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Binuclear Cu(I) complex of (N′1E,N′2E)-N′1,N′2-bis(phenyl(pyridin-2-yl)methylene)oxalohydrazide: Synthesis, crystal structure and catalytic activity for the synthesis of 1,2,3-triazoles

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ABSTRACT

A new binuclear 5-coordinate distorted trigonal bipyramidal Cu(I) complex with (N′1E,N′2E)-N′1,N′2-bis(phenyl(pyridin-2-yl) methylene) oxalohydrazide (H_2bpoh) has been synthesized, and characterized by spectroscopic and single crystal X-ray diffraction techniques. In the complex, H_2bpoh acts as a dibasic hexadentate ligand bonding with two Cu(I) each through a carbonylate-*O*, azomethine-*N*, and pyridyl-*N* atoms. The complex possess a CuN_2OP_2 core with a considerable delocalization of charge on the five-membered chelate rings which forms an unusual intra-molecular π–π stacking and C—H···π interactions. The synthesized complex exhibits excellent catalytic efficiency for a click reaction at room temperature.

1. Introduction

Copper serves as an essential trace metal in biological systems and plays a major role in several enzymatic activities and redox reactions [1]. The striking redox chemistry of copper makes it an attractive catalyst to construct highly functionalized molecules in a regio-selective manner. It can easily attain Cu^0, Cu^I, Cu^{II}, and Cu^{III} oxidation states through one-electron or two-electron processes. In addition, the different oxidation states of copper associate well with a large number of different functional groups via Lewis acid interactions or π-coordination. These features confer a remarkably broad range of activities allowing copper to catalyze the oxidation, and oxidative union of many substrates. It has been recognized as a powerful catalyst in several industrial processes (e.g., phenol polymerization, Glaser–Hay alkyne coupling) stimulating the study of the fundamental reaction steps, and the organometallic copper intermediates [2]. Various studies have revealed that copper is highly versatile with different ligand spheres and different reaction conditions giving rise to a large range of reaction chemistries useful in organic synthesis [3].

Copper(I) complexes with polydentate ligands display a rich structural chemistry as a result of their d^{10} electronic configuration, which enables them to adopt a variety of coordination numbers and geometries [4]. Dihydrazones of 2-benzoyl pyridine may act as a multi-dentate mono- or di-basic ligands because of keto-enol tautomerization. The 2-benzoyl pyridine moiety of the ligand can provide an additional binding site for complexation with the metal ions. The hydrazones of 2-benzoylpyridine and their copper(I) complexes have been used as potent inhibitors of cell growth and function as DNA-binding agents [5]. The DNA binding ability of these compounds is due to planar fragment of hydrazone ligands which can intercalate between DNA base pairs [6]. Hydrazone Schiff bases have structural similarities with neutral biological systems and due to presence of imine group, they are utilized in elucidating the mechanism of transformation of racemization reaction in biological system [7].

Nitrogen-rich heterocyclic motifs are found in a large number of potent drugs used to combat a broad range of diseases and pathophysiological conditions [8]. Particularly, triazole ring has been extensively used as a linkage in bio-conjugation chemistry due to its easy accessibility, hydrolytic, and metabolic stability, water solubility, rigidity, and peptidomimetic character [9]. The click reaction is a highly chemoselective and stereospecific Cu(I)-catalyzed [3 + 2] cycloaddition reaction, in which dipolarophiles react with 1,3-dipoles to form five-membered heterocycles. It is frequently applied in drug discovery, material science, supramolecular chemistry, DNA labeling, and oligonucleotide synthesis [10–13]. Various well-designed methodologies have already been developed to assemble these triazole scaffolds [14]. In particular, the construction of both the 1,4- and 1,5-disubstituted, 1,2,3-triazole

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regioisomers has conventionally been accomplished using 1,3-dipolar cycloaddition of alkynes and organic azides under thermal conditions, mediated by organometallic reagents, as well as under copper or ruthenium catalysis [15–17]. However, these strategies possess some drawbacks such as use of high temperatures and regioselectivity issues. Therefore, the development of efficient, practical, and green synthetic procedures to generate 1,4- and 1,5-disubstituted 1,2,3-triazole modules remains a great challenge. It is interesting to note that the use of copper catalysts in ultra-low levels for an efficient and fast click reaction is an attractive and emerging advance in this field [18].

In view of the above and as a part of our recent investigations on the catalytic application of transition metals and their complexes [19,20], we report herein the synthesis, crystal structure, and catalytic activity of a Cu(I) complex for a click reaction between benzyl halides, sodium azide, and alkynes.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from Sigma–Aldrich Chemicals, USA and Merck Chemicals, India, and used without further purification. Solvents were purified by standard methods. Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 GF_{254} plates (thickness 0.25 mm). Visualization was performed with a 254 nm UV lamp and by staining in I_2 chamber. All the reactions were carried out under an open atmosphere using oven-dried glassware. The precursor bis-(triphenylphosphine) copper(I) nitrate was prepared by the reported procedure [21].

2.2. Synthesis of ligand

The ligand, (*N*′1E,*N*′2E)-*N*′1,*N*′2-bis(phenyl(pyridin-2-yl) methylene) oxalohydrazide (H_2bpoh) was synthesized by the reported method [20], by reacting 50 mL aqueous solution of oxalic acid dihydrazide (5 mmol, 0.59 g) with 50 mL methanolic solution of 2-benzoylpyridine (10 mmol, 1.83 g) in 1:2 molar ratio in a round bottom flask and reflux for 20 h. A white solid product was obtained on cooling at room temperature. Single crystal of the ligand H_2bpoh was obtained from a mixture of dichloromethane and DMSO solution by slow evaporation at room temperature. Yield (80%); M.p. 292 °C. Anal. Calc. for $C_{26}H_{20}N_6O_2$ (448.48): C, 69.63; H, 4.49; N, 18.74. Found: C, 69.55; H, 4.47; N, 18.71%. IR (ν cm^{-1}, KBr): ν(NH) 3387b; ν(C=O) 1690 s; ν(C=N) 1582 m; ν(N—N) 994w. ^{1}H NMR (DMSO-d_6, 300 MHz): δ = 14.08 (br s, NH, Z), 10.28 (br s, NH, E); 8.89–7.39 (m, Ar–H) ppm. ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 160.79 (C = O); 157.48 (C = N); 150.70–124.37 ppm.

2.3. Synthesis of $[Cu_2(bpoh)(PPh_3)_4]\cdot 2CH_2Cl_2$

The $[Cu_2(bpoh)(PPh_3)_4]\cdot 2CH_2Cl_2$ was synthesized by reacting 50 mL solution of bis-(triphenylphosphine) copper(I) nitrate (2 mmol, 1.30 g) in dichloromethane with 50 mL methanolic solution of ligand H_2bpoh (1 mmol, 0.45 g) in 2:1 (M:L) molar ratio. The reaction mixture was stirred on a magnetic stirrer for 24 h at room temperature. The product was slowly crystallized on keeping the above solution in open atmosphere at room temperature. Yield (70%). Orange crystals, M.p. 195 °C. Anal. Calc. for $C_{100}H_{82}Cl_4Cu_2N_6O_2P_4$ (1792.56): Cu, 7.09; C, 67.00; H, 4.61; N, 4.69. Found: Cu, 7.15; C, 67.21; H, 4.60; N, 4.73%. IR (ν cm^{-1}, KBr): ν(C=N) 1572 m; ν(N=C—O$^-$) 1542 m; ν(C—O$^-$) 1276; ν(N—N) 1024 w.

2.4. General procedure for synthesis of 1,2,3-triazoles

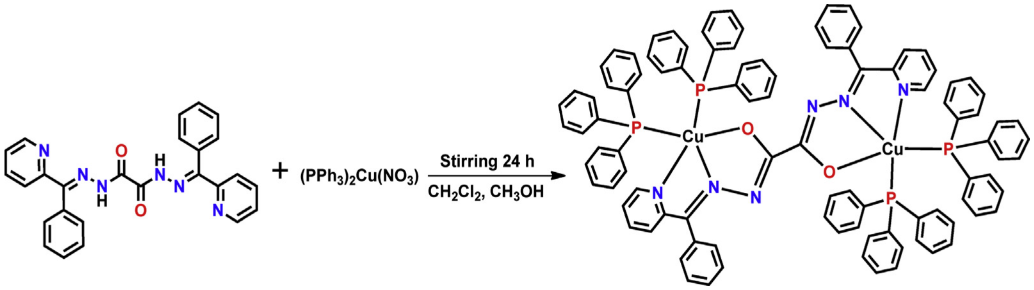
Benzyl halide (10 mmol), sodium azide (10 mmol), alkyne (10 mmol), Cu(I) complex (0.1 mol%) and CH_3CN (2 mL) were added in a 10 mL borosilicate vial. The reaction mixture was stirred at room temperature for 3 h. After completion of the reaction, water was added and the precipitate was filtered off. The product was washed thoroughly with water and dried under open air. The crude products thus obtained were purified through recrystallization from ethanol, and characterized based upon their physical and spectral properties.

2.5. Physico-chemical measurements

The molar conductance of 10^{-3} M solution of the Cu(I) complex in DMSO was measured at room temperature on a Eutech Con 510 conductivity meter. ^{1}H and ^{13}C NMR spectra of the compounds were recorded in DMSO-d_6 on a JEOL AL-300 FT-NMR multinuclear spectrometer. Infrared spectra were recorded in KBr on a Varian 3100 FT-IR spectrophotometer in 4000–400 cm^{-1} region. Single crystal X-ray diffraction data of the Cu(I) complex was obtained at 295(2) K, on a Oxford Diffraction Gemini diffractometer equipped with CrysAlis Pro. Using a graphite mono-chromated Mo Kα (λ = 0.71073 Å) radiation source. The structure was solved by direct methods (SHELXL-97) and refined against all data by full matrix least-square on F^2 using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were included in the refinement at geometrically ideal position and refined with a riding model [22,23]. The MERCURY package and ORTEP-3 for Windows program were used for generating structures [24,25].

3. Results and discussion

It appears from the analytical data that the reaction between bis-(triphenylphosphine) copper(I) nitrate and ligand H_2bpoh occurs in 2:1 (M:L) molar ratio. Both >C=O groups of the ligand enolize and deprotonate during complexation and bonding occurs through two carbonylate-*O* atoms. The reaction is given in Scheme 1.



Scheme 1. Synthesis of $[Cu_2(bpoh)(PPh_3)_4]\cdot 2CH_2Cl_2$.

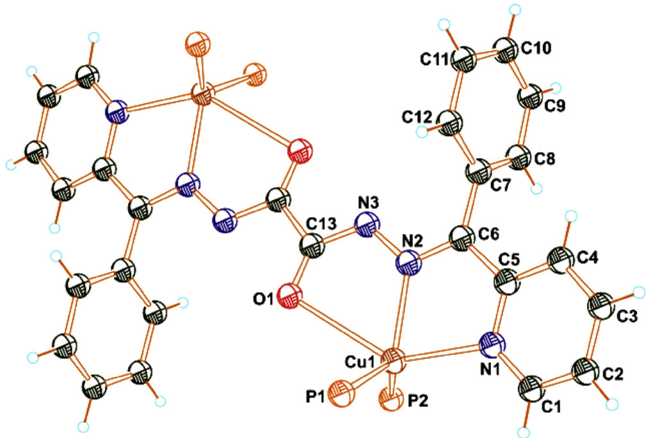


Fig. 1. ORTEP diagram of [Cu_2(bpoh)(PPh_3)4]·2CH2Cl2 (30% probability).

The complex is fairly soluble in water and organic solvents like dichloromethane, chloroform, ethanol, methanol, DMF, and DMSO. It melts with decomposition at temperature 195 °C. 10^{-3} M solution of the complex in DMSO shows molar conductance value 12.14 Ω^{-1} mol^{-1} cm^2 at room temperature, indicating that it is non-electrolyte.

3.1. IR spectra

The IR spectral bands observed at 3387, 1690, 1582, and 994 cm^{-1} in the free ligand are assigned to ν(N—H), ν(C=O), ν(C=N) and ν(N —N), respectively [20]. In the metal complex, the ν(N—H) and ν(C = O) bands disappear due to enolization of both carbonyl groups and a new ν(C = N) and ν(C—O^-) bands appear at 1555 and 1257 cm^{-1}, respectively. In the complex, ν(C=N) band shifts towards lower wave number (25 cm^{-1}) than the ligand, indicating coordination of azomethine-*N* with metal [20]. Furthermore, the shift of ν(N—N) to higher frequency (31 cm^{-1}) in the complex compared to the ligand, suggests the involvement of one of the nitrogen atom of >N—N< in bonding.

Table 1
Selected bond lengths (Å) and angles (°).

Parameter	H_2bpoh	[Cu_2(bpoh)(PPh_3)$_4$]·2CH_2Cl_2
Bond length		
O(1)—C(13)	1.211(7)	1.217(5)
N(3)—C(13)	1.355(8)	1.323(7)
N(3)—N(2)	1.368(4)	1.390(7)
N(2)—C(6)	1.276(7)	1.282(7)
C(5)—C(6)	1.492(9)	1.477(7)
C(5)—N(1)	1.349(5)	1.353(6)
N(1)—C(1)	1.333(8)	1.337(9)
C(6)—C(7)	1.500(6)	1.480(7)
Cu(1)—O(1)		2.792(4)
Cu(1)—N(1)		2.214(5)
Cu(1)—N(2)		2.117(4)
Cu(1)—P(1)		2.268(2)
Cu(1)—P(2)		2.275(2)
Bond angle		
O(1)—C(13)—N(3)	127.2(6)	127.2(5)
N(3)—N(2)—C(6)	118.7(5)	116.8(4)
C(5)—N(1)—C(1)	118.1(5)	118.5(5)
C(13)—N(3)—N(2)	119.1(5)	119.8(4)
O(1)—Cu(1)—N(1)		141.2(2)
O(1)—Cu(1)—N(2)		66.8(1)
N(2)—Cu(1)—N(1)		74.5(2)
P(1)—Cu1—O(1)		82.40(8)
P(2)—Cu(1)—O(1)		92.46(8)
P(1)—Cu(1)—N(1)		113.8(1)
P(2)—Cu(1)—N(1)		100.3(1)
P(1)—Cu(1)—N(2)		107.7(1)
P(2)—Cu(1)—N(2)		114.6(1)
P(1)—Cu(1)—P(2)		131.15(6)
N(2)—Cu(1)—N(1)		74.5(2)

3.2. Single crystal structure of [Cu_2(bpoh)(PPh_3)$_4$]·2CH_2Cl_2

The crystallographic data, structural refinement details of the Cu(I) complex are given in Table S1. Some selected bond length and bond angle parameters of the ligand and Cu(I) complex are given in Table 1. The ORTEP diagram of [Cu_2(bpoh)(PPh_3)$_4$]·2CH_2Cl_2 with the atomic numbering scheme is given in Fig. 1

In the binuclear Cu(I) complex, each metal center is coordinated with N_2OP_2 core by using carbonylate-*O*, azomethine-*N*

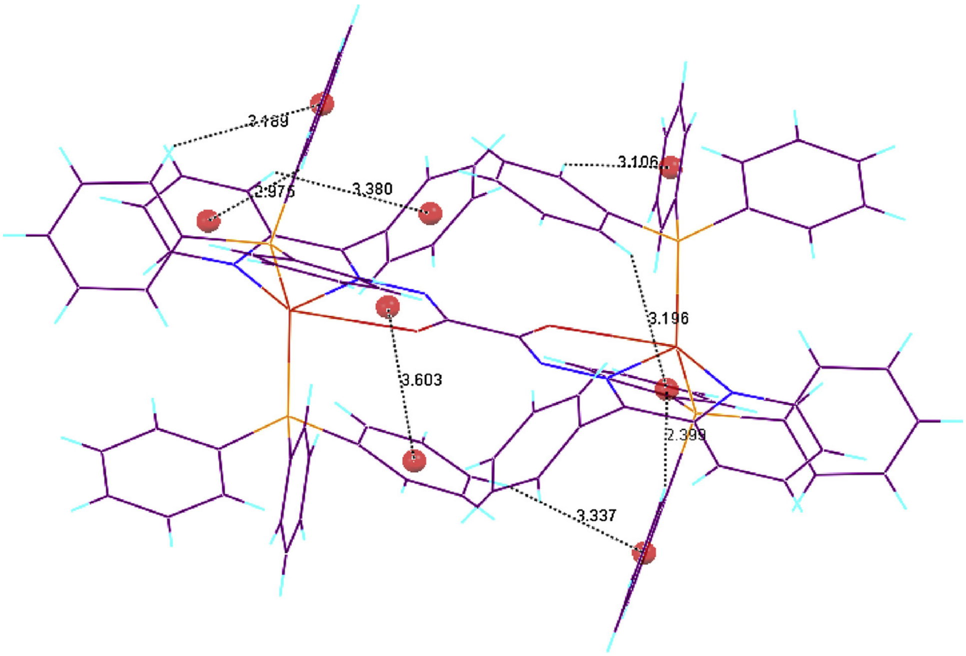
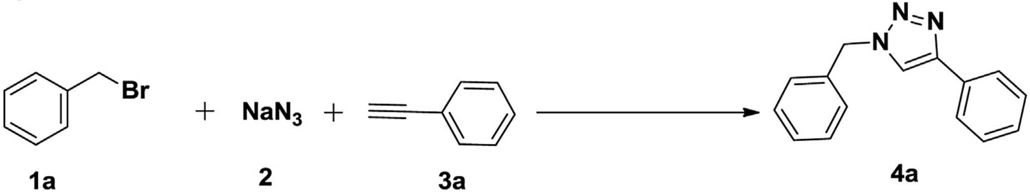


Fig. 2. Intra-molecular π–π stacking and C—H···π interactions along 'c' axis.

Table 2
Optimization of reaction conditions for the model reaction.[a]

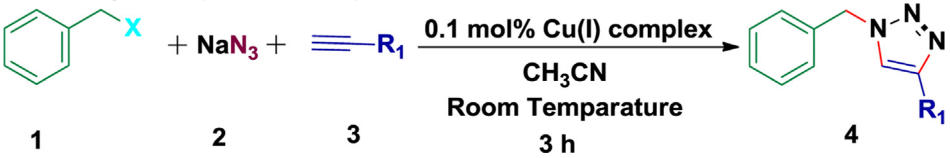


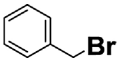
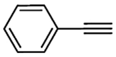
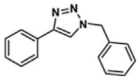
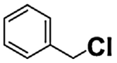
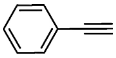
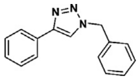
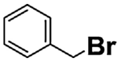
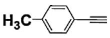
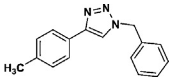
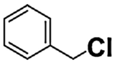
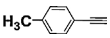
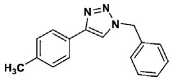
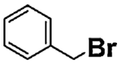
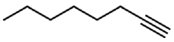
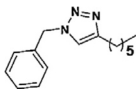
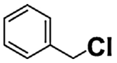
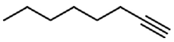
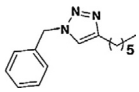
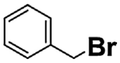
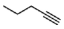
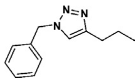
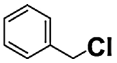
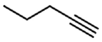
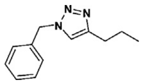
Entry	Catalyst	Loading (mol%)	Solvent	Yield (%)[b]
1.	Cu(I) complex	0.5	CH_3CN	92
2.	Cu(I) complex	0.1	CH_3CN	92
3.	Cu(I) complex	0.05	CH_3CN	60
4.	Cu(I) complex	0.1	1,4-Dioxane	72
5.	Cu(I) complex	0.1	H_2O	50
6.	Cu(I) complex	0.1	DMF	–
7.	Cu(I) $(PPh_3)_2NO_3$	0.1	CH_3CN	45[c]
8.	H_2bpoh	1	CH_3CN	–

[a] Using **1a** (10 mmol), **2** (10 mmol,), **3a** (10 mmol) for 3 h at RT.
[b] Isolated yield.
[c] Reaction conducted for 24 h.

and pyridyl-*N* atoms of ligand, and two phosphorous atoms of triphenylphosphine ligands. The NNO donor sites of the hexadentate ligand form four five-membered CN_2OCu and C_2N_2Cu chelate rings around the metal center. The two metal atoms in the complex are arranged in a trans manner to the coordination sites of ligand. The average bond lengths in the complex are O(1)—C(13)=1.217(5), N(3)—N(2)=1.390(7), N(2)—C(6)=1.282(7), N(3)—C(13)=1.323(7), N(1)—C(1)=1.337(9), C(5)—N(1)=1.353(6), C(5)—C(6)=1.477(7), C(6) —C(7)=1.480(7) Å, respectively, which are longer or shorter than those of the corresponding distances in the ligand and suggest considerable delocalization of π–electrons. The Cu—O(1), Cu—N(1) and Cu—N(2) bond distances

Table 3
Substrate scope for benzyl halide-azide-alkyne click reaction.[a]



Entry	Benzyl halide		Alkyne		Product		Yield (%)[b]
1.		1a		3a		4a	92
2.		1b		3a		4a	90
3.		1a		2b		3b	85
4.		1b		2b		3b	82
5.		1a		2c		3c	74
6.		1b		2c		3c	72
7.		1a		3d		4d	78
8.		1b		3d		4d	71

[a] Reaction conditions: using **1** (10 mmol), **2** (10 mmol, 325 mg), **3** (10 mmol), Cu(I) complex (0.1 mol%, 18 mg) and CH_3CN (2 mL).
[b] Isolated yield.

are 2.792(4) Å, 2.214(5) Å and 2.117(4) Å, respectively, which fall in the range reported for trigonal bipyramidal Cu(I) complexes [26,27]. The N(2)–C(6) distance (1.282(7) Å) in the complex is significantly longer than the ligand (1.276(7) Å) due to coordination of azomethine-*N* to the metal ion. Similarly, the O(1)–C(13) distance (1.217(5) Å) in the complex is slightly longer than the ligand (1.211(7) Å) as a result of involvement of carbonylate-*O* in bonding. The torsion angles N(1)—C(5)—C(6)—C(7) [−168.7°], O(1)—C(13)—N(3)—N(2) [33°], N(1)–C(5)–C(6)–N(2) [145°] and N(3)—N(2)—C(6)—C(7) [29°] indicate that O(1) —N(2), N(1)—N(2) and N(3)—C(7) are (+) syn-periplanar to each other but N(1)—C(7) is (−) anti-periplanar to each other.

The molecular structure of Cu(I) complex is stabilized by edge to face π–π and C —H···π interactions. Edge to face π–π stacking occurs between the centroid of chelate ring and phenyl ring with a contact distance of 3.603 Å (Fig. 2) [28], while C—H ···π interactions occur between phenyl/pyridine protons and the centroid of the pyridine/phenyl rings with contact distances of 2.975, 3.380, 3.106, 3.166, 3.189 and 3.337 Å. The phenyl proton also approaches the centroid of the chelate ring resulting in C—H···π interactions with contact distances of 2.399 and 3.196 Å [20,29].

3.3. Catalytic properties

The catalytic investigation of the Cu(I) complex was initiated using a model reaction involving benzyl bromide (**1a**), sodium azide (**2**) and phenyl acetylene (**3a**). Preliminary screening was conducted by using 0.5 mol% Cu(I) complex in acetonitrile, which delivered the product (**4a**) in 92% yield (Table 2, entry 1). When the catalyst loading was decreased to 0.1 mol%, the product yield remained same (entry 2). However, further lowering of the catalyst loading to 0.05 mol%, decreased the product yield (60%) considerably (entry 3). Various solvents were then screened for their efficiency (entries 4–6), but acetonitrile was proved to be the best. The precursor bis-(triphenylphosphine) copper(I) nitrate was also screened for its efficiency yielding 45% product yield in 24 h (entry 7). The ligand (H_2bpoh) alone was unable to promote the reaction (entry 8).

The optimized reaction conditions were subsequently applied to the reaction of a variety of benzyl halides with different aliphatic and aromatic alkynes (Table 3). It was observed that all the reactions underwent efficiently and provided the corresponding products in high yields (72–92%). Benzyl bromide exhibited better reactivity than benzyl chloride under the investigated conditions. Aliphatic alkynes viz. 1-octyne, and 1-pentyne were also participated well in the reaction and delivered exceedingly good yields (entries 5–8).

4. Conclusions

The present work describes the synthesis and characterization of a binuclear Cu(I) complex using (*N*′1E,*N*′2E)-*N*′1,*N*′2-bis(phenyl(pyridin-2-yl) methylene) oxalohydrazide as a ligand. The molecular structure of the complex has been determined on the basis of its single crystal X-ray diffraction studies. The intramolecular π–π and C—H···π interactions have been observed in the complex which stabilize the molecular structure. The catalytic efficacy of the Cu(I) complex has been effectively explored for the synthesis of 1,2,3-triazole derivatives.

Appendix

CCDC 868390 contains the supplementary crystallographic data for the Cu(I) complex. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e mail: deposit@ccdc.cam.ac.uk. The characterization data of the products are given in supporting information.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.12.003.

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