0.0252 g, 0.1 mmol), MnCl<sub>2</sub>(0.0125 g, 0.1 mmol), water (0.5 mL) and ethanol (1.0 mL) was frozen and sealed under vacuum, then placed inside an oven at 160 °C. The pale yellow block-like crystals were obtained after 24 hours of heating. Calc. for **1**: C 31.62, H 3.64, N 30.74; Found for **1**: C 31.56, H 3.59, N 30.82. IR (KBr, cm<sup>-1</sup>) 3412 (m), 1626 (w), 1609 (s),

1587 (s), 1456 (s), 1423 (m), 1361 (w), 1133 (m), 1019 (m), 816 (w), 753 (w), 709 (m), 640 (w), 453 (w).

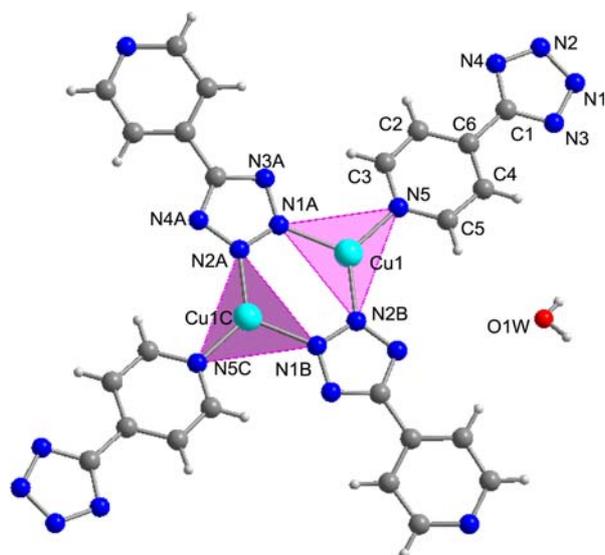
Crystal data of **1** was selected on a Bruker P4 diffractometer with graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 296 K using the  $\theta$ - $2\theta$  scan technique. The crystal structure was solved by direct methods with SHELXS-97 program.<sup>17,18</sup> Detailed information about the crystal data and structure determination for title compound is summarized in Table 1. The selected intra atomic distances and bond angles are given in Table 2. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax (int.code) 44(1223)336-033 or E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk. CCDC NO.: 866658 for **1**.

### Results and Discussion

The pale yellow crystals of the title compound suggest it may be a Cu<sup>I</sup> complex, as we know, most of the Cu<sup>II</sup> compounds are blue or green. The Cu(4-cyanopyridine)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub> (**A**) have been evidenced by two typical peaks around 2300 cm<sup>-1</sup> of the cyano group and 2100 cm<sup>-1</sup> of the azide group in IR spectrum. A series of new peaks around 1626-1424 cm<sup>-1</sup> appeared while the peaks around 2300 cm<sup>-1</sup> and 2100 cm<sup>-1</sup> disappeared in the IR spectrum of title compound, indicating the [2+3] cycloaddition reaction between cyano group and azide anion has occurred.<sup>19-21</sup> In addition, a new broad middle absorption around the 3400 cm<sup>-1</sup> suggests the existence of water molecules in title compound. Crystallographic data of **1** (Table 1) suggest that title compound belong to monoclinic crystal system, C2/c space group. As shown in Figure 1, the basic unit cell of



**Scheme 1.** Preparation of title compound.



**Figure 1.** Polyhedral representation of **1** shows the local coordinated geometry around Cu center has a distorted trigonal planar. Symmetry codes: A(#1):  $-1/2, -z+1/2$ ; B(#2)  $1/2, -y+1/2, z-1/2$ ; C(#3):  $+1/2, y+1/2, -z+1/2$ ; D(#4):  $1/2, -y+1/2, z+1/2$ .

compound **1** contains one central copper metal atom, one tetrazole ligand and one cocrystallized water molecules. Each tetrazole group loses one proton and the oxidation state of copper is clearly +1. As we expected, in the reaction, the  $Mn^{2+}$  act as a Lewis acid catalyst, the  $N^{3-}$  have been reduced to tetrazole group, the  $Cu^{II}$  have been reduced to  $Cu^I$  and the CN group have been oxidized to tetrazole group. To our surprise, although the original intention of our experiment is to prepare the Cu-Mn heterometallic complex, the target compound was turned to be a novel single metal  $Cu^I$  complex; we also performed further experiment using other transition metal salts ( $ZnCl_2$  or  $CdCl_2$ , *et al.*) instead of the  $MnCl_2$  in the same reaction system, the result shows that no corresponding  $Cu^I$  tetrazole complex be obtained. However, when we used other manganese such as  $Mn(ClO_4)_2$ ,  $MnSO_4$ , and  $Mn(CH_3COOH)_2$  *et al.* replacing  $MnCl_2$  in the experiment, we can also get the same structure of title compound. The reason why the presence of  $Mn^{2+}$  instead of  $Zn^{2+}$  or  $Cd^{2+}$  ions can catalyst this reaction may be due to the  $Mn^{2+}$  has the lower reduction potential ( $-1.185$  V) than  $Zn^{2+}$  ( $-0.7618$  V) and  $Cd^{2+}$  ( $-0.4030$  V). As we know, the lower reduction potential, the stronger reducing power.

The local coordination geometry around the Cu ion can be described as a rare irregular trigonal planar which is connected by double  $\beta$  N atoms from different tetrazole groups, one N atom from pyridyl group of another 4-tetrazolepyridine ligand. As shown in Table 1, the bond distance of Cu(1)-N(2)#2 (2.001(10) Å) is slightly longer than that of Cu(1)-N(1)#1 (1.947(10) Å) and Cu(1)-N(5) 1.967(9) Å, also, the bond angles of N(1)#1-Cu(1)-N(5) ( $129.8(4)^\circ$ ) is more than that of N(1)#1-Cu(1)-N(2)#2 ( $115.7(4)^\circ$ ) and N(5)-Cu(1)-N(2)#2 ( $114.5(4)^\circ$ ) suggesting that the  $Cu^I$  center atoms lies in a highly unsymmetrical fashion. As shown in Figures 1 and 2, all the 4-tetrazole pyridine (4-

**Table 1.** Crystal data and structure refinement for **1**

Empirical formula	$C_6 H_6 Cu N_5 O$
Fw	227.70
T, K	296(2)
Wavelength (Å)	0.71073
Crystal system, Space group	Monoclinic, $C2/c$
$a$ , Å	12.640(4)
$b$ , Å	17.343(5)
$c$ , Å	7.839(2)
$\beta$ , ( $^\circ$ )	94.946(4)
$V$ , Å <sup>3</sup>	1712.0(8)
Z	8
$\rho$ (calcd), Mg/m <sup>3</sup>	1.767
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	2.516
F (000)	912
Crystal size (mm <sup>3</sup> )	0.30 × 0.25 × 0.2
$\theta$ range for data collection ( $^\circ$ )	2.00-25.98
Index ranges	$-15 \leq h \leq 10, -16 \leq k \leq 21, -9 \leq l \leq 9$
Reflections collected	4408
Independent reflections	1685 [R(int) = 0.0475]
Data/restraints/parameters	1685 / 3 / 119
Final R indices [ $I > 2\sigma(I)$ ] (6699)	$R1 = 0.0458, wR2 = 0.1132$
R indices (all data)	$R1 = 0.0854, wR2 = 0.1304$
Min., Max. $\rho$ /e Å <sup>-3</sup>	0.487, $-0.353$

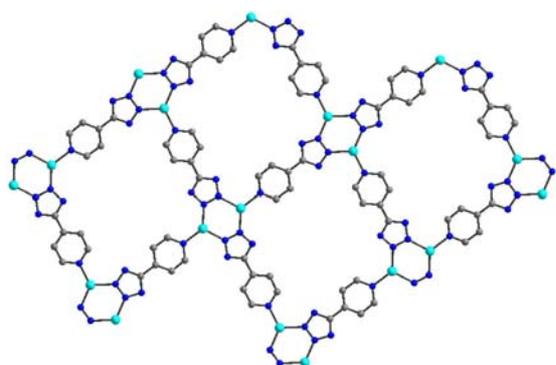
$C_5H_4N-CN_4$ ) ligand in **1** act as tridentate bridging linkers which connect three different Cu atoms through double  $\beta$  site N atoms from tetrazole group and one N atom from pyridyl group. Interestingly, four  $\beta$  site N atoms from double different 4-tetrazole pyridine ligands link the same two Cu atoms by  $\mu_1$  modes, thus forming a binuclear structure which containing an interesting six-membered ring along the Cu1-N1A-N4A-Cu1C-N1B-N2B bonding sequence. The sum of N(1)-N(2)-Cu(1)#4 ( $124.2(8)^\circ$ ), N(2)-N(1)-Cu(1)#3 ( $120.1(8)^\circ$ ), N(1)#1-Cu(1)-N(2)#2, ( $115.7(4)^\circ$ ) is  $360^\circ$ , so we can conclude that all the atoms of six-membered ring lie in the same plane.

As shown in Figure 2, the binuclear copper subunits are further cross-linked by the molecular skeletons of the 4-tetrazole pyridine ligands in an end-to-end mode, thereby

**Table 2.** Selected bond distances (Å) and angles ( $^\circ$ ) for **1**

Bond lengths	
Cu(1)-N(1)#1	1.947(1)
Cu(1)-N(5)	1.967(9)
Cu(1)-N(2)#2	2.001(1)
N(1)-Cu(1)#3	1.947(1)
N(2)-Cu(1)#4	2.001(1)
N(1)#1-Cu(1)-N(5)	129.8(4)
N(1)#1-Cu(1)-N(2)#2	115.7(4)
N(5)-Cu(1)-N(2)#2	114.5(4)
N(2)-N(1)-Cu(1)#3	120.1(8)
N(3)-N(1)-Cu(1)#3	130.1(8)
N(1)-N(2)-Cu(1)#4	124.2(8)
N(4)-N(2)-Cu(1)#4	126.5(8)

Symmetry codes: #1  $-x+1/2, y-1/2, -z+1/2$ ; #2  $x+1/2, -y+1/2, z-1/2$ ; #3  $-x+1/2, y+1/2, -z+1/2$ ; #4  $x-1/2, -y+1/2, z+1/2$

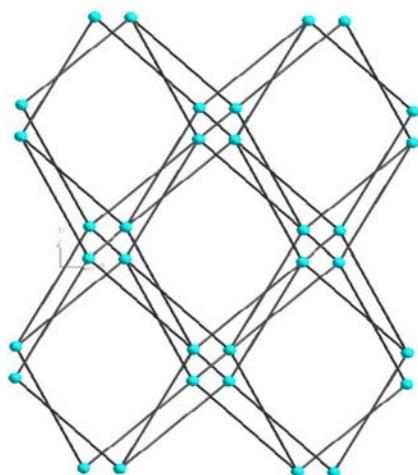


**Figure 2.** The 2-D open network of title complex (H atoms and water molecules are deleted for clarity).

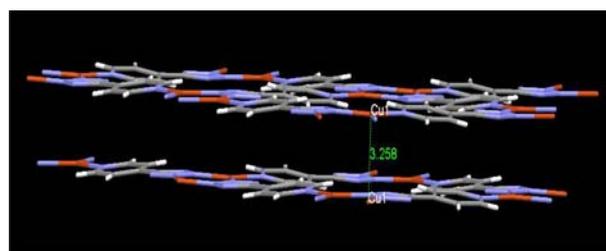
extending the structure into a 2-D open network parallel to the [101] plane. Notably, the 2-D sheet framework contains an interesting rhombic cavities  $ca\ 10.3 \times 7.7\ \text{\AA}$ .

When we simplify the network using the procedure described by Carlucci *et al.*,<sup>22</sup> and remove all the unnecessary elements which have no topological relevance, thus leaving only the essentials represented by nodes and linkers. As discussed above, each 4-tetrazole pyridine ligand links three metal atoms and can be regarded as a three - connector, and each  $\text{Cu}^{\text{I}}$  center links three N atoms of three different 4-tetrazole pyridines. As a result of the simplification, we find that the copper metal atom and the 4-tetrazole pyridine ligand are 3-connected nodes of 2D (4, 3) three connected bimodal net (Figure 3). This kind of (4, 3) three connected bimodal net has been well described by Blatov, V. A. *et al.*<sup>23,24</sup>

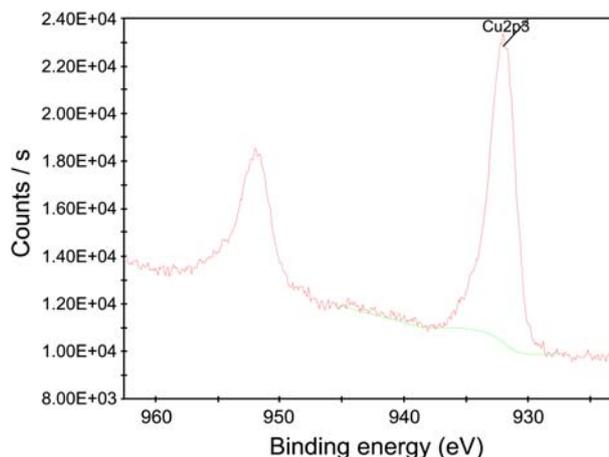
As shown in Figure 4, it should be noted that the  $\text{Cu}(\text{I})$  ions of different layers form  $\text{Cu}^{\text{I}}\cdots\text{Cu}^{\text{I}}$  distances of  $3.257\ \text{\AA}$  that is close to the sum of the van der Waals radii of two copper atoms. To the best of our knowledge, this type of  $\text{Cu}\cdots\text{Cu}$  interaction is obviously stronger than that of tetrazole complex  $[\text{Cu}(\text{Mtt})]_n$  ( $3.484\text{--}3.592\ \text{\AA}$ ) *et al.*<sup>20</sup> and  $\text{Cu}^{\text{I}}$  triazole coordination polymer ( $3.421\ \text{\AA}$ ).<sup>19</sup> The attractive interactions between closed-shell  $d^{10}$  metal centers have



**Figure 3.** Simplified 2-D grid network representation of **1** along the  $c$  axis (Cu cyan). The long straight line stands for 4-tetrazole pyridine.



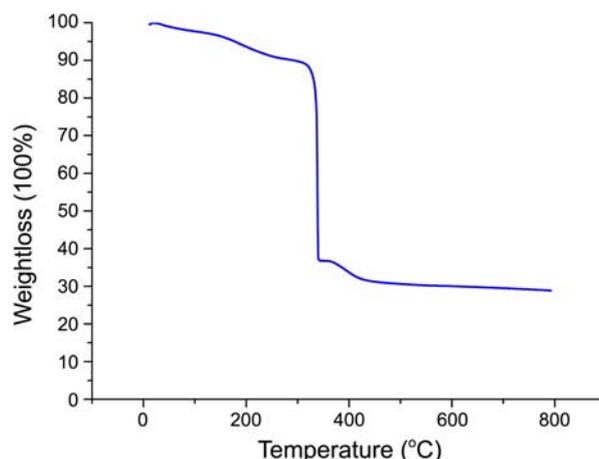
**Figure 4.** A simple  $\text{Cu}\cdots\text{Cu}$  interactions representation of **1**.



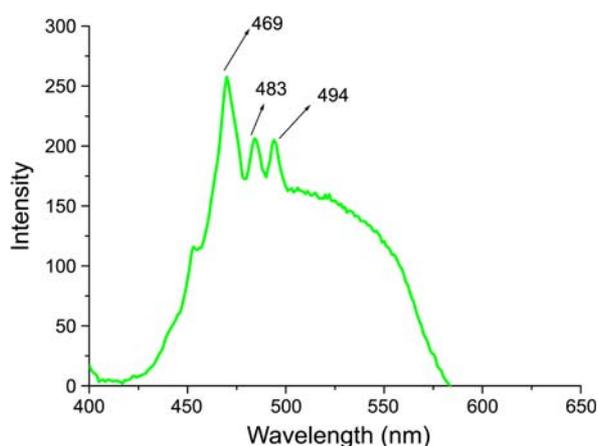
**Figure 5.** Narrow survey XPS of Cu 2p peaks for **1**.

received extensive attention because they play an important role in optical and electronic properties of polynuclear  $d^{10}$  metal complexes.<sup>15,16,25</sup> In addition, there exist a weak interaction uncoordinated water molecules and pyridyl group that are speculated to hold together the molecules of the compound.

To further confirm the oxidation state of copper in target compound, we investigate the XPS in solid state. The result shows that the binding energy of C1s, O1s, and N1s in the title compound is at 285.80, 531.50 and 399.60 respectively. As shown in Figure 5, the narrow survey XPS exhibits that the Cu2p binding energy peak is at 932 eV. The value together with the existence of satellite structure of the



**Figure 6.** Thermo-gravimetric analysis (TGA) curves for **1**.



**Figure 7.** Solid state fluorescent emission spectrum of **1** at room temperature.

observed peaks indicate that most of copper centers have completely filled d-shell corresponding to  $\text{Cu}^{\text{I}}$ ,  $d^{10}$  configuration and are in consistent with values published for other  $\text{Cu}^{\text{I}}$  compounds.<sup>26</sup>

To verified whether the framework of complex **1** is maintained after the removal of guest water molecules. TGA (thermo gravimetric analysis) was used to investigate framework stability. As shown in Figure 6, for complex **1**, there are two obviously weight loss “steps” in the graphic of TGA. The first clean weight loss “step” which looks like a downward slope occurred at *ca.* 77–148 °C (7.97% loss) corresponding to the removal co-crystallized water molecules (7.91%) from the compound **1**. The second obvious weight loss (63.36%) happened at *ca.* 313–331 °C indicates 4 tetrazole pyridine ligand (63.41% per formula unit calculated) was removed from compound **1**.

As is well known, the coordination compound containing  $\text{Cu}^{\text{I}}$  often shows the fluorescence property, but  $\text{Cu}^{\text{II}}$  compound does not. As we expected, at room temperature, solid-state of **1** shows three distinct strong photoluminescence with maxima ( $\lambda_{\text{em}}$  at 469 nm, 483 nm and 494 nm) upon excitation at 355 nm (Figure 7). According to previous research and our investigation on  $\text{Cu}^{\text{I}}$ -tetrazolate compounds,<sup>3,12-15,27,28</sup> the two peaks at about 483 nm and 494 nm (shoulder) may be attributed to a  $[\text{Cu}-\pi^*(\text{tetrazolate})]$  metal-to-ligand charge transfer (MLCT),<sup>19</sup> while another strong peak at about 469 nm in title complex is tentatively probably involved with  $\text{Cu}\cdots\text{Cu}$  [3d-4s] cluster-centered (CC) excited states. Especially, there may exist CC excited states because of the vibronic progression in the spectra and the short  $\text{Cu}\cdots\text{Cu}$  distances in the structures,<sup>25</sup> but it is still uncertain in light of Cotton’s work through DFT calculations, which points out that short  $\text{Cu}\cdots\text{Cu}$  separation does not guarantee a metal-metal bond, and related bonds and angles with the bridging ligands should be taken into account.<sup>25</sup>

### Conclusion

In conclusion, we have successfully synthesized a novel 2D coordination polymer  $\{[\text{Cu}(\text{4-C}_5\text{H}_4\text{N-CN}_4)]\cdot 0.5\text{H}_2\text{O}\}_n$  **1**

constructed by a binuclear copper(I) tetrazole units. The structure analysis shows an interesting  $\text{Cu}\cdots\text{Cu}$  interactions. Complex **1** exhibits a strong green photoluminescence.

**Acknowledgments.** This work was funded by the National Natural Science Foundation of China (Grant No. 21001056 and 21261009), Young Scientist Foundation of Jiangxi Province and Natural Science Foundation of Jiangxi Province (GJJ11453).

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