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Synthesis, Structure and Biological Properties of a Novel Copper (II) Supramolecular Compound Based on 1,2,4-Triazoles Derivatives

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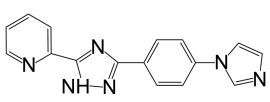
A novel mononuclear supramolecule of copper(II) has been synthesized with Ippyt ligand (Ippyt=3-(4'-imidazole phenyl)-5-(pyrid-2"-yl)-1,2,4-triazole) (**1**). Compound **1**, namely $[Cu(Ippyt)_2(H_2O)_2]$, has been characterized by single-crystal X-ray diffraction, IR spectrum, elemental analysis and thermogravimetric analysis. Structure determination reveals that the elongated-octahedral geometry is formed in the vicinity of the copper (II) atom being coordinated by four nitrogen atoms from two Ippyt ligands occupying the equatorial position and two oxygen atoms from two coordinated water molecules in the axial position, which together form the N_4O_2 donor set. Hydrogen bonding interactions between nitrogen and oxygen atoms result in the set up of a supramolecular network architecture. Biological properties including antibacterial activity and superoxide dismutase (SOD) mimetic activity of compound **1** have been investigated by agar diffusion method and the modified Marklund method, respectively. The results indicate that compound **1** exhibits a stronger antibacterial efficiency than the parent ligand and it also has a certain radical-scavenging activity.

Key Words : Hydrogen bonding, Triazole, Copper (II), Antibacterial activity, SOD-like activity

Introduction

With the development of self-assembly supramolecular chemistry, the rational design and construction of the metal-organic supramolecular networks based on ligand and hydrogen bonding interactions have attracted great attentions[1-5] not only for their intriguing structural motifs, but also for their enormous potential applications in areas such as gas storage,[6-8] magnetism,[9-11] nonlinear optics,[12] catalysis[13-15] as well as biochemistry.[16] In the language of supramolecular construction, the final structures of metal-organic architectures can be effectively influenced by multiple factors[17-19] such as solvent system, temperature, pH value, especially the selection of the bridging ligands and metal ions.[20-22] At this stage, many researches have been devoted to the metal-organic supramolecular architectures derived from aromatic heterocyclic ligands such as the pyridine-based, the imidazole-based as well as the triazole-based ligands which have been widely used as multifunctional linkers to construct compounds with novel structural features and potential properties.[23-30] It has been well documented that the rigid 1,2,4-triazoles possess five-membered aromatic rings containing three nitrogen heteroatoms[31] which can afford coordinate sites to bridge transition metal ions together.[32-37]



Scheme 1. Chemical structure of Ippyt ligand: 3-(4'-imidazole phenyl)-5-(pyrid-2"-yl)-1,2,4-triazole

As an organic triazole-based ligand, Ippyt (Scheme 1) contains both imidazolyl and pyridyl building-blocks which can help to provide more nitrogen coordination sites to meet considerable requirements for the construction of coordination compounds. In addition, Ippyt also tends to provide abundant hydrogen bonds which not only favor the formation of the versatile metal-organic frameworks but also link low-dimensional structures into high-dimensional supramolecular networks. Moreover, many researches have demonstrated that the triazoles fused to another heterocyclic rings have effective antimicrobial activities.[38-41] In recent years, transition metal compounds of triazole-based ligands have been the subject of considerable studies because of their interesting properties and biological activities. However, a survey of the literatures reveals that no work has been carried out on the coordination compounds constructed from the Ippyt ligand.

Besides, copper is an essential micronutrient that has both prooxidant and antioxidant properties. As copper is found in the eukaryotic Cu,Zn superoxide-dismutase (CuZnSOD),[42] some mono-copper compounds which are reported in the previous researches to possess SOD-mimic activities may be tested as model or potential substitutes.[43-49] Among them, some compounds have been demonstrated to possess anti-inflammatory activities, anti-carcinogenic and anti-mutagenic effects.[50,51]

In a word, a new supramolecular structure of copper (II) and Ippyt ligand have been prepared in this work, namely $[Cu(Ippyt)_2(H_2O)_2]$. Crystal structures, infrared spectra, elemental analyses and thermal stability properties have been investigated. In an attempt to determine whether the compound

possesses antioxidant activity, SOD-mimic assays of it have been performed. Furthermore, to explore the possibility of using such compound as a multifaceted drug, the antimicrobial activity of the novel compound is also determined against two classes of bacteria: *E. coli* (Gram−) and *S. aureus* (Gram+).

Experimental

Materials and Physical Measurements. All reagents and solvents employed were commercially available and used as it was received without further purification. The IR spectra were recorded in the range of 4,000-400 cm^{-1} on a Nicolet 170SX FT-IR spectrometer with pressed KBr pellets (5 mg of sample in 500 mg of KBr). Elemental analyses of C, H, and N were determined with a Perkin-Elmer model 240C instrument. Thermogravimetric analyses (TGA) were performed under a NETZSCHSTA 449C thermal analysis instrument from room temperature to 800 ºC under a N_2 atmosphere (flow rate 10 mL· min^{-1}) at a heating rate of 10 ºC·min^{-1}.

Synthesis of $[Cu(Ippyt)_2(H_2O)_2]$ (1). The solution of Ippyt (0.006 g, 0.02 mmol) in 5 mL of *N,N′*-dimethylformamide (DMF) whose pH value was carefully adjusted to 6.5 by dilute ammonia water was layered slowly onto a solution of $Cu(OAc)_2$ (0.008 g, 0.04 mmol) in 5 mL of CH_2Cl_2 including small amounts of methanol. The resulting mixture was kept at room temperature and light blue rectangular crystals were obtained after about three weeks. Yield based on Cu: 0.0011 g, 37.6%. Elemental analysis (%) for $C_{32}H_{26}CuN_{12}O_2$, Found (calcd): C, 56.29 (57.01); H, 3.68 (3.89); N, 24.18 (24.93). IR data (in KBr, cm^{-1}): 3468 (br, s), 3228 (s), 3106 (s), 3046 (s), 3022 (s), 2859 (s), 1656 (s), 1634 (m), 1618 (s), 1602 (s), 1588 (s), 1504 (m), 1450 (s), 1469 (m), 1093 (w), 891 (m), 802(m).

Structure Determination and Refinement. Data collection for compound **1** was carried out on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromated Mo-Kα radiation with radiation wavelength 0.71073 Å at 293(2) K. The intensity data were collected by the *w* scan technique. The structure was solved by direct method and refined with the full-matrix least-squares technique using the SHELXS-97[52a] and SHELXL-97[52b] programs. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C atoms were located at geometrically calculated positions to their carrier atoms and refined with isotropic thermal parameters included in the final stage of the refinement. A summary of the detailed crystallographic data and structure refinement for **1** is given in Table 1, and selected bond lengths and angles of compound **1** are listed in Table 2.

Determination of SOD-like Activity. SOD-like activity of compound **1** was investigated with the modified Marklund method.[53,54] The solutions of **1** were prepared in dimethyl sulfoxide before adding the Tris-HCl buffer (pH 8.2). All the reagents were added according to Table 3. Then put them respectively into 25 ºC water bath for 10 min after homogeneous mixing and 0.30 mL of pyrogallic acid solution (4.0 mmol/mL) which was also held in 25 ºC water bath was added to the mixture immediately. Then the well-mixed mixture was quickly turned into 1 cm quartz cuvette. Finally, the absorbance values of the resulting solutions were measured at 320 nm every 30 seconds after adding in pyrogallic acid for one minute.

Antibacterial Activity. The antibacterial activity of the newly synthesized supramolecule together with the parent ligand has been investigated against gram-positive *Staphylococcus aureus* and gram-negative *Escherichia coli* by the cup plate method with triplicate determination in each

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

Empirical formula	$C_{32}H_{26}CuN_{12}O_2$
Formula weight	674.19
Temperature	293(2) K
Wavelength (Å)	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 12.6375(6) Å α = 90.00º
	b = 11.9361(4) Å β = 103.331(5)º
	c = 10.0100(5) Å γ = 90º
Volume	1469.25(12) $Å^3$
Z, Calculated density (Mg/m^3)	2, 1.524
μ (mm^{-1})	0.798
F (000)	694
Crystal size (mm^3)	0.02 × 0.01 × 0.01 mm
θ range for data collection	2.70 to 25.01º
Reflections collected	8763
Independent reflections	2579 [R_{int} = 0.0594]
Completeness to θ = 25.01	99.9%
Data / restraints / parameters	2579 / 36 / 217
Goodness-of-fit on F^2	1.295
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0626, wR_2 = 0.1364
R indices (all data)	R_1 = 0.1015, wR_2 = 0.1545
Largest diff. peak and hole	1.115 and -0.761 e. $Å^{-3}$

$^aR_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $^bwR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w|F_o^2|^2)]^{1/2}$

Table 2. The selected bond lengths (Å) and angles (°) of **1**

Cu(1)-N(1)= 1.982(3)	Cu(1)- N(4)#1=2.035(3)
Cu(1)- N(1)#1=1.982(3)	Cu(1)- N(4)=2.035(3)
N(1)-Cu(1)-N(1)#1=180.0	C(1)-N(1)-Cu(1)= 114.4(3)
N(1) -Cu(1)-N(4)#1=80.97(14)	N(2)-N(1)-Cu(1)=139.3(3)
N(1)#1-Cu(1)-N(4)#1= 99.03(14)	C(12)-N(4)-Cu(1)=127.1(3)
N(1)-Cu(1)-N(4)= 99.03(14)	C(16)-N(4)-Cu(1)=114.6(3)
N(1)#1-Cu(1)-N(4)= 80.97(14)	N(4)#1-Cu(1)-N(4)= 180.0

Table 3. The system for determining the SOD-like activity of compound **1**

	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**
Tris-HCl (mL)	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Ultrapure water (mL)	4.70	4.50	4.30	4.10	3.90	3.70	3.20	2.70
Compound **1** (mL)	0.00	0.20	0.40	0.60	0.80	1.00	1.50	2.00

case.[55] The nutrient agar medium (peptone, beef extract, NaCl, and agar) and Oxford Cups were used. The abacterial Oxford Cups were carefully placed on the plates which were previously seeded with the test organism Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli*, respectively. Then 240 μL sample solutions at 50, 100, 150, 200 and 250 μg/mL concentrations were injected into each cup. Finally, the plates were incubated for 24 h at 37 ºC in order to diffuse and get inhibition zones. The antibacterial activity around each cup was measured by measuring the diameter of the inhibition zone in millimeter.

The standard strains used were *E. coli* ATCC 35218 and *S. aureus* ATCC 25923. In each case, the suspension of indicator strain was adjusted by stroke-physiological saline solution until the turbidity compared with McFarland standard number 0.5 (10^8 CFU/mL). Stock solutions of compound **1** were prepared in dimethyl sulfoxide (DMSO) which had no effect on the microorganisms in the paper. Controls with DMSO were adequately done.

Results and Discussion

Description of the Structure. Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the monoclinic space group $P2_1/c$. The structure of **1** consists of the neutral mononuclear unit $[Cu(Ippyt)_2(H_2O)_2]$ (Figure 1) which consists of one unique central Cu(II) ion, two Ippyt ligands and two coordinated water molecules in trans-fashion. As is shown in Figure 1, each central Cu(II) adopts a six-coordinated elongated-octahedral geometry (CuN_4O_2) in which Cu(II) is coordinated with two oxygen atoms from two water molecules occupying the apical position, and four nitrogen atoms which include two pyridyl nitrogen atoms and two triazolyl nitrogen atoms from two Ippyt ligands occupying the equatorial plane. The Cu–O and Cu–N bond lengths are 2.531(3) Å and in the range of 1.982(3) Å-2.035(3) Å, respectively.

In compound **1**, two Ippyt ligands respectively act as bidentate ligands in the *cis*-fashion to link one copper atom, which form a basic construct unit. Both hydrogen atoms from the two coordinated waters in each construct unit are involved in constructing hydrogen bonds (O1-H1A···N3=2.917(5) Å and O1-H1B···N6=2.901(6) Å) with the nitrogen atoms which belong to the ligands from other construct units around. And they can be divided into two

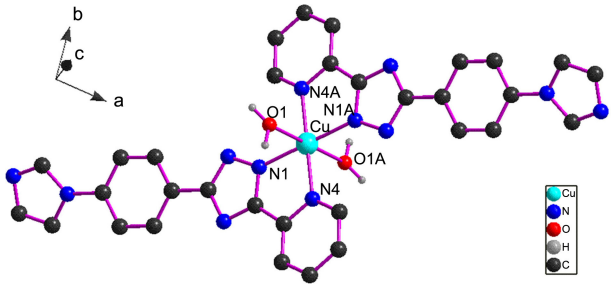


Figure 1. The coordination environment of the copper(II) atom in compound **1**.

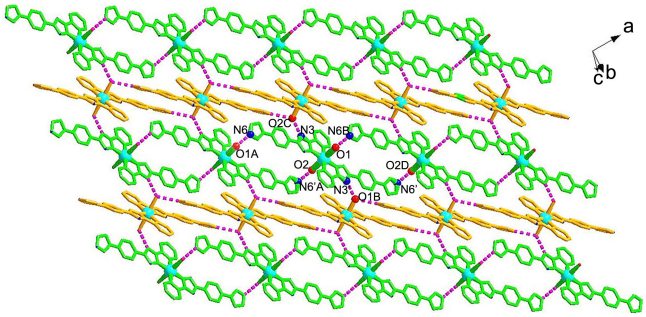


Figure 2. The 2D supramolecular architecture of **1** constructed by hydrogen bonding interactions in the a, c plane.

kinds of hydrogen bonding interactions which are between the coordinated waters and the triazolyl nitrogen atoms [O1B···N3', O2C···N3], between the coordinated waters and the imidazolyl nitrogen atoms [O1···N6B, O2···N6'A, O1A···N6, O2D···N6'] (Figure 2), respectively. As is shown in Figure 2, the construct motifs are interlinked by the hydrogen bonding interactions between oxygen/imidazolyl nitrogen atoms and imidazolyl nitrogen/oxygen atoms from adjacent motifs. Thus, infinite one-dimensional (1D) ring-shaped chains are formed. N3 and N3' are further involved in forming another hydrogen bonding interactions with other neighbouring water oxygen atoms and thus connect the 1D supramolecular chains together to form the two-dimensional (2D) supramolecular architecture in the a,c plane. In this architecture, each adjacent chain is connected parallel but in a fold-paper-like manner and the dihedral angles between two adjacent planes are 23.52º. In addition, the structures are interlinked by different hydrogen bonding interactions and finally result in the three-dimensional (3D) supramolecular network architectures. Due to the coordinated waters and abundant nitrogen atoms from the Ippyt ligands, numerous hydrogen bonding interactions are formed. Then these hydrogen bonds connect the construct units together and thus the 1D structure can be further connected to be a pseudo 3D network (shown in Figure 3).

Thermal Stability. Thermogravimetric analysis (TGA) was carried out in the interest of studying the thermal stability

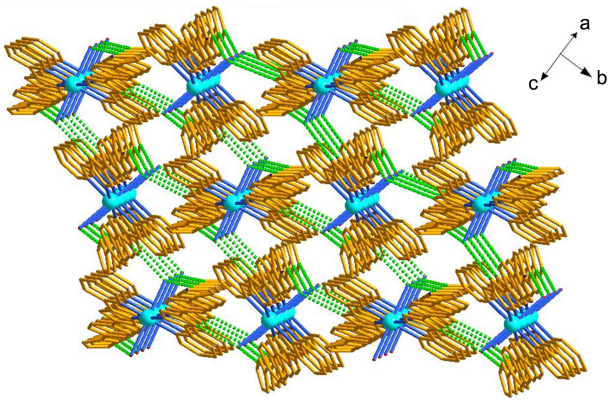


Figure 3. View of 3D-supramolecular architecture formed by the hydrogen bonding interactions in **1**.

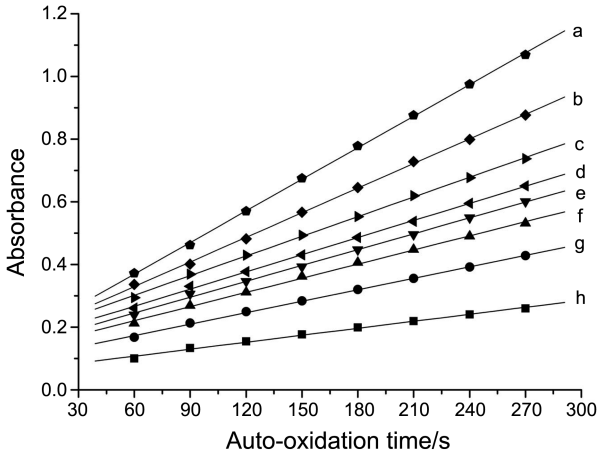


Figure 4. Absorbance *vs*. auto-oxidation time of pyrogallol in Tris-HCl. The concentrations of compound **1** added in samples **a-h** were 0, 5, 10, 15, 20, 25, 37.5 and 50 μg/mL respectively.

of the framework. The TGA curve (Figure S1) shows two main weight loss stages. The initial weight loss of 7.2% in the 50-170 ºC temperature range is corresponding to the removal of the coordinated water molecules (5.34% calculated). When the temperature is above 380 ºC, the product begins to decompose and oxidize. The residual weight percentage at the end of the decomposition of compound **1** is consistent with the formation of CuO, and the observed residue percentage is 10.2% (11.8% calculated).

SOD-like Activity. The SOD-like activity of compound **1** was assayed according to its ability to inhibit the auto-oxidation of pyrogallic acid. In this reaction system, absorbance values were determined at 320 nm and the relationship between the time of auto-oxidation and the absorbance value was shown in Figure 4 and the equation of linear regression was $A = K_0t + K_1$, where A is the absorbance value, K_0 is the slop of the straight line/the speed of auto-oxidation of pyrogallic acid, t is the time of auto-oxidation, K_1 is the intercept of the straight line (*constant*).

In Figure 4, it shows that the rate of auto-oxidation of pyrogallic acid is inhibited. With the increase of the concentration of compound **1**, the slop of the line exhibits a slightly decreasing tendency which also represents the decline of the speed of auto-oxidation. On the other hand, inhibition ratio (η) represents the inhibitory ability and is calculated from the formula: $\eta = (1 - K_0/K_{auto}) \times 100\%$, where K_{auto} is the speed of auto-oxidation of pyrogallic acid.

In addition, by graphing the inhibition rate of auto-oxidation versus the concentrations of the tested solutions

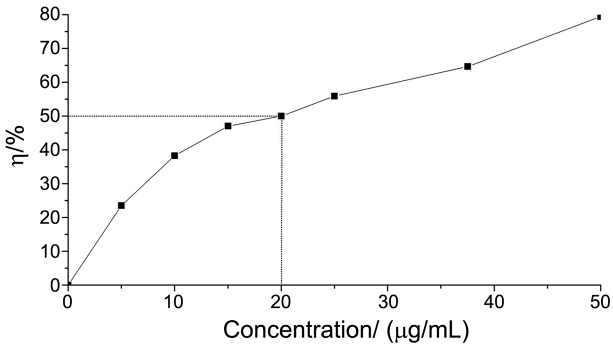


Figure 5. Relationship between the inhibition rate and concentration of compound **1**.

(Figure 5), it is concluded that the greater the concentration of compound **1**, the lower the velocity of auto-oxidation of pyrogallol acid. And the concentration required to produce the inhibition ratio of 50% (IC_{50}) is 20 μg/mL which indicated that this copper compound presented a certain SOD-like activity.[53]

Study of Antibacterial Activity. The antibacterial activity of the ligand and its corresponding compound was evaluated against gram-positive *E. coli* and gram-negative *S. aureus*. The inhibition zones (mm) around each disk were measured after 24 h and the results in terms of the inhibition percentage are listed in Table 4. The inhibition percentages were calculated using the formula: (%) = 100(D–D_0)/(D–6), where D and D_0 are the diameters of the inhibition zones in test and control plates, respectively. The results show that compound **1** has toxicity against both strains. The parent ligand is found to have a certain antibacterial property. However, it is interesting that the biological activity is enhanced upon complexation with the copper ion. The enhanced activity of metal compound compared to the parent ligand may be due to the nitrogen atom around the central metal ion arising from chelation. Such an increased activity for the metal chelates as compared to the free ligand can be explained on the basis of chelation therapy.[56] Chelation considerably reduces the polarity of metal ion because of the partial sharing of its positive charge with the donor groups. On the other hand, compound **1** is found to be slightly more toxic against *E. coli* as compared to *S. aureus.*

Conclusion

In this work, we synthesized a novel supramolecular compound with a construct unit of $[Cu(Ippyt)_2(H_2O)_2]$, in which the copper atom adopts a six-coordinated elongated-

Table 4. The results of antimicrobial activity for ligand and compound **1**

	Average inhibition percentage after 24 h (%)									
	E. coli					*S. aureus*				
Sample solution (μg/mL)	50	100	150	200	250	50	100	150	200	250
Ligand Ippyt	55.22	57.75	58.62	60.00	61.78	50.00	50.00	50.41	53.85	54.89
Compound **1**	55.55	60.26	64.49	64.91	68.25	53.85	56.83	59.73	60.53	64.50

octahedral geometry(CuN_4O_2). In compound **1**, the water molecules play crucial roles in the construction of the final three-dimensional (3D) network architecture because all coordinated waters are involved in constructing hydrogen bonds with triazolyl and imidazolyl nitrogen atoms from other construct units around. SOD-like activity determination shows IC_{50} value of compound **1** is 20 μg/mL which indicates compound **1** has a certain SOD-like activity in comparison with the previous work.[53] Antimicrobial assays indicate that compound **1** exhibits a stronger antibacterial efficiency than the parent ligand arising from the chelation with copper atom.

Supplementary Material. Crystallographic data for the structure reported here has been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC: 873303). The data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/cperl/catreq.cgi (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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