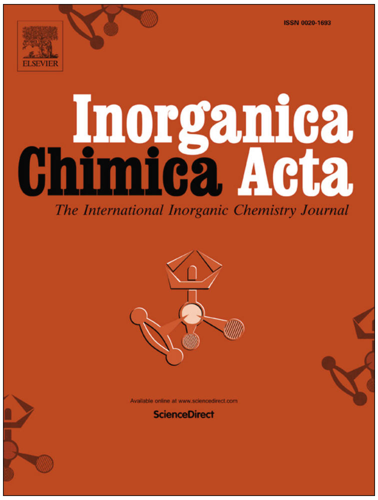

Research paper

Synthesis, characterization and crystal structure of a diketone based Cu(II) complex and its catalytic activity for the synthesis of 1,2,3-triazoles

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Synthesis, characterization and crystal structure of a diketone based Cu(II) complex and its catalytic activity for the synthesis of 1,2,3-triazoles

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Abstract

The synthesis and characterization of complex [Cu(dppo)$_2$] (dppo = 1,3-diphenylpropane-1,3-dione) is reported. The complex has been fully characterized by FT-IR, UV-Vis, elemental analysis and Cyclic Voltammetry. The paramagnetic nature of the complex was confirmed by magnetic measurement and the square planar geometry was ascertained by single crystal X-ray determination. The complex has been found to be a good homogeneous catalyst for the synthesis of 1,2,3-triazole derivatives *via* one-pot reaction of arylboronic acids, sodium azide and alkynes in DMF.

Keywords: Copper complex, cycloaddition, 1,2,3-triazoles

Introduction

1,2,3-Triazoles, a nitrogen-containing five membered heterocyclic compounds have received much interest in the field of medicinal and material chemistry [1]. These compounds have also found applications in synthesis of various agrochemicals, dyes, corrosion inhibitors, biochemicals, polymers and other functional materials like photo-stabilizers and photographic materials [2]. A literature survey indicates that there are several methods available for the synthesis of 1,2,3-triazole derivatives (Scheme 1) [3-10]. The classical method involves the thermal 1,3-dipolar cycloaddition of organic azides with alkynes, discovered by Huisgen in 1963 [11]. Owing to elevated temperature, low yields and lack of selectivity, Sharpless [12] and Meldal [13] modified the method and found that 1,3-dipolar cycloaddition of organic azides with alkynes could be accelerated by using Cu(I) complexes as catalyst [14]. Although initial reports were based on the active Cu(I) catalysts, other workers also used Cu(II) species in these transformations [15]. These reactions were catalyzed by a variety of Cu(II) catalysts or catalytic mixtures such as $CuSO_4$-ascorbate [16], immobilized Cu(II) on polymers or zeolites [17-20], metallic copper turnings [21], and copper nanoparticles [22-23] etc. However, these methods suffered from several drawbacks such as, explosive nature and relative instability of organic azides [24]. The alternative approach involved an *in situ* generation of organic azides [25] from aryl halides or aryl boronic acids and sodium azide.

The development of well characterized homogeneous catalysts for these organic transformations is one of the frontier areas of current research in Chemistry. Due to different interesting properties such as antioxidant, anti-leukemia, antimicrobial, anticancer activities and chelating power of β-Diketones [26], herein we describe the synthesis of a copper(II) complex [Cu(dppo)] from copper chloride and 1,3-diphenyl propane 1,3-dione(dppo) and its application in the synthesis of 1,2,3-triazoles *via* one-step reaction from an arylboronic acid with sodium azide in DMF, followed by a cyclization process with an alkyne under mild reaction conditions.

Scheme 1

Experimental

Materials and instrumentations:

All reagents and solvents for the synthesis and analysis were purchased from commercially sources and used as received without further purification. 1,3-diphenylpropane-1,3-dione (dppo), various phenyl boronic acids and alkynes were purchased from Merck and Sigma Aldrich.

FT-IR spectra were recorded on a Perkin Elmer Spectrometer between 400-4000 cm^{-1} using KBr pellets. Electronic absorption spectral analysis was recorded on a Shimadzu UV-1800 Spectrophotometer in the wave length range of 200-1100 nm. Elemental analyses were carried out using a Heraeus CHN-Rapid elemental analyzer. The NMR spectra of the isolated products were recorded on a Bruker AvIII HD-300 MHz and 400 MHz spectrometer in $CDCl_3$ using TMS as the internal Standard. ESI-MS were recorded by using a model Waters UPLC-TQD. Melting points were recorded with Yazawa micro melting point apparatus. The electrochemical experiments were performed on a CHI660C electrochemical analyzer under oxygen-free conditions. The electrochemical behavior of the dppo ligand (10^{-3} M) and $[Cu(dppo)_2]$ complex (10^{-3} M) was investigated by Cyclic Voltammetry (CV) technique using 0.1M $[nBu_4N][ClO_4]$ as a supporting electrolyte in DMF solvent at an scan rate of 100 mV S^{-1}. The three-component electrode consisted of a glassy carbon working electrode, a SCE reference electrode, and platinum wire as counter electrode.

Synthesis of [Cu(dppo)₂] complex

A methanolic solution of ligand 1,3-diphenylpropane-1,3-dione (dppo) (0.224g, 1.00 mmol) was added dropwise to a clear solution of copper (II) chloride (0.173g, 0.5 mmol) in methanol (10 mL). The resultant mixture was stirred at room temperature for 12 h to produce a greenish precipitate which was filtered and dried under vacuum. Yield: 0.208g (70 %), M.p: 230^o C. The diffraction quality crystals were obtained by slow evaporation of greenish methanolic solution of the complex at room temperature. Anal. Calc. for $C_{30}H_{22}CuO_4$: C, 70.25; H, 4.62. Found: C, 70.65; H, 4.35. Selected FT-IR (KBr), cm^{-1}: ν(partial C=O) 1536, ν(C-C) 1311, ν(Cu-O) 556. UV-Vis [λ_{max}(nm), ε (L mol^{-1} cm^{-1})]: 277 (13550), 354 (17250), 642 (64).

Synthesis of 1,2,3-triazole derivatives

In a 25-mL round-bottom flask, phenylboronic acid (1.0 mmol), NaN_3 (1.5 mmol) were dissolved in DMF (3.5 mL) by stirring for 30 minutes. After this period, an alkyne (1.0 mmol) dissolved in 1mL DMF was added slowly via syringe, followed by addition of 2 mol% of the complex [Cu(dppo)$_2$]. The contents were stirred for 8-12 h at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the product was extracted with ethyl acetate (3 x10 mL) from aqueous phase. The combined organic fractions were dried over Na_2SO_4 and the solvent removed under reduced pressure to afford a crude product, which after purification over Column chromatography using petroleum ether/ethyl acetate in 4:1 as eluting solvents to yielded the pure product as colorless solid.

Single crystal X-ray structure determination of [Cu(dppo)₂] complex

The X-ray diffraction intensity data were measured at 103 K with a Bruker Kappa diffractometer equipped with a CCD detector, employing Mo K α radiation (λ = 0.71073 Å), with the SMART suite of programs [27a]. All data were processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS [27b]. Structural solution and refinement were carried out with the SHELXTL suite of programs [27c]. The integration of the data using a monoclinic unit cell yielded a total of 9213 reflections to a maximum θ angle of 26.47° (0.80 Å resolution), of which 2345 were independent (average redundancy 3.929, completeness = 99.6%, R_{int} = 5.67%, R_{sig} = 5.24%) and 1875 (79.96%) were greater than $2\sigma(F^2)$. A summary of the crystallography data is given in table 1.

Table 1

Results and discussion

The [Cu(dppo)$_2$] complex was synthesized by the reaction of ligand 1,3-diphenylpropane-1,3-dione (dppo) and copper(II)chloride in a 2:1 ratio in methanol at room temperature (Scheme 2). The product was obtained as a greenish solid, insoluble in common solvents but soluble in DMF and DMSO only. The complex was characterized by FT-IR, UV-Vis, Cyclic Voltamogram analysis and the structure was determined by single crystal X-ray crystallography.

The FT-IR spectra of the dppo ligand (Fig. 1) exhibited a strong characteristic peak at 1549 cm^{-1} which is attributed to νC=O. There is also characteristic OH stretching frequency in the enol form of 1,3diphenylpropane 1,3-dione appears as a weak and very broad band at about 3400 cm^{-1} region due to intramolecular hydrogen bond [28a]. The FT-IR spectrum of [Cu(dppo)$_2$] exhibited a peak at 1536 cm^{-1} due to $\nu\mathrm{C}\overset{----}{—}\mathrm{O}$ stretching. The lowering in the νC=O stretching by 13 Cm^{-1} indicates that the CO group is coordinated to the metal [28b]. The FT-IR spectrum of the free ligand indicates a νC-C stretching frequency at 1217 cm^{-1}, however, in the complex this stretching was obtained at 1311 cm^{-1}. An increase in νC-C in the complex may be ascribed to the partial double bond character of C-C bond in the ligand due to delocalization. The band at 556 cm^{-1} was attributed to the νCu-O bonds, and confirmed the coordination of copper with oxygen atom of the dppo ligand [28c].

Fig. 1

The UV-Visible spectra of the dppo ligand and its copper complex are depicted in Fig 2. The dppo ligand shows two absorption bands at 241 nm (ε = 6560 L mol^{-1} cm^{-1}) and 332 nm (ε = 18400 L mol^{-1} cm^{-1}), due to π-π* and n-π* transition of aromatic ring and C=O chromophore, respectively. The electronic spectra of complex are characterized by bathochromic shift in the position of these bands due to metal to ligand charge transfer [29]. An additional characteristic band at 642 nm due to d-d transitions suggests the square planar geometry of the complex. Generally, copper (II) square planar complexes are expected to show three spin allowed transitions namely, ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ($d_{x^2-y^2} \rightarrow d_{z^2}$), ${}^2B_{1g} \rightarrow {}^2B_{2g}$ ($d_{x^2-y^2} \rightarrow d_{xy}$) and ${}^2B_{1g} \rightarrow {}^2E_g$ (d_{x^2-}

$_y{}^2$ → d_{xz}, d_{yz}) in the ground state [30a]. These three bands may overlap together to give a single broad band at 642 in the complex [30b].

Fig. 2

The electrochemical behavior of the dppo ligand (10^{-3} M) and [Cu(dppo)$_2$] complex (10^{-3} M) was investigated by Cyclic Voltammetry (CV) technique using 0.1M [*n*Bu$_4$N][ClO$_4$] as a supporting electrolyte in DMF solvent at an scan rate of 100 mV S^{-1} (Fig. 3). The Cyclic Voltammogram of the ligand shows a reversible peak at $E_{1/2}$= -1.44 V vs. SCE (E_{pc}=-1.48V and E_{pa}=-1.40V) and one irreversible oxidation peak appears at 1.47 V vs. SCE. But in case of copper complex, the ligand based reversible peak shifted to $E_{1/2}$= -1.40 V vs. SCE along with an irreversible oxidation peak appears at 1.52 V vs. SCE. In the Cyclic Voltammogram of the [Cu(dppo)$_2$] complex, it was noticed that the resting potential was at -0.022 V vs. SCE which indicates that copper complex is in +2 oxidation state which undergoes an irreversible cathodic reduction at E= -0.79V vs. SCE followed by the corresponded oxidation peaks at -0.1 V vs. SCE and +0.54 V vs. SCE respectively due to the slow electron transfer process. The above mentioned process only noticed when the Cyclic Voltammogram window was set to -1.0 V vs. SCE to +1.0 V vs. SCE (Fig. 3c). However, upon the full scan range -1.7 V vs. SCE to -1.7 V vs. SCE. A sharp peak at 0.173 V vs. SCE observed which may be attributed due to the formation of radical cation at the ligand centre [31].

Fig. 3

The magnetic moment (μ) of the complex was determined on a Sherwood Scientific magnetic balance and found to be 2.03 B.M, corresponding to one unpaired electron [32]. Therefore, the complex was paramagnetic in nature.

X-ray Crystal Study

Diffraction quality crystals were obtained by the slow evaporation of methanolic solution of complex at room temperature and the structure of the complex has been elucidated by single-crystal X-ray diffraction. The unit of the complex is composed of one Cu(II) ion and two 1,3-diphenylpropane-1,3-dionate units and the complex displays a nearly ideal square planar geometry with monoclinic shape. An ORTEP plot of this complex is shown in fig. 4. All non hydrogen atoms were refined with anisotropic thermal parameters (Fig. 4). The selected bond lengths and angles are given in Table 2. The structure shows that the two molecules of 1,3-

diphenylpropane-1,3-dione ligand are coordinated to copper in the bidentate fashion. It forms two six-member chelate rings with O1A-Cu-O2A and O1A-Cu1-O2A bite angles of 93.11(7) and 86.89(7), respectively. The structure of the complex adopts a square planar geometry with O1A-Cu1-O1A and O2A-Cu1-O2A bond angles of 180 to each which are comparable with reported square planar Cu(II) complexes [33, 34]. The bond length of Cu(1)-O(1)A and Cu(1)-O(2)A was found to be 1.8997(17) Å and 1.9149(17), respectively, which lies in the range of previously reported Cu(II) complexes such as, $[Cu(L)(H_2O)](ClO_4)]$ and $[Cu(L_1)(H_2O)_2]$ [35, 36]. Where L and L1 are the abbreviations of ligands 2-[(3-methoxypropyl)thio]aniline and pyridine-2,6-di carboxylic acid respectively. The C1-C2 and C2-C3 bond lengths were found to be 1.398 Å and 1.396 Å respectively. These values are typical of C-C partial double bonds [37].

Table 2

Fig. 4

Catalytic Studies

The catalytic potential of the complex $[Cu(dppo)_2]$ was explored in a cycloaddition reaction of an arylboronic acid (1 mmol) and substituted phenylacytylene (1 mmol) with NaN_3 (1.5 mmol) at room temperature to form 1,2,3-triazole (Scheme 3). Initially, phenylboronic acid and phenylacetylene were chosen as a model reactant to optimize the reaction conditions. When the reaction was carried out with 1 mol% catalyst loading (Table 1, entry 2) under room temperature, product is isolated in 50 % yield. It was observed that the reaction was completed in 8-10 h using 2 mol % $[Cu(dppo)_2]$ as a catalyst in DMF under atmospheric conditions at room temperature. No significant improvement in yield of triazole was noticed when the catalyst loading was increased from 2 mol% to 5 mol% under optimized reaction conditions (Table 3, entry 3-4). The reaction was carried out in various solvents such as H_2O, CH_3CN, DCE, $PhCH_3$ and CH_3OH (Table 3). The best yield was obtained in DMF (Table 3, entry 4). All other reactions were carried out with 2 mol % of catalyst under optimized conditions.

Scheme 3

Table 3

Different phenylboronic acids, bearing electron-donating and electron-withdrawing and two alkynes were used (Table 4). It was found that both electron withdrawing and electron donating groups at para position in boronic acids could be efficiently converted to the desirable products (Table 4, entry 2-4). On the other hand, between phenylacetylene and *p*-tolyl phenylacetylene, the later gave better yield in less time (Table 4, entry 5-7). However, meta-substituted phenylboronic acid gave a low yield of the product as compared to para substituted ones (Table 4, entry 8). The products were obtained as white solids, soluble in common organic solvents and fully characterized by melting point, ^{1}H NMR and Mass spectra. All data matches with the literature values [38, 39]. The spectra are given in the supporting information. Furthermore, the catalyst [Cu(dppo)$_2$] was compared with previously reported catalysts [40] for the synthesis of 1,2,3-triazole in terms of temperature, catalytic loading, and time etc (Table 5). The earlier reported catalytic systems required large mol % of catalyst, high temperature and prolong reaction time for completion of the reaction. But our catalyst [Cu(dppo)$_2$] gave better yields (up to 86 %) at room temperature using substantially low (only 2 mol %) catalyst loading. The ease of synthesis, low catalyst loading, less reaction time, and high yields of the products at just room temperature make the complex a “good catalyst”.

Table 4

Table 5

A plausible mechanism for Cu(II)-catalysed synthesis of 1,2,3-triazoles cycloaddition is proposed in Scheme 4, based on earlier reports [41]. The proposed mechanism entails the *in situ* generation of Cu(I) from Cu(II) by sodium azide. The next step of the mechanism involves the formation of a copper(I) acetylenide complex through the coordination with alkyne. Then the *in situ* generated aryl azide from arylboronic acid and sodium azide, reacts with copper(I) acetylenide complex followed by cyclization. The last step of the catalytic cycle is the exclusion of the Cu(I) through reductive elimination, to give the desired 1,4-disubstituted 1,2,3-triazoles.

Scheme 4

Conclusion

A new copper(II) complex [Cu(dppo)$_2$] (dppo =1,3-diphenylpropane-1,3-dione) has been synthesized and fully characterized by various physicochemical and spectroscopic techniques including single crystal X-ray diffraction. The complex has square planer geometry as confirmed by the single crystal X-ray structure determination. The square plane is made up of four donor oxygen atoms of the ligand, 1,3-diphenylpropane-1,3-dione. The complex has been found to be an economic and efficient homogeneous catalyst for the synthesis of 1,2,3-triazole derivatives *via* one-step reaction from an arylboronic acid, sodium azide and alkyne. The procedure does not require isolation of the azide intermediates and afforded good-to-excellent yields at room temperature without addition of any additives.

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Supplementary data

CCDC 1441959 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or mail

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List of Scheme's caption

Scheme 1. General Methods for synthesis of 1,2,3-triazoles

Scheme 2. Synthesis of [Cu (dppo)$_2$] complex

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Scheme 4. Plausible mechanism for the synthesis of 1,2,3-triazole

List of figure's caption

Fig. 1. FT-IR spectra of dppo ligand and [Cu(dppo)$_2$] complex

Fig. 2. (a) UV-Vis spectra of dppo ligand (b) [Cu(dppo)$_2$] complex and, (c) d-d transition in UV-Vis spectrum of complex

Fig.3 (a) Cyclic Voltamogram of the ligand (dppo) , (b) [Cu(dppo)$_2$] complex and (c) [Cu(dppo)$_2$] complex in the range of -1.0 V vs. SCE to +1.0 V vs. SCE at scan rates of 100 mV/s

Fig.4. ORTEP diagram of complex [Cu(dppo)$_2$] with the atom labeling scheme (Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity)

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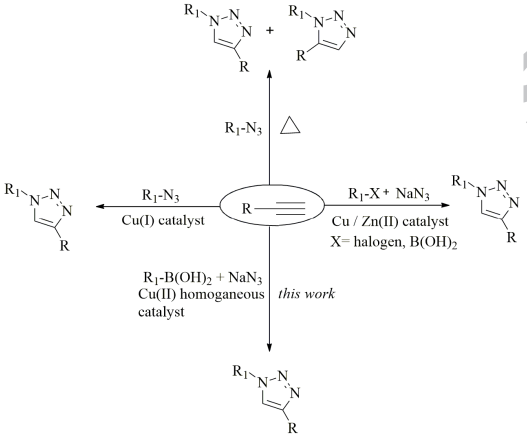
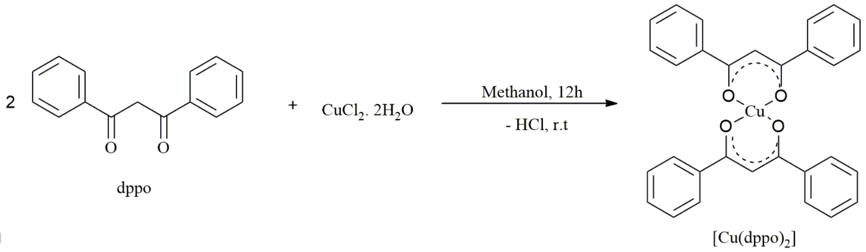
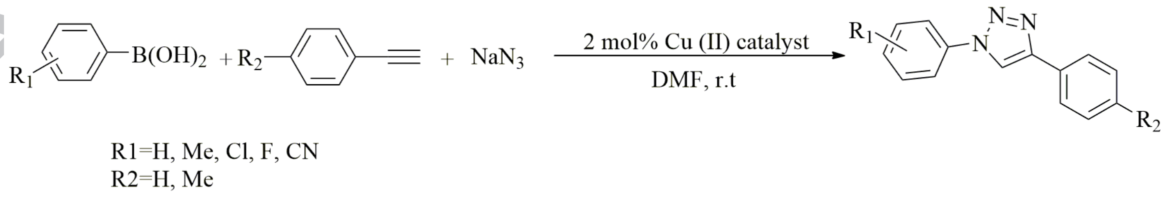
Table 5. A comparison study of catalyst [Cu$(dppo)_2$] with the previous reported catalysts in synthesis of 1,2,3-triazole



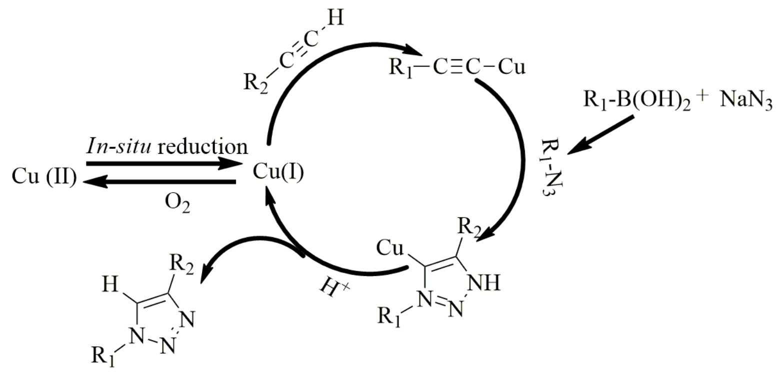
Scheme 1. General methods for synthesis of 1,2,3-triazole



Scheme 2. Synthesis of [Cu$(dppo)_2$] complex



Scheme 3. Synthesis of 1,2,3-triazole derivatives



Scheme 4. Plausible mechanism of 1,2,3-triazole synthesis

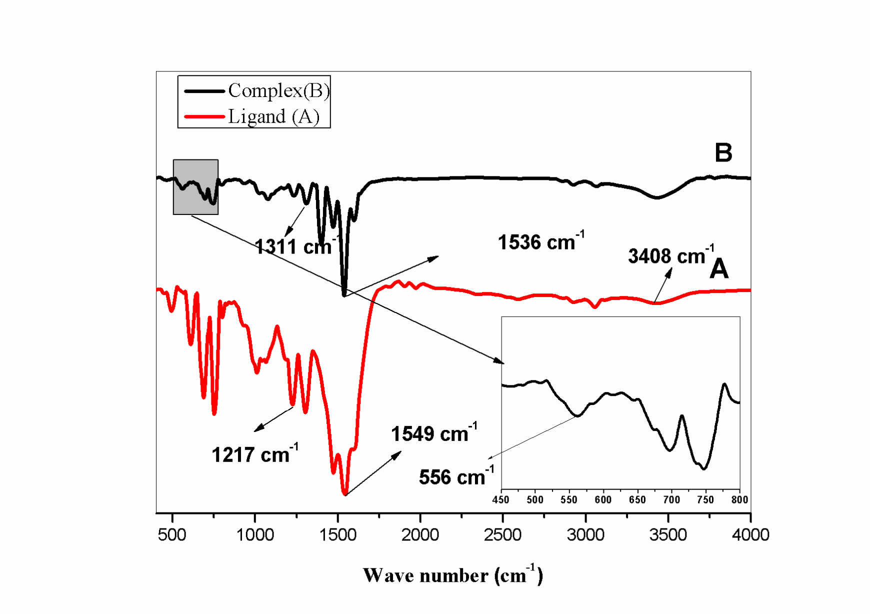


Fig.1. FT-IR spectra of dppo ligand and $[Cu(dppo)_2]$ complex

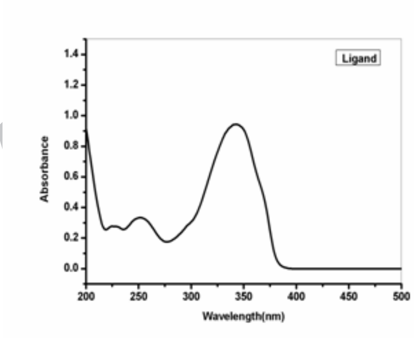


Fig. 2a

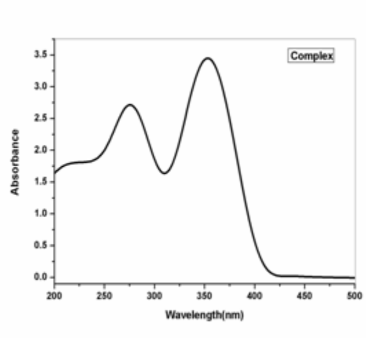


Fig. 2b

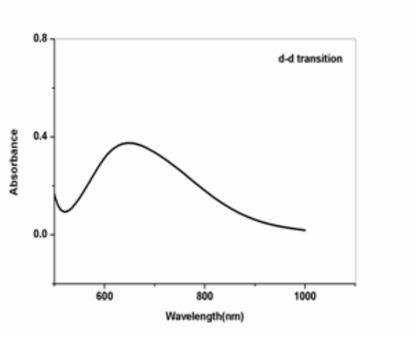


Fig. 2c

Fig.2. (a) UV-Vis spectra of dppo ligand (b) [Cu(dppo)$_2$] complex and, (c) d-d transition in UV-Vis spectrum of complex

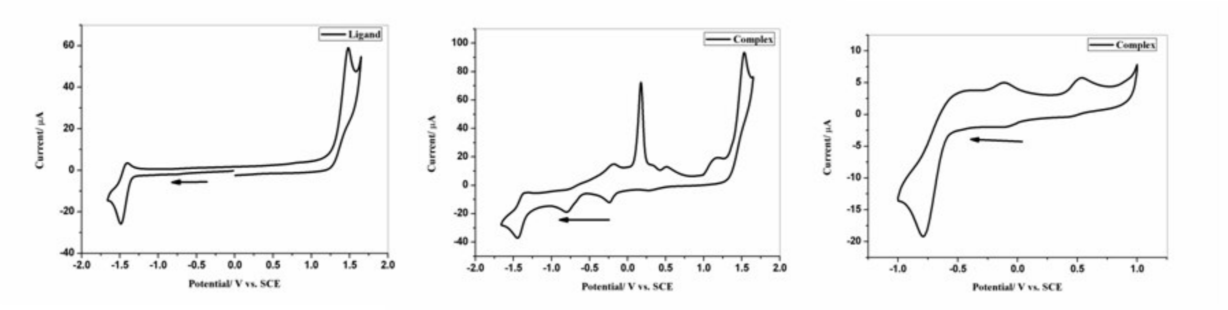


Fig. 3a

Fig. 3b

Fig. 3c

Fig.3. (a) Cyclic Voltamogram of the ligand (dppo), (b) [Cu(dppo)$_2$] complex and (c) [Cu(dppo)$_2$] complex in the range of -1.0 V vs. SCE to +1.0 V vs. SCE at scan rates of 100 mV/s

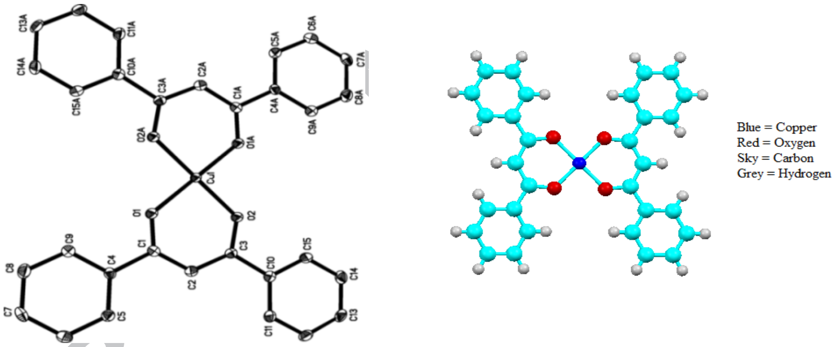


Fig.4. ORTEP diagram of complex [Cu(dppo)$_2$] (Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity)

Table 1. Crystal data and refinement parameters of [Cu(dppo)$_2$] complex

Chemical formula	$C_{30}H_{22}CuO_4$
Formula weight	510.01 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.100 x 0.120 x 0.220 mm

Crystal habit	yellow block
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	a = 25.626(3) Å
	b = 6.0009(5) Å
	c = 16.1255(17) Å
	α = 90°
	β = 114.092(3)°
	γ = 90°
Volume	2263.8(4) $Å^3$
Z	4
Density (calculated)	1.496 g/cm^3
Absorption coefficient	1.002 mm^{-1}
R_{int}	0.0567
$R_1[I>2\delta(I)]$	0.0513
wR_2 (all data)	0.1145

Table 2. Selected bond lengths(Å) and bond angles(°) of $[Cu(dppo)_2]$

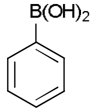
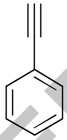
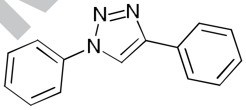
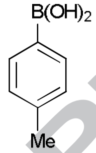
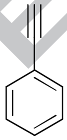
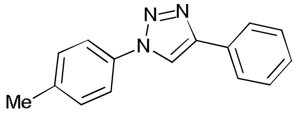
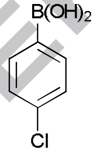
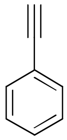
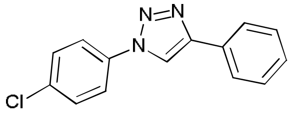
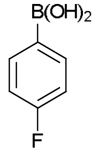
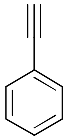
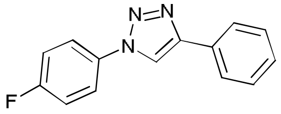
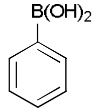
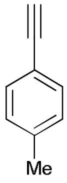
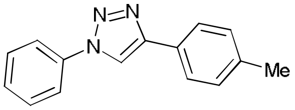
Bond	Length(Å)	Bond	Angles(°)
Cu1-O1A	1.8997(17)	O1A-Cu1-O1A	180.0
Cu1-O2A	1.9149(17)	O1A-Cu1-O2A	93.11(7)
C1-O1A	1.278(3)	O1A-Cu1-O2A	86.89(7)
C1-C2	1.398(3)	O2A-Cu1O2A	180.0
C2-C3	1.396(4)	O1A-Cu1-O2A	86.90(7)
C1-C4	1.500(4)	O1A-C1-C2	124.7(2)
C3-O2A	1.283(3)	C2-C1-C4	120.8(2)
C4-C5	1.395(4)	O2A-C3-C2	124.6(2)
C5-C6	1.385(4)	C2-C3-C10	120.7(2)
C7-C8	1.387(4)	C5-C4-C1	122.8(2)

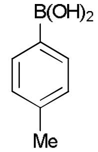
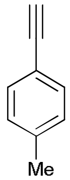
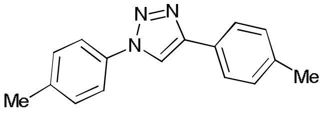
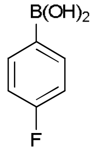
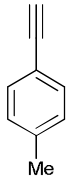
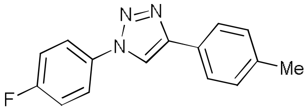
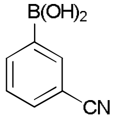
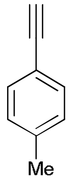
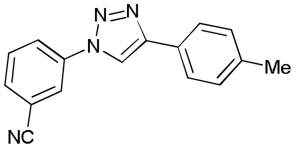
Table 3. Study of reaction optimization conditions

Entry	Solvent	Catalyst Loading (mol %)	Time (h)	Yield, % [a]
1	Water	2	12	21
2	DMF	1	12	50
3	DMF	2	8	78
4	DMF	5	8	75
5	Methanol	5	12	35
6	Acetonitrile	5	24	53
7	Toluene	5	18	45
8	1,2-Dichloroethane	5	24	25

[a] Isolated yields

Table 4. Synthesis of 1,2,3-triazoles from various arylboronic acid and alkynes in presence of Cu(II) catalyst under the optimized reaction conditions

Entry	Boronic Acid	Phenyl-acetylene	Products	Time (h)	Yield* %
1.				9	82
2.				8	86
3.				8.5	75
4.				9.5	70
5.				8.5	70

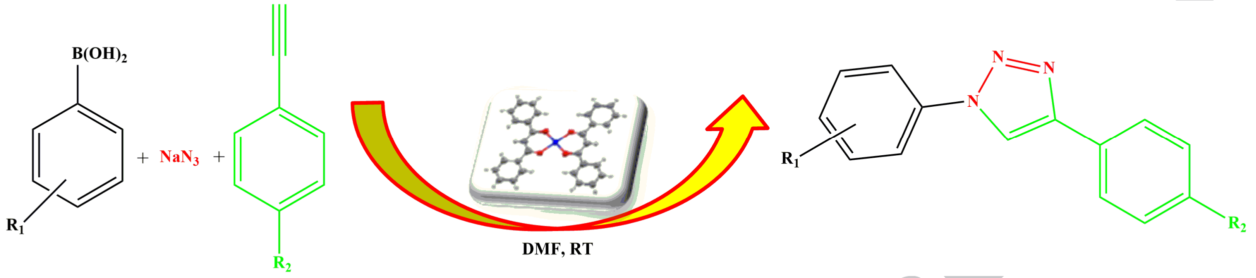
6.				9	74
7.				10	68
8.				12	65

*Isolated yield after work up.

Table 5. A comparison study of catalyst [Cu(dppo)$_2$] with the previous reported catalysts in synthesis of 1,2,3-triazole

Entry	Catalyst	Catalytic loading (mol %)	Temperature (°C)	Time (h)	Yield/Conv. (%)	Ref.
1	Cu/SiO$_2$	20	70	12	93	[40a]
2	[Cu(tzol)$_2$]	2.0	70	12	47	[40b]
3	[Cu(tzol)$_2$]	2.4	70	12	96	[40b]
4	CuSO$_4$-sodium ascorbate	10	80	8.5	89	[40c]
5	[Cu(dppo)$_2$]	2.0	RT	8.0	86	This Work

Graphical Abstract



- [Cu(dppo)$_2$] complex was easily synthesized from CuCl$_2$.2H$_2$O and ligand 1,3-diphenylpropane-1,3-dione (dppo) and the structure determined by single crystal X-ray studies.
- The complex is used as a homogeneous catalyst for the one pot synthesis of 1,4-disubstituted-1,2,3-triazoles from an arylboronic acids, sodium azide and alkynes.
- Good to excellent yields have been achieved at room temperature in less time.