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Syntheses, structures and properties of Zn(II) and Cu(II) complexes based on N2-2-methylenepyridinyl 1,2,3-triazole ligand

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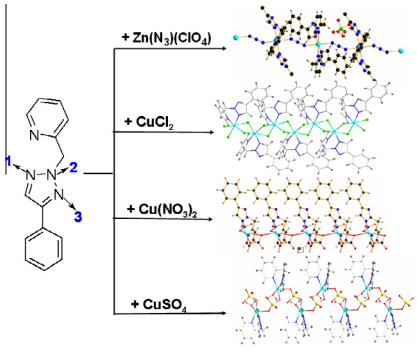
HIGHLIGHTS

- Four Zn(II) and Cu(II) 1,2,3-triazole complexes have been synthesized.
- The anions lead to different molecular self-assembly for three Cu(II) complexes.
- The properties of the complexes have been investigated.

GRAPHICAL ABSTRACT

Four metal coordination compounds based on N2-2-methylenepyridinyl 1,2,3-triazole ligand have been synthesized and characterized. These anions play a pivotal role in the assembly of these supramolecular structures. The fluorescent and electrochemical properties of the complexes have been also investigated.



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ABSTRACT

Four new Zn(II) and Cu(II) coordinated polymers ($[ZnL_2N_3]ClO_4$ (**1**), $[Cu_2L_2(CH_3CN)]Cl_4$ (**2**) $[CuL](NO_3)_2$ (**3**), $[Cu(H_2O)L](SO_4)$ (**4**) L = 2-((4-phenyl-2H-1,2,3-triazol-2-yl)methyl) pyridine (**ptmp**)) have been reported. All the compounds have been characterized by IR spectrum, elemental analyses and X-ray crystallography diffraction. Single-crystal X-ray diffraction analyses show that one-dimensional polymers are formed in these four complexes. Chain-like structures are formed in complex **1**, **2** and **3**, which are connected by azide, chloride and nitrate anions, respectively. In complex **4**, one-dimensional left-handed polymer is formed by a μ_2-SO_4 bridge. The fluorescent and electrochemical properties of these four complexes were investigated. It was found that these three Cu(II) complexes displayed a quenching of fluorescence, while Zn(II) complex exhibited a clear enhanced fluorescence.

Introduction

With the discovery and development of Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction [1], 1,2,3-triazole finds use in research as a popular building block in many fields, including pharmaceutical research [2], materials chemistry [3] and bioconjugation [4]. The CuAAC click reaction produces 1,4-disubstituted 1,2,3-triazoles [5] with high efficiency and selectivity (Scheme 1(a)). Lately, Ru(II)- or base-catalyzed approaches are also developed to produce 1,5-disubstituted 1,2,3-triazoles [6] (Scheme 1(b)). In principle, all the three nitrogen atoms in the 1,2,3-triazole can serve as donor atoms to coordinate with metal

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ions, and some metal complexes have been synthesized based on 1,4 or 1,5-disubstituted 1,2,3-triazole ligands. Many of them show specific topologies [7] and interesting properties such as optical [8], magnetic [9], biological properties [10]. According to some calculated results, the electron density on N1 or N3 nitrogen atom in the 1,2,3-triazole is always higher than that of N2 nitrogen atom [11], so the N2-substituted 1,2,3-triazoles, which offer higher electron density N1 and N3 nitrogen atoms, could be suitable ligands to coordinate with metal ions. However, to the best of our knowledge, very rare metal complexes based on N2-substituted 1,2,3-triazole ligands have been reported so far.

We focus on the synthesis and properties of 1,2,3-triazole derivatives. Herein, we report a new N2-substituted 1,2,3-triazole ligand, 2-((4-phenyl-*2H*-1,2,3- triazol-2-yl)methyl) pyridine (**ptmp**), affording four Zn(II) and Cu(II) coordinated complexes. The synthetic routine for the ligand is outlined in Scheme 2. A Br atom was firstly introduced to 4-phenyl-1,2,3-triazole, then selective alkylation [12,13] was happened in N2 position, successively reduction of the Br atom gave 2-((4-phenyl-*2H*-1,2,3-triazol-2-yl)methyl) pyridine with high overall yield.

Experiment section

Materials and physical and chemical measurements

All reagents were purchased and used without further purification. NMR spectra were recorded on Varian 600 MHz and 400 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (TMS) (0.00 ppm) or $CDCl_3$ (7.26 ppm) for ^1H, $CDCl_3$ (77.0 ppm) for ^{13}C. Flash column chromatography was performed on 200–300 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250μ) and visualized by fluorescence. IR spectra were recorded on a vector 22 FI-IR spectrophotometer using KBr disk. Fluorescence spectra were recorded on a Jasco FP-6500 spectrophotometer. Melting points were measured on a melting point tester RY-1G apparatus and uncorrected. Electrochemical property was recorded on electrochemical workstation with GCE (glassy carbon electrode), SCE (standard calomel electrode) and platinum electrode. Scanning rates were in the range of 20–200 mV/s. The solution was deaerated for 15 min before measurements. The half-wave potentials were calculated approximately from $(E_{pa} + E_{pc})/2$, and the measured error was ±2 mv.

Synthesis of 4-bromo-5-phenyl-2H-1,2,3-triazole

To a solution of 4-phenyl-2H-1,2,3-triazole (745 mg, 5 mmol) in EtOAc (25 mL), was added NBS (1.07 g, 6 mmol) in one portion. The mixture was stirred at room temperature and monitored by TLC. After the completion of the reaction, the mixture was filtered, and the solvent was removed under reduced pressure. The obtained oil was purified by flash column chromatography (eluent: EtOAc/petroleum ether, 1:20, V/V) to give the 4-bromo-5-phenyl-2H-1,2,3-triazole (1.02 g, yield: 91%) as yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 3.6 Hz, 1H), 7.94 (d, J = 7.2 Hz, 2H), 7.69–7.63 (m, 1H), 7.47–7.37 (m, 1H), 7.27–7.2 (M, 1H), 7.13 (d, J = 8.0 Hz, 1H), 5.75 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 149.6, 145.9, 137.1, 128.91, 128.88, 128.6, 127.3, 122.0, 120.3, 60.8.

*Synthesis of 2-((4-phenyl-2H-1,2,3-triazol-2-yl)methyl)pyridine (**ptmp**)*

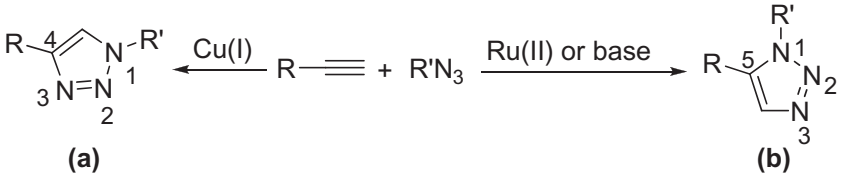
To a solution of 4-bromo-5-phenyl-2H-1,2,3-triazole (448 mg, 2 mmol) in acetone (10 mL), was added 2-(chloromethyl)-pyridinium chloride (279 mg, 2.2 mmol, 1.1 eq) and K_2CO_3(414 mg, 3 mmol, 1.5 eq), the mixture was stirred at room temperature and monitored by TLC. After the completion of the reaction, the mixture was filtered, and the solvent was removed under reduced pressure. The obtained oil was then dissolved in EtOH, and then Pd/C was added, the mixture was filled with H_2 gas and stirred at room temperature. After the completion of the reaction, the mixture was filtered to removed the Pd/C, then the solvent was removed under reduced pressure to give a crude solid. The target product 2-((5-phenyl-2H-1,2,3- triazol-2-yl)methyl)pyridine can be purified by recrystallization from CH_2Cl_2/EtOAc (1:10, V/V) to give the product as white solid (378 mg, yield: 80%). White solid, mp. 68–69 °C, ^1H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, J = 3.6 Hz, 1H), 7.93 (s, 1H), 7.81 (d, J = 7.2 Hz, 2H), 7.67–7.62 (m, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.38–7.33(m, 1H), 7.26–7.19 (m, 1H), 7.03 (d, J = 7.8 Hz, 1H), 5.81 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 149.4, 148.3, 136.9, 131.6, 130.1, 128.8, 128.4, 125.9, 122.8, 121.6, 60.0.

*Synthesis of [Zn(**ptmp**)$_2$N$_3$]ClO$_4$ (complex **1**)*

Sodium azide (11 mg, 0.17 mmol, 4 eq) was dissolved in methanol (2 mL) [14], then the solution was carefully added to a methanol solution (1 mL) of zinc perchlorate hexahydrate (63 mg, 0.17 mmol, 4 eq), the color of the later one turned brown, finally a clear solution obtained. Then 2-((5-phenyl-*2H*-1,2,3-triazol-2-yl)methyl)pyridine (10 mg, 0.04 mmol, 1 eq) in methanol (1 mL) was carefully layered on a fresh prepared $Zn(ClO_4)_2$/NaN_3 solution, which affords clear and colorless crystals two weeks later. The white crystals were collected by filtration (6.7 mg, yield: 47%). m.p. 238–240 °C, Anal. Calc. for $C_{28}H_{24}ClN_{11}O_4Zn$: C 49.50; H 3.56; N 22.68. Found: C 49.38; H 3.66; N 22.79. IR (KBr, cm^{-1}): 3116, 2082, 1480, 1365, 1092, 978.

*Synthesis of [Cu$_2$Cl$_4$(**ptmp**)$_2$] (complex **2**)*

To a solution of 2-((5-phenyl-2H-1,2,3-triazol-2-yl)methyl)pyridine (10 mg, 0.04 mmol) in CH_3CN (2 mL), was added a solution of $CuCl_2$ (11 mg, 0.08 mmol, 2 eq) in methanol (1 mL) carefully, then these solution stand for three weeks to get the green block crystals by filtration (6.3 mg, yield: 81%), m.p. 160–161 °C. Anal. Calc. for $C_{30}H_{27}Cl_4N_9Cu_2$: C 46.05; H 3.04; N 16.11. Found: C 46.20; H 3.23; N 16.08. IR (KBr, cm^{-1}): 2995, 2901, 2361, 1391, 1061, 877.



Scheme 1. The approaches to the syntheses of disubstituted 1,2,3-triazaoles via "click" reactions.