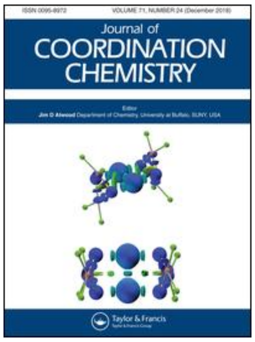

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Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: https://www.tandfonline.com/loi/gcoo20

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**To cite this article:** Sankar Saha, Kinkar Biswas, Pranab Ghosh & Basudeb Basu (2019): New 1,2-dithioether based 2D copper(I) coordination polymer: from synthesis to catalytic application in $A^3$-coupling reaction, Journal of Coordination Chemistry, DOI: 10.1080/00958972.2019.1627339

**To link to this article:** https://doi.org/10.1080/00958972.2019.1627339

JOURNAL OF COORDINATION CHEMISTRY
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# New 1,2-dithioether based 2D copper(I) coordination polymer: from synthesis to catalytic application in A$^3$-coupling reaction

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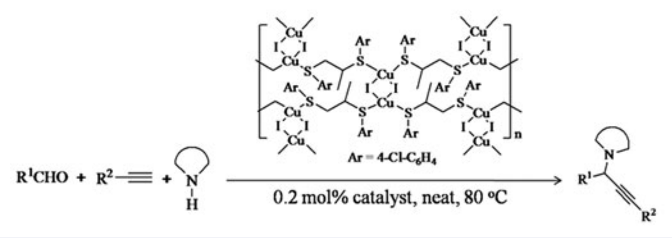
**ABSTRACT**
A new 2D copper(I) coordination polymeric complex has been synthesized from CuI and 1-(1-{4-chlorophenylthio}propan-2-ylthio)-4-chlorobenzene ($[(CuI)_2\{ArSCH_2CH(CH_3)SAr\}_2]_n$, Ar = 4-$ClC_6H_4$) and characterized by high resolution mass spectrometry (HRMS) and single crystal X-ray diffraction techniques. The complex has been employed as a suitable catalyst for a solvent-free, one-pot, three-component A$^3$-coupling reaction. A variety of aromatic and aliphatic aldehydes, terminal alkynes and aliphatic cyclic secondary amines have been used to prepare a library of propargylamines using the 2D-Cu complex at significantly low concentration (0.2 mol%).



**ARTICLE HISTORY**
Received 12 February 2019
Accepted 21 May 2019

**KEYWORDS**
Coordination polymer; 2D-copper(I) complex; solvent-free; A$^3$-coupling; propargyl amine

## 1. Introduction

Coordination polymers of copper halides with infinite network structures composed with organic ligands are widely reported due to the presence of their enthralling physical and chemical properties [1]. For example, Cu(I) halide-based compounds have been widely explored due to their attractive structural characteristics and possible applications in luminescence-based sensors, photophysical phenomena, and biological probes [2]. They also find catalytic applications in various organic transformations [3–8]. *N*- and *P*-based ligands and Cu complexes are employed in catalytic applications

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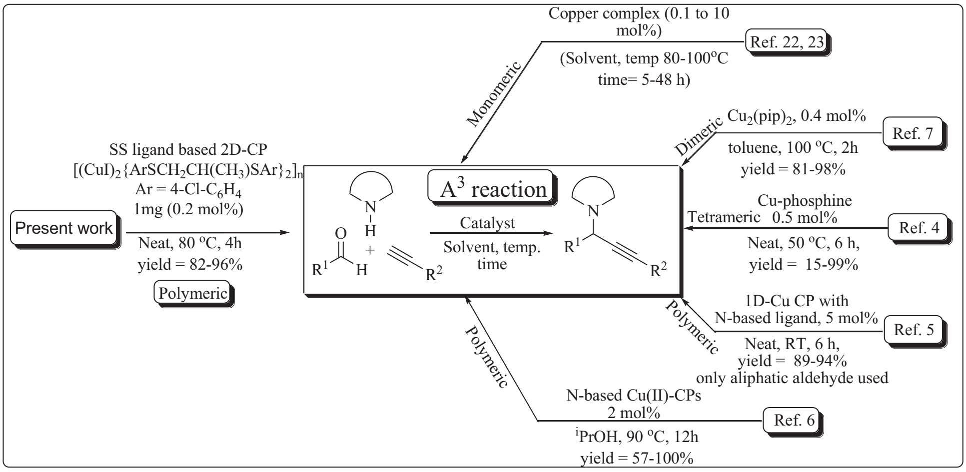
Supplemental data for this article can be accessed https://doi.org/10.1080/00958972.2019.1627339.

[4–9]. Interestingly, metal complexes with 1,2-dithioether ligands are rarely synthesized and used as catalysts except for one recent report that describes the synthesis of a 1,2-dithioether and Cu(I) halide-based 2D complex and its catalytic application in aminomethylation of phenylacetylene. They have shown one example of catalytic use of the complex in the synthesis of propargylamine but the catalyst loading was high (5 mol%) [10]. Propargylamines are versatile building blocks for the preparation of various *N*-containing heterocyclic compounds as well as key intermediates for the synthesis of pharmaceuticals and natural products [11–13]. They also act as key intermediates for the construction of biologically active compounds such as $\beta$-lactams, oxotremorine substrates, conformationally restricted peptides, and therapeutic drug molecules [14]. Because of their importance, many synthetic methods have been developed [15–18].

The classical methodologies are less attractive due to their low tolerance of functional groups, harsh reaction conditions, and operational difficulty [19, 20]. However, the most direct and efficient method for the preparation of propargylamines can be achieved through transition-metal catalyzed three-component coupling between an aldehyde, an amine and a terminal alkyne, which is commonly known as an $A^3$-coupling reaction [21]. Among various synthetic methods, the copper-catalyzed $A^3$-coupling is the most common due to its easy availability, low cost, low toxicity, and high reactivity [22, 23].

Trivalent phosphorus ligands have been used to control the metal center that lead to metal catalysts with improved reactivity and stability. Garcia et al. reported a diallylphosphine-tetrameric copper(I) complex catalyzed $A^3$-coupling reaction for preparing propargylamine [4]. Apart from the phosphorous ligands, nitrogen-based Cu(I) compounds have also been used for $A^3$-coupling reaction. For example, a nitrogen-based 1-D Cu(I)-coordination polymer [5], a benzotriazole-based homogeneous and air-stable Cu-coordination compounds [6], and a dicopper (I) complex based on 2-picolyliminomethyl ligand [7] have been used in $A^3$-coupling reactions. A thioether-based Schiff base Cu(I) complex has been used as the catalyst for an asymmetric type $A^3$-coupling reaction [24]. Since the use of only CuI as catalyst requires prolonged times to complete the reaction, the presence of a co-catalyst or microwave irradiation is mandatory for facile $A^3$-coupling reactions [9, 25]. Interestingly, though the *S*-based copper complexes are widely known, their catalytic applications are quite limited as compared to the corresponding *N*- and *P*-based copper complexes. We report herein the synthesis of a new coordination polymer of CuI attached to the bidentate 1,2-dithioether [1-(1-(4-chlorophenylthio)propan-2-ylthio)-4-chlorobenzene] and characterize it by single crystal X-ray diffraction. The 2-D Cu(I)-1,2-dithioether coordination polymer catalyst works efficiently in $A^3$-coupling reactions under solvent-free condition at 80 °C to afford propargylamines in good to excellent yields. A summary of the previous catalytic $A^3$-coupling reactions along with the present work has been schematically presented in Scheme 1. This clearly shows the catalytic application of various Cu(I) monomeric and polymeric complexes based on *P*- and *N*-ligands in $A^3$-coupling reactions. However, to the best of our knowledge, there is no example of a polymeric 2D Cu(I) complex with 1,2-*SS*-based bidentate ligands used as the catalyst for the synthesis of propargylamines via $A^3$-coupling reaction. The present work thus demonstrates not only a new CuI-based complex as the catalyst for three-component reaction, but also shows the potentiality of using 1,2-dithioethers as the chelating ligands for making metal complexes and their catalytic applications in organic reactions.



Scheme 1. Various copper complexes used as catalysts in A$^3$-coupling reaction.

## 2. Experimental

### 2.1. Materials and methods

Phenylacetylene, *p*-bromophenylacetylene, and cyclohexylcarboxaldehyde were purchased from Sigma – Aldrich and used directly as obtained. Benzaldehyde and salicylaldehyde were purchased from Merck and used without purification. All other aldehydes were purchased from SD Fine Chemical Limited, India. Morpholine, piperidine, and pyrrolidine were purchased from Lancaster and used after distillation. The solvents were purchased from Thomas Baker (Chemicals) Pvt. Ltd., India and used after distillation. All the products were purified by column chromatography on 60–120 mesh silica gels (SRL, India). For TLC, Merck plates coated with silica gel 60, $F_{254}$ were used. The catalyst was weighed by using a Mettler-Toledo digital balance (0.1 mg sensitivity). FT-IR spectra were recorded with a FT-IR-8300 SHIMADZU spectrophotometer using a KBr pellet for solid compounds and neat for semi-solid or liquid compounds. $^1$H and $^{13}$C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, on a Bruker AV 300 spectrometer in $CDCl_3$. Splitting patterns of protons were described as s (singlet), d (doublet), t (triplet), bs (broad singlet), dd (doublet of doublet), and m (multiplet). Chemical shifts (δ) were reported in parts per million (ppm) relative to TMS as internal standard. *J* values (coupling constant) were reported in Hz (Hertz). $^{13}$C NMR spectra were recorded with complete proton decoupling ($CDCl_3$: δ 77.0 ppm). HRMS was performed by a Micromass Q-TOF Spectrometer under ESI (positive mode) at the Indian Association for the Cultivation of Science.

### 2.2. Crystal structure determination

Suitable crystals of the compound were obtained by slow evaporation of its saturated solution using the diffusion method. Single-crystal diffraction studies were carried out using a Bruker D8 Quest CMOS diffractometer with a Mo Kα (l = 0.71073 Å) sealed tube. The data frames were obtained using the program APEX3 and processed using the program SAINT in APEX3 [26]. The structures were solved by direct methods and refined using the SHELXTL-2014/7 program [27]. The structures were refined by full-matrix least-squares (SHELXL2014-7) on $F^2$ [28]. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogens were positioned at their idealized positions using a riding model. The molecular structure figures were prepared using DIAMOND version 3.2 [29]. Table 1 provides the data collection and structure solving parameters for the compound. Selected bond distances and angles for the compound are given in Tables 2 and 3.

### *2.3. General procedure of preparing CuI-L (1,2-bis(4-chlorophenylthio)-propane)-coordination complex (1) Catena-poly [di-μ-iodido-bis[(1,2-bis(4-chlorophenylthio)-propane)-copper (I)]]*

The dithioether ligand (**L**) was synthesized according to our previously reported procedure [30]. **L** (329 mg, 1.0 mmol) and CuI (95 mg, 0.5 mmol) in acetonitrile (2 mL) were

**Table 1.** Crystal data, data collection, and structure refinement for the complex.

| | |
|---|---|
| Formula | $C_{15}H_{14}Cl_2CuIS_2$ |
| Formula weight | 519.73 |
| Temperature/K | 296(2) |
| Description | Block |
| Color | White |
| Crystal system | Orthorhombic |
| Space group | Pbca |
| a/Å | 10.0087(5) |
| b/Å | 15.4384(10) |
| c/Å | 23.6978(14) |
| Cell angle ($\alpha$) | 90° |
| Cell angle ($\beta$) | 90° |
| Cell angle ($\gamma$) | 90° |
| Cell volume/Å$^3$ | 3661.7(4) |
| Cell formula units Z | 8 |
| Density (calculated) g/cm$^3$ | 1.886 |
| θ Range for data collection/deg | 2.42–27.48 |
| F(000) | 2016 |
| Crystal size/mm | 0.216, 0.284, 0.320 |
| Absorption co-efficient ($\mu$) | 3.389 |
| Index ranges | $-12 \leq h \leq 13$<br>$-20 \leq k \leq 20$<br>$-30 \leq l \leq 30$ |
| Reflections collected | 62648 |
| Independent reflections | 4182 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| R-equivalents | 0.0285 |
| Sigma I/net I | 0.0119 |

**Table 2.** Selected bond lengths.

| Bond | Length |
|---|---|
| I3–Cu1 | 2.6119(4) |
| I3–Cu1 | 2.6182(4) |
| Cu1–S2 | 2.3539(7) |
| Cu1–S1 | 2.3990(7) |
| Cu1–I3 | 2.6182(4) |
| Cu1–Cu1 | 2.8979(8) |
| S1–C4 | 1.779(2) |
| S1–C1 | 1.828(2) |
| S1–Cu1 | 2.3990(7) |

**Table 3.** Selected bond angles.

| Bond | Angle |
|---|---|
| Cu1–I3–Cu1 | 67.296(15) |
| S2–Cu1–S1 | 96.07(2) |
| S2–Cu1–I3 | 123.28(2) |
| S1–Cu1–I3 | 110.344(19) |
| S2–Cu1–I3 | 102.56(2) |
| S1–Cu1–I3 | 110.42(2) |
| I3–Cu1–I3 | 112.705(15) |

taken in a 25 mL round-bottomed flask. The mixture was stirred at room temperature for 4 h and then refluxed for 24 h. After cooling to room temperature, petroleum ether was added dropwise to the solution and the solution kept in a refrigerator. After two days, shining white crystals of the complex were separated by simple filtration, followed by washing with dry petroleum ether (2 × 5 mL), and finally dried in a vacuum desiccator. The 2-D polymeric complex compound (**1**) from CuI and 1,2-dithioether was found in 74% yield (384 mg).

### *2.4. General procedure for A$^3$-coupling reaction*

A mixture of aldehyde (1.0 mmol), secondary amine (1.0 mmol), terminal acetylene (1.1 mmol), and the polymer catalyst (~1.0 mg) was magnetically stirred at 80 °C in an open reaction vessel for hours. The progress of the reaction was monitored by TLC. After completion of the reaction (disappearance of the alkyne spot on TLC), the reaction mixture was cooled to room temperature, dichloromethane (5 mL) was added, concentrated, and adsorbed on silica gel. The dry silica-adsorbed material was passed through a bed of silica gel in a column and elution with a light petroleum:ethyl acetate solvent mixture (in varying proportions) afforded the desired propargylamine.

## 3. Results and discussion

### *3.1. Characterization of the complex*

The CuI-1,2-dithioether 2-D polymeric complex (**1**) was characterized by $^1$H NMR, $^{13}$C NMR spectroscopy, HRMS spectrometry (Supplementary Materials) and by single crystal X-ray diffraction (XRD) techniques. The $\delta$ values of proton and carbon in complex (**1**) were shifted downfield compared to the ligand (**L**) in both $^1$H NMR and $^{13}$C NMR spectra, indicating the formation of the complex. Single crystal XRD analysis (Table 1) revealed that **1** crystallizes in the orthorhombic *P*bca space group and shows a polymeric propagation in the form of the $[(CuI)_2\{ArSCH_2CH(CH_3)SAr\}_2]_n$ (Ar = 4-$ClC_6H_4$) metallopolymer (Figure 1) [31–33]. The ORTEP diagram of the complex is given in Figure 1(a). The 2D-network is built up of dimeric $Cu_2I_2$ units which are interconnected via dithioether ligands. Within the cluster core, the Cu–I bond lengths range between 2.6119(4) and 2.6182(4) Å. The interatomic distance between two Cu within the $Cu_2I_2$ cluster is 2.8979(8) Å, significantly larger than the sum of the van der Waals radius (2.80 Å) [34]. The mean Cu–S bond length, range between 2.3539(7) and 2.3990(7) Å, is a

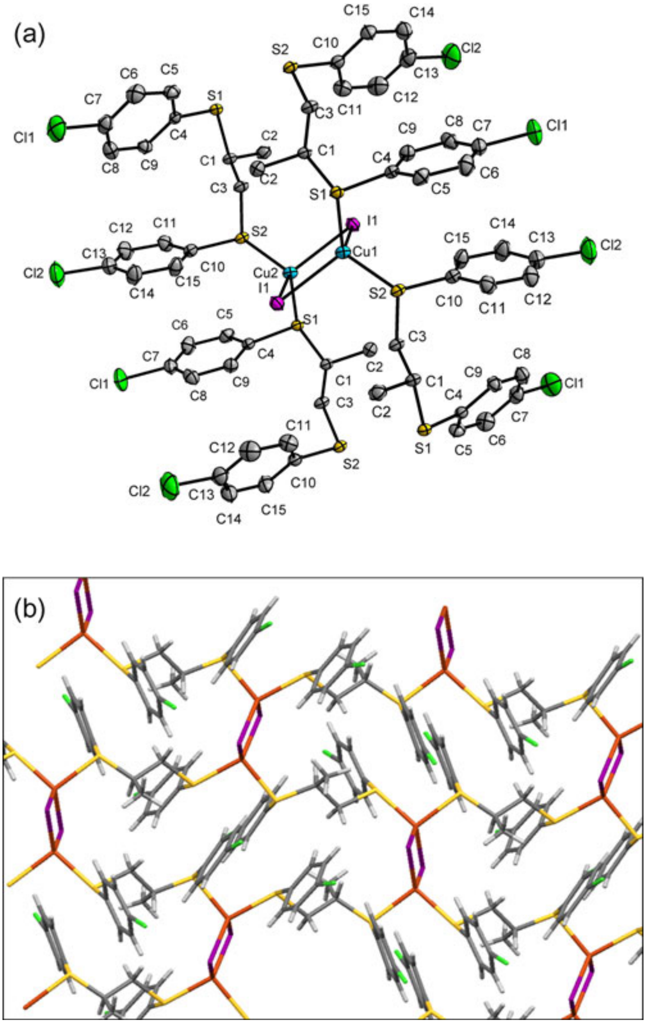


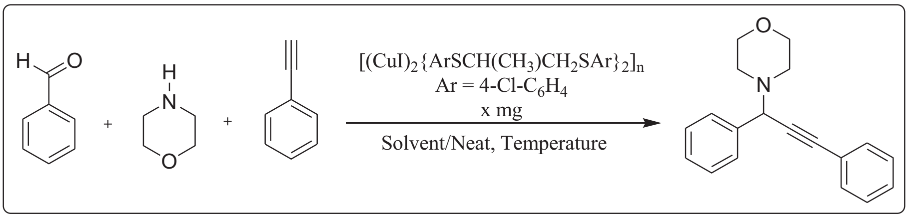
**Figure 1.** (a) ORTEP diagram of the ($[(CuI)_2\{ArSCH_2CH(CH_3)SAr\}_2]_n$, Ar = 4-$ClC_6H_4$) complex, **1**. (b) Two-dimensional framework of complex **1**.

little in excess of that seen in $[\{Cu(\mu\text{-}I)_2Cu\}_2\{\mu\text{-}PhS(CH_2)_3SPh\}_2]_n$ (2.3465 Å) and ($[(CuI)_2\{ArS(CH_2)_3SAr\}_2]_n$, Ar = 4-$FC_6H_4$); range between 2.3339(11) and 2.3551(12) Å) [31, 35]. The angle Cu … I … Cu is 67.296(15)° and the angle I … Cu … I is 112. 705(15)° in the metallocluster. The polymeric framework of **1** is formed by the connection of $Cu_2I_2$ unit and four 1,2-dithioether linkers **L**. Each 1,2-dithioether coordinates via its *S*-donor atoms to two $Cu_2I_2$ units, while each $Cu_2I_2$ unit connects with four 1,2-dithioether ligands (**L**). This gives a 2-D shaped network matrix topology (Figure 1(b)). The crystal data, data collection, and structure refinement of the polymeric complex are given in Table 1. Selected bond lengths and angles of the complex are also given in the Tables 2 and 3, respectively. The refined bond length and angles are given in the Supplementary Materials (Tables S1 and S2, respectively, under 2.2).

### 3.2. The catalytic activity of copper complex 1

The catalytic activity of the complex towards A$^3$-coupling reactions was optimized in a model reaction of phenyl acetylene, benzaldehyde, and morpholine under varying catalyst loading, different temperatures and solvents (Table 4). Initially, the reaction of phenylacetylene (1.1 mmol), benzaldehyde (1.0 mmol), and morpholine (1.0 mmol) was performed in acetonitrile at 60 °C for 8 h using 5 mg of the complex as catalyst. A trace amount of conversion was achieved (entry 1). Raising the temperature of the medium from 60 to 80 °C gave 40% yield of the product (entry 2). Using polar hydroxylic solvents *e.g.* ethanol and water, the yield of the product was ~50% (entries 3 and 4). In a binary solvent mixture (acetonitrile:water = 1:1), the conversion was increased to 65% (entry 5). When the reaction was studied under neat conditions, the yield of the product was significantly increased to 91% (entry 6). Decreasing the amount of the catalyst from 5.0 mg to 3.0 and 1.0 mg (±0.1 mg) (approx. 0.2 mol%), respectively, did not affect the overall yield of the product (90% yield in both cases; entries 7 and 8). Reducing the reaction time did not show any significant drop in the yield of the desired product (entries 9 and 10). A reaction performed without any catalyst did not produce any desired product after 24 h (entry 11). On the other hand, conducting the experiment at room temperature showed traces of product after 24 h (entry 12). We also performed the reaction using CuI as the catalyst under similar reaction conditions affording the product in relatively lower yield (55%; entry 13). Among the different conditions attempted, the best condition was optimized as the presence of 1 mg

Table 4. Optimization of reaction conditions for the 2-D Cu(I)-polymeric complex catalyzed A$^3$-coupling reaction.



| Entry | Solvent | Cu-catalyst (mg) | Temp. (°C) | Time (h) | Yield[a] (%) |
|---|---|---|---|---|---|
| 1 | Acetonitrile | 5 | 60 | 8 | Traces |
| 2 | Acetonitrile | 5 | 80 | 8 | 40 |
| 3 | Ethanol | 5 | 80 | 8 | 52 |
| 4 | Water | 5 | 80 | 8 | 50 |
| 5 | Acetonitrile:water | 5 | 80 | 8 | 65 |
| 6 | Neat | 5 | 80 | 8 | 91 |
| 7 | Neat | 3 | 80 | 8 | 90 |
| 8 | Neat | 1 | 80 | 8 | 90 |
| 9 | Neat | 1 | 80 | 6 | 88 |
| **10** | **Neat** | **1 ± 0.1 ~ 1**[b] | **80** | **4** | **88** |
| 11 | Neat | – | 80 | 24 | No reaction |
| 12 | Neat | 1 | RT | 24 | Traces |
| 13[c] | Neat | 1 | 80 | 4 | 55 |

Reaction conditions: phenyl acetylene (1.1 mmol), benzaldehyde (1.0 mmol) and morpholine (1.0 mmol), Cu-complex (5 mg to 1 mg), Neat.

[a] Isolated yield after purification through column chromatography over silica gel.

[b] Error in the measurement of the catalyst is ±0.1 mg.

[c] CuI was used as catalyst.

The bold values refer to the optimized reaction conditions used for the reaction.

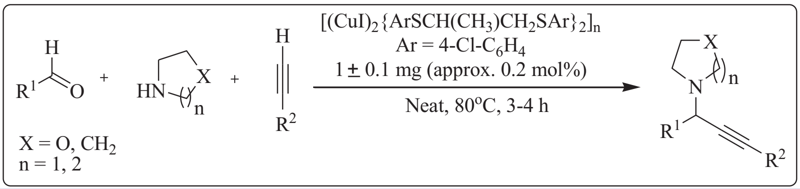
(±0.1 mg) (approx. 0.2 mol%) catalyst under solvent-free and aerobic conditions at 80 °C (entry 10).

In order to explore the generality of the optimized reaction conditions, different types of substrates such as secondary amines with different types of aldehydes were allowed to react with terminal acetylenes. Very good to excellent isolated yields of the products have been achieved under this protocol (Table 5). In Table 5, it is clearly evident that various aldehydes including electron releasing or withdrawing groups such as OMe, OH, Br, Cl as well as benzaldehyde reacted smoothly with terminal alkynes (phenyl acetylene and 4-bromophenyl acetylene) and cyclic secondary amines (morpholine, piperidine and pyrrolidine). Furthermore, the reaction of an alicyclic aldehyde (cyclohexanecarboxaldehyde) and straight-chain aliphatic aldehyde (*n*-heptanal) with morpholine and phenylacetylene were performed efficiently and afforded the desired products in brilliant yields (entries 9 and 10).

### 3.3. Probable mechanism

The most possible mechanism of the A$^3$-coupling reaction is believed to proceed *via* the activation of the C$_{sp}$–H bond of the terminal alkyne by the copper catalyst (here the new coordination 2D polymer complex derived from CuI and 1,2-dithioether). The resulting four-coordinate alkynyl–Cu intermediate (3), formed by the dissociation of one thioether ligand, then reacts with the iminium ion generated *in situ* from aldehyde and secondary amine to produce the corresponding propargylamine product. The proposed mechanism is outlined in Scheme 2.

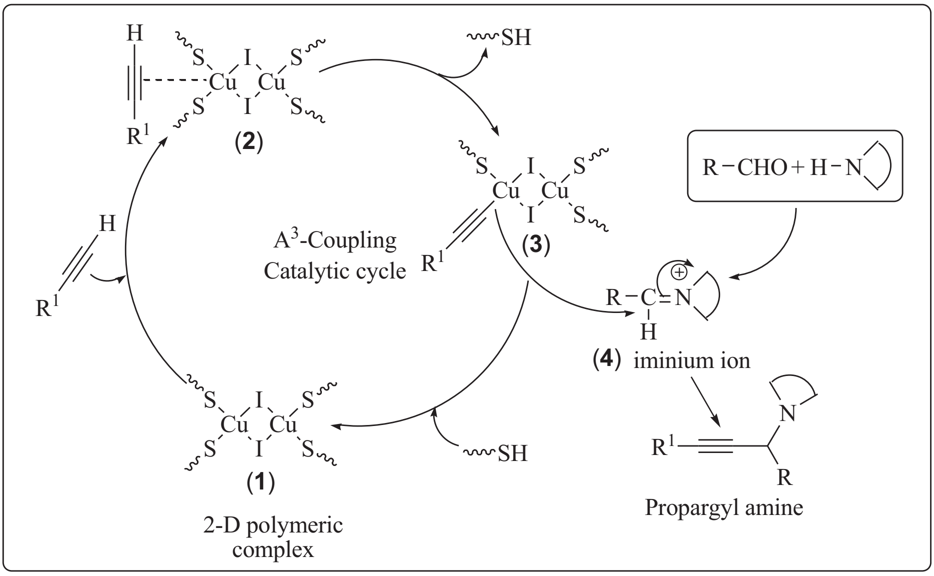
**Table 5.** Catalytic activities of the 2-D Cu(I)-polymeric complex catalyzed A$^3$-coupling reaction.



| Sl No. | Aldehyde | 2° Amine | Alkyne | Time (h) | Yield[a] (%) |
|---|---|---|---|---|---|
| 1 | $4-\mathrm{OMe}-C_6H_4CHO$ | Morpholine | Ph—≡ | 4 | 87 |
| 2 | $4-\mathrm{Br}-C_6H_4CHO$ | Morpholine | Ph—≡ | 4 | 92 |
| 3 | $4-\mathrm{C1}-C_6H_4CHO$ | Morpholine | Ph—≡ | 4 | 96 |
| 4 | $2-\mathrm{C1}-C_6H_4CHO$ | Morpholine | Ph—≡ | 4 | 88 |
| 5 | $C_6H_5CHO$ | Morpholine | Ph—≡ | 4 | 88 |
| 6 | $3,5-\mathrm{Br}-C_6H_3CHO$ | Morpholine | Ph—≡ | 4 | 95 |
| 7 | $4-\mathrm{OMe}-C_6H_4CHO$ | Morpholine | $4-\mathrm{Br}-C_6H_4$—≡ | 4 | 92 |
| 8 | $2-\mathrm{OH}-C_6H_4CHO$ | Morpholine | $4-\mathrm{Br}-C_6H_4$—≡ | 3 | 85 |
| 9 | $\mathrm{Cy}-\mathrm{CHO}$ | Morpholine | Ph—≡ | 3.5 | 91 |
| 10 | $n-C_6H_{13}-\mathrm{CHO}$ | Morpholine | Ph—≡ | 3.5 | 86 |
| 11 | $4-\mathrm{OMe}-C_6H_4CHO$ | Piperidine | Ph—≡ | 4 | 93 |
| 12 | $2-\mathrm{OH}-C_6H_4CHO$ | Piperidine | Ph—≡ | 3 | 90 |
| 13 | $4-\mathrm{OMe}-C_6H_4CHO$ | Pyrrolidine | Ph—≡ | 4 | 82 |
| 14 | $2-\mathrm{OH}-C_6H_4CHO$ | Pyrrolidine | Ph—≡ | 3 | 92 |
| 15 | $4-\mathrm{OMe}-C_6H_4CHO$ | Pyrrolidine | $4-\mathrm{Br}-C_6H_4$—≡ | 4 | 91 |

Reaction conditions: phenyl acetylene/4-bromo phenyl acetylene (1.1 mmol), aldehyde (1.0 mmol) and morpholine/piperidine/pyrrolidine (1.0 mmol), Cu-complex (1 ± 0.1 mg, approx. 0.2 mol%) in neat condition.

[a] Isolated yield after purification through column chromatography by silica gel.



Scheme 2. A probable mechanism of Cu(I)-complex catalyzed $A^3$-coupling reaction.

## 4. Conclusion

We have demonstrated the synthesis and characterization of a new 2D-Cu(I) coordination polymer of 1,2-dithioether ligands (*SS*, bidentate) and its catalytic application in $A^3$-coupling reactions for the synthesis of various propargylamine derivatives under solvent-free conditions. Easy preparation of the copper complex, low catalyst loading (0.2 mol%), mild catalytic conditions and wider applicability to different reacting partners are notable features. The catalyst however performs better in the case of cyclic secondary amines. As the dithioether-based chelating ligands and corresponding copper complexes are less known in catalysis, we expect that the present work would encourage newer *S,S*-based copper complexes for catalytic applications. The choice of chloro-substituted ligands, however, does not carry any specific significance except physical parameters, easy characterization, *etc*.

## Disclosure statement

No potential conflict of interest was reported by the authors.

## Funding

This work was supported by the Science and Engineering Research Board of India under Grant Number EMR/2015/000549.

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