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# Solvent-Dependent Oxime–Azide and Oxime–Nitrile Coupling: Crystallographic and Catalytic Studies

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This study describes the solvent-dependent conversion of an oxime under identical reaction conditions ( $[\text{Cu}(\text{bipy})\text{Cl}_2]/\text{NaN}_3/5\text{-Br-H}_2\text{salox}/\text{TEA} = 1:2:1:2$  molar ratio;  $\text{bipy} = 2,2'$ -bipyridyl,  $5\text{-Br-H}_2\text{salox} = 5\text{-bromosalicylaldoxime}$ ,  $\text{TEA} = \text{triethylamine}$ ), but in different solvents. In  $\text{DMSO}/\text{CH}_2\text{Cl}_2$  (2:1 v/v) only tetrazole is formed, whereas iminoacylation in MeCN and simple complexation takes place in MeOH. The formed tetrazole and iminoacylated ligands further undergo complexation with metal ions, as evidenced from single-crystal X-ray diffraction studies and ESI-

MS analyses. Mechanistic models have been proposed in which coordination-assisted bonding of sodium azide across the  $-\text{C}=\text{N}-\text{OH}$  double bond occurs to form a tetrazole and oxime–MeCN coupling forms an iminoacylated ligand. The former is a catalytic reaction, as evidenced from a turnover number of approximately 50, whereas the latter is stoichiometric in nature. This is the first report to demonstrate the dependence of solvent polarity on oxime transformation reactions through structural elucidation.

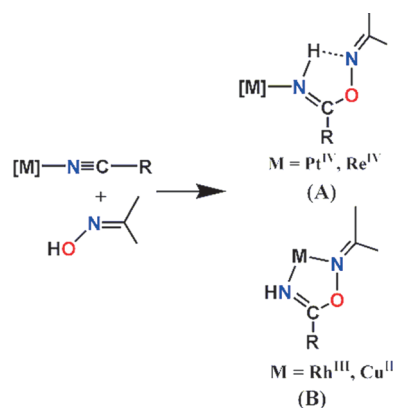
## Introduction

Tetrazoles are popular N-heterocycles<sup>[1]</sup> with potential applications in pharmaceuticals as lipophilic spacers<sup>[2]</sup> and carboxylic acid surrogates,<sup>[3]</sup> in special explosives, in photography,<sup>[4]</sup> in information storage technology,<sup>[5]</sup> and finally as precursors for a variety of N-heterocycles.<sup>[6]</sup> The formal [2+3] cycloaddition of azides and nitriles are the most popular synthetic route to form tetrazoles. However, evidence in the literature indicates that the mechanism of the reaction is different for different azide species. When an organic azide is used as the dipole, it reacts only with highly activated nitriles as dipolarophiles<sup>[7]</sup> to give 1-alkylated tetrazole.<sup>[8]</sup>

Although the nitrile–azide click reaction does not occur only with heat, the copper catalyst is used to promote the electrocyclicization of the intermediate alkynyl azide,<sup>[9]</sup> but the importance of the copper(I/II)–azide interaction has been relatively understated.<sup>[10,11]</sup> Interestingly, there are very few reports in which the conversion of oxime derivatives into tetrazoles are discussed.<sup>[12]</sup> Tetrazole formation from oxime occurs in a step-wise fashion in which dehydration of aldoximes afford nitriles ( $\text{RCH}=\text{NOH} \rightarrow \text{R}-\text{C}\equiv\text{N} + \text{H}_2\text{O}$ ), which then react with an azide to give the tetrazole.<sup>[12,13]</sup> Recently, the effects of different solvents and reaction temperature on nitrile–azide coupling reactions have been investigated and DMSO was found to be the

best solvent for such transformations, giving high yields.<sup>[12–14]</sup> Hence, replacement of nitriles by oximes and investigating the influence of the nature of the solvent on its direct conversion to tetrazoles are the two motives that prompted us to perform this study.

On the other hand, the reactions of aldoximes or ketoximes as nucleophiles towards electrophilically activated ligands containing double and triple bonds are limited, but have been known for some time.<sup>[15,16]</sup> This intriguing addition of oxime species to coordinated organonitriles in platinum(IV) and rhenium(IV) complexes results in stable monodentate iminoacylated ligands (Scheme 1 A) that simultaneously coordinate to the metal center<sup>[17–20]</sup> (Scheme 1 B). So far, these reactions were favored by the coordinatively activated organonitriles. Another interesting feature of phenolate oximes is that they can simply

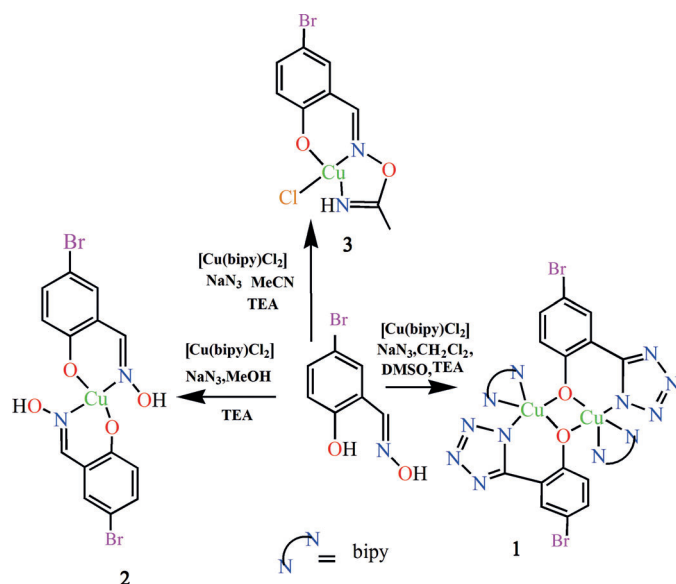


**Scheme 1.** Addition of oxime species to coordinated organonitriles in platinum(IV) and rhenium(IV) complexes to give stable monodentate iminoacylated ligands (A) that simultaneously coordinate to the metal center (B).

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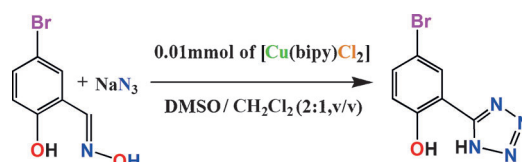
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**Scheme 2.** A schematic representation of the strategies for the formation of complexes 1–3. TEA = triethylamine.

coordinate to a metal center such as  $\text{Cu}^{\text{II}}$  to give a pseudo-macrocyclic monomer complex.<sup>[21]</sup>

Herein, we report the solvent-dependent conversion of oxime in the presence of  $[\text{Cu}(\text{bipy})\text{Cl}_2]$  (bipy = 2,2'-bipyridyl), thereby forming three different complexes, 1, 2, and 3, in three different solvents (Scheme 2). These complexes have been characterized by single-crystal X-ray diffraction techniques. The conversion of oxime to tetrazole can be catalyzed by  $[\text{Cu}(\text{bipy})\text{Cl}_2]$ ; this occurs only in a  $\text{DMSO}/\text{CH}_2\text{Cl}_2$  (2:1 v/v) solvent system. On the other hand, in MeCN, iminoacylation and concomitant coordination to the metal center occurs in a concerted way, whereas in MeOH simple coordination to the metal center occurs. We have also examined the catalytic effi-



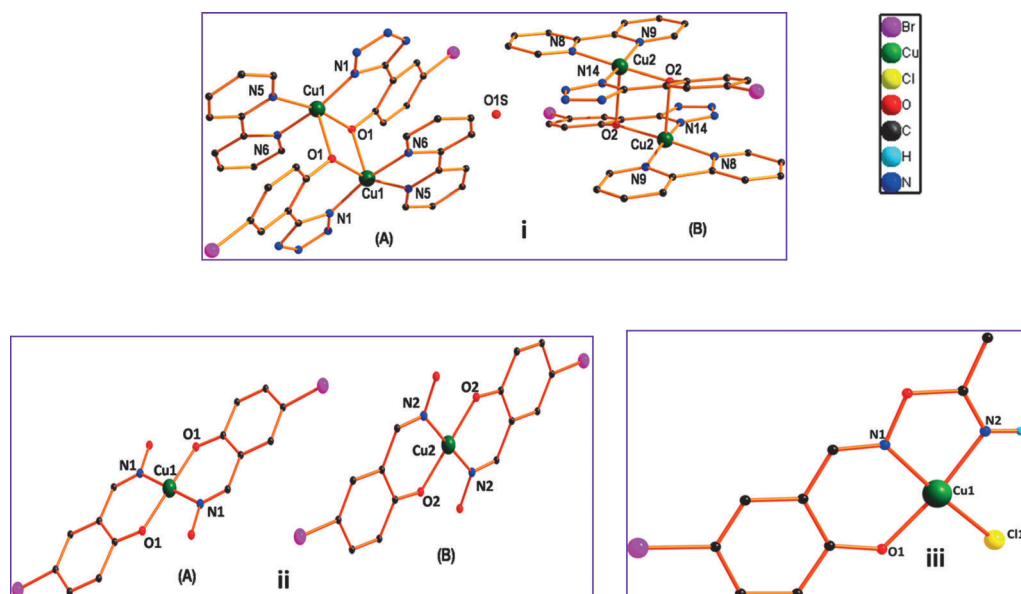
**Scheme 3.** A catalytic conversion of oxime ligand to tetrazole.

ciency of this transformation (Scheme 3) through quantification and analysis of the products by HRMS and  $^1\text{H}$  NMR spectroscopy studies.

## Results and Discussion

### Structural description of 1–3

Dimeric  $\text{Cu}^{\text{II}}$  complex 1 was prepared by a one-pot transformation of oxime in the presence of  $[\text{Cu}(\text{bipy})\text{Cl}_2]$  as a catalyst to give a tetrazole, which subsequently coordinates to the metal center to give phenoxo-bridged dimeric complex 1 under stoichiometric reaction conditions. Single-crystal X-ray diffraction studies show that complex 1 crystallizes in the triclinic system with space group  $\bar{P}1$ . Both  $\text{Cu}^{\text{II}}$  atoms are penta-coordinated; each is coordinated by N1 and O1 atoms of 5-bromo-2-(tetrazolato-5-yl)phenolate, ligand  $\text{L}^{2-}$ , and atoms N5 and N6 from a neutral bipyridyl ligand to form the equatorial plane (Figure 1 i), while the sole axial position is occupied by the bridging phenoxo oxygen atom (O1; symmetry code:  $a = x, y, z$ ;  $b = x, -y, -z$ ). In the unit cell, there are two crystallographically independent dimeric units A and B and one molecule of water of crystallization (Figure S1 in the Supporting Information). Both units are isostructural, but with small differences in bond



**Figure 1.** Coordination environment of a) 1, b) 2, and c) 3. All hydrogen (except N–H) atoms are omitted for clarity.

| Table 1. Selected bond lengths and angles of complex 1. |          |                            |            |
|---|----------|----------------------------|------------|
| Bond lengths [Å]  |          | Bond angles [°]            |            |
| <b>unit A</b>   |          |                            |            |
| Cu1–O1  | 2.325(3) | O1–Cu1–N1                  | 99.67(12)  |
| Cu1–N5  | 2.020(4) | O2 <sup>[b]</sup> –Cu2–N9  | 89.58(12)  |
| Cu1–N6  | 2.007(3) | Cu1–O1–Cu1 <sup>[a]</sup>  | 93.89(10)  |
| Cu1–N1  | 1.951(3) | O1–Cu1–N5                  | 88.68(12)  |
| Cu1–O1 <sup>[a]</sup>                                   | 1.923(3) | O1–Cu1–N6                  | 95.56(12)  |
|   |          | O1–Cu1–N6                  | 95.56(12)  |
|   |          | O1–Cu1–O1 <sup>[a]</sup>   | 86.11(10)  |
|   |          | N1–Cu1–N5                  | 102.89(15) |
|   |          | N1–Cu1–N6                  | 164.43(15) |
|   |          | O1 <sup>[a]</sup> –Cu1–N1  | 88.74(13)  |
|   |          | N5–Cu1–N6                  | 80.60(14)  |
|   |          | O1 <sup>[a]</sup> –Cu1–N5  | 167.92(13) |
|   |          | O1 <sup>[a]</sup> –Cu1–N6  | 89.05(13)  |
| <b>unit B</b>   |          |                            |            |
| Cu2–O2  | 2.437(3) | O2–Cu2–N14                 | 98.96(11)  |
| Cu2–N14   | 1.954(4) | O2–Cu2–O2b                 | 86.29(10)  |
| Cu2–O2 <sup>[b]</sup>                                   | 1.924(3) | N8–Cu2–N9                  | 80.79(14)  |
| Cu2–N8  | 2.024(3) | N8–Cu2–N14                 | 101.36(14) |
| Cu2–N9  | 1.999(4) | O2 <sup>[b]</sup> –Cu2–N8  | 169.48(13) |
|   |          | O2–Cu2–N8                  | 89.77(11)  |
|   |          | Cu2–O2–Cu2 <sup>[b]</sup>  | 93.71(10)  |
|   |          | N9–Cu2–N14                 | 168.93(14) |
|   |          | O2–Cu2–N9                  | 91.88(11)  |
|   |          | O2 <sup>[b]</sup> –Cu2–N14 | 88.90(12)  |

[a] 1–x, 2–y, 1–z. [b] 1–x, 1–y, 2–z.

lengths and angles (Table 1). In unit **A**, Cu–O/N bond lengths fall in the range 1.931–2.232 Å and Cu···Cu distances of 3.112 Å; in unit **B**, Cu–O/N bond lengths fall in the range 1.926–2.428 Å and Cu···Cu distances of 3.20 Å. The hydrogen-bonding interactions in complex **1** are given in Figure S2a in the Supporting Information.

The reaction between [Cu(bipy)Cl<sub>2</sub>] and 5-Br-H<sub>2</sub>salox in the presence of NaN<sub>3</sub> in MeOH and TEA as a base does not lead to the formation of tetrazole, but rather to the formation of complex **2**, which takes place in quantitative yield. Single-crystal X-ray diffraction studies reveal that complex **2** (Figure 1 ii) crystallizes in the triclinic space group  $\bar{P}1$ . The Cu<sup>II</sup> atom is tetra-coordinated with two bidentate NO donor ligands, namely, through N1 and O1, and their symmetry-related counter atoms in a square-planar geometry. In the unit cell, there are also two crystallographically independent asymmetric units **A** and **B** with some differences in bond lengths and angles (Table 2). In the asymmetric units, both monomers are intramolecularly hydrogen bonded through the phenolate oxygen and oxime proton (–C=NOH) to form a pseudo-macrocyclic framework (Figure S2b in the Supporting Information).

Complex **3** is a mononuclear Cu<sup>II</sup> species (Figure 1), which crystallizes in the triclinic space group  $\bar{P}1$ . The Cu<sup>II</sup> atom here is also tetra-coordinated with one tridentate iminoacylated ligand through N1, O1, and N2 and one chloride ion (Cl1) to give a square-planar geometry. Important bond lengths and angles are listed in Table 3. The hydrogen-bonding interactions of complex **3** are given in Figure S2c in the Supporting Information.

| Table 2. Selected bond lengths and angles of complex 2. |          |  |           |
|---|----------|--|-----------|
| Bond lengths [Å]  |          | Bond angles [°]                          |           |
| <b>unit A</b>   |          |  |           |
| Cu1–N1  | 1.931(4) | O1–Cu1–N1                                | 91.69(14) |
| Cu1–O1  | 1.903(3) | O1–Cu1–O1 <sup>[a]</sup>                 | 91.87(14) |
| Cu1–N1 <sup>[a]</sup>                                   | 1.931(4) | O1–Cu1–N1 <sup>[a]</sup>                 | 180.00    |
| Cu1–O1 <sup>[a]</sup>                                   | 1.903(3) | O1i–Cu1–N1                               | 88.31(14) |
|   |          | N1–Cu1–N1 <sup>[a]</sup>                 | 88.31(14) |
| <b>unit B</b>   |          |  |           |
| Cu2–O3  | 1.895(3) | O3–Cu2–N2                                | 180.00    |
| Cu2–N2  | 1.935(4) | O3 <sup>[b]</sup> –Cu2–N2                | 88.14(14) |
| Cu2–O3 <sup>[b]</sup>                                   | 1.895(3) | O3 <sup>[b]</sup> –Cu2–N2 <sup>[b]</sup> | 91.87(14) |
| Cu2–N2 <sup>[b]</sup>                                   | 1.935(4) |  |           |

[a] 2–x, 1–y, –z. [b] 1–x, 2–y, 1–z.

| Table 3. Selected bond lengths and angles of complex 3. |            |                 |            |
|---|------------|-----------------|------------|
| Bond lengths [Å]  |            | Bond angles [°] |            |
| Cu1–Cl1   | 2.2242(17) | Cl1–Cu1–O1      | 94.36(13)  |
| Cu1–O1  | 1.902(4)   | Cl1–Cu1–O2      | 148.37(11) |
| Cu1–O2  | 2.846(4)   | Cl1–Cu1–N1      | 168.50(18) |
| Cu1–N1  | 1.936(5)   | Cl1–Cu1–N2      | 98.03(17)  |
| Cu1–N2  | 1.939(5)   | O1–Cu1–O2       | 116.37(15) |
|   |            | O1–Cu1–N1       | 89.72(19)  |
|   |            | O1–Cu1–N2       | 166.9(2)   |
|   |            | O2–Cu1–N1       | 126.80(17) |
|   |            | O2–Cu1–N2       | 52.12(18)  |
|   |            | N1–Cu1–N2       | 78.9(2)    |

### Catalytic studies and mechanistic details

During a systematic investigation of ternary ([Cu<sup>II</sup>(bipy)Cl<sub>2</sub>], 5-Br-H<sub>2</sub>salox + N<sub>3</sub><sup>–</sup>) reactions, we examined the influence of solvent polarity on the chemical and structural identity of the products. Scheme 2 displays the various combinations of solvents and products thus obtained in each case.

An initial attempt involved the reaction between equimolar quantities of [Cu(bipy)<sub>2</sub>Cl<sub>2</sub>] and 5-Br-H<sub>2</sub>salox in the presence of two equivalents of NaN<sub>3</sub> and TEA in DMSO/CH<sub>2</sub>Cl<sub>2</sub> (2:1 v/v); this resulted in a light-green reaction solution that finally yielded **1**. The structure of **1** was confirmed by single-crystal X-ray diffraction studies and also by ESI-MS<sup>+</sup> analysis (Figure S6 in the Supporting Information). The molecular structure of **1** (Figure 1) reveals the presence of a deprotonated 4-bromo-2-(1*H*-tetrazol-5-yl)phenol in the form of a Cu<sup>II</sup> complex.

In another set of reactions, the catalytic behavior of [Cu(bipy)Cl<sub>2</sub>] was explored under the following reaction conditions: [Cu(bipy)Cl<sub>2</sub>] (0.01 mmol), 5-Br-H<sub>2</sub>salox (1 mmol), and NaN<sub>3</sub> (2 mmol) in DMSO/CH<sub>2</sub>Cl<sub>2</sub> (10 mL; 2:1 v/v) at approximately 70 °C for 20 h. The product thereby formed was extracted with diethyl ether, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and finally the solvent was removed to give the solid product, which was characterized by HRMS (positive mode) and <sup>1</sup>H NMR spectroscopy (Figure 2); these results clearly demonstrated the formation of tetrazole as the sole product. Within this time, the turnover number (TON) was calculated to be 38 with approximately 100% selectivity. It was also noted that, when this reaction

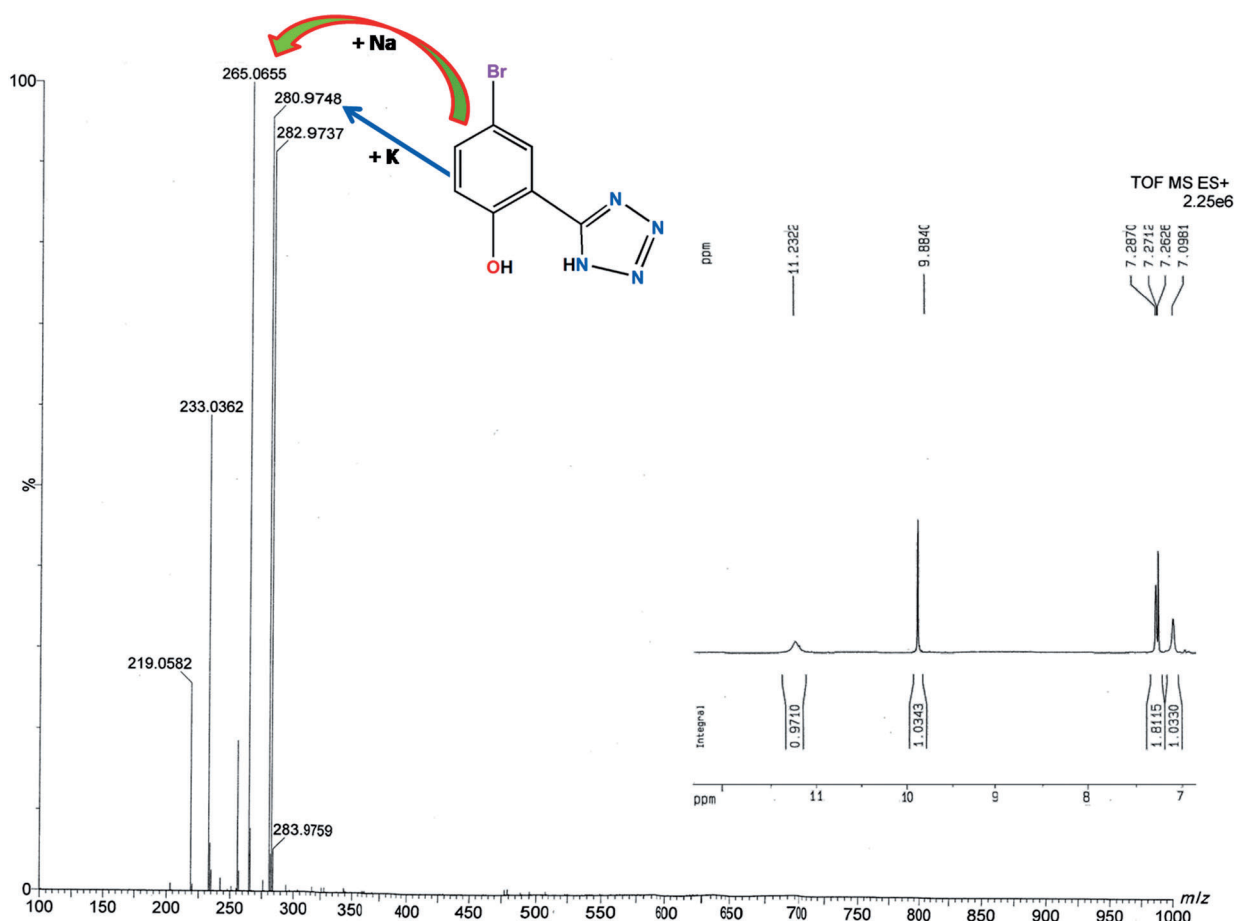


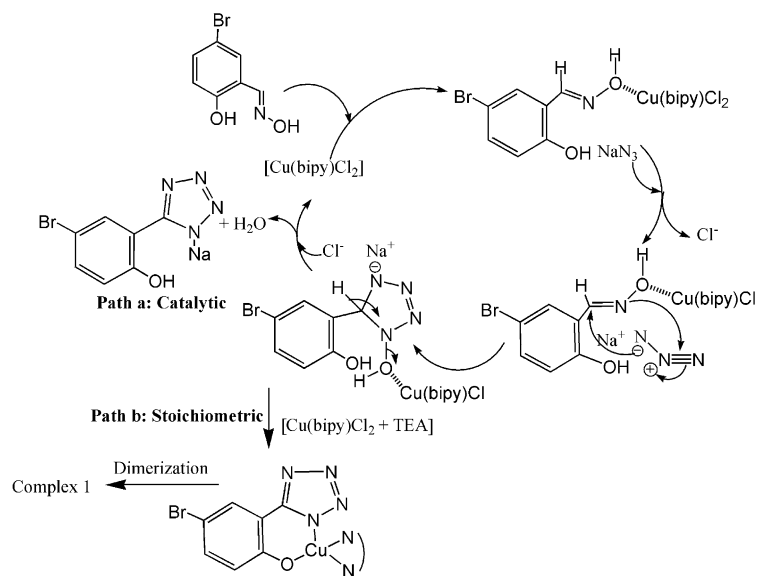
Figure 2. ESI-MS (positive) spectrum of the catalytic reaction product (tetrazole ligand) and the corresponding  $^1\text{H}$  NMR spectrum (inset).

was performed without external base (TEA), the conversion increased and led to a TON of approximately 50.

It was further noted that the yield of tetrazole was lower when the reaction was performed at room temperature; this may be due to trapping of the catalyst as complex 1, which may be unstable at high temperature and favor the catalytic cycles proceeding.

A tentative mechanism for the catalytic transformation of oxime to tetrazole by coupling with  $\text{N}_3^-$  in the presence of  $[\text{Cu}(\text{bipy})\text{Cl}_2]$  in  $\text{DMSO}/\text{CH}_2\text{Cl}_2$  (2:1 v/v) is given in Scheme 4. We propose that nitrile formation does not occur in an intervening step, but rather it proceeds in a concerted way. It is proposed that direct nucleophilic attack of an azide ion onto the electron-deficient carbon atom of the  $-\text{C}=\text{N}-\text{OH}$  moiety with concomitant cycloaddition occurs to give tetrazoles. Here, coordination of the oxime oxygen atom to the metal ion in  $[\text{Cu}(\text{bipy})\text{Cl}_2]$  activates the oxime moiety by facilitating the cycloaddition of  $\text{NaN}_3$  across the  $\text{C}=\text{N}$  bond. Thus, the two-step conversion of oxime to tetrazole ( $-\text{C}=\text{N}-\text{OH} \rightarrow -\text{CN} \rightarrow \text{tetrazole}$ ) can be replaced by a single-step, concerted process.<sup>[12]</sup> The dehydration of oxime to nitrile requires specific reagents and high temperature; these are absent from our reaction medium.<sup>[12,13]</sup> The

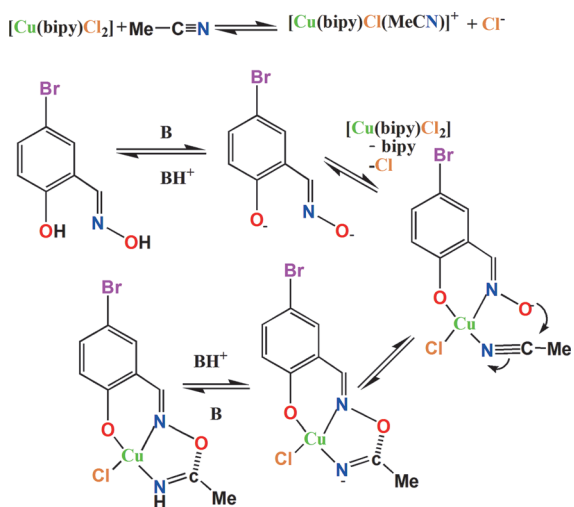
coordination of  $-\text{C}=\text{N}-\text{OH}$  to copper(II) through the oxime oxygen atom will favor removal of oxime OH group, making the attack of the azide ion across the  $\text{C}=\text{N}$  bond more facile. If



Scheme 4. Proposed mechanism for the copper-mediated oxime-azide coupling to form a tetrazole.

[Cu(bipy)Cl<sub>2</sub>] is coordinated by a nitrogen atom and a phenolate oxygen atom to form a chelate ring, removal of the OH group might be more difficult and the catalyst, [Cu(bipy)Cl<sub>2</sub>], will be trapped permanently, which will terminate the catalytic cycle. Thus, we propose coordination of –C=N–OH to the Cu<sup>II</sup> center by the O atom to give an unstable intermediate, which subsequently undergoes attack by NaN<sub>3</sub> across the C=N bond and removal of the oxime OH group.<sup>[14]</sup> However, when the reaction is performed in stoichiometric proportions, the formed tetrazole reacts immediately with [Cu(bipy)Cl<sub>2</sub>] to give complex **1** in quantitative yield. Parallel reactions under identical reaction conditions, but in the absence of [Cu(bipy)Cl<sub>2</sub>], do not lead to the formation of trace amounts of tetrazoles (Figure S7 in the Supporting Information); this, on the other hand, firmly establishes the metal ion/complex catalyzed transformation of oxime to tetrazole in the presence of sodium azide.

When we performed this reaction in MeOH, THF, acetone, or other low-boiling solvents alone, no tetrazole formation took place; rather simple, mononuclear, pseudo-macrocyclic complex **2** formed. This was confirmed by single-crystal X-ray diffraction studies and also by ESI-MS<sup>+</sup> analysis (Figure S6 in the Supporting Information). On the other hand, when we performed the same reaction in MeCN, traditional oxime–nitrile coupling was favored over cycloaddition to give the tetrazole. The in situ formation of iminoacylated ligand L<sup>–</sup> is best described by nucleophilic attack of the oximate oxygen atom of 5-Br-H<sub>2</sub>salox to the unsaturated carbon atom of the nitrile group of MeCN (Figure S6 in the Supporting Information). The question now arises as to whether the oximate oxygen attacks the carbon atom of MeCN present in the bulk or in the coordinated state (Scheme 5). To check these possibilities, we recorded the IR spectrum of [Cu(bipy)Cl<sub>2</sub>] in MeCN, and it was observed that MeCN did coordinate to the metal center because there were two IR stretching frequencies at  $\tilde{\nu}=2294$  and  $2252\text{ cm}^{-1}$ , which corresponded to coordinated and free MeCN, respectively. The shift in the IR frequency by  $42\text{ cm}^{-1}$  (Figure S8 in the Supporting Information) is normal and occurs



**Scheme 5.** Proposed mechanism for the copper-mediated oxime–nitrile coupling.

in the range of  $\tilde{\nu}=40\text{--}130\text{ cm}^{-1}$ .<sup>[19]</sup> To confirm the involvement of the metal ion/complex in the formation of the iminoacylated product we performed parallel reactions under identical conditions, but in the absence of [Cu(bipy)Cl<sub>2</sub>], and it was observed that the oxime remained unreacted during the entire course of the reaction without any sign of the formation of iminoacylated product, as evidenced from ESI-MS (–) analysis (Figure S7 in the Supporting Information). Similar observations were made by Raptopoulou et al.,<sup>[22]</sup> who used simple copper(II) ions and proposed that oxime–MeCN coupling occurred with bulk MeCN. Herein, we observed that activation of MeCN through metal coordination was a prerequisite for the reaction.

In the transformation of the oxime to the tetrazole, in the presence of an azide ion, the solvent played a vital role. DMSO, which is a polar aprotic solvent (Na<sup>+</sup>), is heavily solvated and makes the anion (N<sub>3</sub><sup>–</sup>) free and like a ‘naked ion’, thereby increasing its nucleophilicity to attack the electron-deficient carbon center in –C=N–OH. On the other hand, when using methanol as a polar solvent, both Na<sup>+</sup> and N<sub>3</sub><sup>–</sup> become solvated simultaneously within the solvent cage through ion–dipole interactions (MeOH can form hydrogen bond with the azide), which reduce the nucleophilicity of N<sub>3</sub><sup>–</sup> to such an extent that it cannot promote the cycloaddition reaction of oxime for tetrazole formation.

### Magnetic properties

The  $\chi T$  value for **1** at 300 K is  $0.94\text{ cm}^3\text{ mol}^{-1}\text{ K}$ , and is in accordance with the expected value for two uncoupled copper(II) ions ( $0.91\text{ cm}^3\text{ mol}^{-1}\text{ K}$ , considering  $g=2.2$ ; Figure 3). The  $\chi T$  product remains constant as the temperature decreases, until approximately 50.0 K. It then decreases faster and finally reaches  $0.67\text{ cm}^3\text{ mol}^{-1}\text{ K}$  at 1.8 K. This overall behavior is characteristic of a very weak, antiferromagnetically coupled copper(II) dimer.

The data were fitted by using the spin Hamiltonian given in Equation (1), in which the spin operator,  $S$ , is defined<sup>[23]</sup> as  $S = S_{\text{Cu1}} + S_{\text{Cu2}}$ :

$$H = -JS_{\text{Cu1}}S_{\text{Cu2}} + g\beta HS \quad (1)$$

The best fit parameters were found for  $J = -1.3(1)\text{ cm}^{-1}$  and  $g = 2.23(1)$ , with a very good agreement factor  $R = 2 \times 10^{-5}$ ;  $R$  is defined by Equation (2):

$$R = \frac{\sum (\chi T_{\text{exp},T} - \chi T_{\text{calcd}})^2}{\sum \chi T_{\text{exp},T}^2} \quad (2)$$

The sign and magnitude of  $J = -1.3(1)\text{ cm}^{-1}$  reveals that the two copper(II) centers in complex **1** are very weakly antiferromagnetically coupled. The EPR spectra of all complexes are given in Figure S9 in the Supporting Information.

### Conclusion

The main objective of this study was to explore the effect of solvent polarity on the single-step transformation of oxime to

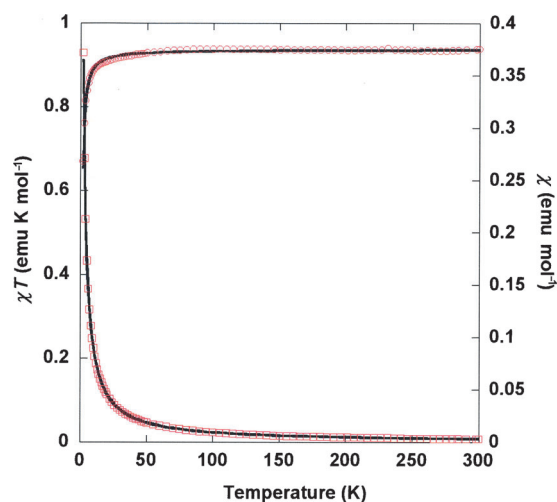


Figure 3. Temperature dependence of  $\chi$  ( $\square$ ) and  $\chi T$  ( $\circ$ ) for **1**. The full lines correspond to the best fit of the data.

tetrazole in the presence of  $[\text{Cu}(\text{bipy})\text{Cl}_2]$  as a catalyst. For this purpose, we performed the same reaction ( $[\text{Cu}(\text{bipy})_2\text{Cl}_2] + \text{H}_2\text{Br-salox} + \text{NaN}_3$  in a 1:1:2 molar ratio in the presence of TEA (2.0 equiv) as a base) in different solvents, namely, DMSO/ $\text{CH}_2\text{Cl}_2$ , MeOH, THF, and MeCN, which varied widely with respect to their dielectric constants. It was interesting to note that in DMSO/ $\text{CH}_2\text{Cl}_2$  medium tetrazole formation occurred smoothly and immediately reacted with  $[\text{Cu}(\text{bipy})\text{Cl}_2]$  to give dinuclear complex **1**. Under catalytic conditions and at  $70^\circ\text{C}$ , the TON of tetrazole was 38 with approximately 100% selectivity, whereas in the absence of TEA this transformation is increased to give a TON of approximately 50. On the other hand, in solvent (MeOH/MeCN) different products are formed.

## Experimental Section

### Materials and reagents

Starting materials such as 5-bromosalicylaldehyde (Lancaster), hydroxylamine hydrochloride (Merck, India), anhydrous  $\text{Na}_2\text{SO}_4$  (Merck), triethylamine (Merck, India), and sodium azide (Merck, India) were of reagent grade and used as received.  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (Merck, Germany) and bipy (Spectrochem, India) were used for the preparation of  $[\text{Cu}(\text{bipy})\text{Cl}_2]$ . Solvents such as methanol, diethyl ether, acetonitrile,  $\text{CH}_2\text{Cl}_2$ , and DMSO (Merck, India) were of reagent grade and dried before use.

### Physical measurements

Elemental analyses were performed by using a PerkinElmer 240 elemental analyzer. IR spectra ( $\tilde{\nu} = 400\text{--}4000\text{ cm}^{-1}$ ) were recorded as KBr pellets on a Nicolet Magna IR 750 series-II FTIR spectrophotometer.  $^1\text{H}$  NMR spectra were recorded in  $[\text{D}_6]\text{DMSO}$  on a Bruker 300 MHz NMR spectrophotometer by using tetramethylsilane ( $\delta = 0$ ) as an internal standard. EPR spectra were recorded as solid samples on an X-band EPR spectrometer (Model: JEOL, JES-FA 200).

### Crystallography

Single-crystal X-ray data for **1–3** were collected at room temperature on a Bruker SMART APEX-II CCD diffractometer by using graphite monochromated  $\text{Mo}_{\text{K}\alpha}$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). Data integration and reductions were processed with SAINT+ software.<sup>[24]</sup> Structures were solved by direct methods and then refined on  $F^2$  by the full-matrix least-squares technique with SHELX-97<sup>[25]</sup> and SHELXTL<sup>[26]</sup> crystallographic software packages. The molecular views and hydrogen-bonding patterns were drawn by using DIAMOND-3.2 and Mercury 3.0 software packages. The crystallographic data for **1–3** are given in Table 4.

CCDC 900536 (**1**), 984812 (**2**), and 914811 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### Magnetic measurements

Magnetic measurements were performed by using a Quantum Design squid-vibrating sample magnetometer (SVSM). The static susceptibility measurements were performed in the 300–1.8 K temperature range with an applied field of 5 kOe. Magnetization measurements at different fields at a given temperature confirmed the absence of ferromagnetic impurities. Data were corrected for the sample holder and diamagnetism was estimated from Pascal constants.

### Preparation of the 5-Br- $\text{H}_2\text{salox}$ ( $\text{H}_2\text{L}$ )

$\text{NH}_2\text{OH}\cdot\text{HCl}$  (2.76 g, 40 mmol) in water (20 mL) was added to a solution of 5-bromosalicylaldehyde (4.02 g, 20 mmol) in ethanol (60 mL) with stirring.  $\text{Na}_2\text{CO}_3$  (4.00 g, 40 mmol) in water (20 mL) was then added and the resulting mixture was heated at  $80^\circ\text{C}$ . The progress of the reaction was monitored by TLC (solvent: 1/1 hexanes/EtOAc) and found to be completed within 3–5 h. The reaction mixture was filtered through a pad of Celite and a solid precipitated upon subsequent concentration; this precipitate was collected by filtration and washed with cold water. Recrystallization from methanol gave the product as a needle-like crystalline material (2.55 g, 59%). M.p.  $133\text{--}134.5^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta = 6.87$  (d,  $J = 8.75\text{ Hz}$ , 1H), 7.36 (dd,  $J = 9\text{ Hz}$ , 2H), 7.65 (brs, 1H; phenolic OH), 8.15 (s, 1H; methyne), 9.84 ppm (s, 1H; N–OH).

### Metal precursor $[\text{Cu}(\text{bipy})\text{Cl}_2]$

$[\text{Cu}(\text{bipy})\text{Cl}_2]$  was prepared by following a method reported in the literature.<sup>[27]</sup>

### Preparation of **1**

The one-pot reaction between 5-Br- $\text{H}_2\text{salox}$  and  $\text{NaN}_3$  in the presence of  $[\text{Cu}(\text{bipy})\text{Cl}_2]$  and TEA in DMSO/ $\text{CH}_2\text{Cl}_2$  gave 5-bromo-2-(tetrazolato-5-yl)phenol, which subsequently coordinated to  $[\text{Cu}(\text{bipy})\text{Cl}_2]$  to give **1**. In a typical procedure,  $[\text{Cu}(\text{bipy})\text{Cl}_2]$  (0.290 g, 1.0 mmol) was added to a pale-yellow solution of 5-Br- $\text{H}_2\text{salox}$  (0.216 g, 1.0 mmol) in DMSO/ $\text{CH}_2\text{Cl}_2$  (30 mL; 2:1 v/v). The addition of TEA (0.202 g, 2.0 mmol) resulted in a green solution, which was stirred for an additional 20 min. Then sodium azide (0.13 g, 2.0 mmol) was added and stirring was continued for an additional 2 h at room temperature. The reaction mixture was then filtered and the filtrate was set aside undisturbed for slow evaporation.

**Table 4.** Crystallographic data and details of the structure determination for 1–3.

|   | 1  | 2   | 3   |
|---|--|---|---|
| formula   | C <sub>34</sub> H <sub>22</sub> Br <sub>2</sub> Cu <sub>2</sub> N <sub>12</sub> O <sub>3</sub> | C <sub>14</sub> H <sub>10</sub> Br <sub>2</sub> CuN <sub>2</sub> O <sub>4</sub> | C <sub>9</sub> H <sub>8</sub> BrClCuN <sub>2</sub> O <sub>2</sub> |
| M <sub>w</sub>                                    | 933.54   | 493.59  | 355.07  |
| crystal system                                    | triclinic  | triclinic   | triclinic   |
| space group                                       | $\bar{P}1$ (no. 2)   | $\bar{P}1$ (no. 2)  | $\bar{P}1$ (no. 2)  |
| a [Å]   | 8.0981(4)  | 4.3940(2)   | 7.4794(8)   |
| b [Å]   | 11.8943(5)   | 8.1448(4)   | 7.7956(8)   |
| c [Å]   | 19.2588(7)   | 21.3588(10)   | 10.7861(12)   |
| $\alpha$ [°]                                      | 105.530(2)   | 82.121(2)   | 88.665(7)   |
| $\beta$ [°]                                       | 101.767(2)   | 89.994(2)   | 81.377(7)   |
| $\gamma$ [°]                                      | 95.953(2)  | 89.995(2)   | 65.790(7)   |
| V [Å <sup>3</sup> ]                               | 1724.92(13)  | 757.18(6)   | 566.59(11)  |
| Z   | 2  | 2   | 2   |
| $\rho_{\text{calcd}}$ [g cm <sup>-3</sup> ]       | 1.797  | 2.165   | 2.081   |
| $\mu(\text{MoK}\alpha)$ [mm <sup>-1</sup> ]       | 3.606  | 6.740   | 5.673   |
| F(000)  | 924  | 478   | 346   |
| absorption correction                             |  |   |   |
| index ranges                                      | –10:10;–15:15;–25:25   | –5:5;–10:10;–28:28  | –9:9;–9:9;–13:13  |
| reflins collected                                 | 27 190   | 11 807  | 8010  |
| independent reflins ( $R_{\text{int}}$ )          | 7957(0.052)  | 3677(0.131)   | 2466 (0.063)  |
| no. of parameters                                 | 478  | 213   | 146   |
| GOF   | 1.01   | 0.83  | 0.86  |
| $R_1/wR_2$ ( $I > 2\sigma(I)$ )                   | 0.0454(5151)   | 0.0348(1924)  | 0.0553 (1755)   |
| $R_1/wR_2$ (all data)                             | 0.1336   | 0.0883  | 0.1762  |
| min and max residual density [e Å <sup>-3</sup> ] | –1.31, 1.15  | –0.68, 0.49   | –1.46, 1.09   |

After 3 weeks, green, rectangular, block-shaped crystals formed and were collected by filtration (0.28 g, 60% based on copper content). IR:  $\tilde{\nu}$  = 2076.5 (s;  $\nu_{\text{(tetrazole)}}$ ), 1624 cm<sup>-1</sup> ( $\nu_{\text{(N=C)}}$ ); elemental analysis calcd (%) for C<sub>34</sub>H<sub>22</sub>Br<sub>2</sub>Cu<sub>2</sub>N<sub>12</sub>O<sub>3</sub> (935.55): C 43.65, H 2.58, N 17.96; found: C 43.79, H 2.65, N 18.12.

### Preparation of 2

The reactants and their proportions were the same as those used in the preparation of 1, but with a difference in the solvent system. MeOH was used instead of a mixture of DMSO/CH<sub>2</sub>Cl<sub>2</sub> (0.321 g, 65% based on copper content). IR: 1615 cm<sup>-1</sup> (vs;  $\nu_{\text{(N=C)}}$ ); elemental analysis calcd (%) for C<sub>14</sub>H<sub>10</sub>Br<sub>2</sub>CuN<sub>2</sub>O<sub>4</sub> (493.59): C 34.06, H 2.04, N 5.67; found: C 33.81, H 2.10, N 5.60.

### Preparation of 3

The synthetic procedure and proportion of reactants were the same as those used in the preparation of 1 or 2, but MeCN was used as the reaction medium (0.22 g, 62% based on copper content). IR:  $\tilde{\nu}$  = 1614 cm<sup>-1</sup> (vs;  $\nu_{\text{(N=C)}}$ ); elemental analysis calcd (%) for C<sub>9</sub>H<sub>8</sub>BrClCuN<sub>2</sub>O<sub>2</sub> (355.07): C 30.44, H 2.27, N 7.88; found: C 30.61, H 2.35, N 7.65. (**Caution!** Azide salts are very toxic and potentially explosive and they should be handled with extreme care.)

### Catalytic synthesis of 5-substituted 1H-tetrazole

A mixture of oxime (0.216 g, 1.0 mmol), sodium azide (0.13 g, 2.0 mmol), catalyst (2.9 mg, 0.01 mmol), and DMSO/CH<sub>2</sub>Cl<sub>2</sub> (10 mL; 2:1 v/v) was added to a 25 mL round-bottomed flask and heated at 70 °C on an oil bath for 20 h under vigorous stirring. The reaction mass was cooled to room temperature. The products thus formed were extracted with diethyl ether (3 × 20 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed to give the solid

product, which was characterized by HRMS (positive mode) and <sup>1</sup>H NMR spectroscopy (Figure 2).

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