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Synthesis and crystal structures of salen-type Cu(II) and Ni(II) Schiff base complexes: Application in [3+2]-Cycloaddition and A^3-coupling reactions

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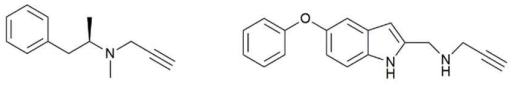
The synthesis of two new salen-type Schiff base complexes of the type [Cu(L)].*0.5*H_2O, **1**, and [Ni(L)], **2**, are described from the reaction of 6,6'-[(1E,1'E)-(cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene)bis(3-(diethylamino)phenol)] salen-type Schiff base ligand (H_2L) with $Cu(OAc)_2.H_2O$ and $Ni(OAc)_2.4H_2O$ in methanol at room temperature, respectively. The complexes are isolated as coloured crystalline solids and characterized by elemental analysis, FTIR, UV-visible spectroscopy and single crystal X-ray diffraction studies. The paramagnetic nature of the complex **1** was confirmed by EPR studies, having g_{iso}= 2.076 which indicated a distorted square planar geometry of the complex. Contrary to this, the nickel complex was found to be diamagnetic in nature and it was additionally characterized by ^{1}H NMR. The crystal structures of complex **1** and **2** confirm the distorted square planar geometry of both the complexes. The complex **1** was found to be a better catalyst for the synthesis of series of 5-substituted 1*H*-tetrazoles from nitriles and sodium azide *via* [3+2]-cycloaddition and in A^3-coupling reaction of aldehydes, secondary amines and terminal alkynes with low catalyst loading (0.7 and 0.9 mol % respectively) as compared to complex **2**. The complex **1** is novel in the sense that, being a homogeneous catalyst, it can be recovered almost quantitatively in both reactions and recycled up to four times to afford good yields of the corresponding products.

Introduction

The tetradentate Schiff base, salen-type ligand and their complexes have allured much interest since Jacobsen's discovery of chiral manganese(III) salen Schiff base catalysts in the asymmetric epoxidation of unfunctionalised olefins in 1990s.[1] Salen-Schiff base transition metal complexes have been extensively studied because of their prospective use as catalysts in a wide range of C-C and C-N bond formation reactions such as cyclopropanations, aziridination, asymmetric cycloaddition reactions, and A^3-coupling etc.[2] Among different type of reactions, C-N bond formation reactions mediated by salen-type transition metal complexes has attracted much interest in recent decade.[3] The construction of the C-N bonds of aromatic compounds is particularly important to medicinal chemists.[4] Nitrogen containing heterocyclic moiety is an integral part of several natural products and many synthetic organic compounds exhibiting interesting biological activities.[5-7] Among various heterocycles reported, tetrazoles are very important class of compounds. Tetrazoles have been used as ligands in coordination chemistry,[8] stabilizers in photographic industry,[9] linkers for selective covalent attachment of synthetic groups to biopolymers,[10] antihypertensive[11] and antiviral drugs[12] and ligating aryl thiotetrazolyl acetanilides with HIV-1 reverse transcriptase.[13]

Due to wide applications of tetrazoles and their derivatives, concerted efforts have been directed towards the development new synthetic methodologies.[14] Among them, [3+2]-cycloaddition, first reported by Hantzsch and Vagt, is the most widely used procedure to access 5-substituted 1*H*-tetrazoles from sodium azide and organic nitriles.[15] Numerous catalysts have been reported for this reaction; such as $Zn(OTf)_2$,[16] $Cu_2(OTf)_2$,[17] $Fe(OAc)_2$,[18] BF_3-OEt_2,[19] $Cu(NO_3)_2.3H_2O$,[20] $Cu(OAc)_2$,[21] $AgNO_3$,[22] Fe_3O_4@SiO_2/salen Cu(II),[23] Zn/Al hydrotalcite,[24] CoY zeolites,[25] γ-Fe_2O_3,[26] nano-ZnO/Co_3O_4,[27] nano-$CuFe_2O_4$,[28] Ni-Ferrite NPs[29], AlPO-5 microporous molecular sieves,[30] Pd-SMTU@boehmite nanoparticles,[31] and [Pd SBT@MCM41][32] etc. Majority of the methods suffers from one or more drawbacks such as long reaction time, high catalyst loading, elevated temperature, low yields, tedious workup of the reaction mixture etc.

Multi-component reactions (MCRs) are another very powerful tool in the armoury of an organic chemist for the synthesis of complex organic compounds *via* a one-pot methodology[33]. An attractive example of MCRs is the A^3-coupling reaction.[34] Propargylamines, the final product of an A^3-coupling reaction, are important intermediates for the synthesis of many nitrogen-containing natural products and potential therapeutic molecules such as l-Deprenil and PF960IN (Fig. 1).[35] Due to the versatile applications, propargylamine have been usually prepared by the nucleophillic attack of lithium acetylides and Grignard reagents on imines or their derivatives.[36] However, these methods have certain limitations such as moisture sensitivity and the requirement for stringent reaction conditions. Various homogenous[37-46] and heterogeneous[47-53] catalysts have been reported for the synthesis of propargylamines. However, recovery and recyclability of most of the homogeneous catalysts is still an issue. Therefore, there is a considerable scope for design and development of structurally well characterized, robust, and recyclable catalysts for this reaction.



l-Deprenil **PF960IN**

Fig. 1 Propargylamine moiety containing drugs

In continuation of our ongoing research interest in the synthesis, structural characterization and catalytic applications of transition

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metal complexes in organic synthesis,[54-58] we herein describe the synthesis and characterization of two new salen-type Schiff base complexes [Cu(L)].*0.5*H_2O, **1** and [Ni(L)], **2** and their application in the synthesis of 5-substituted 1*H*-tetrazoles and propargylamines.

Experimental

Materials and instrumentations

All reagents and solvents for the synthesis and analysis were purchased from Merck and Sigma Aldrich and used as received without further purifications.
FTIR spectra were recorded on a Perkin Elmer Spectrometer in the range of 400-4000 cm^{-1} using KBr pellets. Electronic absorption spectra were recorded on a Shimadzu UV-1800 Spectrophotometer in the wave length range of 200-900 nm. The Cyclic Voltammetry (CV) analysis were performed on a CHI660C electrochemical analyzer under oxygen-free conditions. The CV studies were performed on [Cu(L)].0.5H_2O complex (10^{-3} M) using 0.1 M [nBu_4N][ClO_4] as a supporting electrolyte in DMF solvent at a 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. The ^1H and ^{13}C NMR spectra of the isolated products were recorded on a Bruker AvIII HD-400 MHz spectrometer in DMSO-d_6 and $CDCl_3$ using TMS as the internal Standard. Melting points were recorded on a Yazawa micro melting point apparatus.

General synthesis of Salen-type Schiff base complexes [M(L)].*x*H_2O

The ligand H_2L was prepared by reported method.[59] A methanolic solution of ligand H_2L (0.464 g, 1.0 mmol) was added dropwise to a clear solution of $Cu(OAc)_2.H_2O$ (0.200 g, 1.0 mmol) or $Ni(OAc)_2.4H_2O$ (0.248 g, 1.0 mmol) in methanol (10 mL). The solution was stirred at room temperature for 8 h and resultant dark brown for Cu(II) and reddish brown precipitate for Ni(II) complexes, were filtered, washed with cold ethanol and dried in vacuum over anhydrous $CaCl_2$. Single crystals suitable to X-ray crystallography were grown over a period of two weeks on standing a concentrated solution of the complex in DMF.
Complex [Cu(L)].0.5H_2O ***1****:* Yields: 0.481 g, 90 %, m.p = 286 ^oC, R_f = 0.36 (EtOAc), Anal. Calc. for C_{28} H_{39} Cu N_4 $O_{2.50}$: C, 62.84; H, 7.35; N, 10.47; O, 7.47. Found: C, 62.67; H, 7.48; N, 10.23; O, 7.28. FTIR (KBr), cm^{-1}: 1584 ν (C=N), 2857-2931 ν (CH_2), 1318 ν (C=C_{ring}), 619 ν (Cu-O), 512 ν (Cu-N). UV-vis [λmax(nm)]: 346, 566.
Complex [Ni(L)] ***2****:* Yields: 0.459 g, 88 %, m.p = 330 ^oC, R_f =0.57 (EtOAc), Anal. Calc. for C_{28} H_{38} Ni N_4 O_2: C, 64.51; H, 7.35; N, 10.75. Found: C, 64.39; H, 7.24; N, 10.89. FTIR (KBr), cm^{-1}:1590 ν (C=N), 2857-2931 ν (CH_2), 1325 ν (C=C_{ring}), 523 ν (Ni-O), 442 ν (Ni-N). ^1H NMR ($CDCl_3$, 25 ^0C, 400 MHz): δ 7.03 (s, 2H, *H*-CN), δ 6.79 (d, *J* = 8 Hz, 2H, Ar *H*), 6.15 (d, *J* = 2 Hz, 2H, Ar *H*), 5.94 (m, 2H, Ar *H*), 3.24 (q, *J* = 2 Hz, 8H, -CH_2), δ 2.90 (m, 2H, cyclohexane ring), δ 2.29 (d, 2H, *J* = 6.8, cyclohexane), δ 1.78 (d, *J* = 0.8, 2H, cyclohexane ring), δ 1.20 (m, 4H, cyclohexane ring), δ 1.08 (t, 12H, *J* = 7.2 Hz, -CH_3). UV-vis [λmax(nm)]: 377, 557.

General procedure for the synthesis of 5-substituted 1*H*-tetrazoles

A mixture of nitrile (1.0 mmol), and sodium azide (0.078g, 1.2 mmol) were placed in 25-mL round-bottomed flask in DMSO (5 mL). The catalyst (0.7 mol %) was added to the reaction mixture and allowed to react at 110^{o}C for 4-6 h. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled down to room temperature and recrystallized salen Cu(II) was removed by filtration and the filtrate was treated with HCl (2N, 10ml) and then with ethyl acetate (3x10 mL). The resultant organic layer was separated, washed with water and dried over Na_2SO_4.The solvent was removed under reduced pressure to give crude product which was purified by column chromatography using petroleum ether/ethyl acetate (1:4) as an eluent. Products were characterized by ^1H and ^{13}C NMR studies.

General procedure for the synthesis of propargylamines

A mixture of aldehyde (1.0 mmol), secondary amine (1.0 mmol), alkyne (1.2 mmol) and catalyst (0.9 mol %) was stirred in a 25-mL round-bottomed flask at 80 °C for 5-8 hrs in toluene (5-mL). The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled down to room temperature and recrystallized salen Cu(II) was removed by filtration and then solvent was removed under vacuum. The crude product was washed with water and extracted with ethyl acetate (3x10 mL). It was purified by the column chromatography using silica gel and ethyl acetate: petroleum ether as an eluent. Products were characterized by ^1H NMR and ^{13}C NMR studies.

Crystallographic studies

The X-ray diffraction data were collected on a Bruker Kappa diffractometer at 203(2) K and 293 K equipped with a CCD detector, employing Mo K α radiation (λ = 0.71073 Å), with the SMART suite of programs.[60] All data were processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS.[61] Structural solution and refinement were carried out with the SHELXTL suite of programs.[62] 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. A summary of the crystallographic and refinement data of complexes are given in Table 1.

Table 1 Crystal data and refinement parameters of [Cu(L)].*0.5*H_2O and [Ni(L)] complexes

CCDC	**1576528**	**1813608**
Empirical formula	C_{28} H_{39} Cu N_4 O_{2-50}	C_{28} H_{38} N_4 Ni O_2
Formula weight	535.17	521.33
Temperature	203(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	P-1	P 2_1/n
Unit cell dimensions		
a	9.4610(11) Å	12.0046(13)Å
b	15.3673(17) Å	8.5202(9)Å
c	19.021(2) Å	26.095(2)Å
α	92.716(3)°	90°
β	93.956(3)°	92.104(9)°
γ	102.009(3)°	90°
Volume	2693.1(5) $Å^3$	2667.2(5) $Å^3$
Z	4	4
Density (calculated)	1.320 mg/m^3	1.298 mg/m^3
Absorption coefficient	0.845 mm^{-1}	0.759 mm^{-1}
F(000)	1136	1112
Crystal size	0.420 x 0.140 x 0.080 mm^3	0.1 x 0.1 x 0.1 mm^3
Theta range for data collection	1.357 to 26.173°	1.842 to 29.425°
Index ranges	-11<=h<=6,18<=k<=19,-23<=l<=23	-15<=h<=15,-7<=k<=10, -33<=l<=35
Reflections collected	20273	14110

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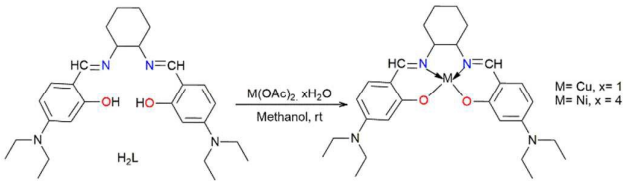
Completeness to theta = 25.242°	98.7 %	100 %
Absorption correction	None	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	10518 / 239 / 702	6171/125/368
Goodness-of-fit on F^2	0.936	1.014
Final R indices [I>2sigma(I)]	R1 = 0.0709, wR2 = 0.1363	R1 =0.0541, wR2 =0.1138
R indices (all data)	R1 = 0.1722, wR2 = 0.1721	R1 =0.1134, wR2 =0.1357
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	0.723 and -0.919 e.Å^{-3}	0.567 and -0.285 e.Å^{-3}

Results and discussion

The Salen-type Schiff base ligand 6,6'-[(1E,1'E)-(cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene)bis(3-(diethylamino)phenol)] (H_2L) was synthesized as an off-white solid in 89 % yield by the reported method.[60] The reaction of H_2L with $Cu(OAc)_2.H_2O$ and $Ni(OAc)_2.4\ H_2O$ in methanol at room temperature afforded complexes $[Cu(L)].0.5H_2O$, **1**, and [Ni(L)], **2**, as dark brown and red brown solids, respectively (Scheme1) in high yields (88-90 % yields). The complexes were air stable, insoluble in water and benzene, and soluble in other common organic solvents such as CH_2Cl_2, $CHCl_3$, CH_3CN, DMF and DMSO. The complexes were fully characterized by elemental analysis, FTIR, UV-vis and single crystal X-ray diffraction studies. In addition, paramagnetic nature of complex **1** was confirmed by EPR spectroscopy. The complex **2** was found to be diamagnetic and it was also characterized by ^{1}H NMR.



Scheme 1 Synthesis of complexes

X-ray crystallography

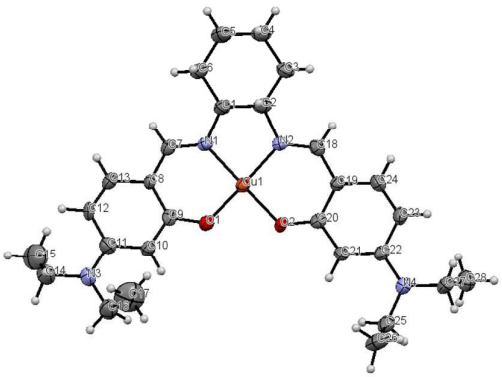
Diffraction quality crystals of complexes **1** and **2** were grown over a period of two weeks on standing a concentrated solution of the respective complex in DMF at room temperature. The structures of the complexes have been elucidated by single-crystal X-ray diffraction studies.

Structure description of complex $[Cu(L)].0.5H_2O$, 1

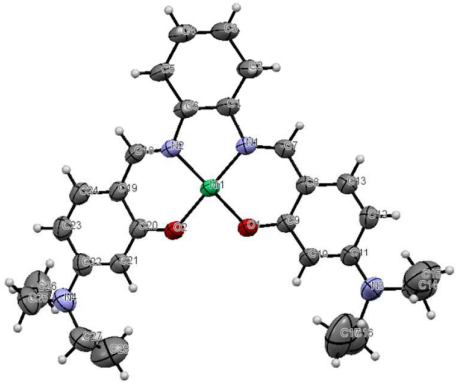
The ORTEP diagram of the complex $[Cu(L)].0.5H_2O$ along with the atom numbering scheme is depicted in Fig. 2(a). The crystal data and structural refinement parameters are summarized in Table 1 and selected bond lengths and bond angles are given in Table 1S. The central copper(II) ion adopts a distorted square planar geometry, ligated to two phenolate oxygen and two imine nitrogen of tetradentate Salen-type ligand forming one five membered and two six membered ring. In Cu(II) complex, the bond length of Cu(1)-O(1), Cu(1)-O(2), Cu(1)-N(1) and Cu(1)-N(2) are 1.903(3), 1.910(3), 1.925(4) and 1.928(4), respectively. The bond angles O(1)-Cu(1)-O(2), O(1)-Cu(1)-N(1), O(2)-Cu(1)-N(1), O(1)-Cu(1)-N(2) are 90.17(15), 93.81(18),169.75(16), 165.92(16) respectively. The bond angle and bond length are in close agreement to the other square planar Cu(II) complex.[63]

Structure description of complex [Ni(L)], 2

The ORTEP diagram of the complex [Ni(L)] along with the atom numbering scheme is depicted in Fig. 2(b). The crystal data and structural refinement parameters are summarized in Table 1 and selected bond lengths and bond angles are given in Table 1S. Molecular structure of the complex revealed that nickel atom in the complex [NiL] have distorted square planar .The ligand H_2L coordinate to Ni atom in tetradentate manner through two phenolate oxygen and two imine nitrogen forming one five membered and two six membered ring. In Ni(II) complex, Ni(1)-O(1), Ni(1)-O(2), Ni(1)-N(1) and Ni(1)-N(2) bond length are 1.840(3), 1.856(3), 1.851(4) and 1.850(3), respectively. The bond angles O(1)-Ni(1)-O(2), O(1)-Ni(1)-N(1), O(2)-Ni(1)-N(1),O(1)-Ni(1)-N(2) are 85.0(1),95.0(2), 176.5(2) and 178.0(2), respectively. The bond angle and bond length are in close agreement with the previously reported Ni(II) complexes.[63]



(a) $[Cu(L)].0.5\ H_2O$



(b) [Ni(L)]

Fig. 2 ORTEP diagram of (a) Cu(II) (Thermal ellipsoids are drawn at the 50% probability level. Water molecule have been omitted for Cu(II) complex) and, (b) Ni(II) Salen-type Schiff base complexes with the atom labelling scheme (Thermal ellipsoids are drawn at the 50% probability level.)

FTIR spectra of ligand and complexes **1** and **2** are shown in Fig. 3. The FTIR spectrum of free ligand shows characteristic bands at 3298, 2850-2923 and 1620 cm^{-1} corresponding to ν (OH), ν $(CH_2)_{cyclohexane}$ and ν (C=N) of azomethine group, respectively.[64] However the FTIR spectra of complexes **1** and **2** showed band at 1584 cm^{-1} and 1590 cm^{-1} attributed to ν (C=N), respectively. A

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comparison of the spectra of free ligand with the complexes, indicated that the ν (C=N) has been lowered by 36 cm^{-1} for Complex **1** and 30 cm^{-1} for complex 2, supporting the coordination of azomethine nitrogen atom to Cu^{2+} and Ni^{2+} metal ions.[65] The disappearance of ν OH band in the FTIR spectra of both the complexes and appearance of two additional bands 619 and 512 cm^{-1} for ν (Cu-O) and ν (Cu-N) and 523 and 442 cm^{-1} for ν (Ni-O) and ν (Ni-N) respectively, confirms the deprotonation of the -OH group and supports the coordination of phenolate oxygen atom to metal ions.

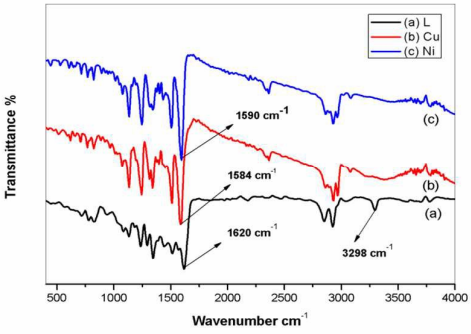


Fig. 3 FTIR spectra of (a) Ligand (b) $[Cu(L)].0.5H_2O$, **1** and (c) [Ni(L)], **2** complex

The UV-vis spectra of the ligand and complexes **1** and **2** are shown in Fig. S3. The UV-vis spectrum of the ligand shows peaks at 309 nm due to π-π^* transition localised on the aromatic rings and a low intensity band at 351 nm due to the n-π^*excitation of the lone pair on the imine nitrogen atom to the π^* orbital on the C=N fragment.[66] However, a comparison of the UV-Vis spectra of the complexes with the ligand indicated a slight shift in the position and intensity of this band at around 346 and 377 nm in complex **1** and 319 and 359 nm in complex **2** respectively. The spectra of the Cu(II) and Ni(II) complexes also shows an additional broad band at 566 and 557 nm due to d-d transitions assignable to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ respectively, suggesting the distorted square planar geometry of the complexes.[67]

The X-band EPR spectrum of the complex **1** recorded at room temperature is shown in the Fig. 4. The EPR spectrum of the powdered complex at 300 K, revealed an isotropic behaviour with broad signal having g_{iso}= 2.076 with no hyperfine structure and confirmed a distorted square planar geometry of the complex.[68]

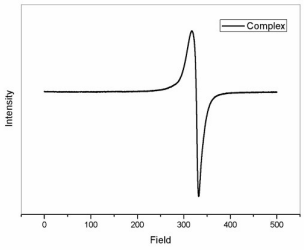
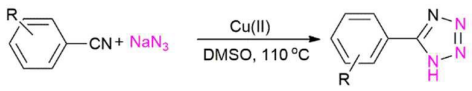


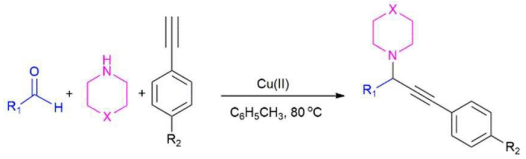
Fig. 4 EPR spectrum of $[Cu(L)].0.5H_2O$

The ^{1}H NMR spectra of ligand and complex **2** are shown in Fig. S1-S2. The ^{1}H NMR spectrum of H_2L in $CDCl_3$ showed one broad singlet at δ13.79 due to presence of O*H* proton. The azomethine proton (C*H*=N) appeared at δ7.93 as a singlet and the phenyl protons of the free ligand are observed in the range of δ6.89-6.03 as multiplets. The CH_2 and CH_3 protons of 4-(diethylamino)-2-hydroxybenzaldehyde moiety in the free ligand appeared as quartet and triplet at δ3.32 and δ1.14, respectively. The -C*H* resonance of the cyclohexane ring are recorded as multiplets at δ3.14. The methylene resonances (-CH_2) of the cyclohexane ring were observed in the range of δ1.94-1.42 as multiplets. A comparision of the ^{1}H NMR spectrum of complex **2** with the free ligand indicated upfield shift of the azomethine proton (C*H*=N) at δ7.03 from δ7.93. The CH_2 and CH_3 protons of 4-(diethylamino)-2-hydroxybenzaldehyde moiety in the complex **2** appeared as quartet and triplet at δ3.24 and δ1.08, respectively. The -C*H* protons of cyclohexane ring is shifted to upfield at δ2.90 and the methylene resonances (-CH_2) of cyclohexane ring appeared in the range δ 1.78-1.06 in the spectrum of complex **2.** The disappearance of -O*H* proton signal in ^{1}H NMR spectrum of complex **2** confirms the deprotonation of -OH group.[67]

The catalytic activity of complexes **1** and **2** were screened for the synthesis of 5-substituted 1*H*-tetrazoles and propargylamines (Scheme 2-3). Initially the catalytic studies were performed for synthesis of tetrazoles choosing benzonitrile and sodium azide as a model substrates. Various parameters such as catalyst loading, solvent, temperature and time were studied and optimized. The results are summarised in Table 2. When the reaction was carried out in absence of catalyst in DMSO at 110 °C, no product was obtained even after 24 h (Table 2, entry 1). However, in presence of 0.4 mol % complex **1**, 40 % yield of the product was obtained in 9h (Table 2, entry 2). Increasing catalyst loading to 0.7 mol %, resulted in 96 % yield of the desired product in 4 h at 110 °C (Table 2, entry 3). However further increase in catalyst loading to 1 mol % did not improve the yield of the product (Table 2, entry 4). Therefore, 0.7 mol % of the catalyst loading was found to be optimum (Table 2, entry 3). In order to find the best solvent, reaction was carried out in different solvents such as CH_3CN, $C_6H_5CH_3$, DMF and DMSO (Table 2). Among all the solvents used DMSO was found to be the best solvent (Table 2, entry 3). The reaction was also carried out at different temperatures, i.e. at 90, 110, 120, 140 °C (Table 2, entries 9-11). The best yield of the product was obtained at 110 °C (Table 2, entry 3). Further, the effect of time was also investigated (Table 2) and the best yield was obtained in 4 h (Table 2, entries 3, 12). The reaction was also performed with complex **2** under optimized conditions. Although the product was formed but in low yield (30 %) as compared to the complex **1** which may be due to the weaker interaction of Ni ion with nitrile than Cu ion (Table 2, entry 5). The best results were obtained with 0.7 mol % catalyst loading of complex **1**, at 110 °C in DMSO in 4 h (Table 2, entry 3).



Scheme 2 Synthesis of 5-substituted 1*H*-tetrazoles



Scheme 3 Synthesis of propargylamines

Table 2 Optimization of reaction conditions for Synthesis of 5-substituted 1*H*-tetrazoles[a]

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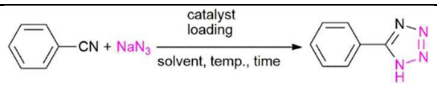
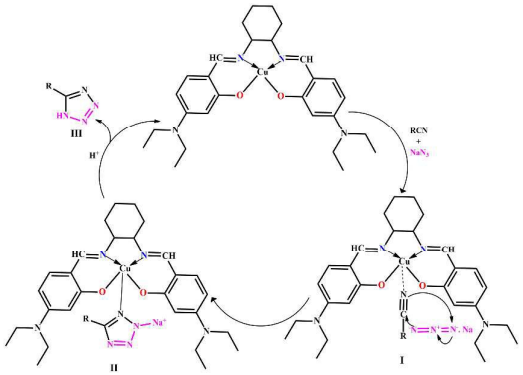


Entry	Catalyst	Catalyst loading (mol %)	Solvent	Temperature (°C)	Time (h)	Yield[b] (%)
1	-	-	DMSO	110	24	-
2	Cu(II)	0.4	DMSO	110	9	40
3	Cu(II)	0.7	DMSO	110	4	96
4	Cu(II)	1	DMSO	110	4	96
5	Ni(II)	0.7	DMSO	110	4	30
6	Cu(II)	0.7	DMF	110	4	70
7	Cu(II)	0.7	CH_3CN	80	4	30
8	Cu(II)	0.7	$C_6H_5CH_3$	110	5	35
9	Cu(II)	0.7	DMSO	90	12	75
10	Cu(II)	0.7	DMSO	120	4	96
11	Cu(II)	0.7	DMSO	140	4	96
12	Cu(II)	0.7	DMSO	110	8	96

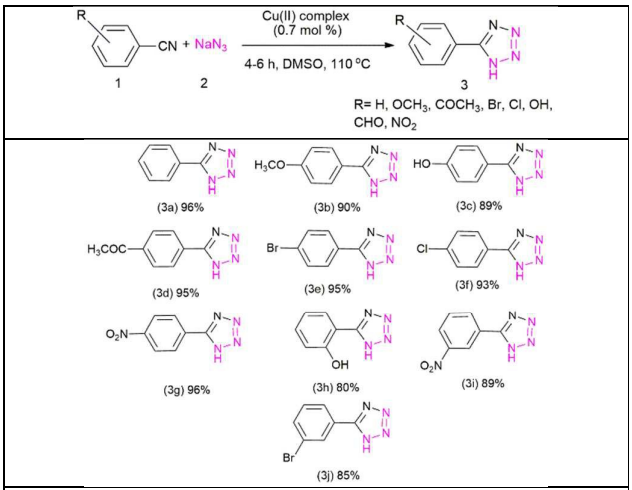
[a]Reaction conditions: Benzonitrile (1.0 mmol), NaN_3 (1.2mmol).
[b]Isolated yield.

With the optimized reaction conditions in hand, the scope of the reaction was extended to a variety of substituted nitriles with sodium azide. Aromatic nitriles bearing electron withdrawing group such as -$COCH_3$, -Br, -Cl, and -NO_2 results in higher yield (Table 3, entries 3d-g, i-j) while nitriles bearing electron donating groups such as -OCH_3 and -OH results in lower yield as compared to nitriles bearing electron withdrawing groups (Table 3, entry 3b-c,h). This is due to faster cycloaddition reaction of aromatic nitriles with electron withdrawing substituents rather than the reaction of aromatic nitrile compound with electron donating as the presence of electron withdrawing group, increases the polarity of the cyanide group (-I effect), favouring the reaction.[69] However, substituents at para and meta position resulted in excellent yield (Table 3, entries 3c,i,j) as compared to ortho substituent's due to steric hindrance (Table 3, entries 3h).The isolated products were fully characterized by ^{1}H and ^{13}C NMR (Figure S9-S17). A plausible mechanism for the reaction, based on previous reports,[20,69] is suggested in Scheme 4. The proposed mechanism entails coordination of nitrogen atom of the nitrile group to Cu(II) as the initial step to form complex **I**. The complex **I** serves as an ideal template for the [3+2]-cycloaddition reaction between activated nitrile an azide. Interestingly, the cycloaddition reaction in absence of the catalyst, did not proceed even after prolong refluxing time at 110 °C (Table 3, entry 1). This clearly indicates the role of Cu^{2+} as a Lewis acid in the activation of the nitrile. After [3+2]-cycloaddition between the C≡N bond of nitrile and azide, a five-membered heterocyclic ring was formed (**II**). Protonolysis of the intermediate **II** by 2 N HCl yielded the 5-substituted 1*H*-tetrazole **III**. In order to ascertain the efficiency of the new catalysts, a comparison was made with some previously reported catalysts [21-23] (Table 4). The results indicate that the complex **1** exhibited better catalytic activity as compared to other reported catalyst. The complex **1** afforded products at low catalyst loadings, in short reaction time, and high yields. Easy synthesis, stability and recyclability of the homogenous catalyst are some of the additional characteristics of the complex 1 that makes it a better catalyst as compared to the reported catalysts.



Scheme 4 A plausible reaction mechanism for the 5-substituted 1*H*-tetrazole

Table 3 The reaction of various benzonitrile with sodium azide under optimized reaction conditions[a,b]



[a]Reaction conditions: Benzonitrile (1.0 mmol), NaN_3 (1.2mmol).
[b]Isolated Yield

Table 4 A comparison study of synthesized [Cu(L)].0.5H_2O complex with some of the previous reported catalysts for 5-substituted 1*H*-tetrazoles

Entry	Catalyst	Catalyst loading (mol%)	Temp. (°C)	Time (h)	Yields (%)	Reference
1	$AgNO_3$	10	120	5-5.5	87	22
2	$Cu(OAc)_2$	20	120	12	96	21
3	Salen complex of Cu(II)	0.4	120	6-12	92	23
4	[Cu(L)].0.5H_2O	0.7	110	4-6	96	This work

To enhance the scope of our studies, [Cu(L)].*0.5*H_2O, **1,** was also tested for the synthesis of propargylamines. Initially benzaldehyde, piperdine and phenylacetylene were chosen as model substrates. The results are summarized in Table 5. When the reaction was carried out in the absence of the catalyst in toluene at 80 °C for 24 h, no product was obtained (Table 5, entry 1). However in presence of 0.5 mol % of Cu(II) complex, 35% yield of desired product was obtained (Table 5, entry 2) in 9h. Further catalyst loading was increased to 0.7 mol % and 0.9 mol % resulted in 85 % and 93 % yield of the product respectively, in 7 h in toluene (Table 5, entries 3-4). However no significant improvement in yield was observed on increasing catalyst loading to 1 mol % (Table 5, entry 5). Thus 0.9 mol % of catalyst

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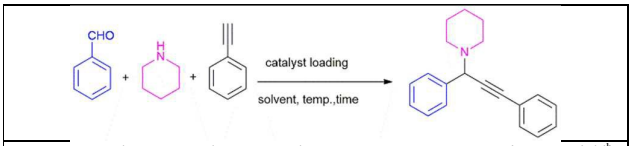
loading was found to be optimum (Table 5, entry 4). The effect of solvents was investigated in presence of the optimized catalyst (Table 5, entries 4-8). The best result was obtained in toluene (Table 5, entry 4). When, the reaction was carried out without solvent, 50 % yield of the desirable product was obtained in 7h (Table 5, entry 9).To investigate the effect of temperature, the reaction was performed at RT, 50 °C, 80 °C and 100 °C (Table 5, entries10-12) and the best result was obtained at 80 °C (Table 5, entry 4). Additionally, the effect of time was also investigated, maximum yield obtained in 7h (Table 5, entry 4). The reaction was also carried out using 0.9 mol % of complex **2** as catalyst, resulted in low yield as compared to Cu(II) complex (Table 5, entry 13). The reason for this is may be due to the fact that Cu ions can form stronger complexes with acetylenes than nickel.[47] Thus, the best yield (93%) was achieved in the presence of 0.9 mol% of Cu(II) catalyst in $C_6H_5CH_3$ solvent at 80 °C in 7 h (Table 5, entry 4).

Table 5 Optimization of reaction conditions for Synthesis of propargylamines[a]



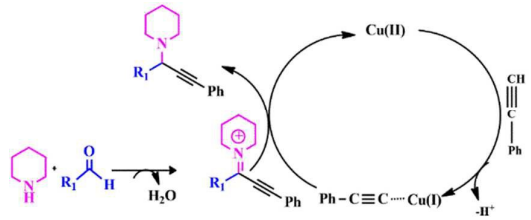
Entry	Catalyst	Catalyst loading (mol %)	Solvent	Temperature (°C)	Time (h)	Yield[b] (%)
1	-	-	$C_6H_5CH_3$	80	24	-
2	Cu(II)	0.5	$C_6H_5CH_3$	80	9	35
3	Cu(II)	0.7	$C_6H_5CH_3$	80	7	85
4	Cu(II)	0.9	$C_6H_5CH_3$	80	7	93
5	Cu(II)	1	$C_6H_5CH_3$	80	7	93
6	Cu(II)	0.9	DMF	80	7	50
7	Cu(II)	0.9	C_2H_5OH	80	7	55
8	Cu(II)	0.9	CH_3CN	80	7	80
9	Cu(II)	0.9	-	80	7	50
10	Cu(II)	0.9	$C_6H_5CH_3$	100	7	90
11	Cu(II)	0.9	$C_6H_5CH_3$	50	8	75
12	Cu(II)	0.9	$C_6H_5CH_3$	RT	10	30
13	Ni(II)	0.9	$C_6H_5CH_3$	80	7	25
14	Cu(II)	0.9	$C_6H_5CH_3$	80	10	93
15	Cu(II)	0.9	$C_6H_5CH_3$	80	8	93

[a]Reaction conditions: Aldehyde 1 (1mmol), Amine 2 (1mmol), Alkyne 3 (1.2 mmol)
[b]Isolated yield

The scope and applicability of the catalyst was examined to various aldehyde, amines and alkynes under optimized conditions. Aryl aldehyde with electron withdrawing groups such as -Br, -Cl, -CHO and $-NO_2$, (Table 6, entries 4d-h) afforded high yields as compared to electron donating groups such $-CH_3$ and -OH (Table 6, entries 4c,j). Aliphatic aldehyde such as formaldehyde also resulted in good yield (Table 6, entry 4m). The reaction with secondary cyclic amines, i.e. piperdine and morpholine also proceeded well to afford the corresponding propargylamine in good yields (Table 6, entries 4a-m) under optimized conditions. Attempts to isolate products with aromatic amines, such as aniline and benzyl amine, were unsuccessful presumably due to the low nucleophilicity of the aromatic amines. Interestingly, 2-thiophenecarbaxaldehyde also reacted well to afford the corresponding propargylamine in 85 % yields (Table 6, entry 4i). Reactions using substituted and unsubstituted alkynes also afforded corresponding products in high yields (Table 6, entries 4a-m). The isolated products were fully characterized by ^1H and ^{13}C NMR (Figure S18-S30).

Further, the change of oxidation state was confirmed by Cyclic Voltammetry (CV). The CV studies were performed on [Cu(L)].0.5H_2O complex (10^{-3} M) using 0.1 M [nBu_4N][ClO_4] as a supporting electrolyte in DMF solvent at a scan rate of 100 mV S^{-1} (Fig. S7). The CV plot showed one quasi-reversible peak at $E_{1/2}$ = 0.46 V vs. SCE ($E_{p/a}$ = 0.51 V, $E_{p/c}$ = 0.41 V vs. SCE) corresponding to the Cu^{II}/Cu^{I} redox couple, supporting the formation of a Cu(I) intermediate during the catalytic reaction.[70] The irreversible peak at $E_{1/2}$ = -1.39 V vs. SCE ($E_{p/a}$= -1.33 V, $E_{p/c}$= -1.45 V vs. SCE) is due to ligand based reduction and one irreversible anodic peak at potential 0.74 V vs. SCE is due to ligand based oxidation.[59]

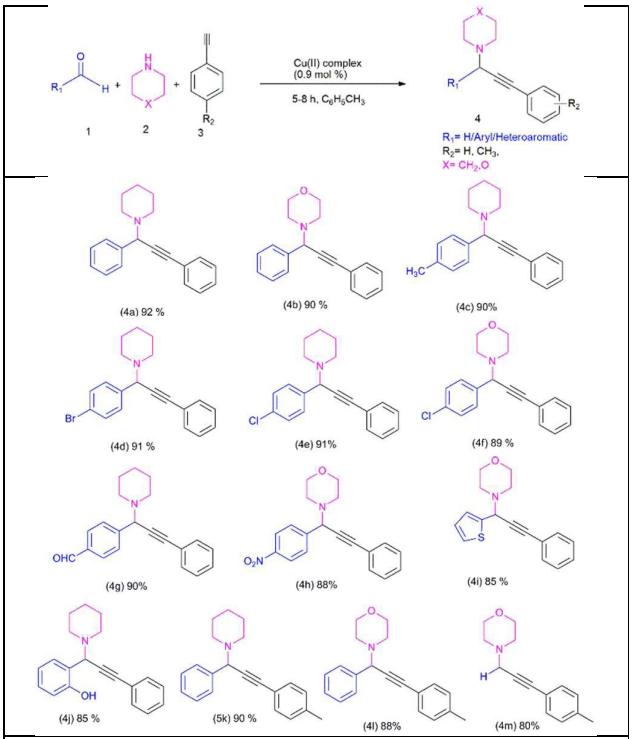
A plausible mechanism for reaction, based on previous reports [47,48] is suggested in Scheme 5. The A^3-coupling reaction proceeds by the activation of C-H bond of the terminal alkyne by the Cu(II) complex. The copper-acetylide intermediate then reacted to the iminium ion prepared in situ from the aldehyde and the amine to afford the corresponding propargylamine.



Scheme 5 A plausible reaction mechanism for the propargylamines

A comparison was also made with some of the previous reported catalysts for A^3-coupling reactions. The results indicate that the complex **1** exhibited better catalytic activity as compared to some of other reported catalyst in terms of catalyst loading, temperature and time etc. (Table 7).[37-39,47]

Table 6 Synthesis of propargylamines from aldehydes, amines and alkynes[a,b]



[a]Reaction conditions: Aldehyde 1 (1mmol), Amine 2 (1mmol), Alkyne 3 (1.2 mmol)
[b]Isolated Yield

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Table 7 A comparison study of synthesized [Cu(L)].0.5H_2O complex with some of the previous reported catalysts for A^3-coupling reactions

Entry	Catalyst	Catalyst loading (mol %)	Temp. (°C)	Time (h)	Yields (%)	Reference
1	CuI	2	120	5	78	37
2	Gold(III) salen	0.05	40	24	94	38(a)
3	[Au(C^N)Cl_2]	1	40	24	82	39
4	Cu(II) salen complex	3	80	2.5	95	47
5	[Cu(L)].0.5H_2O	0.9	80	5-8	93	This work

Reusability of catalyst

Recovery and reusability of the catalyst were studied for both the reactions under the optimized condition. A reaction of benzonitrile and sodium azide in DMSO and benzaldehyde, piperdine and phenylacetylene in $C_6H_5CH_3$ was chosen as a model reaction. After completion of the reaction, it was cooled down to room temperature in open atmosphere and allowed to stand overnight. During this period, the complex crystallized from the reaction mixture which can be easily separated by simple filtration. The complex, after washing with water and methanol, was dried and reused up to four time to afford good yields of the product. A marginal decrease in the catalytic activity of the complex **1** was observed from the first to forth cycle (Fig. S4). The identity of the recovered catalyst was confirmed by comparing its R_f value, melting point, FTIR (Fig. S5-S6) and cyclic voltammetry (Fig. S7) with the original complex.

Conclusions

In conclusion, two new salen-type Schiff-base complexes [Cu(L)].0.5H_2O **1** and [Ni(L)], **2**, have been synthesized and characterized by various spectroscopic techniques and structure of the complexes confirmed by single crystal X-ray structure determination. The catalytic application of Cu(II) complex has been demonstrated in the synthesis of 5-substituted 1*H*-tetrazoles (10 reactions) and A^3-coupling reactions (13 reactions). The reactions proceeded smoothly at a low catalyst loading and the catalyst can be recycled up to four times in both the reactions. The complex 2 was not found to be a good catalyst for these reactions as low yields of products were obtained with this complex.

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Supporting Information

CCDC 1576528 and **1813608** contain 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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The synthesis of two new salen-type Schiff base complexes of the type [Cu(L)].*0.5*H_2O, **1**, and [Ni(L)], **2**, and their application in the synthesis of 5-substituted 1*H*-tetrazoles and propargylamines are described. The complex **1** is novel in the sense that, being a homogeneous catalyst, it can be recovered almost quantitatively in both reactions by filtration and recycled up to four times to afford good yields of the corresponding products.