

Synthesis, Crystal Structure and Catalytic Activity of a Hexa- μ -chloro-tetrakis-(1-triphenylmethyltriazole)- μ_4 -oxo-tetracopper(II)^①

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ABSTRACT A new Cu(II) complex, [Cu₄Cl₆O(1-TrTz)₄] where 1-TrTz is 1-trityl-1*H*-[1,2,4]triazole, was synthesized by the reaction of 1-trityl-1*H*-[1,2,4]triazole with two hydrated cupric chlorides, and its structure was characterized by X-ray single-crystal diffraction. [Cu₄Cl₆O(1-TrTz)₄] is of monoclinic system, space group *P2*₁/*c*, *a* = 12.5024(13), *b* = 26.400(3), *c* = 28.588(3) Å, β = 112.807(4)°, *V* = 8698.1(16) Å³, *Z* = 4, ρ_{calc} = 1.411 g/cm³, μ = 1.265 mm⁻¹, *F*(000) = 3772, the final *R* = 0.1293 and *wR* = 0.3644 for 55774 observed reflections (*I* > 2 σ (*I*)), *R*(all data) = 0.1972, *wR*(all data) = 0.3989, completeness to theta of 25.242 is 99.9% and *GOF* = 1.103. In the structure of [Cu₄Cl₆O(1-TrTz)₄], the central O atom is tetrahedral and is coordinated with four Cu atoms. The distance between copper and oxygen bond is 1.909(6) Å. In addition, the catalytic property of this complex was investigated and it could effectively catalyze the Ullmann coupling reaction of various (hetero)aryl chlorides with azoles.

Keywords: Cu(II) complex, 1-trityl-1*H*-[1,2,4]triazole, Ullmann coupling reaction, azoles;

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1 INTRODUCTION

Copper-catalyzed Ullmann coupling reactions play an important role in academia and industry due to its low cost and toxicity, and have been widely used in the synthesis of organic compounds^[1-4]. Traditionally, the reaction usually required higher temperature. In recent years, with the development of various effective ligands, the reaction temperature is gradually moderate. However, most of the Ullmann coupling reactions still need expensive and active (hetero)aryl iodides or (hetero)aryl bromides, and high catalyst loading is also uneconomical^[5]. Therefore, the development of efficient catalysts is still a challenge.

Nitrogen-containing ligands are commonly used in Ullmann coupling reactions, which are mainly due to their non-toxic, cheap and stable to air and moisture. At present, the reported nitrogen-containing ligands are mainly diamines^[6-11], phenanthroline^[12-16], 8-hydroxyquinolines^[17, 18], Schiff base^[19], 2,2'-bipyridine^[20] and other nitrogen-con-

taining ligands^[21, 22].

Herein, 1-trityl-1*H*-[1,2,4]triazole was selected as a ligand to react with two hydrated cupric chlorides and a new hexa- μ -chloro-tetrakis-(1-triphenylmethyltriazole)- μ_4 -oxo-tetracopper(II) was obtained. Furthermore, the catalytic activity of new complex for Ullmann coupling reaction was also investigated.

2 EXPERIMENTAL

2.1 Materials and methods

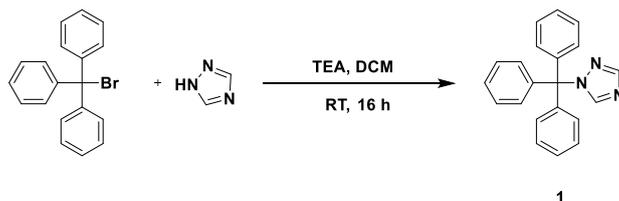
Triphenylmethyl bromide, 1,2,4-triazole and triethylamine were purchased from Tianjin Heowns Biochemical Technology Co., Ltd (Tianjin, China). Dichloromethane was obtained from Tianjin Sixth Chemical Reagent Factory (Tianjin, China). X-ray diffraction data were collected on a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE III 400MHz NMR at room temperature.

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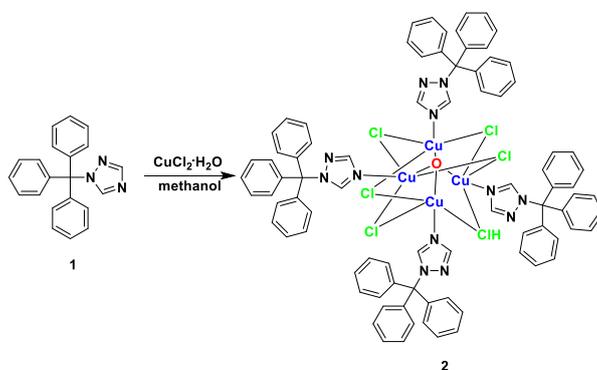
2.2 Synthesis of compound 1^[23]



A 25 mL round-bottom flask was charged with 1,2,4-triazole (500 mg, 7.25 mmol) and dichloromethane (DCM, 10.0 mL). Then, 2 mL triethylamine (TEA) and a solution of triphenylmethyl bromide (2.34 g, 7.25 mmol) in 10 mL DCM were added dropwise under an ice-water bath. After the mixture was stirred for 16 h, 10 mL water was added. The aqueous layer was extracted with DCM (2 × 20 mL) and combined organic phases were dried over Na₂SO₄. After the

solvent was evaporated, the white powder was obtained. The crude product was purified by recrystallization from methanol to give pure compound **1** as a white powder. Yield: 2.14 g, 95%. ¹H NMR (400 MHz, CDCl₃) δ 8.07 (s, 1H), 8.03 (s, 1H), 7.34 (s, 9H), 7.14~7.13 (m, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 151.6, 145.6, 141.9, 129.9, 128.3, 128.1, 78.1 ppm.

2.3 Synthesis of complex 2



A round-bottom flask was charged with compound **1** (40 mg, 0.128 mmol), CuCl₂·2H₂O (21.8 mg, 0.128 mmol), and methanol (3 mL). The mixture was heated at 60 °C for 5 h. After cooling to room temperature, the crude product was obtained by filtration. Then, the crude product was purified by recrystallization from dichloromethane to give complex **2** as a yellow crystal. Yield: 8.3 mg, 30%.

2.4 X-ray crystal structure determination

A yellow single crystal of complex **2** (0.22mm × 0.21mm × 0.18mm) was selected on a glass fiber for measurement. The X-ray crystallographic data were collected on a Bruker

SMART APEX II CCD diffractometer with a graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) using a φ - ω scan technique in the range of $1.09 \leq \theta \leq 26.50^\circ$ at 296(2) K. The structure of complex **2** was solved by direct methods and refined by applying a full-matrix least-squares procedure based on F^2 using values SHELXS-2014/7^[24]. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms bound to carbon atoms were positioned geometrically and refined using a riding model. The representative bond lengths and bond angles of complex **2** are listed in Table 1.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.	Dist.	Bond
Cu(1)–O(1)	1.909(6)	Cu(2)–O(1)	1.899(6)	Cu(3)–O(1)	1.878(6)	Cu(4)–O(1)	1.904(7)
Cu(1)–N(1)	1.953(9)	Cu(2)–N(4)	1.939(10)	Cu(3)–N(7)	1.931(8)	Cu(4)–N(10)	1.925(10)
Angle	(°)	Angle	(°)	Angle	(°)	Angle	(°)
O(1)–Cu(1)–N(1)	176.0(4)	O(1)–Cu(2)–N(4)	176.8(4)	O(1)–Cu(3)–N(7)	177.6(4)	O(1)–Cu(4)–N(10)	178.6(4)
O(1)–Cu(1)–Cl(4)	86.9(2)	O(1)–Cu(2)–Cl(5)	85.8(2)	O(1)–Cu(3)–Cl(1)	85.9(2)	O(1)–Cu(4)–Cl(2)	86.7(2)
N(1)–Cu(1)–Cl(4)	91.2(3)	N(4)–Cu(2)–Cl(5)	90.9(3)	N(7)–Cu(3)–Cl(1)	94.7(3)	N(10)–Cu(4)–Cl(2)	94.5(3)
O(1)–Cu(1)–Cl(5)	84.6(2)	O(1)–Cu(2)–Cl(3)	87.8(2)	O(1)–Cu(3)–Cl(6)	87.4(2)	O(1)–Cu(4)–Cl(4)	85.5(2)
Cl(4)–Cu(1)–Cl(5)	122.27(14)	Cl(5)–Cu(2)–Cl(6)	119.79(13)	Cl(6)–Cu(3)–Cl(2)	116.5(10)	Cl(2)–Cu(4)–Cl(4)	118.6(12)

3 RESULTS AND DISCUSSION

3.1 Syntheses of compound 1 and complex 2

Compound **1** was synthesized according to the reported literature^[23]. Reacting 1,2,4-triazole with triphenylmethyl bromide in DCM in the presence of TEA at room temperature gave compound **1** as a white powder. Complex **2** as a yellow crystal (30% yield) was obtained by the coordination of compound **1** with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in methanol at 60 °C.

3.2 Crystal structure of complex 2

X-ray single-crystal diffraction showed complex **2** crystallized in monoclinic space group $P2_1/c$. X-ray single-

crystal structure of complex **2** is shown in Fig. 1. The tetranuclear complex molecule is composed of four Cu atoms and a central O atom to form a tetrahedral structure. Each Cu atom is connected to the other three Cu atoms by bridging Cl atoms, and to the 1-trityl-1*H*-[1,2,4]triazole ligand by N atoms. According to the graph and data analysis, the tetrahedral Cu_4O has a very slight deformation (three Cu–O–Cu bond angles are about 110°, two Cu–O–Cu bond angles are 108°, and another is 109°). The Cu–O bond lengths fall in the range of 1.878~1.909 Å, the Cu–Cl distances vary from 2.394 to 2.528 Å, and the angles around Cu are in the 176.0~178.6° region.

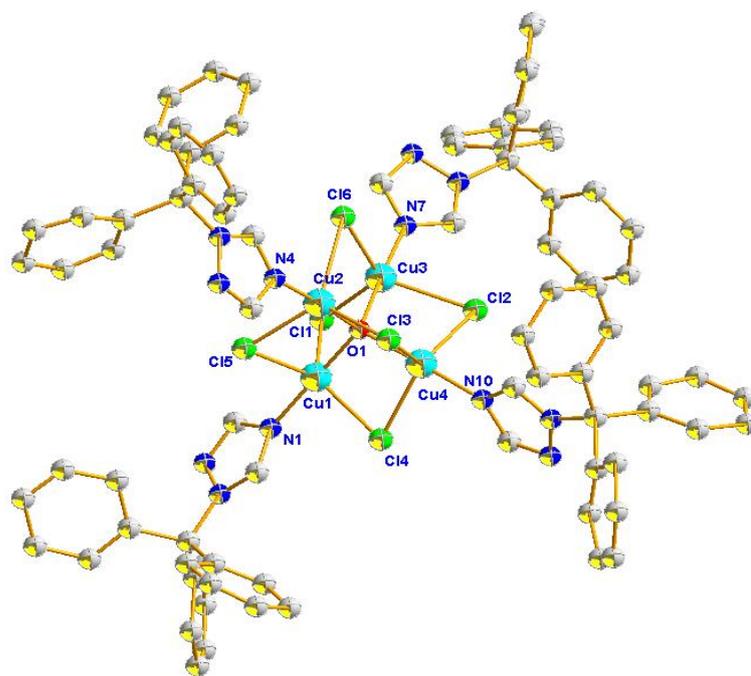


Fig. 1. X-ray single-crystal structure of complex **2**. All hydrogen atoms are omitted for clarity. Symmetry code: $1-x, 0.5+y, 0.5-z$

Complex **2** was analyzed by PLATON Windows Taskbar crystal software and no classical hydrogen bonds were found. However, a three-dimensional (3D) supramolecular network was constructed by connecting plentiful non-classical intermolecular hydrogen bonds (C–H...Cl bonds), as shown

in Fig. 2. The distances between the acceptors and donors for C(40)–H(40)...Cl(4), C(62)–H(62)...Cl(5) and C(83)–H(83)...Cl(5) hydrogen bonds are 2.851, 2.846, and 2.567 Å, respectively (Table 2).

Table 2. Hydrogen Bonds for Complex 3 (Å, °)

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠DHA	Symmetry code
C(40)–H(40)...Cl(4)	0.93	2.85	3.782(12)	130	$1-x, 0.5+y, 0.5-z$
C(62)–H(62)...Cl(5)	0.93	2.84	3.776(12)	129	$2-x, 0.5+y, 0.5-z$
C(83)–H(83)...Cl(5)	0.93	2.56	3.497(14)	151	$2-x, 0.5-y, 0.5+z$

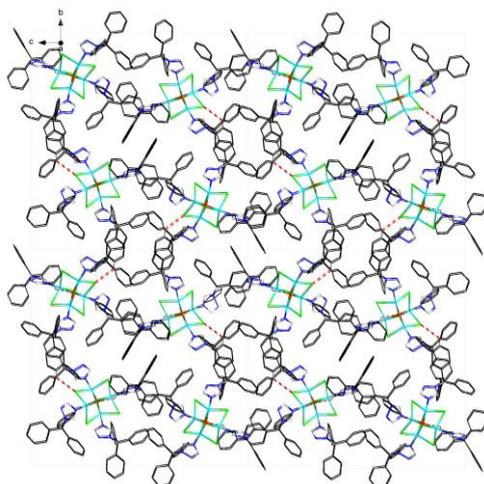


Fig. 2. View of the 3D supramolecular network formed by hydrogen bonds (dashed lines)

3.3 Catalytic property

The catalytic property of complex **2** was investigated by using it to catalyze the Ullmann coupling reactions of various (hetero)aryl chlorides with azoles. The reactions were carried out under the following conditions: (hetero)aryl chlorides (1 equiv), azoles (1.2 equiv), and Cs_2CO_3 (2 equiv) in DMF in the presence of **2** at 80 °C for 48 h, and the results are shown in Table 3. Imidazole, benzimidazole, 1,2,4-triazole, 4-phenyl-1H-imidazole and 2-methylimidazole all react well with *p*-chloronitrobenzene and gave the corresponding

coupling products in high to excellent yield (98%, 98%, 98%, 95% and 80%, respectively) within 48 h (entries 1~5). However, for 2-methylimidazole and 2-methylbenzimidazole, the coupling reactions didn't go smoothly and the yields of the products were moderate (50% and 40%, respectively) (entries 6 and 7). Meanwhile, 2-chloroquinoline and 2-chloropyridine also used as substrates. Both 2-chloroquinoline and 2-chloropyridine could couple with imidazole and got good yields (85% and 80%). Meanwhile, 2-chloropyridine also reacted well with 4-phenyl-1H-imidazole with a yield of 78%.

Table 3. Coupling of Various (Hetero)aryl chlorides with Azoles^a

entry	product	yield (%)	entry	product	yield (%)
1		98%	6		50%
2		98%	7		40%
3		98%	8		85%
4		95%	9		80%
5		80%	10		78%

^a Reactions condition: (hetero)aryl chlorides (1 equiv), azoles (1.2 equiv) and Cs_2CO_3 (2 equiv) in DMF at 80 °C for 48 h.

^b Yields were determined by GC-MS analysis.

4 CONCLUSION

In summary, a new tetranuclear copper complex [Cu₄Cl₆O(1-TrTz)₄] was constructed *via* the reaction of 1-trityl-1*H*-[1,2,4]triazole with two hydrated cupric chlorides, and its structure was characterized by X-ray single-

crystal diffraction. The tetranuclear copper complex molecule was connected into a 3D network via plentiful weak non-classical C–H...Cl hydrogen bonds. Furthermore, complex **2** could be used as a catalyst to effectively catalyze the Ullmann coupling reaction of various (hetero)aryl chlorides with azoles under mild conditions.

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