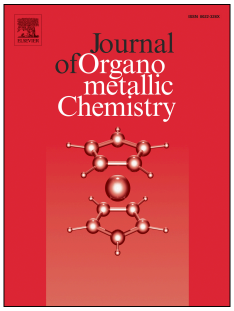

Unprecedented formation of a *μ*-oxobridged polymeric copper(II) complex: Evaluation of catalytic activity in synthesis of 5-substituted 1*H*-tetrazoles

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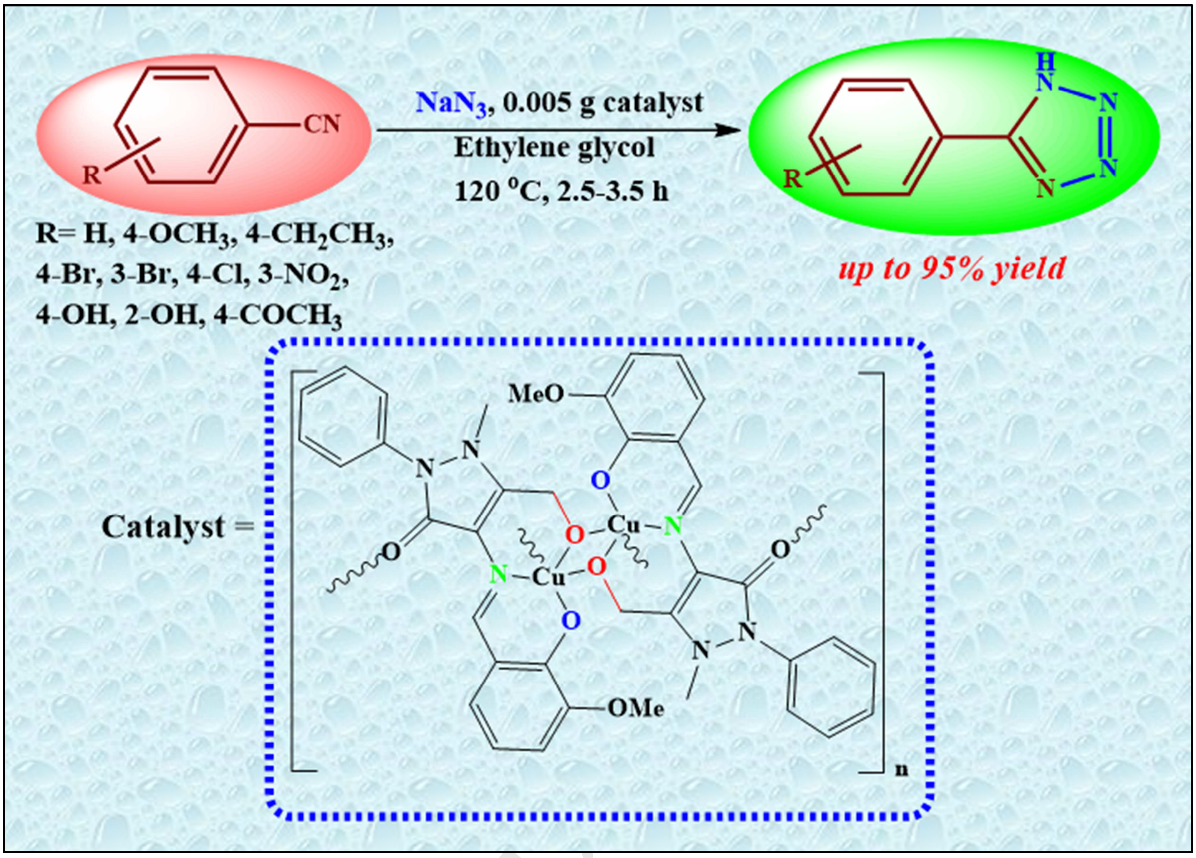
Graphical Abstract:



Unprecedented formation of a μ-oxobridged polymeric copper(II) complex: Evaluation of catalytic activity in synthesis of 5-substituted 1*H*-tetrazoles

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Abstract

The reaction of $CuCl_2.2H_2O$ with Schiff base ligand, 4-[(2-hydroxy-3-methoxybenzylidene)amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3-one] (hmdpH), in 1:1 molar ratio led to a novel and unprecedented oxo-bridged polymeric copper(II) complex, $[Cu(\mu\text{-}O)(hmdp)]_n$. The complex was isolated as crystalline solid and characterized by FTIR, UV-visible and EPR spectroscopic techniques. The molecular structure of the complex was also determined by single crystal X-ray diffraction studies. The formation of the complex is unique and unprecedented in the sense that one of the CH_3 group of the 4-aminoantipyrene unit of the Schiff base ligand is oxidized *in situ* to CH_2OH, during the complex formation. The catalytic potential of the complex has been demonstrated in the synthesis of a series of 5-substituted 1*H*-tetrazoles via [3+2]-cycloaddition reactions of substituted benzonitriles and sodium azide in ethylene glycol.

Keywords

Schiff base; polymeric copper(II) complex; crystal structure; [3+2]-cycloaddition reaction; 5-substituted 1*H*-tetrazoles

1. Introduction

Among various *N*-heterocycles, tetrazoles are the most stable five membered ring comprising of four nitrogen atoms. In general, heterocyclic compounds have been used as excellent ligands in coordination chemistry [1]. Majority of heterocycles also exhibit interesting biological/pharmaceutical activity [2]. Owing to lower toxicity and higher lipophilicity of tetrazoles, they have been used as isosteric replacement in drugs [3], antidiabetics [4], antibiotics [5] and HIV-inhibitors [6].

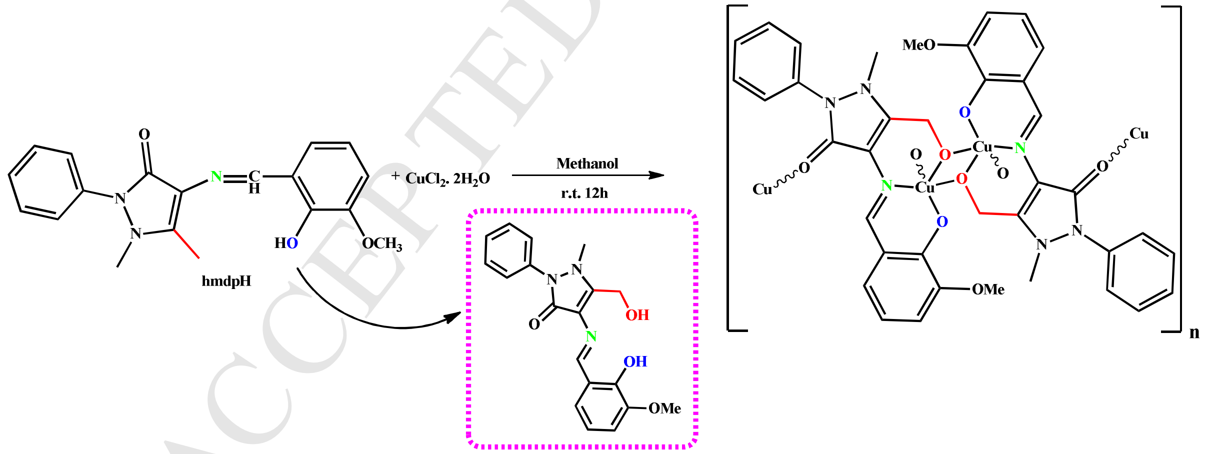
Because of the widespread range of applications of tetrazole derivatives, several preparative methods for synthesis of tetrazole derivatives are described in the literature [7]. The most common method to synthesize a tetrazole is the [3+2] cycloaddition reaction between an organic nitrile and an azide in presence of an acid [8]. However, during the last few years, the synthesis of 5-substituted 1-*H* terazoles have been reported using a large number of homo- and heterogeneous catalysts, such as ZnO [9], $ZnBr_2$ [10] $Zn(OTf)_2$ [11], Cu_2O [12], $Fe(OAc)_2$ [13], $InCl_3$ [14], $AgNO_3$ [15], $Cu(OTf)_2$ [16], $Pd(PPh_3)_4$ [17], $CuSO_4.5H_2O$ [18], $Cu(NO_3)_2.\ 3H_2O$ [19], $In(OTf)_3$ [20], silica-supported ZnS nanospheres [21], Cu-Zn alloy nanopowder [22], Zn/Al hydrotalcite [23], Mw-Pd/Co Nanoparticles [24], zinc hydroxyapatite [25], nano-ZnO/Co_2O_3 [26a], ZnO nanoflakes [26b], CoY zeolite [27], Pt NPs@AC [28a], CAES [28b], $CuFe_2O_4$ nanoparticles [29], and $Ln(OTf)_3$-SiO_2 [30], [Pd-SMTU@boehmite] [31a], [Pd-SBT@MCM-41] nanoparticles [31b], monodisperse carbon black decorated Pt nanoparticles [32a], and Pt NPs@rGO [32b] etc. from an organic cyanide and sodium azide. Although most of these methods are worthwhile, many of the prevailing methods suffer from one or more of the drawbacks such as long reaction time, elevated temperature, low yield, harsh reaction conditions, tedious workup and use of hazardous solvents. In some cases, where alkyltin-based reagents are used as co-catalysts, toxic hydrazoic acid is formed [33] as by product which is a major concern from green chemistry point of view. In this respect, a more environmental-friendly, stable, and easy to handle cheap catalytic systems are desirable.

By virtue of good thermal and chemical stability, simple and easy synthesis, Schiff bases are recognized as suitable ligands to develop new catalysts with various metals [34]. Consequently, Schiff base metal complexes have played a pivotal role in catalysis and find miscellaneous industrial applications [35]. Motivated by these results and our on-going research interest in developing air- and moisture-stable transition metal-based catalysts for various organic transformations [36], we report herein the synthesis and characterization of a novel and an unprecedented oxo-bridged polymeric copper(II) complex $[Cu(\mu\text{-}O)(hmdp)]_n$, and its catalytic application in synthesis of a wide range of 5-substituted 1*H*-tetrazoles by the reaction of various substituted benzonitriles and sodium azide involving a [3+2]-cycloaddition.

2. Results and Discussion

2.1. Synthesis and characterization

The Schiff base ligand (hmdpH) was synthesized in 81% yield by the reported method [37] and isolated as yellow crystalline solid, m.p. 205-207°C. The drop-wise addition of a clear solution of $CuCl_2.2H_2O$ (0.086 mg, 0.50 mmol) in 5 mL methanol to methanolic suspension of the ligand hmdpH (0.168 g, 0.50 mmol) at room temperature resulted in the precipitation of reddish brown powder (**Scheme 1**). The complex was found to be insoluble in benzene, toluene, dichloromethane and water but soluble in methanol, DMF and DMSO. Initially, the complex was characterized by FTIR, UV-visible, and EPR spectroscopy. Due to ambiguity about the structure, single crystals of the complex, suitable for X-ray crystallography were grown from a saturated solution in DMF on prolonged standing over three weeks. Moreover, the molecular structure of the complex was resolved by single crystal X-ray crystallography which confirmed the formation of a μ-oxo bridged polymeric complex. *The formation of the complex is unique and unprecedented in the sense that one of the* CH_3 *group of the 4-aminoantipyrene unit of the Schiff base ligand is oxidized in situ to* CH_2OH*, during the complex formation*. At present, the exact mechanism of this structural change in the ligand in presence of Cu^{2+} in solution, is ambiguous but the source of oxygen is likely to be the atmospheric air [38].



Scheme 1. Synthesis of polymeric copper (II) complex

The FTIR spectrum of the Schiff base ligand exhibited three prominent peaks at 1665 cm^{-1}, 1593 cm^{-1} and 1242 cm^{-1} corresponding to ν (C=O), ν (C=N) of azomethine group and OH in plane bending, respectively (**Fig. S1**). The data is consistent with the literature [37]. The FTIR spectrum of the complex exhibited two prominent peaks at 1659 cm^{-1} and 1579 cm^{-1} due to ν (C=O), and ν (C=N), respectively. A comparison of the FTIR spectra of the complex and the ligand clearly indicated that the ν (C=N) stretching frequency was shifted to lower wavenumber by 14 cm^{-1} (i.e. from 1593 cm^{-1} in free ligand to 1579 cm^{-1} in the complex) which confirmed the coordination of the nitrogen atom of the azomethine group of the ligand to the metal center [39]. The C=O stretching frequency of the pyrazole ring of the Schiff base ligand was shifted to lower wavenumber by a magnitude of 06 cm^{-1} only, upon complexation. This indicated the coordination of the C=O group of pyrazole ring of the Schiff base ligand to metal ion to form a polymeric chain. The disappearance of OH (in plane bending) peak of the ligand in the FTIR spectrum of the complex also substantiated the deprotonation of the hydroxyl group and the emergence of a new peak at 547 cm^{-1} due to ν Cu-O indicated the coordination of the phenolic oxygen to the copper [40].

The UV-vis absorption spectra of the ligand and copper(II) complex measured in methanol at room temperature in the range of 200-1000 nm are depicted in **Fig. S2**. In the UV-vis spectrum of Schiff base ligand, four distinct absorption bands were observed at 235, 284, 335 and 414 nm. The bands at 235 and 284 nm were attributed due to π-π* transition of the aromatic ring and the bands at lower energies (at 335 and 413 nm**)** were associated with the n-π* of the azomethine group [41]. Upon coordination to Cu(II), all bands were shifted to higher wavelengths due to LMCT which confirmed that the nitrogen of the azomethine was involved in the coordination with Cu(II) ion [41-42]. The presence of an additional broad band at 695 nm in the UV spectrum of the complex may be ascribed to the forbidden d-d transitions of copper and indicated the distorted square pyramidal geometry of the complex. The d-d transitions in copper (II) complexes have been reported to be of low energy due to the Jahn-Teller distortion [42].

The EPR spectrum of complex, recorded at room temperature, is shown in **Fig. 1**. The EPR spectrum of the powdered complex revealed an isotropic behavior with sharp signal and without any hyperfine splitting. The g_{iso} value was calculated to be 2.14 which indicated a distorted square pyramidal geometry of the complex [43].

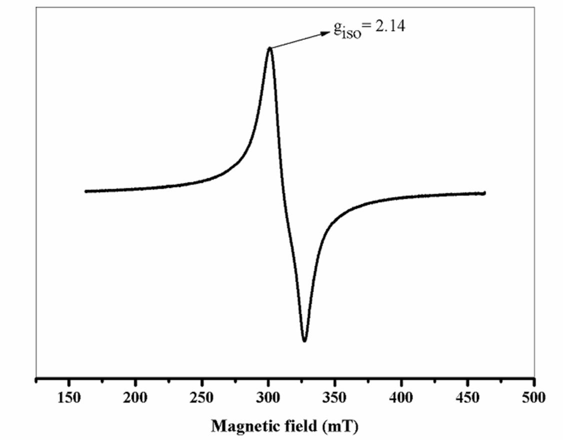


Fig 1. EPR spectrum of copper(II) complex

2.2. Description of the crystal structure of [Cu(μ-O)(hmdp)]$_n$

Diffraction quality crystals of the complex were grown by slow evaporations of DMF solution of the complex and structure of the complex was further confirmed by X-ray crystallography. An ORTEP drawing of the complex is shown in **Fig. 2.** A summary of the crystallographic and refinement data of complex is given in **Table 1** and selected bond lengths and bond angles are given in **Table S1**. X-ray analysis reveals that complex crystallizes in monoclinic system, having space group P 1 21/c 1. The structure analysis of the complex shows that complex is a one dimensional polymer built up from asymmetric monomer units in which Cu(II) ion is surrounded by five donor atom. Copper atoms centrally bound through two bridging oxygen atoms with Cu-O bond length of 1.938(2) Å. The asymmetric units are further bridged by oxygen atom of C=O group of pyrazole ring of the Schiff base ligand, forming the polymeric chain in copper complex. Interestingly, the CH_3 group of 4-aminoantipyrene analogue of Schiff base ligand has been oxidized to CH_2OH, which bridges with two copper atoms *via* deprotonation. In the complex, the azomethine nitrogen atom and oxygen of orthovanilate are coordinating to the copper atoms forming two six-membered chelate ring, having Cu1-O1 and Cu1-N1 bond length 1.884(2) Å and 1.947(3) Å, respectively. The inter-atomic Cu1-Cu1A distance and Cu1-O301-Cu1 bridge angle in complex are 3.0101(8) Å and 102.83(10)^o, respectively, which are in close agreement with the values reported for other similar type of copper complexes containing two and one-atom bridging ligands [44]. The four-membered $Cu_2(\mu\text{-}O)_2$ unit is co-planar with a Cu1-O301-Cu1-O301 torsion angle of 0.00(8)^o. Thus, each copper center in polymeric chain, is ligated by one azomethine nitrogen atom, two bridging oxygen atoms, one oxygen atom of orthovaniline moities and oxygen atom of C=O group of pyrazole ring forming five coordinated distorted square-pyramidal geometry around each of the copper atoms. The coordination geometry around the Cu(II) atom is a distorted square pyramidal as structure index τ value of 0.12 as defined by Addison et al. [45] (The structure index is defined as $\tau = (\beta\text{-}\alpha)/60$, where α and β are the largest coordination angles; $\tau = 0$ for an ideal square pyramidal and $\tau = 1$ for a trigonal bipyramidal).

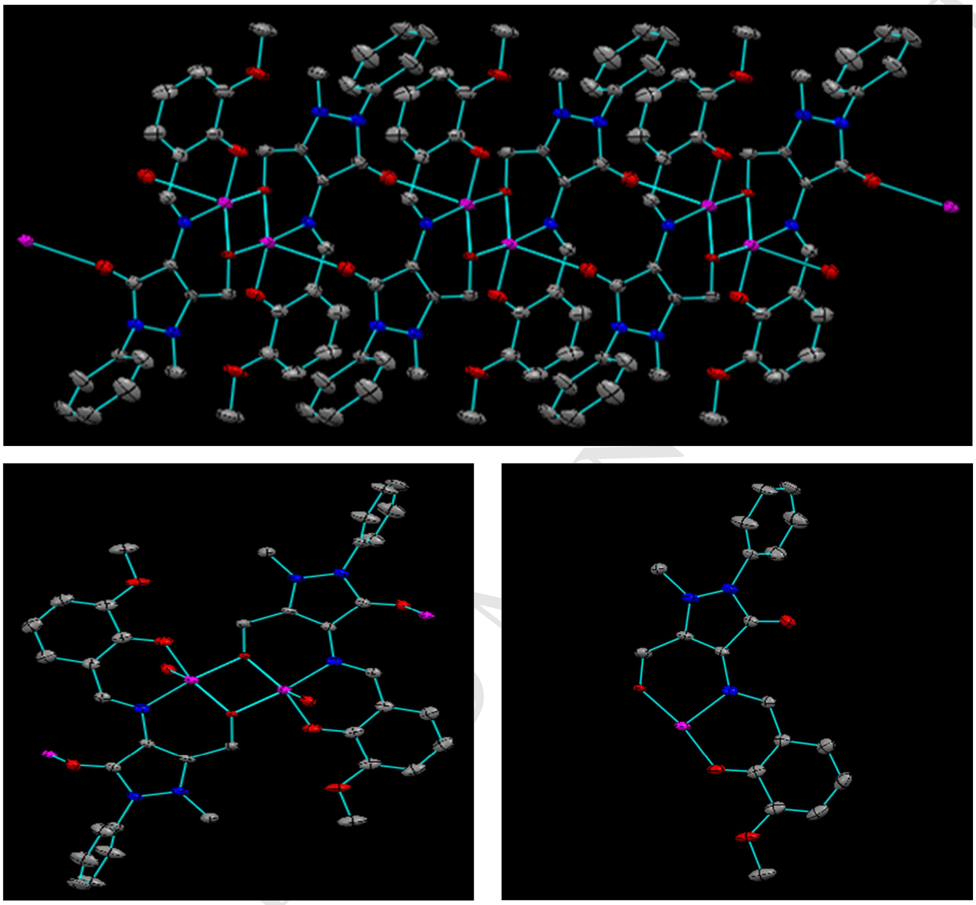


Fig. 2. ORTEP diagram of the polymeric copper chain (top); binuclear unit of polymeric copper(II) complex (bottom right side) and asymmetric unit of the polymeric complex (bottom left side). Non-H atoms are shown with displacement ellipsoids at the 50% probability level (red: oxygen; blue: nitrogen; magenta: copper; grey: carbon)

Table 1. Crystal data and refinement parameters of copper(II) complex

Crystal data	
Chemical formula	$C_{19}H_{17}CuN_3O_4$
Formula weight	414.90

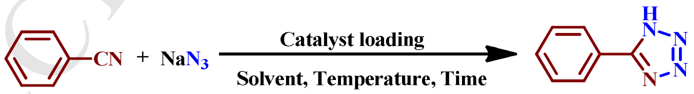
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal size	0.08 x 0.12 x 0.22 mm
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 7.8548(5) Å;
	b = 12.6281(5) Å
	c = 17.1032(8) Å;
	α = 90°;
	β = 97.088(2)°;
	γ = 90°
Volume	1683.52(16) $Å^3$
Z	4
Density (calculated)	1.637 Mg/cm^3
Absorption coefficient	1.330 mm^{-1}
F(000)	852
Data collection and structure refinement	
Theta range for data collection	2.40 to 26.50°
Index ranges	-9<=h<=9, -15<=k<=14, -18<=l<=21
Reflections collected	11996
Independent reflections	3495 [R(int) = 0.0948]
Function minimized	Σ w$(F_o^2 - F_c^2)^2$
Data / restraints / parameters	3495 / 6 / 252
Goodness-of-fit on F^2	1.010
Final R indices	2556 data; I>2σ(I)
R.M.S. deviation from mean	0.119 $eÅ^{-3}$

Catalytic activity of copper(II) complex in the synthesis of 5-substituted 1H tetrazole:

After synthesis and characterization of the copper(II) polymeric complex, its catalytic activities was examined in the synthesis of 5-substituted 1*H* tetrazole *via* [3+2]-cycloaddition reaction of nitriles with sodium azide (**Table 2 & Table 3**).

In order to optimize the appropriate reaction condition, a model reaction of benzonitrile (1.0 mmol) and sodium azide (1.2 mmol) was carried out and various reaction parameters such as, catalyst loading, solvents, temperature and time were studied. The results are summarized in Table 2. When the reaction was carried out in the absence of the catalyst in ethylene glycol at 120°C for 24 h, no product was obtained (Table 2, entry 1). After that, the reaction was carried out in presence of 0.003 g copper(II) complex at 120°C for 3 h, product was obtained in 79% yields (Table 2, entry 2). Further screening of the catalyst loading showed that, when the reaction was carried out with 0.005 g copper(II) complex, the desired product was obtained in 91% yield within 3 h at 120°C (Table 2, entry 5). Increasing the amount of catalyst (0.008 g) had no beneficial effect on the yield of the product (Table 2, entry 7). Thus, it was concluded that 0.005 g loading of the catalyst was optimal (Table 2, entry 5). After optimization of the catalyst loading, the effect of solvents in the reaction was also investigated by conducted in various solvents such as water, THF, DMF, DMSO, ethanol, methanol etc. (Table 2, entries 8-13). Though DMF and DMSO gave satisfied yield of the product (Table 2, entries 8-9), considering the green chemistry approach, the all reactions were carried out in environmentally benign ethylene glycol as green solvent and it gave 91% yield of the product (Table 2, entries 5-7). To investigate the effect of temperature, the reaction was performed at 90°C, 120°C and 140°C, the best result was obtained at 120°C (Table 2, entries 3-6). Thus, the optimal reaction conditions and best yield (91%) was achieved in the presence of 0.005 g of copper(II) catalyst in ethylene glycol as solvent at 120°C within 3 h.

Table 2. Optimization of reaction parameters for the reaction of benzonitrile with sodium azide

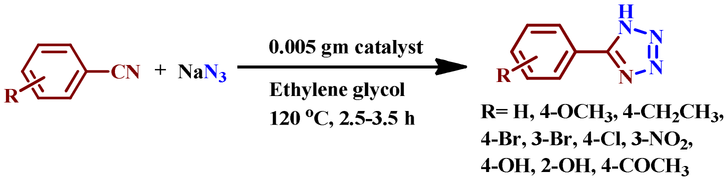


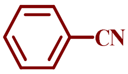
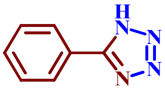
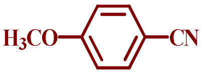
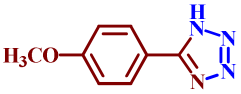
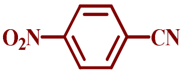
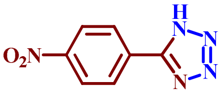
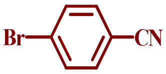
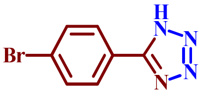
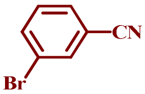
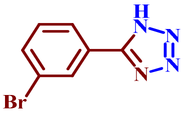
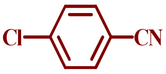
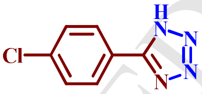
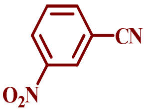
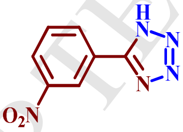
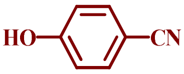
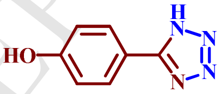
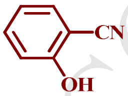
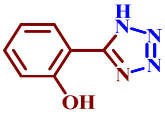
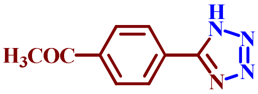
Entry	Catalyst loading (g)	Solvent	Temp (°C)	Time (h)	Yield (%)
1	------	Ethylene glycol	120	24	-
2	0.003	Ethylene glycol	120	3	79
3	0.003	Ethylene glycol	90	3	43
4	0.003	Ethylene glycol	120	3	81

5	**0.005**	**Ethylene glycol**	**120**	**3**	**91**
6	0.005	Ethylene glycol	140	3	90
7	0.008	Ethylene glycol	120	3	91
8	0.005	DMSO	120	3	89
9	0.005	DMF	120	3	84
10	0.005	CH_3OH	65	12	53
11	0.005	CH_3CH_2OH	80	12	50
12	0.005	H_2O	100	12	trace
13	0.005	THF	100	12	15

After optimizing the reaction conditions, the scope and applicability of the catalyst was examined to various substituted benzonitrile with sodium azide. The results are summarized in Table 3. As variety of benzonitrile bearing electron-donating and electron-withdrawing substituents were successfully employed and the corresponding 5-substituted 1*H*-tetrazole derivatives are obtained in good to excellent yields (Table 3, entries 2-10). But benzonitrile having electron-donating substituents require longer reaction time than benzonitrile comprising electron-withdrawing groups. For instance, $-NO_2$, -Br, -Cl and also $-COCH_3$, that incorporate electron-withdrawing communities (Table 3, entries 3-7 & 8), react more quickly in better yields compared to the nitriles made up of electron-releasing groups like $-OCH_3$, -OH (Table 3, entries 2, 8 & 9) and these observations may be due to the electrophilic nature of the benzonitrile i.e. the presence of electron withdrawing groups increases the polarity of the cyanide group inductively [46]. The substituent at *o*-position (Table 3, entry 9) and substituent at *m*-position (Table 3, entry 5) gave lower yield than *p*-position (Table 3, entries 4 & 8), presumably due to steric effect. The products were obtained as white to off-white crystalline solid and fully characterized by melting point, FTIR and ^1H NMR (Fig. S3-S12). Furthermore, the catalytic activity of the synthesized complex was also compared with some of the previously reported catalyst [15,19,26b,27,31a]. The results show that our catalytic system exhibits a better catalytic activity than some of the earlier reported catalysts in terms of yields, catalyst loading, reactions time, TON and TOF (Table 4).

Table 3. Copper(II)-catalyzed synthesis of 5-substituted 1*H*-tetrazoles [a]



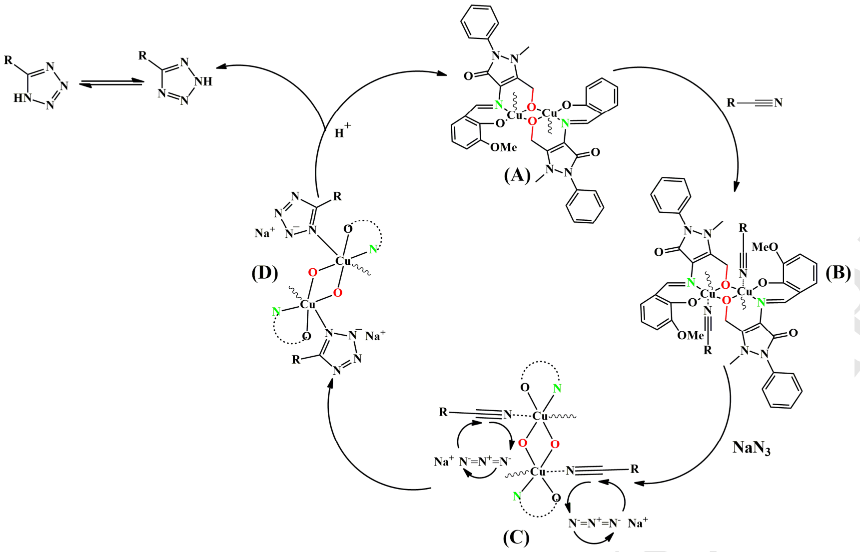
Entry	Nitriles	Product	Time (h)	Yield (%) [b]	TON [c]	TOF (h^{-1}) [d]
1			3	91	74.72	24.90
2			3.5	94	77.48	22.14
3			3.5	93	76.58	21.88
4			2.5	94	77.50	31.00
5			2.5	93	76.77	30.70
6			2.5	95	78.50	31.40
7			2.5	92	75.72	30.28
8			3.5	92	76.01	21.72
9			3.5	90	73.97	21.13
10			3	93	76.50	25.50

[a] Reaction condition: Nitriles (1.0 mmol), NaN_3 (1.2 mmol)
[b] Isolated yields after column chromatography
[c] TON= moles of product formed per mole catalyst
[d] TOF= TON/time (h) of the reaction.

Table 4. A comparison study of the synthesized polymeric copper(II) complex with some of the reported catalysts

Entry	Catalyst	Conditions Solvent/Temp./Time	TON	TOF (h^{-1})	Yields %	Ref.
1	10 mol% (17 mg) $AgNO_3$	DMF/120 ^oC/5h	~	~	83	[15]
2	10 mol% (24 mg) $CuNO_3.\ 3H_2O$	DMF/ 120 ^oC/16h	~	~	92	[19]
3	100 mg ZnO nanoflakes	DMF/ 125 ^oC/14h	1.77	0.13	87	[26b]
4	20 mg CoY zeolite	DMF/ 120 ^oC/14h	36.96	2.64	90	[27]
5	20 mg [Pd-SMTU@boehmite]	PEG-400/ 120 ^oC/2.5h	31.65	12.66	95	[31a]
6	5 mg $[Cu(\mu\text{-}O)(hmdp)]_n$	Ethylene glycol/ 120 ^oC/3h	74.72	24.90	91	*This-work*

A plausible reaction mechanism for the synthesis of 5-substituted 1*H*-tetrazoles using synthesized copper(II) complex as catalyst, is proposed in Scheme 2 based on earlier reports [16, 19]. Initially, coordination of nitrogen atoms of nitrile with Cu(II) takes place and forms complex **B**. After that, the [3 + 2]-cycloaddition between the pre coordination of the nitrogen atom of the C≡N bond with azide ion takes place and readily to form the intermediate **D,** which accelerate the cyclization step. This idea is supported by performing the reaction in the absence of copper(II) complex as catalyst. Without any catalyst, cycloaddition reaction is not completed even after a long period of time (Table 2, entry 1). Protonolysis of intermediate **D** by 2 N HCl to affords the 5-substituted 1*H*-tetrazole as white solid.



Scheme 2. Plausible reaction mechanism for the synthesis of 5-substituted 1*H*-tetrazoles

3. Conclusion

In summary, an unprecedented oxo-bridged polymeric copper(II) complex $[Cu(\mu\text{-}O)(hmdp)]_n$ has been synthesized and characterized by FTIR, UV-visible, EPR and single crystal X-ray diffraction study. The oxidation of one of the CH_3 group of the 4-aminoantipyrene unit of the Schiff base ligand to CH_2OH during the complex formation in air is unprecedented. However, the exact mechanism of oxidation of CH_3 group to CH_2OH is unambiguous at present. The future studies will focus on to unravel the mechanistic aspect of this transformation. The complex exhibited better catalytic activity for the synthesis of a wide range of 5-substituted 1*H*-tetrazoles as compared to some of the previously reported catalysts in terms of yields, catalyst loading, reactions time, TON and TOF. The ease of synthesis, air-stability, and good catalytic activity are some of the key characteristics of the synthesized complex to make it as an interesting and active catalyst for organic synthesis.

4. Experiment

4.1. Materials and Instrumentations:

All reagents and solvents for the synthesis and analysis were commercially available and used as received without further purification.

FT-IR spectra were recorded using KBr pellets on a Perkin Elmer Spectrometer in the range of 4000-400 cm^{-1}. Electronic absorption spectral analysis was recorded on a Shimadzu UV-1800

Spectrophotometer in the wave length range of 200-1100 nm. ^{1}H NMR spectra of the isolated products were recorded on a Bruker Avance-II HD-400 MHz spectrometer in $(CD_3)_2SO$ using TMS as the internal Standard. The EPR spectra were recorded at room temperature on JES-FA200 ESR spectrometer (JEOL-Japan).

4.2. Synthesis of Schiff base ligand 4-[(2-hydroxy-3-methoxybenzylidene) amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3-one] (hmdpH):

The Schiff base ligand (hmdpH) was synthesized by the reported method [37]. A solution of 4-aminoantipyrene (0.204 g, 1 mmol) in ethanol (5 mL) was added drop wise to an ethanolic solution (5 mL) of ortho-vaniline (0.1522 g, 1 mmol). The resultant solution was heated to reflux for a time of 6 h to produce yellow solid. The reaction mixture was cooled to room temperature and the precipitate was filtered, washed with cold ethanol and dried in vacuum over anhydrous $CaCl_2$. Yield: 0.233 g, 81%. M.P. 205 ^oC. Selected FT-IR (KBr), cm^{-1}: 1665 (C=O str., Ar.), 1593 (C=N str.), 1460 (C=C str.), 1242 (OH in plane bending), 1137(C-O-C str.) UV-Vis [λ_{max}(nm)]: 235, 284, 335 and 414.

4.3. Synthesis of complex [Cu(μ-O)(hmdp)]$_n$:

A methanolic solution of $CuCl_2$. $2H_2O$ (0.086 g, 0.50 mmol) was added drop-wise to a suspension of the Schiff base ligand (**hmdpH**) (0.168 g, 0.50 mmol) in methanol (5 mL). The reaction mixture was stirred for 12 h at room temperature to give a brownish precipitate which was filtered, washed with cold methanol and dried vacuum over anhydrous $CaCl_2$. The precipitate was re-crystallized from DMF. Suitable single crystals for X-ray crystallography were grown over a period of weeks from a concentrated solution of the complex in DMF.

Selected FT-IR (KBr), cm^{-1}: 1,659 (C=O str., Ar.), 1579 (C=N str.), 1,460 (C=C str.), 547 (Cu-O str.), 499 (Cu-N str.). UV-Vis [λ_{max}(nm)]: 270, 338, 418, 514, 695.

4.4. General procedure for the synthesis 5-substituted 1-H tetrazoles:

In 25 mL round-bottomed flask, sodium azide (0.076 g, 1.2 mmol) and polymeric copper(II) complex (0.005 g) were added to a solution of benzonitrile (0.103 g, 1 mmol) in ethylene glycol (3 mL) with stirring at room temperature. The reaction temperature was raised up to 120 °C for 3 h. The reaction was monitored by TLC at regular intervals. After completion of the reaction, the reaction mixture was cooled to room temperature and treated with 10 mL HCl (2N) and extracted with 10 mL ethyl acetate. The resulted organic layers were separated and washed with 2x10 mL distilled water, dried over anhydrous sodium sulphate and evaporated under reduced pressure.

The residue was then purified by column chromatography on silica gel (100-200 mesh) to afford the corresponding products.

4.5. X-ray structure determination:

The X-ray diffraction data were collected on a Bruker Kappa diffractometer at 153(2) K equipped with a CCD detector, employing Mo K α radiation (λ = 0.71073 Å), with the SMART suite of programs [47]. All data were processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS [48]. Structural solution and refinement were carried out with the SHELXTL suite of programs [49]. The structures were refined (weighted least squares refinement on F^2) to convergence. All the non-hydrogen atoms in all the compounds were refined anisotropically by full-matrix least-squares refinement. Precise unit-cell parameters were determined by a least-squares fit of 2556 reflections of the highest intensity, chosen from the whole experiment.

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Supplementary data

CCDC 1578086 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. Supporting information also includes experimental details and characterization data for synthesized compounds.

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Highlights:

- Synthesis and characterization of Schiff base ligand derived an unprecedented polymeric copper(II) complex
- Single crystal X-ray diffraction study confirmed a distorted square pyramidal geometry around the Cu(II) ion
- The complex has been found to be a very good catalyst for the synthesis of 5-substituted 1*H*-tetrazoles
- Ethylene glycol used as green solvent for the synthesis of 5-substituted 1*H*-tetrazoles