



Copper and silver- (N,N'- bis [2-hydroxy-1- naphthylmethyldene] -1,2-diaminoethane) complexes as efficient catalysts for the formation of 1,4-disubstituted triazoles.

Safaa Eldin H. Etaiw*, Mohamed B. Elzarie and Marwa M. Rashad

Department of Chemistry, Faculty of Science, University of Tanta, 31527-Tanta, Egypt

Abstract: The reactions of copper and silver ions with N,N'-bis(2-hydroxy-1-naphthylmethyldene)-1,2-diamino ethane (H₂L) afford the complexes [CuL], 1 and [AgHL], 2. H₂L and the complexes 1 and 2 were investigated by elemental analyses, molar conductance and spectral measurements. The elemental analysis data suggest the stoichiometric ratio 1:1 [M:L]. The molar conductance measurements reveal the presence of non-electrolytic nature of the complexes. Spectral data indicated the versatility of H₂L as tetra-dentate ligand via NONO with Cu and Ag atoms forming square planar and tetrahedral geometries, respectively. These complexes have good catalytic activity in click reactions to prepare 1-benzyl -4- bromo triazole and 1-benzyl-4-phenyl triazole. **Key words:** click reaction, Copper, Silver, supramolecular polymers, Catalysis.

Key words: Schiff base, Copper, Silver, Complexes, Catalysis, Click reactions

Introduction:

Co-ordination compounds exhibit different characteristic properties which depend on the metal ion to which they are bound as well as the type of ligand, etc. These metal complexes have found extensive applications in various fields of human interest [1-3]. With increasing knowledge of the properties of functional groups, as well as the nature of donor atoms and the central metal ion, ligands with more selective chelating groups, i.e., imines or azomethanes, which are more commonly known as Schiff bases, are used for complex formation studies. Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions since they frequently exhibit unusual structural properties [4-6]. These properties have resulted in wide applications in different chemical fields [7-10]. The synthesis and characterization of extended bridged polynuclear complexes is a subject of great interest because of their potential applications in catalysis and materials chemistry [11-13]. Many binuclear complexes where the metal atoms are bridged by extended dicarboxylato ligands such as μ -terephthalate, μ -oxalate, μ -butene dicarboxylate have been reported [14-18]. Generally, Schiff-bases have played a seminal role in the development of modern coordination chemistry, but also they can be found at key points in the development of inorganic

biochemistry, catalysis and optical materials. The Ag (I) ion is regarded as a soft acid that favors the coordination of soft bases, such as ligands that contain sulfur and unsaturated nitrogen. Complexes of silver (I) and N-heterocyclic ligands lead to the production of interesting geometric configurations and photophysical properties [19-21]. However, only a few examples of Ag (I)-containing Schiff-base complexes and coordination polymers have been studied in detail to date [22]. Copper (II) complexes show distorted octahedral and tetrahedral symmetries due to d₉ configuration. The distortion is usually seen as axial elongation consistent with the lability and geometric flexibility of the complex [23-26].

Therefore, typical Cu (II) complexes have square planar or square pyramidal geometries with weakly associated ligands in the axial positions, but some copper (II) complexes possess trigonal bipyramidal geometry [23-26].

The present work introduces the syntheses and characterization of a Schiff base ligand derived from 2-hydroxy naphthaline -1-carbaldehyde and ethylenediamine and its Ag^I and Cu^{II} complexes. These complexes are prepared to be used as catalysts in

bioconjugate areas have increased exponentially over the last decade [29].

2. Experimental

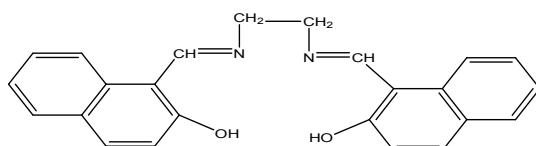
2.1. Materials and instrumentation

All chemicals used in this study were of the purest grade and used without further purification. Benzyl bromide [purity 98%], propagyl bromide [80%wt solution in toluene stabilized], phenylacetylene [purity 98%] and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were obtained from Acros. Sodium azide and sodium ascorbate [ASSay 99%] were obtained from Universal fine chemicals. Dichloromethane [purity 99%], diethyl ether, absolute ethyl alcohol [purity 98%] and acetone [purity 98%] were obtained from Sd fine chemical limited. Acetonitrile HPLC gradient grade was obtained from Fisher chemical. Thin-layer Chromatography [TLC] was carried out by using plastic sheets pre-coated with silica gel 60 F₂₅₄ [Merck] and was visualized under 254 nm UV-light. Elemental analyses were performed on a Perkin-Elmer 2400 automatic elemental analyzer. The metal analysis was carried out by dissolving the substance by digestion the sample in $\text{H}_2\text{SO}_4/\text{HNO}_3$. The oxidation of organic groups by HNO_3 was completed when NO--fumes no more appeared then the metals were measured by Perkin-Elmer 5000 atomic absorption spectrophotometer. Infrared spectra were recorded on a Bruker vector 22 spectrophotometer applying KBr discs in the range of 4000–400 cm^{-1} . Electronic absorption spectra in the visible and ultraviolet regions were measured on a Shimadzu 3101 PC spectrophotometer as a Nujol mull matrix. The magnetic susceptibility was determined with a Magnetic susceptibility balance 436 Devon Park Drive (USA) using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. Molar conductivities measurements were carried out in DMSO using Sybron-Barnstead conduct meter (Meter-PM.6, E= 3406). The thermogravimetric analysis (TGA) was performed on Shimadzu AT-50 thermal analyzer in nitrogen atmosphere with heating rate 10 $^{\circ}\text{C}/\text{min}$.

2.2 Syntheses

2.2.1 Synthesis of Schiff base ligand (*N,N'*- bis [2-hydroxy-1-naphthyl methylidene] -1,2-diaminoethane); H_2L

A hot solution (60°C) of ethylenediamine [10 mmol, 0.67 mL] was mixed with a hot solution (60°C) of 2-hydroxy naphthaline -1-carbaldehyde [20 mmol, 3.44 gm.] in 50 mL of ethanol. The resulting Mixture was left under reflux for 2h and the solid yellow product formed was separated by filtration and washed by diethyl ether and ethanol.

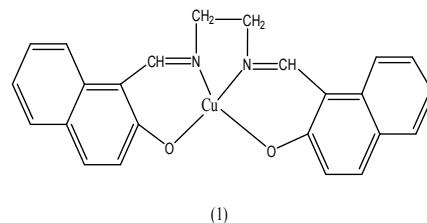


Scheme 1 *N,N'*- bis [2-hydroxy-1-naphthyl methylidene] -1,2-diaminoethane

2.2.2 Synthesis of Copper (II), **1**, and Silver (I), **2**, Schiff base complexes

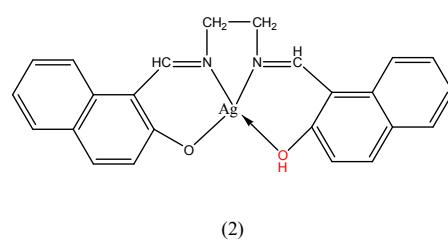
The complexes were prepared by the addition of a hot aqueous solution (60°C) of the cupric chloride [2

mmol, 0.19 gm.] or silver nitrate [2 mmol, 0.18 gm.] in an ethanol-water mixture [1:1, 25 mL] to the hot solution of the Schiff base ligand [1 mmol, 0.2 gm.] in the same solvent [1:1, 25 mL]. The resulting mixture was stirred under reflux for 1h until the complex



precipitated. The complexes CuL and AgHL were

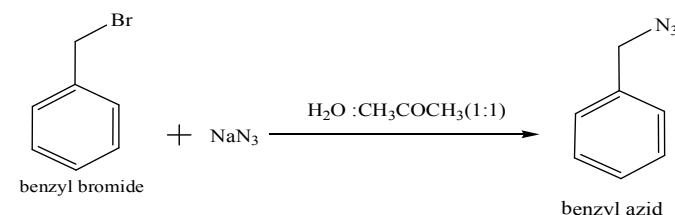
collected by filtration and washed with [1:1] ethanol-water.



Scheme 2 copper (1) and silver (2) - Schiff base complexes

2.2.3 Synthesis of benzyl azide

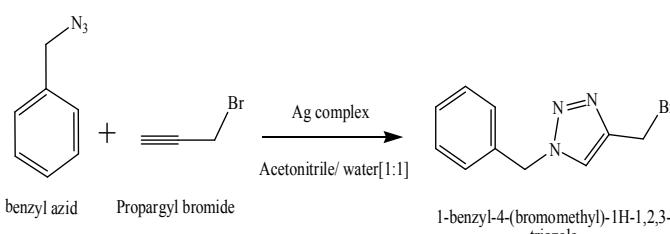
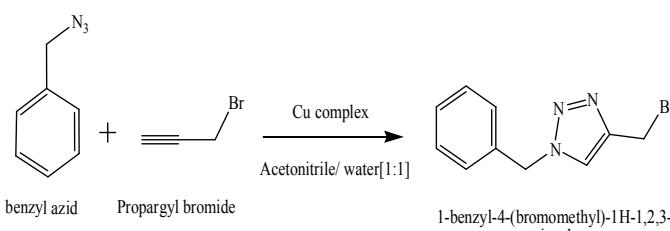
Sodium azide (1.4 gm., 2.5 equiv.) and Benzyl bromide (1mL, 1.5 equiv.) are dissolved in mixture of acetone and water (1:1, 20 mL) by stirring in 100 mL round-bottom flask under close system over night at room temperature, then leaving the mixture to evaporate acetone. The benzyl azide was extracted with water (1×10 mL) and diethyl ether (2×10 mL).



2.2.4 Synthesis of 1-benzyl- 4-bromo triazole

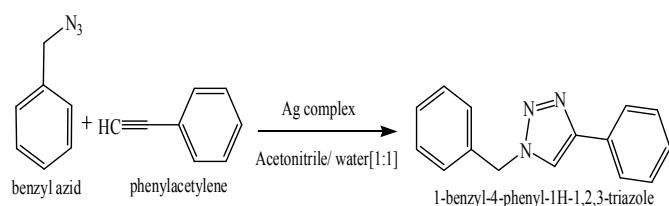
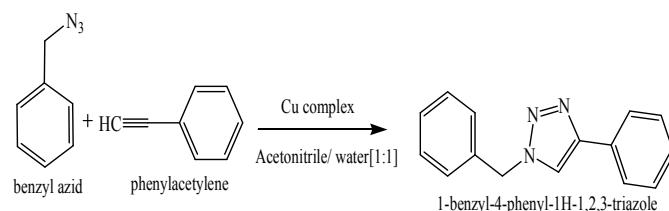
Propagyl bromide (1 equiv. 0.09 gm.) and (2 equiv. 0.19 gm.), benzyl azide ((1 equiv. 0.12 mL) and (2 equiv. 0.25 mL) and the catalyst (0.025, 0.05, 0.1, 0.15 equiv.) were mixed in presence of acetonitrile and water mixture (1:1, 20

mL). The mixture was stirred at room temperature or with gentle heating to deliver exclusively the corresponding 1, 4 - triazole



2.2.5 Synthesis of 1-benzyl-4-phenyl triazole

Phenyl acetylene (1 equiv. 0.1 mL) and (2 equiv. 0.22 mL), benzyl azide (1 equiv. 0.12 mL) and (2 equiv. 0.25 mL) and catalyst (0.025 ,0.05 ,0.1 ,0.15 equiv.) in presence of acetonitrile and water mixture (1:1, 20 mL) and stirring the mixture at room temperature or with gentle heating to deliver exclusively the corresponding 1,4-triazole .



3 Results and Discussion

3.1 Characterization of Schiff base ligand and the complexes 1 and 2

The level of the purity of H_2L has been checked by running TLC on a silica gel coated plate using $EtOAc-EtOH$ (6:4, v/v) as the eluent. The elemental analysis data of the H_2L ligand and its copper and silver complexes agree well with the proposed compositions, Table 1. The isolated complexes are insoluble in common organic solvents but easily soluble in a mixture of acetonitrile- water mixture and DMF or DMSO. The molar conductance values of the complexes 1 and 2 fall in the range $6.7-8.3\ \Omega^{-1}\ mol^{-1}\ cm^2$ indicating that the two complexes are non-electrolytes, Table 1. The structure of the prepared Schiff-base ligand and its complexes 1 and 2 have been confirmed on the basis of analytical data, IR, electronic absorption spectra,

molecular modeling study , melting point , mass spectroscopy, thermal analysis and 1H - NMR. The Ag-complex 2 is diamagnetic while the magnetic moment value of Cu (II)- complex 1 is 1.71 BM. This value is quite close the spin-only value of 1.73 BM for Cu (II) [30]. This indicates the presence of single unpaired electron suggesting the square planer structure for the complex 1.

3.2 Infrared spectra of Schiff base (H_2L) and its metal complexes 1 and 2

The IR- spectra of the complexes 1 and 2 are compared with that of the free ligand H_2L in order to determine the coordination sites that may involve in chelation, Table 2 and Fig. 1. The band due to ν_{OH} (phenolic) appears at $3427\ cm^{-1}$ in the spectrum of H_2L which suffers shift to lower wavenumber; $3408\ cm^{-1}$, supporting participation of oxygen atom of one hydroxyl group in the coordination sphere of the silver atom. On the other hand, this band disappears in the spectrum of the complex 1 indicating the covalent nature of the bond between the oxygen atoms and copper. The band due to $\nu_{C=N}$ of H_2L at $1641\ cm^{-1}$ is shifted to lower wavenumbers (1623 and $1637\ cm^{-1}$) in the spectra of complexes 1 and 2, respectively, indicating the participation of the azomethane nitrogen in coordination. New bands are found in the spectra of the complexes in the regions 505 and $518\ cm^{-1}$, which are assigned to M-O stretching vibrations. The band at 477 and $441\ cm^{-1}$ for 1 and 2, respectively, has been assigned to M-N stretching vibrations indicating the participation of the azomethane nitrogen and oxygen atoms in the coordination sphere. Therefore, from the IR spectra, it is concluded that H_2L ligand behaves in different manners, according to nature and valence of the metal, as a mono- or bi-negative tetradentate ligand via the phenolic and the azomethane groups.

3.3 The electronic absorption spectra of H_2L and its metal complexes 1 and 2

The UV-Vis absorption spectra of the maximum absorption wavelengths (λ_{max}) for H_2L and its complexes are listed in Table 3 and Fig. 2. The absorption spectrum of H_2L is characterized by five absorption bands while the spectra of 1 and 2 display four bands in the region of 200-450 nm. The first three bands resemble those observed in the spectra of naphthalene at 221, 286 and 312 nm [31]. Thus, the high intensity band at 212-225 nm can be attributed to ${}^1B_b \leftarrow {}^1A$ transitions within the naphthyl moiety. The second and the third bands at 252-265 nm and 310-315 nm can be assigned to the ${}^1L_a \leftarrow {}^1A$ and ${}^1L_b \leftarrow {}^1A$ transitions within the naphthyl moiety, respectively. The fourth band in the spectrum of H_2L at 355 nm can be assigned to $n-\pi^*$ transitions of the azomethane group which disappears in the spectra of 1 and 2 indicating participation of the azomethane group in coordination sphere of Cu and Ag atoms. The broad low energy band at 385-425 nm can be assigned to the charge transfer interaction involving the whole molecule. This band suffers blue shift due to participation of the nitrogen and oxygen atoms in complex formation.

3.4 NMR-spectra of H_2L and its metal complexes 1 and 2

The ^1H NMR spectra of the Schiff base ligand, H_2L and the complexes **1** and **2** are shown in [Table 4](#) and [Fig. 3](#). The ^1H -NMR spectrum of H_2L shows sharp singlet at 9.175 ppm, corresponding to the hydroxyl protons which disappears on deuteration. The multi signals within the range of 7.20–7.39 ppm are assigned to the aromatic protons of naphthyl rings. Also, the spectrum displays a sharp signal at 3.269 ppm corresponding to CH_2 protons of the ethylene diamine bridge. In addition, the doublet at 8.029–8.054 ppm can be attributed to absorbance of the protons of the azomethane groups. The ^1H -NMR spectrum of the Cu(II)-complex, **1** was compared with that of the parent Schiff base, [Fig. 3](#). The multiple signals of the naphthyl and azomethane protons appear as broad signals at 7.57–7.87 and 8.52 ppm, respectively suggesting participation of the azomethane nitrogen in coordination with Cu(II). The disappearance of the OH signal at 9.175 ppm, in the spectrum of H_2L confirms involvement of the two anionic oxygen atoms in the coordination sphere of Cu(II) atom. The signal of the CH_2 protons appears at 3.31 ppm. On the other hand, the ^1H -NMR spectrum of **2** displays the same signals of H_2L . The presence of the OH signal at 9.152 ppm indicates that only one OH group is ionized. The NMR-spectra support the formation of N_2O_2 coordination sphere around the Cu(II) and Ag(I) atoms.

3.5 Thermal analyses of H_2L and the metal complexes **1** and **2**

The thermal analysis of H_2L ligand takes place in three steps [Table 5](#) and [Fig. 4](#). The first step occurs from 121 to 306 °C and corresponds to the release of the one OH group [Obs. 17 g mol⁻¹; Calcd 17 g mol⁻¹]. This step is followed by the release of the $[\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}]$ fragment from 306 to 393 °C [Obs. 225.216 g mol⁻¹; Calcd . 225 g mol⁻¹]. The third step from 393 to 999 °C corresponds to the release of $[\text{C}_{10}\text{H}_6]$ group [Obs. 125.85 g mol⁻¹ ; Calcd 126 g mol⁻¹]. Thus, H_2L ligand is stable up to 121 °C . The complex **1** is stable up to 211 °C after which it starts decomposition via five stages of weight loss, [Fig. 5](#). In this case, thermolysis starts by loss of the one oxygen atom from 211 to 342 °C [Obs. 16.3 g mol⁻¹; Calcd 16 g mol⁻¹]. This step is followed by removal of $[\text{C}_{10}\text{H}_6\text{O}]$. The two steps are followed by the release of $[\text{C}_2\text{H}_3\text{N}]$ fragment at 380–536 °C and 536–740 °C [Obs. 41.2 g mol⁻¹ ; Calcd 41 g mol⁻¹]. The last step corresponds to the release of the $[\text{C}_{10}\text{H}_6]$ fragment from 740 to 1000 °C [Obs. 126.2 g mol⁻¹; Calcd 126 g mol⁻¹]. The residue obtained in this case is coincident with copper. The decomposition of complex **2** takes place in four steps, [Fig. 6](#). In this case, thermolysis starts by loss of the $[\text{C}_3\text{H}_5\text{N}]$ fragment from 129 to 319 °C [Obs. 54.69 g mol⁻¹; Calcd 55 g mol⁻¹]. This step is followed by release of the $[\text{C}_{20}\text{H}_{13}\text{O}]$ fragment from 319 to 411°C [Obs. 269.04 g mol⁻¹; Calcd 269 g mol⁻¹]. Third step from 411 to 717 °C corresponds to the release of [CHN] group [Obs. 27.04 g mol⁻¹; Calcd 27 g mol⁻¹]. The last step is the release of one oxygen atom from 717 to 999 °C [Obs. 16.1 g mol⁻¹; Calcd 16 g mol⁻¹]. The residue obtained in this case is coincident with silver. Thus, complex **2** is stable up to 129 °C.

3.6 Molecular modeling

We performed cluster calculations using DMOL[®] program [32] in Materials Studio package [33], which is designed for the realization of large scale density functional theory (DFT) calculations. DFT semi-core pseudopods calculations (dspp) were performed with the double numerica basis sets plus polarization functional (DNP). The DNP basis sets are of comparable quality to 6-31G Gaussian ba-sis sets [34]. Delley et al. showed that the DNP basis sets are more accurate than Gaussian basis sets of the same size [33]. The RPBE functional [35] is so far the best exchange–correlation functional [36] based on the generalized gradient approximation (GGA) which is employed to take account of the exchange and correlation effects of electrons. The geometric optimization is performed without any symmetry restriction. The geometric optimization is performed without any symmetry restriction. The molecular structure along with atom numbering and HOMO–LUMO representation of the complexes **1** and **2** are shown in [Figs. 7 and 8](#). The Cu atoms acquire slightly distorted square plane geometry where Cu29 atom coordinates to two nitrogen and two oxygen atoms (N_2O_2) forming two six and one five member rings. The bond lengths and bond angles are in the normal range reported for the proto-type compounds. The photo-induced charge redistribution over the whole molecular skeleton of the complexes **1** and **2** is well represented by plot of the Frontier molecular orbitals (HOMO and LUMO) as illustrated in [Figs. 7 and 8 \(b,c\)](#). E_{HOMO} is a quantum chemical descriptor which is often associated with the electron donating ability of the molecule. High value of E_{HOMO} indicates a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy. However, E_{LUMO} indicates the ability of the molecule to accept electrons. The HOMO electronic density distribution for the complex **1** can be represented as localization of charge density on the (N_2O_2 -Cu) center, en fragment and C1, C2, C6, C14, C16 and C24 of the naphthyl moiety. In the case of LUMO level, the charge is mostly localized that can facilitate the donation from the ligand to Cu29 atom. Quantum chemical parameters for **1** (E_{HOMO} , E_{LUMO} and the energy gap, $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) are found to be -4.794, -3.263 and 1.531 e.v. respectively.

3.7 Click reaction

We reported here a homogeneous, well defined copper (II) complex **1** which is used as catalyst in click reaction. We prepared the 1- benzyl - 4 – [bromomethyl] – 1H - 1,2,3-triazole by adding the mixture of propargyl bromide [Alkyne], benzyl azide [Azide] and copper (II) complex [catalyst] in presence the sodium ascorbate to reduce the Cu (II) to Cu (I) in solvent acetonitrile and water at room temperature. Full conversion in yield [100%] of azide /alkyne [2:1] to triazole required the use of [0.1 equivalent] of catalyst complex **1** within 1h at room temperature [[Table 6; entry 3](#)]. Above reaction was occurred in the best condition because the triazole was formed in a short time and high yield. To check the efficiency of the catalyst **1** , this reaction was repeated two times on the initial catalyst by using identical quantities of azide / alkyne to provide [100% yield] conversion within 2h and 2:30h [[Table 6; entries](#)

5,6]. Using 0.1 equivalent of catalyst complex 1 under otherwise conditions of [Table 6; entry 3] at 40°C and 60°C . We observed that by increasing the temperature allowed conversion of azide / alkyne to triazole after 50min and 20min [Table 6; entries 7, 8]. On the other hand, Using 0.1 equivalent of in case of silver (I) complex 2 as catalyst under the same conditions of the copper complex catalyst. It was observed that the silver catalyst 2 is the most efficient than the copper catalyst 1 [Table 7; entry 3] because the triazole was formed after 30min at room temperature. But when we were comparing these results with results of copper (II) acetate and silver nitrate , we observed that the triazole was formed after 4:15h and 25:30h [Table 8; compound 1,2] So , the copper and silver complexes 1 and 2 catalysis were more efficient catalysts than copper acetate and silver nitrate catalysis .On the other hand, when we used phenyl acetylene as alkyne instead of the propargyl bromide with benzyl azide and the complex 1 and 2 as a catalysts in the solvent of the acetonitrile and water [1:1] at room temperature to prepare 1-benzyl -4-phenyl -1H-1,2,3-triazole. Full conversion in yield [100%] of azide/alkyne [2:1] to triazole required 0.1 equivalent of catalyst complex 1 in presence of sodium ascorbate to reduce of Cu(II) to Cu(I) within 2:15h at room temperature [Table 9; entry 3] . Above reaction was occurred in the best conditions because the triazole was formed in the short time and high yield. To check efficiency of the catalyst complex 1 , This reaction was repeated two times on the initial catalyst using the same quantities of azide/ alkyne to provide 100% conversion within 1:30h and 61min [Table 9 ; entries 5, 6] . Using 0.1equivalent of catalyst complex1 under other conditions of [Table 9; entry 3] at 40°C and 60°C. We observed that by increasing the temperature allowed conversion of azide/alkyne to triazole after 25min and 15min [Table 9; entries 7, 8]. On the other hand.using 0.1 equivalent of in case of silver (I) complex 2 as catalyst under the same conditions of the copper catalyst. It was observed that the silver catalyst 2 is the most efficient than the copper catalyst 1 [Table 10; entry 3] because the triazole was formed after 30min at room temperature. But when we were comparing these results of copper (II) acetate and silver nitrate , we observed that the triazole was formed after 3:30h and 30h [Table 11 ; compound 1 , 2] so, the copper and silver complexes 1 and 2 catalysts are more efficient catalysts than the copper acetate and silver nitrate catalysts.

References

- [1] N.V. Tverdova, E.D. Pelevina, N.I. Giricheva, G.V. Girichev, N.P. Kuzmina, O.V. Kotova, J. Mol. Struct. 1012 (2012) 151–161.
- [2] K.Y. Lau, A. Mayr, K.K. Cheung, Inorg. Chim. Acta 285 (1999) 223.
- [3] A.D. Garnovskii, I.S. Vasil Chenko, Russ. Chem. Rev. 71 (2002) 943–996
- [4] C. Anitha, C. D. Sheela, P. Tharmaraj, S. Sumathi, Spectrochim. Acta, Part A 96 (2012) 493–500
- [5] A. M. A. Alaghaz, B. A. El-Sayed, A. A. El-Henawy, R. A. A. Ammar, Mol. Struct. 1035 (2013) 83–93
- [7] M. B. Halli, R. B. Sumathi, M. Kinni, Spectrochim. Acta, Part A 99 (2012) 46–56
- [8] A. Chakraborty, P. Kumar, K. Ghosh, P. Roy, Eur. J. Pharmacol. 647 (2010) 1–12
- [9] M. S. Alam, J. H. Choi, D. U. Lee, Med. Chem. 20 (2012) 4103–4108
- [10] C. A. Wegermann, P. Strapasson, S. M. M. Romanowski, A. Bortoluzzi, R. R. Ribeiro, F. S. Nunesa, S. M. Drechsel. App. Catalysis A: General 454 (2013) 11–20
- [11] A. M. A. Ibrahim, S. M. A. Al-Ashqar, Spectrochim. Acta, Part A 92 (2012) 238–244
- [12] B. Tamami, S. Ghasemi. Appl. Catalysis A: General 393 (2011) 242–250
- [13] P. M. Forster, A. K. Cheetham, Angew. Chem. Int. Ed Engl. 41 (2002) 457–459
- [14] P. Ayyappan, O. R. Evans, W. Lin, Inorg. Chem. 40 (2001) 4627–4632
- [15] S. S. Massoud, F. A. Mautner, R. Vicente, H. N. Sweeney, Inorg. Chim. Acta 359 (2006) 1489–1499
- [16] F. A. Mautner, R. Vicente, F. R. Y. Louka, S. S. Massoud, Inorg. Chim. Acta 361(2008) 1339–1384
- [17] S. S. Massoud, K. T. Broussard, F. A. Mautner, R. Vicente, M. K. Saha, I. Bernal, Inorg. Chim. Acta 361(2008) 123–131.
- [18] L. Jiang, X. L. Feng, T. B. Lu, Cryst. Growth Des 5(2005) 1469–1475.
- [19](a) Catalano, V. J.; Kar, H. M.; Garnas, J. *Angew. Chem., Int. Ed.* 1999, 38, 1979–1982. (b) Zhang, G. q.; Yang, G. q.; Yang, L. y.; Chen, Q. q.; Ma, J. S. *Eur. J. Inorg. Chem.* 2005, 1919–1926. (c) Huang, X. C.; Zheng, S. L.; Zhang, J. P.; Chen, X. M. *Eur. J. Inorg. Chem.* 2004, 5, 1024–1029. (d) Ren, C. X.; Ye, B. H.; He, F.; Cheng, L.; Chen, X. M. *CrystEngCommun* 2004, 6, 200–206.
- [20] (a) Dong, Y.-B.; Cheng, J.-Y.; Ma, J.-P.; Huang, R.-Q.; Smith, M. D. *Cryst. Growth Des.* 2005, 5, 585–591. (b) Catalano, V. J.; Malwitz, M. A. *Inorg. Chem.* 2003, 42, 5483–5485. (c) Kang, Y.; Seward, C.; Song, D.; Wang, S. *Inorg. Chem.* 2003, 42, 2789–2797. (d) Ouyang, X. M.; Liu, D. J.; Okamura, T. a.; Bu, H. W.; Sun, W. Y.; Tang, W. X.; Ueyama, N. *Dalton Trans.* 2003, 1836–1845. (e) Yam, V. W. W.; Lo, W. Y.; Zhu, N. *Chem. Commun.* 2003, 2446–2447.
- [21] (a) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Ning, G. L.; Kojima, T. *J. Am. Chem. Soc.* 1998, 120, 8610–8618. (b) Schmidbaur, H.; Bublak, W.; Huber, B.; Reber, G.; Muller, G. *Angew. Chem., Int. Ed. Engl.* 1986, 25, 1089–1090. (c) Che, C. M.; Yip, H. K.; Li, D.; Peng, S. M.; Lee, G. H.; Wang, Y. M.; Liu, S. T. *J. Chem. Soc., Chem. Commun.* 1991, 1615–1617. (d) Wu, C. D.; Ngo, H. L.; Lin, W. *Chem. Commun.* 2004, 1588–1589.
- [22] (a) Liu, M.; Xu, G.; Liu, Y.; Chen, Q. *Langmuir* 2001, 17, 427–431. (b) Chen-jie, F.; Chun-ying, D.; Hong, M.; Cheng, H.; Qing-jin, M.; Yong-jiang, L.; Yu-

- hua, M.; Zhe-ming, W. *Organometallics* 2001, 20, 2525-2532. (c) Patra, G. K.; Goldberg, I. *Cryst. Growth Des.* 2003, 3, 321-329. (d) Hou, H.; Li, G.; Song, Y.; Fan, Y.; Zhu, Y.; Zhu, L. *Eur. J. Inorg. Chem.* 2003, 2325-2332. (e) Dong, Y. B.; Zhao, X.; Huang, R. Q.; Smith, M. D.; zur Loye, H. C. *Inorg. Chem.* 2004, 43, 5603-5612. (f) Dong, Y. B.; Zhao, X.; Tang, B.; Wang, H. Y.; Huang, R. Q.; Smith, M. D.; zur Loye, H. C. *Chem. Commun.* 2004, 220-221.
- [23] Rusere, L.N., Shalumova, T., Tanski, J.M., et al., *Polyhedron*, 2009, vol. 28, p. 3804.
- [24] Pang, Y., Cui, S., Li, B., et al., *Inorg. Chem.*, 2008, vol. 47, p. 10317.
- [25] Giricheva, N.I., Giricheva, G.V., Kuzmina, N.P., et al., *J. Struct. Chem.*, 2009, vol. 50, p. 52.
- 44, 686-698; e) K. A. Winans, C. R. Bertozzi, *Chem. Biol.* 1998, 5, R313-R315; f) K. J. Yarema, L. K. Mahal, R. E. Bruehl, E. C. Rodriguez, C. R. Bertozzi, *J. Biol. Chem.* 1998, 273, 31168-31179; g) E. Saxon, C. R. Bertozzi, *Science* 2000, 287, 2007-2010; h) Q. Wang, T. R. Chan, R. Hilgraf, V. V. Fokin, K. B. Sharpless, M. G. Finn, *J. Am. Chem. Soc.* 2003, 125, 3192-3193; i) R. Breinbauer, M. Kohn, *ChemBioChem* 2003, 4, 1147-1149; j) V. D. Bock, H. Hiemstra, J. H. Van Maarseveen, *Eur. J. Org. Chem.* 2006, 51-68; k) A. Wang, N. W. Bairn, R. S. Johnson, D. A. Tirrell, K. Grabstein, *ChemBioChem* 2008, 9, 324-330; l) F. Amblard, J. H. Cho, R. F. Schinazi, *Chem. Rev.* 2009, 109, 4207-4220; m) T. Fekner, X. Li, M. M. Lee, M. K. Chan, *Angew. Chem.* 2009, 121, 1661; *Angew. Chem. Int. Ed.* 2009, 48, 1633-1635.
- [30] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, sixth ed., Wiley, New York, 1999.
- [26] Mouni, L., Akkurt, M., Yildirm, S.O., et al., *J. Chem. Crystallogr.*, 2010, vol. 40, p. 169.
- [27] Huisgen, R. 1,3-dipolare Cycloadditionen - ruckschau und ausblick. *Angew. Chem. Int. Edit.* 1963, 75, 604-637.
- [28] Tornoe, C.W.; Christensen, C.; Meldal, M. Peptidotriazoles on solid phase: 1,2,3-triazoles by regiospecific copper(I)-catalyzed 1,3-dipolar cycloadditions of terminal alkynes to azides. *J. Org. Chem.* 2002, 67, 3057-3064.
- [29] For selective publications, see: a) *Chem. Asian J.* 2011, 6, 2568-2847 (thematic review issue); b) X. Li, *Chem. Asian J.* 2011, 6, 2606-2616; c) E. M. Sletten, C. R. Bertozzi, *Acc. Chem. Res.* 2011, 44, 666-676; d) M. D. Best, M. M. Rowland, H. E. Bostic, *Acc. Chem. Res.* 2011,
- [31] H.H. Jaffe, M. Orchin, Theory and Applications of Ultraviolet Spectroscopy, 5th edn. (Wiley, New York, 1970).
- [32] (i) B. Delley, *J. Chem. Phys.* 92 (1990) 508-517; (ii) B. Delley, *Int. J. Quantum Chem.* 69 (1998) 423-433; (iii) B. Delley, *J. Chem. Phys.* 113 (2000) 7756-7764; (iv) X. Wu ana, A.K. Ray, *Phys. Rev. B* 65 (2002) 85403-85409; (v) A. Kessi, B. Delley, *Int. J. Quantum Chem.* 68 (1998) 135-144.
- [33] Materials Studio v 5.0 Copyright (2009). Accelrys Software Inc.
- [34] W.J. Hehre, L. Radom, P.V.R. Schleyer, J.A. Pople, *Initio Molecular Orbital Theory*, John Wiley, New York, (1986).
- [35] B. Hammer, L.B. Hansen, J.K. Nørskov, *Phys. Rev. B* 59 (1999) 7413-7421.
- [36] A. Matveev, M. Staufer, M. Mayer, N. Rösch, *Int. J. Quantum Chem.* 75 (1999) 863-873.

Table 1 Analytical and physical data for the Schiff base H₂L and its complexes

| Compound | Empirical formula | Color | Melting point (°C) | Elemental Analysis Found [Calc.] % | | | | Am ohm ⁻¹ mol ⁻¹ Cm ² |
|------------------|--|-----------------|--------------------|------------------------------------|---------------|----------------|------------------|--|
| | | | | %C | %H | %N | %M | |
| H ₂ L | C ₂₄ H ₂₀ N ₂ O ₂ | Yellow | 215 - 217 | 77.9 [78.13] | 4.2 [4.19] | 6.8 [7.73] | ----- | ----- |
| 1 | C ₂₄ H ₁₈ N ₂ O ₂ Cu | Deep green | 325 - 327 | 67.25 [67.05] | 4.0 [4.19] | 6.4 [6.51] | 14.60 [14.78] | 8.3 |
| 2 | C ₂₄ H ₁₉ N ₂ O ₂ Ag | Greenish yellow | 300 - 302 | 60.39 [60.44] | 3.9 [3.98] | 5.60 [5.87] | 22.87 [22.98] | 6.7 |

Table 2 Characteristic IR vibrations (cm⁻¹) of H₂L ligand and the complexes, 1 and 2

| Compound | v O-H | v C-H Aryl | v C-H Alkyl | v C=C | v C-N | v C-O | v C=N | v M←O | v M←N |
|------------------|-------|------------|-------------|-----------|-------|-------|-------|-------|-------|
| H ₂ L | 3427 | 3044 | 2939 | 1539-1494 | 1359 | 1259 | 1641 | - | - |
| 1 | - | 3047 | 2935 | 1538-1509 | 1350 | 1254 | 1623 | 518 | 477 |
| 2 | 3408 | 3041 | 2937 | 1539-1493 | 1357 | 1210 | 1637 | 505 | 441 |

Table 3 Electronic absorption spectra of H₂L and the complexes 1 and 2

| compound | $\lambda_{\text{abs}}(\text{nm})$ | Assignment |
|------------------|-----------------------------------|--|
| H ₂ L | 212 | ¹ B _b ← ¹ A |
| | 265 | ¹ L _a ← ¹ A |
| | 310 | ¹ L _b ← ¹ A |
| | 355 | n-π* |
| | 425 | C T |
| 1 | 220 | ¹ B _b ← ¹ A |
| | 255 | ¹ L _a ← ¹ A |
| | 315 | ¹ L _b ← ¹ A |
| | ----- | n-π* |
| | 420 | C T |
| 2 | 225 | ¹ B _b ← ¹ A |
| | 252 | ¹ L _a ← ¹ A |
| | 310 | ¹ L _b ← ¹ A |
| | ----- | n-π* |
| | 385 | C T |

Table 4 ¹H NMR spectral data of H₂L ligand and its complexes 1 and 2

| Compound | TGA range (°C) | Mass loss | | Assignment | Residue |
|------------------|-------------------|--------------|--------------|---|---------|
| | | Calc. (%) | Found (%) | | |
| H ₂ L | 121 - 306 | 17 | 17 | OH C ₁₄ H ₁₃ N ₂ O C ₁₀ H ₆ | ----- |
| | 306 - 393 | 225 | 225.216 | | |
| | 393 - 999 | 126 | 125.85 | | |
| 1 | 211 - 342 | 16 | 16.3 | O C ₁₀ H ₆ O C ₂ H ₃ N C ₂ H ₃ N C ₁₀ H ₆ | Cu |
| | 342 - 380 | 142 | 142.1 | | |
| | 380 - 536 | 41 | 41.2 | | |
| | 536 - 740 | 41 | 41.2 | | |
| | 740 - 1000 | 126 | 126.2 | | |
| 2 | 129 - 319 | 55 | 54.69 | C ₃ H ₅ N C ₂₀ H ₁₃ O CHN O | Ag |
| | 319 - 411 | 269 | 269.04 | | |
| | 411 - 717 | 27 | 27.04 | | |
| | 717 - 999 | 16 | 16.1 | | |

Table 5 Thermogravimetric analysis (TGA) of H₂L and its metal complexes

| Compound | δ (CH-aliphatic) | δ (CH-Ar) | δ (CH ₂) | δ (OH) |
|------------------|-------------------------|------------------|-----------------------------|---------------|
| H ₂ L | 8.029 – 8.054 | 7.2 – 7.739 | 3.269 | 9.157 |
| 1 | 8.523 | 7.574 – 7.873 | 3.310 | ----- |
| 2 | 8.02 – 8.052 | 7.173 – 7.739 | 3.301 | 9.152 |

Table 6 Optimization with Copper catalysis in the click reaction [benzyl azide\ propagyl bromide]

| Entry | Cat (eq.) | Temp (°C) | Azide | Alkyne | Time | Yield (%) |
|-------|-----------|-----------|-------|--------|-------|-----------|
| 1 | 0.025 | r.t | 2 | 1 | 3:30h | 100% |
| 2 | 0.05 | r.t | 2 | 1 | 4:15h | 100% |
| 3 | 0.1 | r.t | 2 | 1 | 1h | 100% |
| 4 | 0.15 | r.t | 2 | 1 | 2:30h | 100% |
| 5 | 0.1 | r.t | 2.5 | 1.25 | 2h | 100% |
| 6 | 0.1 | r.t | 3 | 1.5 | 2:30h | 100% |
| 7 | 0.1 | 40 | 2 | 1 | 50min | 100% |
| 8 | 0.1 | 60 | 2 | 1 | 20min | 100% |
| 9 | 0.1 | r.t | 1 | 1 | 1:30h | 100% |
| 10 | 0.1 | r.t | 1 | 2 | 1:14h | 100% |

Table 7 Optimization with silver catalysis in the click reaction [benzyl azide \ propagyl bromide]

| Entry | Cat (eq) | Temp (°C) | Azide | Alkyne | Time | Yield |
|-------|----------|------------|-------|--------|-------|-------|
| 1 | 0.025 | r.t | 2 | 1 | 2h | 100% |
| 2 | 0.05 | r.t | 2 | 1 | 2:22h | 100% |
| 3 | 0.1 | r.t | 2 | 1 | 30min | 100% |
| 4 | 0.15 | r.t | 2 | 1 | 2h | 100% |
| 5 | 0.1 | r.t | 2.5 | 1.25 | 40min | 100% |
| 6 | 0.1 | r.t | 3 | 1.5 | 1h | 100% |
| 7 | 0.1 | 40 | 2 | 1 | 27min | 100% |
| 8 | 0.1 | 60 | 2 | 1 | 20min | 100% |
| 9 | 0.1 | r.t | 1 | 1 | 45min | 100% |
| 10 | 0.1 | r.t | 1 | 2 | 2:30h | 100% |

Table 8 Using Copper Acetate(1) and silver nitrate (2) as catalyst with benzyl azide and propagyl bromide

| Compound | Cat (eq) | Azide | Alkyne | Time | yield |
|----------|----------|-------|--------|---------|-------|
| 1 | 0.1 | 2 | 1 | 4:15 h | 100% |
| 2 | 0.1 | 2 | 1 | 25:30 h | 100% |

Table 9 Optimization with Copper catalyst 1 in the click reaction [benzyl azide\phenyl acetylene]

| Entry | Cat (eq) | Temp (°C) | Azide | Alkyne | Time | Yield |
|-------|----------|-----------|-------|--------|-------|-------|
| 1 | 0.025 | r.t | 2 | 1 | 2:13h | 100% |
| 2 | 0.05 | r.t | 2 | 1 | 1:20h | 100% |
| 3 | 0.1 | r.t | 2 | 1 | 30min | 100% |
| 4 | 0.15 | r.t | 2 | 1 | 1h | 100% |
| 5 | 0.1 | r.t | 2.5 | 1.25 | 1h | 100% |
| 6 | 0.1 | r.t | 3 | 1.5 | 1:15h | 100% |
| 7 | 0.1 | 40 | 2 | 1 | 27min | 100% |
| 8 | 0.1 | 60 | 2 | 1 | 20min | 100% |
| 9 | 0.1 | r.t | 1 | 1 | 3:14h | 100% |
| 10 | 0.1 | r.t | 1 | 2 | 62min | 100% |

Table 10 Optimization with silver catalyst 2 in the click reaction [benzyl azide\phenyl acetylene]

| Compound | Cat(eq) | Azide | Alkyne | Time | Yield |
|----------|---------|-------|--------|--------|-------|
| 1 | 0.1 | 2 | 1 | 3:30 h | 100% |
| 2 | 0.1 | 2 | 1 | 30 h | 100% |

Table 11 Using copper acetate (1) and silver nitrate (2) as catalyst with benzyl azide and phenyl acetylene

| Entry | Cat (eq) | Temp (°C) | Azide | Alkyne | Time | Yield |
|-------|----------|-----------|-------|--------|-------|-------|
| 1 | 0.025 | r.t | 2 | 1 | 2:30h | 100% |
| 2 | 0.05 | .t | 2 | 1 | 4h | 100% |
| 3 | 0.1 | r.t | 2 | 1 | 2:15h | 100% |
| 4 | 0.15 | r.t | 2 | 1 | 3:30h | 100% |
| 5 | 0.1 | r.t | 2.5 | 1.25 | 1:30h | 100% |
| 6 | 0.1 | r.t | 3 | 1.5 | 61min | 100% |
| 7 | 0.1 | 40 | 2 | 1 | 25min | 100% |
| 8 | 0.1 | 60 | 2 | 1 | 15min | 100% |
| 9 | 0.1 | r.t | 1 | 1 | 2:40h | 100% |
| 10 | 0.1 | r.t | 1 | 2 | 2:35h | 100% |

Figures

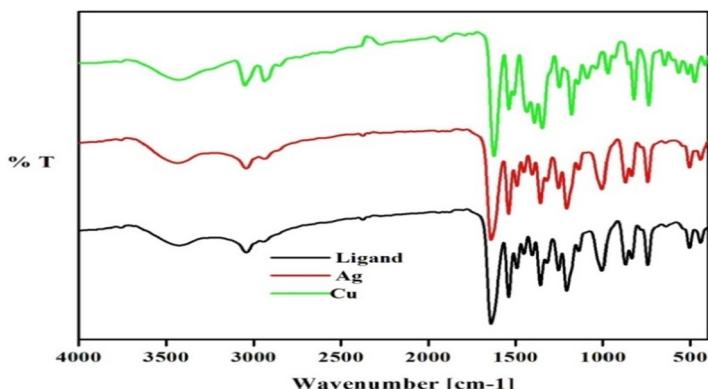
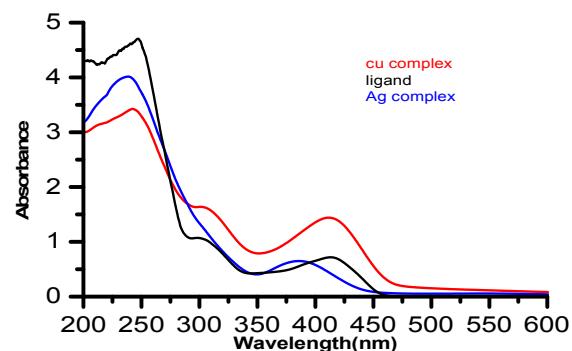
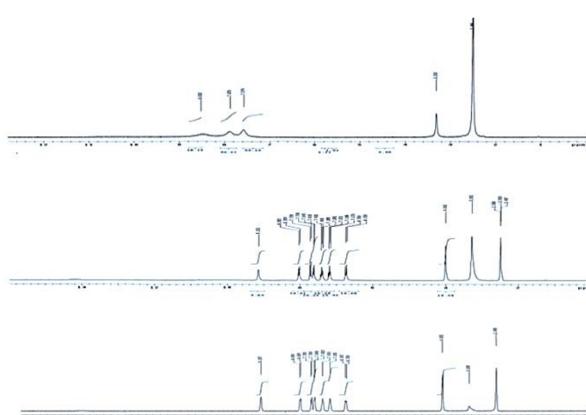
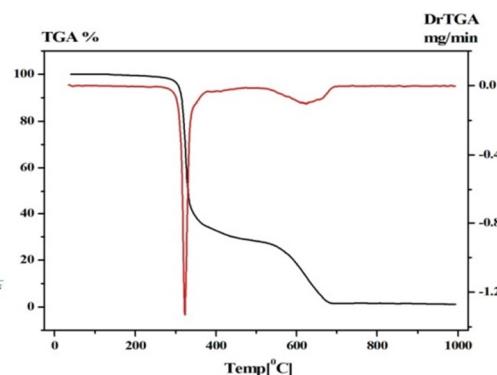
Figure 1 The IR spectrum of H_2L ligand and the complexes 1 and 2

Figure 2 Electronic absorption spectra of schiff base ligand and the complexes 1 and 2

Figure 3 ^1H -NMR spectrum of H_2L ligand Schiff base complexes 1 and 2Figure 4 TGA and DTG curves of the H_2L ligand

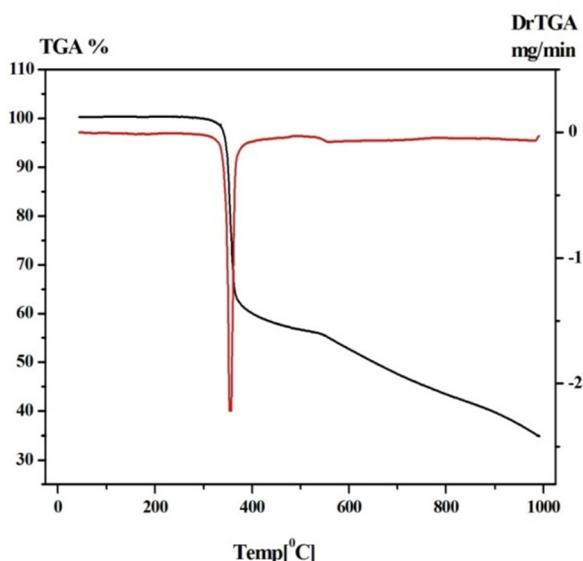
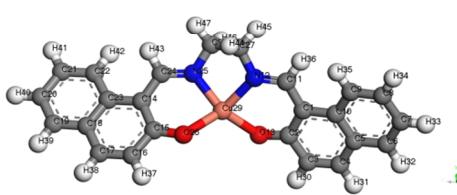
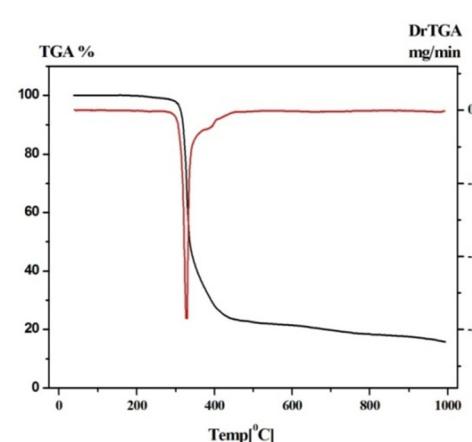
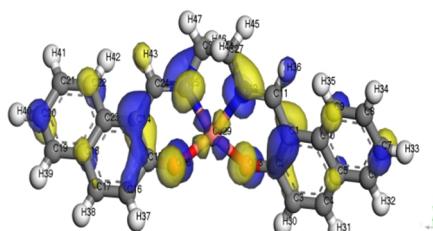


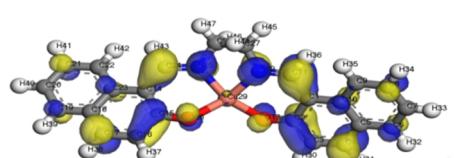
Figure 5 TGA and DTG curves of complex 1
Figure 6 TGA and DTG curves of complex 2



Cu- complex, (a)



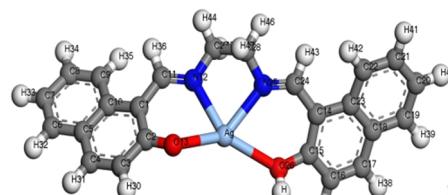
Cu-HOMO, (b)



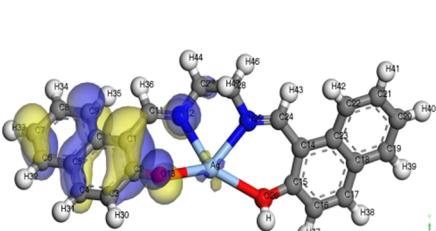
Cu-LUMO, (c)

Figure 7 (a) Optimized geometry of complex 1,
(b,c) HOMO–LUMO representation of 2

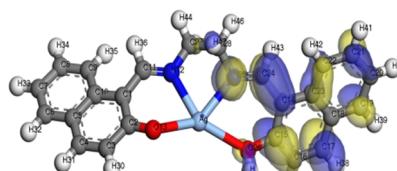
متراکبات النحاس والفضة لمشتقات ثنائي الأمين حفازة للحصول على ١،٤-ثنائي الإستبدال للتراي آزول



Ag Complex, (a)



Ag HOMO, (b)



Ag- LUMO, (c)

Figure 8 (a) Optimized geometry of complex 2,
(b,c) HOMO–LUMO representation of 1

تحضير متراکبات النحاس والفضة لثنائي الأمين وإستعمالها كحفازة لتفاعلات كيميائية محددة ودراسة كاملة لخصائص هذه المتراکبات . الإستفادة من هذه المتراکبات كحفازة تجاه تفاعلات الإضافية الحلقيّة التي تحتوى على الأزيد والألكاين بالمقارنة مع أملاح اسيتات النحاس او نترات الفضة والتي تستخدمنى تكوين التفاعلات الإضافية الحلقيّة للحصول على ١،٤-ثنائي الإستبدال للتراي آزول.