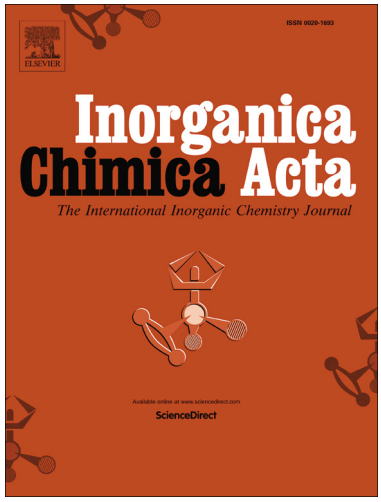

Research paper

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Two new Copper(II) complexes with chelating N,O-type bidentate ligands: Synthesis, characterization, crystal structure and catalytic activity in azide-alkyne cycloaddition reaction

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Abstract

Tetra-coordinated copper(II) complexes, [CuL_2] and [$Cu(phox)_2$], were synthesized by reaction of 1-((4-bromophenylimino)methyl)naphthalen-2-ol, HL, and 2-(2′-hydroxyphenyl)-2-oxazoline, Hphox, ligands with copper acetate, respectively. The complexes were characterized using FT-IR spectroscopy, elemental analyses, and their solid state structures were confirmed by single crystal X-ray diffraction. The catalytic activity of the complexes was evaluated in one-pot azide–alkyne cycloaddition (AAC) click reaction in water without need of any additional agent. The [CuL_2] complex showed high catalytic activity in this reaction and 1,2,3-triazole derivatives were produced in moderate to good yields.

***Keywords*:** copper; azide–alkyne cycloaddition; 1, 2, 3-triazoles; N,O-bidentate ligands

Introduction

Huisgen 1,3-dipolar cycloaddition is a valuable and powerful method for synthesis of aromatic five-membered heterocycles containing nitrogen atoms specially 1,2,3-triazoles [1]. A very wide variety of applications that have been reported for 1,2,3-triazoles in diverse research fields including synthesis of organic compounds and inorganic complexes [2–5], surface science [6,7], polymer [8–10] and material chemistry [11,12], reveal the importance of this reaction.

Furthermore, these type of compounds exhibit various biological activities like HIV-1 inhibition [13], anticancer [14], anti-tubercular [15], antiviral [16], antifungal [17] and antibacterial agents [18]. These unique properties and impressive applications justify improvement of old procedures and development of new and efficient methods for the one-pot synthesis of 1,2,3-triazoles in mild reaction condition. The most important modification for the uncatalyzed Huisgen 1,3-dipolar cycloaddition reaction was conducted by Sharpless and Meldal in 2002 [19,20]. They were successfully able to catalyze this non-selective reaction by copper salts and produce 1,4-disubstituted 1,2,3-triazoles selectively. Cu-catalyzed alkyne–azide cycloaddition (CuAAC) is the premier example of the click reactions which its concept is introduced by Sharpless group for the first time [21]. In situ reduction of inexpensive copper(II) sources (mostly $CuSO_4$) in the presence of reducing agent (e.g. sodium ascorbate) is the most common reaction condition that has been used in the subsequent reports. The drawback of this methods is the instability of organic azides and the potential risk of explosion of these components [22]. To avoid this problem in developed procedures, organic azides are generated in situ by reacting of organic halides or aryl boronic acids with sodium azide. Recently, the catalytic system including Cu(II) sources in homogeneous and heterogeneous form have been reported where the reaction occurs in the absence of reducing agents and also organic azides are generated in situ from organic halides or aryl boronic acids and NaN_3 [23–32]. Among these catalytic systems, the special attention is devoted to which are active in water and the isolation of the azide intermediates is not required. Moreover, water is a green solvent that makes purification of products easier and in situ generated organic azides are immediately consumed in the next step of the reaction.

In this work, we describe the synthesis of two new water insoluble Cu(II) complexes with 1-((4-bromophenylimino) methyl) naphthalen-2-ol and 2-(2′-hydroxyphenyl)-2-oxazoline ligands, and the use of these complexes as catalysts in the one-pot azide-alkyne cycloaddition (AAC) reaction in the presence of water as a solvent without any additional reducing agents or bases.

2. Experimental

2.1. Materials and general methods. All chemicals used were analytical reagent grade. All solvents purchased from Merck were reagent grade and were used without further purification. IR spectra in the region of 4000-400 cm^{-1} were recorded in KBr pellets with a Unicam Matson 1000 FT-IR spectrophotometer. The elemental analyses (CHN) of compounds were done using a Carlo ERBA Model EA 1108 elemental analyzer. The ^{1}HNMR spectra of the free ligands were obtained using a Bruker FT-NMR 500 MHZ spectrometer in DMSO-d_6. Melting points were taken on a Gallenkamp melting point apparatus. 2-(2′-Hydroxyphenyl)-2-oxazoline, Hphox, was prepared according to the reported procedure [33]. Single crystals of **1** and **2** suitable for X-ray diffraction analysis, were grown by slow evaporation of the solvent from the ethyl acetate and dimethylformamide solution of **1** & **2**, respectively. X-ray intensity data were collected using the full sphere routine by φ and ω scans strategy on the Agilent *SuperNova* dual wavelength EoS S2 diffractometer with mirror monochromated Mo *Kα* radiation (λ = 0.71073 Å) for **1** and Cu *Kα* (λ = 1.54184 Å) for **2**, respectively. For all data collections the crystals were cooled to 150 K using an Oxford diffraction Cryojet low-temperature attachment. The data reduction, including an empirical absorption correction using spherical harmonics, implemented in *SCALE3 ABSPACK* scaling algorithm [34], was performed using the *CrysAlisPro* software package for **1** and **2** [35]. The crystal structures of **1** and **2** were solved by direct methods using the online version of *AutoChem 2.0* in conjunction with *OLEX2* suite of programs implemented in the *CrysAlis* software and then refined by full-matrix least-squares (*SHELXL-97*) on F^2 [36,37]. The non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were positioned geometrically in idealized positions and refined with the riding model approximation, with U_{iso}(H) = 1.2 or 1.5 U_{eq}(C). For the molecular graphics the program SHELXTL was used [38]. All geometric calculations were carried out using the *PLATON* software [39]. The difference Fourier map of crystal **1** shows a high peak (2.2 e.Å^{-3}) with almost 10% occupancy. It was assigned to oxygen atom of water molecule but it was not possible to locate its hydrogen atoms because of the very low occupancy. The crystal of **2** was seriously twinned with a refined BASF ration of 0.986(1)/0.014(1).

2.2. 1-((4-bromophenylimino) methyl) naphthalen-2-ol (HL).

The Schiff base ligand (HL) was synthesized via a condensation reaction of 2-hydroxy-1-naphthaldehyde and 4-bromoaniline. 4-Bromoaniline (0.516 g, 3 mmol) in ethanol (10 mL) was added slowly to a stirred solution of 2-hydroxy-1-naphthaldehyde (0.516 g, 3mmol) in hot ethanol (10 mL), then the solution was refluxed for 4 h. The reaction was allowed to cool down gradually to room temperature, the chilled ethanol solution gave yellow microcrystals. The obtained yellow crystalline solid was collected by filtration, washed twice with ethanol and recrystallized by methanol. Yield 78 %, M.p. 163 °C. Calcd. C, 62.60; H, 3.71; N, 4.29 %. Found: C, 62.51; H, 3.71; N, 4.32 %. Selected IR frequency (KBr disk, cm^{-1}): 1603 ($\nu_{C=N}$). ^1H NMR (500 MHz, DMSO-d_6): δ 15.55 (s, 1H, NH), 9.67 (s, 1H, ═CH─NH─), 8.51 (d, 1H, ring H), 7.96 (d, 1H, arom. H), 7.81 (d, 1H, arom. H), 7.55-7.69 (m, 5H, arom. H), 7.37 (t, 1H, arom. H), 7.04 (d, 1H, ring H).

2.3. Synthesis of [Cu(phox)$_2$] (1). A methanolic solution (15 mL) of $Cu(OAc)_2.H_2O$ (0.2 g, 1 mmol) was mixed with a methanolic solution (10 mL) of the ligand, 2-(2′-hydroxyphenyl)-2-oxazoline, (0.326 g, 2 mmol). The resultant mixture was refluxed for 4 h and the resulting greenish product was recovered by filtration, washed with methanol and dried in air. M.p. 248 °C. Anal. Calc. for $C_{18}H_{16}CuN_2O_4$: C, 55.74; H, 4.16; N, 7.22; Found: C, 55.62; H, 4.08; N, 7.30. Selected IR frequency (KBr disk, cm^{-1}): 1625 ($\nu_{C=N}$).

2.4. Synthesis of [CuL$_2$] (2). To a solution of $Cu(OAc)_2.H_2O$ (0.2 g, 1 mmol) in 15 mL of ethanol, a solution of ligand, 1-((4-bromophenylimino) methyl) naphthalen-2-ol (0.652 g, 2 mmol) in 15 mL of hot ethanol was added. The mixture was refluxed for 5 h to produce a brown precipitate which was filtered, washed with hot ethanol and dried under vacuum. M.p. 304 °C (dec.). Anal. Calc. for $C_{34}H_{22}Br_2CuN_2O_2$: C, 57.20; H, 3.11; N, 3.92; Found: C, 57.08; H, 3.10; N, 3.81. Selected IR frequency (KBr disk, cm^{-1}): 1615 ($\nu_{C=N}$).

2.5. General procedure for CuAAC reaction

To a reactor containing alkyne (0.5 mmol), the organic halide (0.55 mmol), NaN_3 (0.55 mmol) and H_2O (2 mL), complexes (1) and (2) separately as a catalyst were added. The reaction mixture was stirred at 70 °C for 8-12 h and completion of the reaction was judged by thin layer chromatography (TLC). Water (5 mL) was added to the resulting mixture and the product was extracted with ethyl acetate (2 x 10 mL) from the aqueous phase. The organic layer was dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to give the

corresponding 1,2,3-triazoles. Further purification needs to be done in the case of complex **1** due to its low solubility in ethyl acetate. To obtain the pure products, after extraction with ethylacetate the reaction mixture was filtered and the residue was subjected to column chromatography (eluent, 30% EtOAc in n-hexane).

3. Results and discussion

3.1. Characterization

The complex [$Cu(phox)_2$] was obtained by the reaction of the Hphox ligand (2 equiv.) and $Cu(OAc)_2.H_2O$ (1 equiv.) in methanol at reflux conditions. The fast color change from bluish-green to the pale green solution during the synthetic procedure indicated the coordination of ligand to Cu^{II} center. Complex **1** is soluble in CH_2Cl_2, $CHCl_3$, DMF, DMSO, low soluble in EtOAc and insoluble in water. The complex [CuL_2] was obtained by treatment of copper(II) acetate mono-hydrate with HL in a 1:2 ratio in ethanol at reflux conditions. Complex **2** was obtained as brown solid, insoluble in common organic solvents but soluble in DMF, DMSO and insoluble in water. The reaction pathways are shown in scheme 1. The complexes **1** and **2** were characterized by FT-IR spectroscopy and elemental analyses. The elemental analyses data in each complex are consistent with the formulations of bis(ligand)metal species. Moreover, the molecular structures of these complexes were confirmed by single crystal X-ray crystallography. Both complexes are insensitive to oxygen or moisture and can be handled in air. Enol–imine and keto–amine are tautomeric forms that could be existed for the HL ligand, where the aldehyde that Schiff base is derived from, playing a decisive role in the relative stabilities of the tautomeric forms [40]. The ^1H NMR spectrum of HL showed the signals corresponding to NH and ═CH─NH─ at 15.55 and 9.67 ppm, respectively. Therefore, NMR spectroscopy only can detect the keto form of HL [41], whereas in its solid state structure which was determined before, both forms have been reported [42]. Comparison of the FT-IR spectra of Cu(II) complexes with that of the free ligands revealed that the $\nu_{C=N}$ vibrations in the free ligand Hphox were shifted to the lower frequencies from 1641 to 1625 cm^{-1} in **1** and another ligand HL shifted to the higher frequencies from 1603 to 1615 cm^{-1} in **2**. This shift in $\nu_{C=N}$ vibrations clearly indicating that the imine nitrogen of the Hphox and the azomethine nitrogen of the HL are strongly coordinated to the metal center [43–45].

3.2. Single crystal X-ray structure analysis

The solid state structures of complexes **1** and **2** were determined by X-ray crystallography and are shown with their atom labelling scheme in Fig. 1 and 2. Details of data collection and refinement parameters are given in Table 1. Selected bond lengths and angles of **1** and **2** are listed in Table 2. Both complexes crystallize in monoclinic system with space group $P2_1/c$. The asymmetric unit of both complexes comprises half of the molecule. The geometry around Cu atom in both complexes is almost a square planar with N2O2 donor atoms of the ligands. The bite angle of Hphox and HL ligands is 88.41(10) and 89.1(2)°, respectively. The crystal packing of **1** shows extended one-dimensional chain running parallel to *ac*-plane and further connected through intermolecular π···π interactions with centroid to centroid distances 3.3833(16)–3.9221(2) Å [*Cg1*...*Cg2* = 3.3833(16), *Cg1*...*Cg3* = 3.3833(16), *Cg1*...*Cg4* = 3.8910(17), *Cg2*...*Cg2* = 3.9221(2), *Cg2*...*Cg3* = 3.9221(2), *Cg3*...*Cg3* = 3.9220(2) Å; *Cg1* = O7/C8/N9/C10/C11, *Cg2* = Cu13/O12/C1A/C2A/C8A/N9A, *Cg3* = Cu13/N9/C8/C2/C1/O12A, and *Cg4* = C1–C6]. The crystal packing of **2** is stabilized by the intermolecular C8···Br [3.427(8) Å], short contact parallel to *ac*-plane which are further forming a column by the intermolecular π···π interactions down the *b*-axis.

3.3. Catalytic Activity

In order to evaluate the catalytic properties of the complexes in the AAC, the reaction of benzyl chloride, sodium azide, and phenyl acetylene was chosen as a model one. The reaction conditions were optimized with respect to the solvent, quantity of catalyst, reaction time and the reaction temperature. The optimization results for catalysts are shown in Tables 3 and 4. First, the AAC reaction was examined without catalyst and no product was obtained after 12 h (entries 1, Table 3). When the catalyst loading was increased from 0.52 to 2.58 mol%, and from 0.28 to 1.40 mol%, respectively for **1** and **2**, isolated yield increased sharply from 29 to 75% for **1** and 77 to 95% for **2.** A further increase in the quantity of catalyst to 5.16 and 2.80 mol% for **1** and **2**, respectively, shows no substantial effect on the yield (entries 7 and 13, Table 3). Different solvents such as water, ethanol, acetone, toluene, and chloroform, were employed to assess the effect of the solvent for this cycloaddition reaction and results showed that poor yields are obtained in organic solvents. Interestingly, water was found to be the most effective solvent for this reaction (Table 4). High reactivity was observed by both of the catalysts when the reaction mixture was warmed to 70 °C (entries 14-21, Table 3). The reaction is completed at 12 h and an

effective improvement in yield of triazole was observed with increasing reaction time from 8 to 12 h (entries 22 and 23, Table 3). Next, the AAC reaction between diversely substituted phenyl acetylenes and benzyl halides were carried out under the optimal conditions to produce the corresponding 1,2,3-triazoles (Table 5). The existence of electron withdrawing and electron donating groups on the benzyl halides and the phenyl acetylenes have a low effect on the resulting yields (entries 2-6). The reaction yield could be affected by some factors such as steric hindrance and coordination ability of substrates to Cu center. The *o*-methyl benzyl chloride was less reactive than the *p*-methyl benzyl chloride due to higher steric hindrance (entries 2 and 3). The obtained results for both catalysts indicated that benzyl chloride is slightly more reactive than benzyl bromide (entries 9–13). When propargyl alcohol or 2-methyl-3-butyn-2-ol was used as a terminal alkyne, the reaction proceeded smoothly to give the corresponding products in moderate yields (entries 7, 8, 12 and 13). The lower reaction yields are probably due to the complexation of copper by alcoholic hydroxy groups [46]. Furthermore, 2-methyl-3-butyn-2-ol gave lower yields compared to the propargyl alcohol owing to the high steric hindrance.

Also, we investigated the reusability of catalyst **2**. For this purpose, according to insolubility of complex 2 in water and ethyl acetate after each recycle this complex was separated from the reaction mixture by filtration and then washed twice with distilled water and ethyl acetate, dried at 45 °C for 30 min, and reused for AAC reaction of benzyl chloride, phenyl acetylene, and NaN_3 at 70 °C for 12 h (Fig. 3). After three uses the reaction yield is reduced to 41% and this decrease in the catalytic activity is mainly attributed to structural changes of the complex **2**, this change in the structure is confirmed by comparison of the IR data for the fresh and recycled catalyst (Fig. 4). As it is clear from Figures 3 and 4 the results suggest that the catalyst **2** has poor recyclability due to structural changes and decomposition of the complex.

Finally, we compared the catalytic reactivity of catalyst **2** with recently reported catalytic systems in the AAC reaction. Although, the presence of sodium ascorbate and inert atmosphere are vital in some catalytic systems (entries 3 and 4, Table 6). Our catalytic system works without needing to an inert atmosphere and any additional reducing agents. Furthermore, the previously reported systems often required much amount of catalyst (entries 1, 2, 3, 5 and 6), high temperature (entry 3) and long reaction times (entries 1, 2 and 4) for more progress of the reaction. Other advantages of the present catalytic systems are, in situ generation of organic

azides, simple catalyst preparation, easy and quick isolation of products and use of water as a green solvent.

Conclusions

Two copper(II) complexes were synthesized by reactions of copper(II) acetate monohydrate with 2-(2′-hydroxyphenyl)-2-oxazoline and 1-((4-bromophenylimino) methyl) naphthalen-2-ol ligands. Both complexes exhibited a quasi-planer coordination environment at the copper(II) centers. The X-ray diffraction studies revealed the coordination of these ligands to the metal center in a chelate way via N- and O-donor atoms. The catalytic behavior of the **1** and **2** complexes was investigated in the one-pot protocol for the synthesis of 1,4-disubstituted 1,2,3-triazoles. Complex 2 was found to be an efficient catalyst for the AAC reaction that has been active in water.

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Appendix A. Supplementary material

CCDC Nos. 1533524-1533525 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version.

References

[1] R. Huisgen, Angew. Chem., Int. Ed. Engl. 2 (1963) 565–598.

[2] K. Kumar, D. Konar, S. Goyal, M. Gangar, M. Chouhan, R.K. Rawal, V.A. Nair, J. Org. Chem. 81 (2016) 9757–9764.

[3] U.K. Bhagat, Kamaluddin, R.K. Peddinti, Tetrahedron Lett. 58 (2017) 298–301.

[4] D. Schweinfurth, S. Strobel, B. Sarkar, Inorg. Chim. Acta 374 (2011) 253–260.

[5] S. V. Kumar, W.K.C. Lo, H.J.L. Brooks, J.D. Crowley, Inorg. Chim. Acta 425 (2015) 1–6.

[6] A. Espinoza-Vázquez, G.E. Negrón-Silva, R. González-Olvera, D. Angeles-Beltrán, H. Herrera-Hernández, M. Romero-Romo, M. Palomar-Pardavé, Mater. Chem. Phys. 145 (2014) 407–417.

[7] J.P. Collman, N.K. Devaraj, C.E.D. Chidsey, Langmuir 20 (2004) 1051–1053.

[8] R.J. Thibault, K. Takizawa, P. Lowenheilm, B. Helms, J.L. Mynar, J.M.J. Fréchet, C.J. Hawker, J. Am. Chem. Soc. 128 (2006) 12084–12085.

[9] J. Hu, K. Peng, J. Guo, D. Shan, G.B. Kim, Q. Li, E. Gerhard, L. Zhu, W. Tu, W. Lv, M.A. Hickner, J. Yang, ACS Appl. Mater. Interfaces 8 (2016) 17499–17510.

[10] Y.-G. Sun, X. Gao, G. Xiong, W.-H. Zong, F. Ding, Z. Xu, S.-J. Wang, L.-X. You, B.-Y. Ren, E.-J. Gao, Inorg. Chim. Acta 409 (2014) 497–502.

[11] A.S. Kumar, N. Kommu, V.D. Ghule, A.K. Sahoo, J. Mater. Chem. A. 2 (2014) 7917.

[12] S. Garg, J.M. Shreeve, J. Mater. Chem. 21 (2011) 4787–4795.

[13] N. Pribut, C.G.L. Veale, A.E. Basson, W.A.L. van Otterlo, S.C. Pelly, Bioorg. Med. Chem. Lett. 26 (2016) 3700–3704.

[14] X. Li, Y. Lin, Y. Yuan, K. Liu, X. Qian, Tetrahedron 67 (2011) 2299–2304.

[15] D.G. Ghiano, A. de la Iglesia, N. Liu, P.J. Tonge, H.R. Morbidoni, G.R. Labadie, Eur. J. Med. Chem. 125 (2016) 842-852.

[16] A. Montagu, V. Roy, J. Balzarini, R. Snoeck, G. Andrei, L.A. Agrofoglio, Eur. J. Med. Chem. 46 (2011) 778–786.

[17] Y. Qin, S. Liu, R. Xing, K. Li, H. Yu, P. Li, Int. J. Biol. Macromol. 61 (2013) 58–62.

[18] P.V.B. Reddy, V. K. Prasad, G. Manjunath, P.V. Ramana, Ann. Pharm. Fr. 74 (2016) 350–357.

[19] V.V. Rostovtsev, L.G. Green, V.V. Fokin, K.B. Sharpless, Angew. Chem., Int. Ed. 41 (2002) 2596–2599.

[20] C.W. Tornøe, C. Christensen, M. Meldal, J. Org. Chem. 67 (2002) 3057–3064.

[21] H.C. Kolb, M.G. Finn, K.B. Sharpless, Angew. Chem., Int. Ed. 40 (2001) 2004–2021

[22] E.F. V. Scriven, K. Turnbull, Chem. Rev. 88 (1988) 297–368.

[23] C. Zhou, J. Zhang, P. Liu, J. Xie, B. Dai, RSC Adv. 5 (2015) 6661–6665.

[24] B.S.P.A. Kumar, K.H.V. Reddy, K. Karnakar, G. Satish, Y.V.D. Nageswar, Tetrahedron Lett. 56 (2015) 1968–1972.

[25] L. Cao, C. Liu, X. Tang, X. Yin, B. Zhang, Tetrahedron Lett. 55 (2014) 5033–5037.

[26] A. Akbari, N. Arsalani, M. Amini, E. Jabbari, J. Mol. Catal. A Chem. 414 (2016) 47–54.

[27] Y. Jiang, D. Kong, J. Zhao, W. Zhang, W. Xu, W. Li, G. Xu, Tetrahedron Lett. 55 (2014) 2410–2414.

[28] B. Kaboudin, R. Mostafalu, T. Yokomatsu, Green Chem. 15 (2013) 2266–2274.

[29] C.Z. Tao, X. Cui, J. Li, A.X. Liu, L. Liu, Q.X. Guo, Tetrahedron Lett. 48 (2007) 3525–3529.

[30] S. Layek, S. Kumari, Anuradha, B. Agrahari, R. Ganguly, D.D. Pathak, Inorg. Chim. Acta 453 (2016) 735–741.

[31] S. Mohammed, A.K. Padala, B.A. Dar, B. Singh, B. Sreedhar, R.A. Vishwakarma, S.B. Bharate, Tetrahedron 68 (2012) 8156–8162.

[32] M. Amini, A. Bayrami, M.N. Marashi, A. Arab, A. Ellern, L.K. Woo, Inorg. Chim. Acta 443 (2016) 22–27.

[33] H.R. Hoveyda, V. Karunaratne, S.J. Rettig, C. Orvig, Inorg. Chem. 31 (1992) 5408–5416.

[34] R. C. Clark, and J. S. Reid, *Acta Cryst*. A64 (1995) 887–897.

[35] *SuperNova Eos S2* System: Empirical absorption correction, 2011,CrysAlis-Software package, Oxford Diffraction Ltd.

[36] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, H., *J. Appl. Cryst*. 42 (2009) 339–341 and Agilent (2012). *AutoChem 2.0*, in conjunction with OLEX2. Agilent Technologies UK Ltd, Yarnton, Oxfordshire, England.

[37] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.* 32 (1999) 115–119.

[38] G. M. Sheldrick, *Acta Cryst*. A64 (2008) 112–122.

[39] A. L. Spek, *Acta Cryst*. D65 (2009) 148–155.

[40] M. Flores-Leonar, N. Esturau-Escofet, J.M. Méndez-Stivalet, A. Marín-Becerra, C. Amador-Bedolla, J. Mol. Struct. 1006 (2011) 600–605.

[41] S. Ziegenbalg, D. Hornig, H. Görls, W. Plass, Inorg. Chem. 55 (2016) 4047–4058.

[42] A. Rauf, A. Shah, S. Abbas, U. A. Rana, S. Ud-Din Khan, S. Ali, Z.-ur-Rehman, R. Qureshi, H.-B. Kraatz, F. B. Gariepy, Spectrochim. Acta, Part A, Mol. Biomol. Spec. 138 (2015) 58-66.

[43] D. Cinčić, B. Kaitner, Cryst. Eng. Comm. 13 (2011) 4351–4357.

[44] M. Hoogenraad, K. Ramkisoensing, W.L. Driessen, H. Kooijman, A.L. Spek, E. Bouwman, J.G. Haasnoot, J. Reedijk, Inorg. Chim. Acta 320 (2001) 117–126.

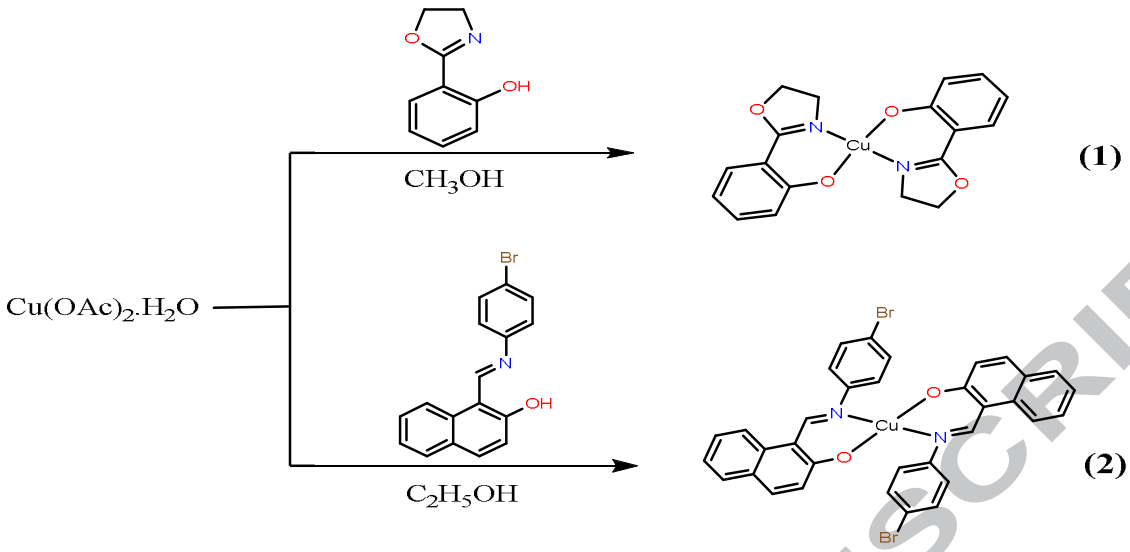
[45] M. Amini, M. Khaksar, A. Arab, R.M. Jahandizi, M. Bagherzadeh, D.M. Boghaei, A. Ellern, L. Keith Woo, Transit. Met. Chem. 41 (2016) 97–105.

[46] I. Jlalia, F. Gallier, N. Brodie-Linder, J. Uziel, J. Augé, N. Lubin-Germain, J. Mol. Catal. A: Chem. 393 (2014) 56–61.

[47] K.R. Reddy, K. Rajgopal, M.L. Kantam, Synlett 6 (2006) 957–959.

[48] N.A. Dangroo, A.A. Dar, B.A. Dar, Tetrahedron Lett. 55 (2014) 6729–6733.

[49] B. Han, X. Xiao, L. Wang, W. Ye, X. Liu, Chin. J. Catal. 37 (2016) 1446–1450.



Scheme 1. Synthesis of complexes 1 and 2.

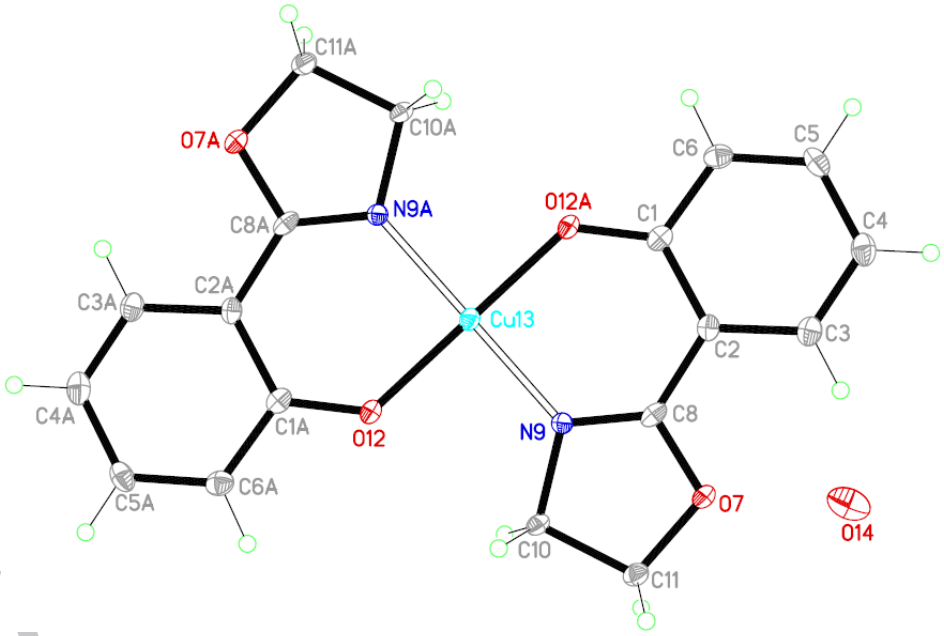


Figure 1. The ORTEP of 1 with atoms labelling and ellipsoids probability of 40%. The A suffix is for symmetry code, -x + 2, -y + 1, -z + 2.

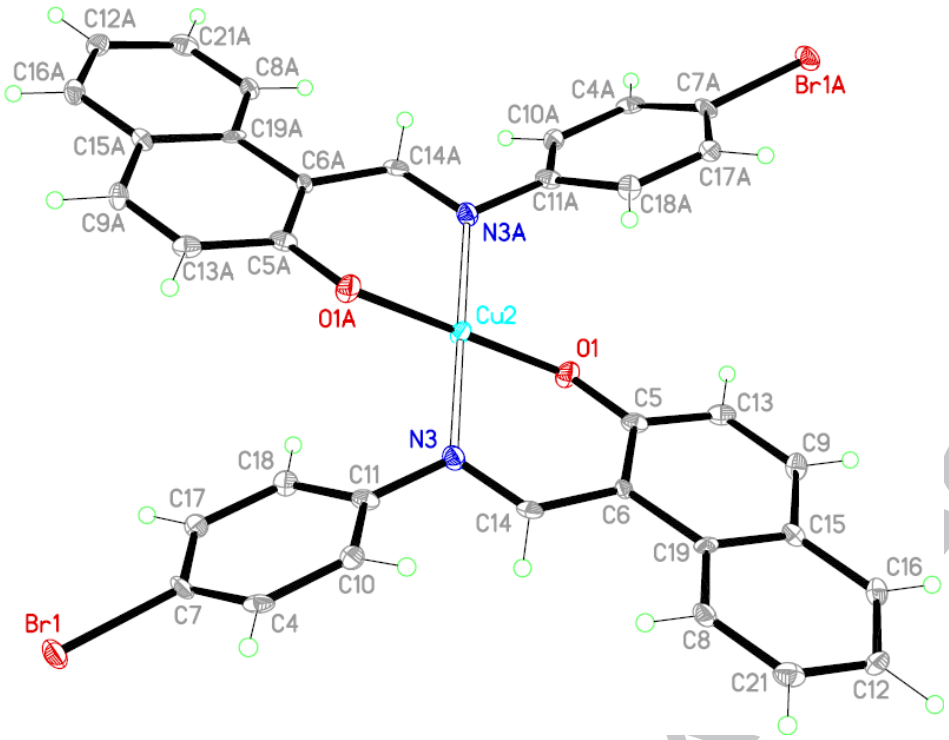


Figure 2. The ORTEP of 1 with atoms labelling and ellipsoids probability of 40%. The A suffix is for symmetry code, -x + 1, -y, -z + 1.

Table 1. Crystal data and refinement parameters for **1** and **2**

Complex	**1**	**2**
Empirical formula	$C_{18}H_{16}CuN_2O_4$	$C_{34}H_{22}Br_2CuN_2O_2$
Formula mass	387.87	713.89
Crystal size (mm)	0.10 × 0.15 × 0.25	0.10 × 0.18 × 0.35
Colour	dark green	brown
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
θ_{max} (°)	26	30
a (Å)	5.5259(2)	17.2389(5)
b (Å)	19.4152(8)	3.87926(13)
c (Å)	7.4422(3)	19.2704(6)
β (°)	102.882(4)	93.123(3)
V (Å^3)	778.35(6)	1286.78(7)
Z	2	2
D_{calc} *(Mg/m^3)*	1.655	1.843
μ *(mm^{-1})*	1.430	5.144
F (000)	398	710
Index ranges	$-6 \le h \le 6$	$-21 \le h \le 21$
	$-24 \le k \le 24$	$-4 \le k \le 4$
	$-9 \le l \le 9$	$-19 \le l \le 23$
No. of measured reflns.	20190	2782
No. of independent reflns./R_{int}	1584/0.0451	2539/0.2243
No. of observed reflns. $I > 2\sigma(I)$	1531	2360
No. of parameters	122	182
Goodness-of-fit (GOF)	1.244	1.183
R_1 (observed data)	0.0447	0.0740
wR_2 (all data)	0.1032	0.1659

Table 2. Selected bond lengths and angles for **1** and **2**

Bond lengths (Å)	**1**	**Bond lengths**	**2**
Cu(13)–O(12)	1.901(2)	Cu(2)–O(1)	1.913(6)
Cu(13)–N(9)	1.958(2)	Cu(2)–N(3)	2.005(7)
N(9)–C(8)	1.290(4)	O(1)–C(5)	1.313(9)
O(7)–C(8)	1.350(4)	N(3)–C(11)	1.417(10)
O(7)–C(11)	1.452(4)	N(3)–C(14)	1.300(10)
N(9)–C(102)	1.290(4)	C(6)–C(14)	1.426(10)
Bond angles (°)		**Bond angles (°)**	
O(12)–Cu(13)–N(9)	88.41(10)	O(1)–Cu(2)–N(3)	89.1(2)
O(12)–Cu(13)–O(12A)[a]	180.00	O(1)–Cu(2)–O(1A)[b]	180.00
O(12)–Cu(13)–N(9A)[a]	91.59(10)	O(1)–Cu(2)–N(3A)[b]	91.0(2)
C(8)–O(7)–C(11)	107.6(2)	Cu(2)–O(1)–C(5)	123.9(5)
Cu(1)–N(9)–C(8)	126.0(2)	Cu(2)–N(3)–C(11)	122.9(5)

a and b are for -x + 2, -y + 1, -z + 2 and -x + 1, -y, -z + 1 symmetry codes, respectively.

Table 3. The effect of time, temperature and the amount of catalyst on the cycloaddition of benzyl chloride with phenyl acetylene in the presence of sodium azide.[a]

Entry	Cat. loading (mol %)	Temp. (^{o}C)	Time (h)	Yield (%)[b]
1	-	70	12	0
2	**1**(0.52)	70	12	29
3	**1**(1.03)	70	12	53
4	**1**(1.55)	70	12	55
5	**1**(2.07)	70	12	63
6	**1**(2.58)	70	12	75
7	**1**(5.16)	70	12	76
8	**2**(0.28)	70	12	77
9	**2**(0.56)	70	12	79
10	**2**(0.84)	70	12	82
11	**2**(1.12)	70	12	90
12	**2**(1.40)	70	12	95
13	**2**(2.80)	70	12	95
14	**1**(2.58)	r.t.	12	12
15	**1**(2.58)	40	12	15
16	**1**(2.58)	50	12	20
17	**1**(2.58)	60	12	52
18	**2**(1.40)	r.t.	12	21
19	**2**(1.40)	40	12	25
20	**2**(1.40)	50	12	73
21	**2**(1.40)	60	12	86
22	**1**(2.58)	70	8	47
23	**2**(1.40)	70	8	78

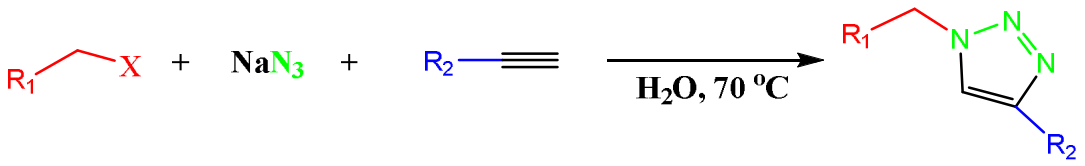
[a] Reaction conditions: 0.5 mmol of phenylacetylene, 0.55 mmol of benzyl chloride, 0.55 mmol of sodium azide, 2 mL of H_2O. [b] Isolated yields.

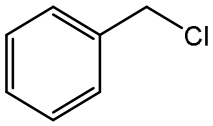
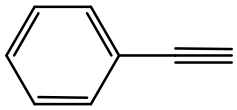
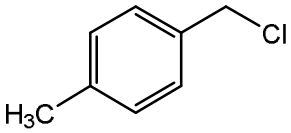
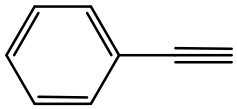
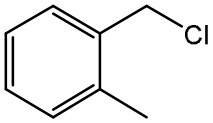
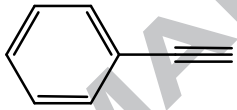
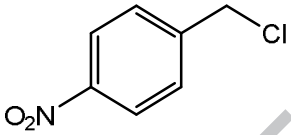
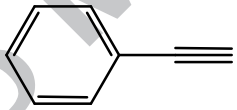
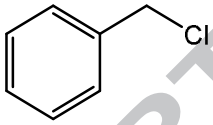
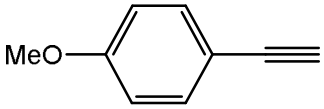
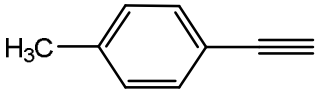
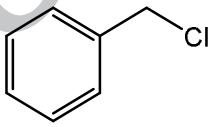
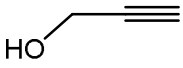
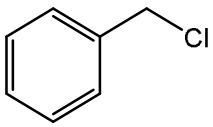
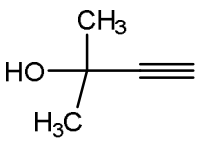
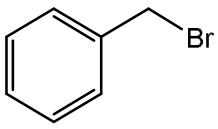
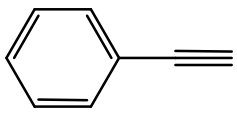
Table 4**.** Effect of solvent on the cycloaddition of benzyl chloride with phenyl acetylene and sodium azide.[a]

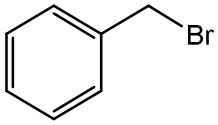
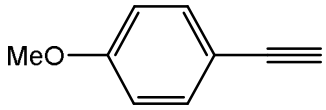
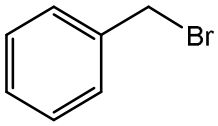
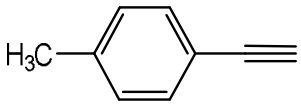
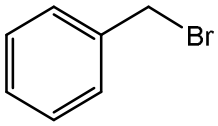
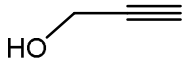
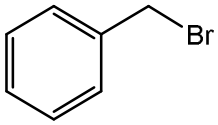
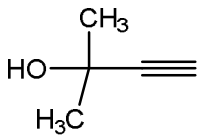
Entry	Solvent	Yield (%)[b]	
		[Cu(phox)$_2$]	[CuL$_2$]
1	acetone	17	12
2	ethanol	23	31
3	chloroform	10	12
4	toluene	5	13
5	water	75	95

[a] Reaction conditions: 0.5 mmol of phenylacetylene, 0.55 mmol of benzyl chloride, 0.55 mmol of sodium azide, solvent 2 mL, 70˚C, 12h. [b] Isolated yields.

Table 5. Cycloaddition of alkyl halides with terminal alkynes in the presence of Cu(II) catalysts and NaN_3 under the optimized reaction conditions.[a]



Entry	Aliphatic halide	Alkyne	Yield (%)[b]	
			[Cu(phox)$_2$]	[CuL$_2$]
1			75	95
2			74	91
3			68	82
4			64	89
5			73	96
6			75	93
7			46	63
8			41	58
9			70	87

10			75	91
11			69	85
12			44	59
13			42	46

[a] Reaction conditions: 0.5 mmol of terminal alkyne, 0.55 mmol of alkyl halide, 0.55 mmol of sodium azide, 2 mL of H_2O. [b] Isolated yields.

Table 6. Recently reported catalytic systems for AAC in the presence of Cu(II) complexes.

Entry	Catalyst	Conditions	Yield (%)	Ref.
1	$Cu(OAc)_2 \cdot H_2O$	Catalyst (20 mol%) / H_2O /20 h / r.t.	77	[47]
2	Cu(NO3)2·3H2O	Catalyst (20 mol%) / H_2O /20 h / r.t.	13	[47]
3	$CuSO_4$-sodium ascorbate	$CuSO_4$-sodium ascorbate (10 mol % each)/acetone: water (1:1)/8.5 h/80 °C	89	[48]
4	$[Cu(Npy_2pz)]_2(PF_6)_2$	Catalyst (0.2mol%), sodiumL-ascorbate (1 mol%)/MeOH/16 h/ /25 °C/N_2	99	[49]
5	$[Cu(dppo)_2]$	Catalyst (2 mol%)/DMF/8 h/ r.t.	86	[30]
6	$[Cu(tzol)_2]$	Catalyst (2.4 mol%)/H_2O/12 h/70°C	96	[32]
7	$[CuL_2]$	Catalyst (1.40 mol%)/H_2O/12 h/70°C	95	Present work

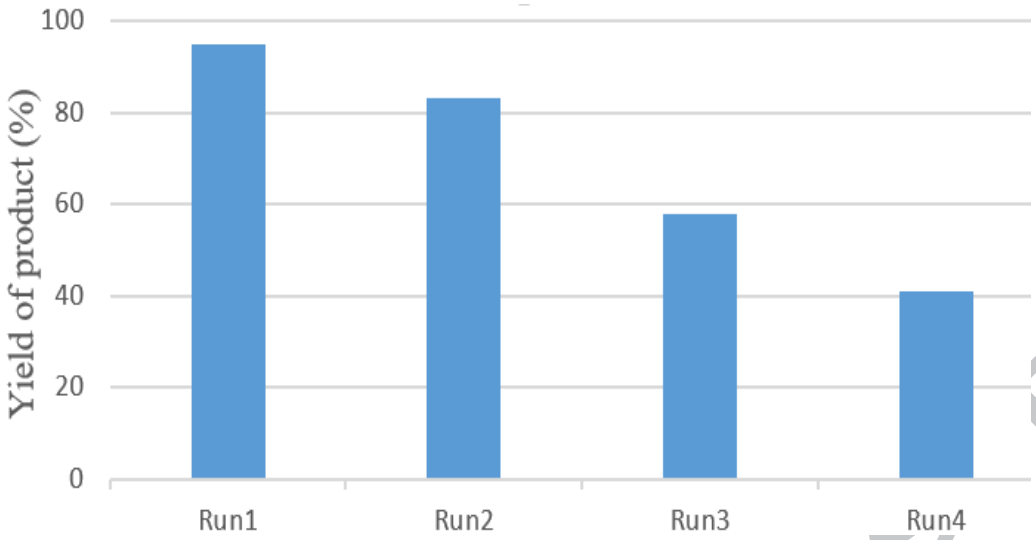


Figure 3. Recyclability and reusability study of complex 2 in the AAC reaction.

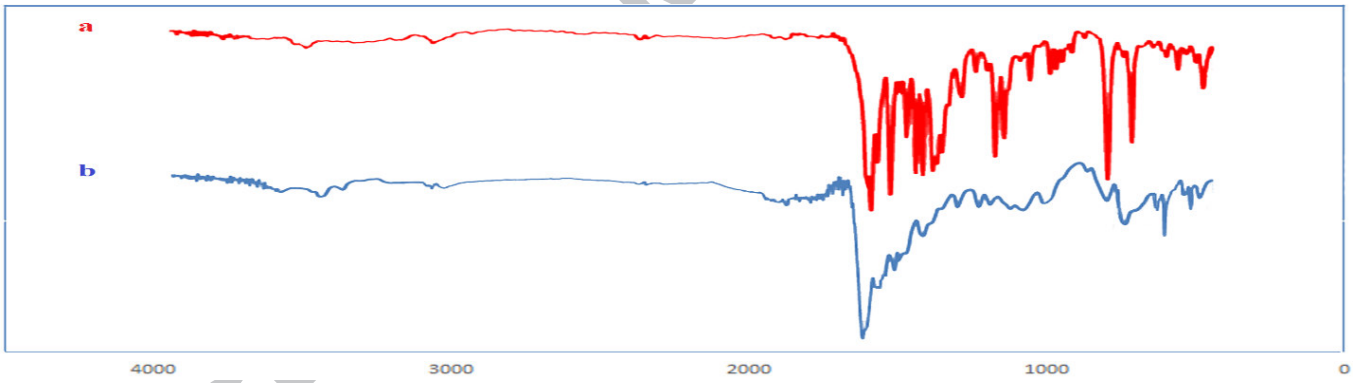
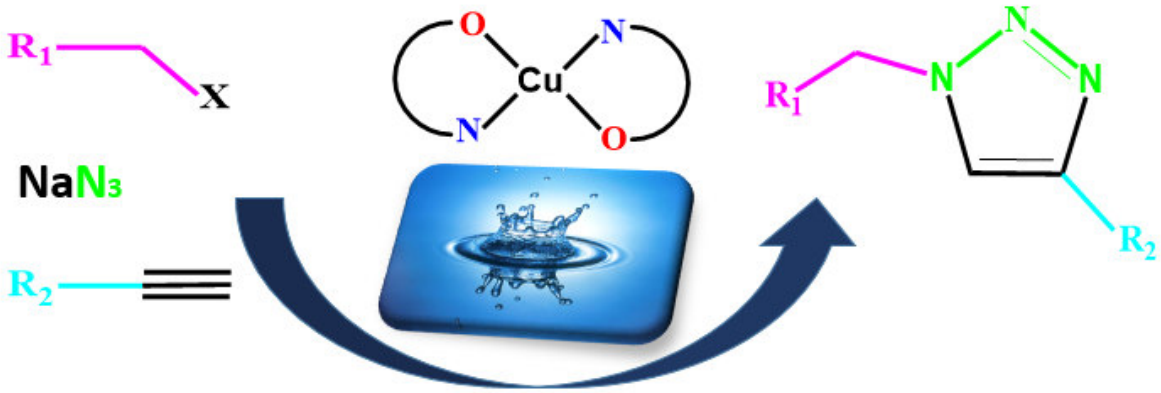


Figure 4. IR spectrum of (a) fresh and (b) reused catalyst [CuL_2].

Graphical Abstract



Highlights

- The copper (II) complexes were prepared with chelating N,O-type bidentate ligands.
- Crystal structure of the both complexes was discussed.
- The catalytic activity of the complexes was investigated in one-pot azide–alkyne cycloaddition reaction that completed in water.
- Moderate to good yields have been achieved at mild reaction condition.