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Macrocyclic tetranuclear copper (I) complex bearing a N-heterocyclic carbene ligand: Synthesis, structure, and catalytic properties

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ABSTRACT

A rare macrocyclic tetranuclear copper (I) complex $([Cu_4(2)_2](PF_6)_4)$ of phenanthroline-based NHC ligand has been prepared and characterized by NMR, ESI-MS spectroscopy, and X-ray diffraction analysis. The complex displays a novel twisted macrocyclic conformation and weak intramolecular Cu–Cu interactions. The complex is found to exhibit high catalytic activity in the Cu-catalyzed azide–alkyne cycloaddition (CuAAC) reaction in an air atmosphere at room temperature in a MeCN/H₂O mixture solution.

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N-heterocyclic carbenes and their transition metal complexes have been the focus of intense research in organometallic chemistry [1] and homogeneous catalysis [2–5]. Polydentate N-heterocyclic carbene (NHC) ligands bearing both C and N donating atoms offer opportunities for the construction of bi- and multi-nuclear organometallic complexes [6,7]. Recently, a type of metallamacrocycle has been constructed using poly-NHC ligands as building blocks [8–10]. For example, Hahn et al. [11] explored a series of metallosupramolecule complexes using rigid polycarbene ligands as donor atoms via metal-controlled self-assembly. Jin et al. [12] reported a series of self-assembled metallacycles with an NHC palladium complex as the corner element and a flexible pyridine-based ligand as the building block. Several coinage metal–NHC clusters involving Ag, and Au centers have been reported [11,13,14]. However, reports of macrocyclic copper (I) complex based on N-heterocyclic carbene ligand are rare.

Phenanthroline as a commonly ligand has been widely used in coordination chemistry and homogeneous catalysis. Our previous research showed that N-(1,10-phenanthrolin-2-yl)imidazolylidenes are versatile ligands and their nickel and palladium complexes are quite efficient cross-coupling catalysts [15], heterobimetallic Pd/Cu complex shows good activity for tandem Click/Sonogashira reactions [16], and a series of Ru complexes display unique photophysical and electrochemical properties [17]. Excellent activities observed with these transition metal complexes of phenanthroline-based NHC ligands encouraged us to explore the chemistry of copper compounds. Herein, we report the synthesis, structure, and catalytic activity of the novel macrocyclic tetranuclear copper (I) complex supported by phenanthroline-based NHC ligand.

All the chemicals were obtained from commercial suppliers and used without further purification. 2-iodo-1,10-phenanthroline [15] and 2-(1H-imidazol-1-yl)-1,10-phenanthroline (1) [18] were prepared according to the known procedure. Reaction of 2-(1H-imidazol-1-yl)-1,10-phenanthroline (1) with dibromethane and subsequent addition of NH₄PF₆ to the methanol solutions of the resulting imidazolium bromide yielded the corresponding hexafluorophosphate [H₂(2)](PF₆)₂ in yield of 60% (Scheme 1). The imidazolium salt was characterized by ¹H and ¹³C NMR spectroscopy [19]. ¹H NMR spectra in DMSO-d₆ show downfield resonance signals at ca. 10.7 ppm assignable to the acidic NCHN proton of the imidazolium salt.

Treatment of the in situ generated silver–NHC complex from $H_2(2)(PF_6)_2$ and Ag_2O with excess copper power or 2 equiv. of Cul in acetonitrile afforded tetranuclear copper–NHC complex $[Cu_4(2)_2](PF_6)_4$ (**3**) in yield of 75% (Scheme 1). The tetranuclear copper complex **3** was characterized by elemental analysis,¹H and ¹³C NMR spectroscopy [20]. ¹H NMR spectrum of complex **3** in DMSO- d_6 shows the complete disappearance of acidic 2H-imidazolium proton, which is diagnostic for the loss of the carbonium protons and the formation of metal carbene complex. In the ¹³C NMR spectrum of complex **3**, the resonance due to the carbonic carbon was observed at 182.5 ppm, which is consistent with the reported values in the range of 215.6–149.5 ppm for copper–NHC complexs [1]. The complex was isolated as a yellow solid that is stable to air in the solid and in solution. ESI-MS spectrum of **3** in acetonitrile shows the base peak at 1697.61 amu due to $[Cu_4(2)_2](PF_6)_3]^+$, and the second largest peak at 776.12 amu assigned to $[Cu_4(2)_2](PF_6)_2]^{2+}$.

Complex **3** was additionally characterized by X-ray crystallography. Yellow single crystals of complex **3** suitable for an X-ray diffraction

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Scheme 1. Synthesis of complex 3.

study were grown from acetonitrile solution and diethyl ether. Details of the X-ray structure crystallographic data and refinement details are in [21]. The molecular structure of complex 3 is depicted in Fig. 1. The complex consists of the cation unit $[Cu_4(2)_2]^{4+}$ and four hexafluorophosphate anions with two acetonitriles of crystallization. Complex **3** crystallizes in the monoclinic space group C2/c. The remaining atoms of the cation are related by a crystallographic 2-fold symmetry. Each copper ion is three-coordinate in a trigonal planar ligand environment of two nitrogen atoms of phenanthroline and one NHC carbon center. Four carbon ligators stem from two ligands forming an unusual fourteen-membered ring with the cuprous ion. The four copper ions between two bi-carbene ligands in $[Cu_4(2)_2](PF_6)_4$ form a distorted square arrangement featuring two short (Cu1-Cu2 2.617 Å) and two long (Cu1...Cu1A 5.798 Å, Cu2... Cu2A 5.743 Å) separations. The shortest Cu1–Cu2 separation (2.617(2) Å) is slightly shorter than the sum of van der Waals radii of two copper atoms, which shows a weak metal-metal interaction in complex 3. The shortest Cu–Cu distance is slightly higher than reported Cu–Cu separations (2.4907 to 2.5150 Å) of the triangular Cu(I)-NHC clusters [22,23] and shorter than the reported tripodal Cu(I)–NHC complexes(2.7557 to 2.9078 Å) [24]. The Cu–C_{carbene} bond distances are found in the range of 1.851(14)–1.871(13) Å which are shorter than reported copper–carbene complexes (1.884–2.05 Å) [22,23,25–30]. Also interestingly, this complex contain a fourteen-membered metallamacrocycle, which is linked together by four copper, four nitrogen and six carbon atoms (Fig. 1, right).

Since the Cu-catalyzed azide–alkyne cycloaddition (CuAAC) reaction discovered by Meldal and Sharpless in 2002 [31], it has become a popular atom-economic process. This reaction has been proved to be accelerated by Cu(I) species supported by polydentate sulfur ligands [32] and NHC ligand[33] under mild conditions. With the tetranuclear copper complex in hand, we investigated its catalytic activity in the CuAAC reaction of benzyl azide and phenylacetylene. The reactions were monitored by ¹H NMR analysis after appropriate intervals



Fig. 1. ORTEP drawing of [Cu₄(2)₂](PF₆)₄ (3). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and anions have been removed for clarity.

Table 1

Solvent and catalyst optimization studies^{*a*}.



Entry	Solvent	Yield % ^b
1	Neat	25
2	H ₂ O	11
3	CH₃CN	45
4	DMSO	12
5	t -BuOH/H ₂ O(V/V = 1/1)	Trace
6	$CH_3CN/H_2O(V/V = 1/1)$	67
^c 7	$CH_3CN/H_2O(V/V = 1/1)$	>99

Reaction condition: "(azidomethyl)benzene 1.0 mmol, ethynylbenzene 1.2 mmol, catalyst 0.0050 mmol, solvent 2 mL, RT, 3 h. ^bH NMR conversion of (azidomethyl)benzene, ^ccatalyst 0.0075 mmol.

within 3 h. At a complex loading of 0.5 mol%, the effect of solvents was studied. It is noted that CuAAC reaction often uses t-BuOH/H₂O as solvent. A first screening of different solvents revealed exceptional activity of **3** in MeCN/H₂O (v/v 1:1) in the air atmosphere using 0.5 mol% catalyst loading, giving rise to the cycloadduct in 67% yield (Table 1). Having identified MeCN/H₂O as the best solvent for the reaction, we next investigated catalyst loading for this reaction. Gratifyingly, upon increasing the catalyst concentration to 0.75 mol%, the reaction proceeded in nearly quantitative yield (Table 1).

Having optimized the reaction conditions, complex **3** was applied to the cycloaddition reaction of electron-rich, electron-poor, and dialkyne at room temperature in MeCN/H₂O to give the corresponding triazoles in high yields (Table 2, entries 1–5). However, the cycloaddition reaction of 1,4-diethynylbenzene with benzyl azide only obtains the mono-triazole product (Table 2, entry 3), which may be ascribed to the low solubility of triazole derivates in MeCN/H₂O solution. Thus the resultant product bears additional alkynyl offering opportunity for the construction of more complex triazole compound. Moreover, 2-(azidomethyl)pyridine was also successfully employed in this reaction in 96% yield (Table 2, entry 5).

The promising catalytic behavior of complex **3** for Cu-catalyzed azide–alkyne cycloaddition (CuAAC) reaction encouraged us to explore its application in three-component (alkyl halide, sodium azide, and alkyne) cycloaddition reaction [34] (Table 3). Catalyst **3** again performed well in above optimize condition to give the desired products (entries 1–5) in good to excellent isolated yields (85–94%).

In conclusion, we have designed and synthesized a novel Cu₄ cluster complex representing the first tetranuclear copper (I) complex supported by N-heterocyclic carbene ligand. The complex displays a novel twisted macrocyclic conformation and weak intramolecular copper–copper interactions. Each copper ion is three-coordinate in a trigonal planar ligand environment of two nitrogen atoms of phenanthroline and one NHC carbon

Table 2

Azide-alkyne cycloaddition catalyzed with complex 3.





Table 3

Three-component CuAAC reaction promoted by tetranuclear copper complex 3.





center. Complex **3** is found to exhibit high catalytic activity in the Cucatalyzed azide–alkyne cycloaddition (CuAAC) reaction in an air atmosphere at room temperature in a MeCN/ H_2O mixture solution.

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Appendix A. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-number: 871837. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk. Supplementary data related to this article can be found online at http://dx. doi.org/10.1016/j.inoche.2012.05.007.

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2H), 8.96 (d, J = 8.8 Hz, 2H), 8.50 (s, 2H), 8.59 (d, J = 8.0 Hz, 2H), 8.41–8.39 (m, 4 H), 8.14 (b, 4 H), 7.90–7.87 (m, 2 H), 7.05 (s, 2 H) ppm. ¹³C NMR (100 MHz, d_6 -DMSO): δ 150.7, 145.5, 144.6, 144.3, 141.9, 137.9, 137.3, 129.9, 129.5, 128.8, 126.5, 124.0, 120.7, 114.4, 59.7 ppm.

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