

# [Cu<sub>30</sub>I<sub>16</sub>(mtpmt)<sub>12</sub>(μ<sub>10</sub>-S<sub>4</sub>): an unusual 30-membered copper(i) cluster derived from the C–S bond cleavage and its use in heterogeneous catalysis†‡

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**The Cu(i)-mediated C–S bond cleavage of 5-methyl-4-(*p*-tolyl)pyrimidine-2-thiol (mtpmtH) gave one 30-nuclear cluster [Cu<sub>30</sub>I<sub>16</sub>(mtpmt)<sub>12</sub>(μ<sub>10</sub>-S<sub>4</sub>), one polymeric complex [(bmtmps)Cu(μ-I)]<sub>n</sub> and one tetranuclear complex [(bmtpmds){Cu(μ-I)}<sub>2</sub>]<sub>2</sub>; the 30-nuclear cluster displayed excellent catalytic performances in the coupling reactions of *N*-heterocycles and arylboronic acids and could be recycled and reused.**

High nuclear copper coordination complexes are of great interest because of their synthetic challenges<sup>1</sup> and their potential applications in advanced materials<sup>2</sup> and catalysis.<sup>3</sup> The inorganic<sup>4</sup> and/or organic sulfur<sup>5</sup> ligands are frequently used to prepare these high nuclear Cu(i) complexes. Among the organosulfur ligands, nitrogen-donor-containing thiolates such as pyridine-2-thiolate or pyrimidine-2-thiolate ligands could be employed in the assembly of mono-, di-, tri-, tetra-, hexa-nuclear and polymeric complexes,<sup>6</sup> which may largely depend on their coordination modes (Scheme S1, ESI†).<sup>7</sup> These ligands have also shown a rich redox chemistry based on both oxidative formation and reduction cleavage of the C–S bond.<sup>8</sup> However, the inorganic sulfur ligands generated *in situ* from the C–S bond rupture of pyrimidine-2-thiol ligands have been less explored for synthesizing high nuclear Cu(i) clusters.<sup>9</sup>

On the other hand, when bulk CuI was reacted with various organic nitrogen and/or sulfur donor ligands, its 3D framework could be cleaved into various [Cu<sub>x</sub>I<sub>y</sub>]<sup>x–y</sup> motifs. These motifs may interact with those coexisting in these systems like organic ligands and counter ions to form the corresponding [Cu<sub>x</sub>I<sub>y</sub>]-based coordination complexes.<sup>10</sup> Then could these *in situ*-generated [Cu<sub>x</sub>I<sub>y</sub>]<sup>x–y</sup>

motifs be employed to capture the possible S-containing species derived from the copper(i)-mediated C–S bond cleavage of a thiol? With these in mind, we employed 5-methyl-4-(*p*-tolyl)pyrimidine-2-thiol (mtpmtH) as a substrate to react with CuI under solvothermal conditions. This system did proceed with an intriguing Cu(i)-assisted C–S bond cleavage and several cleaved species such as a unique S<sub>4</sub><sup>2–</sup> ion, organic thioethers and disulfides were trapped by different [Cu<sub>x</sub>I<sub>y</sub>] motifs to form a set of [Cu<sub>x</sub>I<sub>y</sub>]-based coordination complexes, one 30-nuclear cluster [Cu<sub>30</sub>I<sub>16</sub>(mtpmt)<sub>12</sub>(μ<sub>10</sub>-S<sub>4</sub>)] (**1**), one polymeric complex [(bmtmps)Cu(μ-I)]<sub>n</sub> (bmtmps = bis(5-methyl-4-(*p*-tolyl)pyrimidin-2-yl)sulfide) (**2**) and one tetranuclear complex [(bmtpmds){Cu(μ-I)}<sub>2</sub>]<sub>2</sub> (bmtpmds = 1,2-bis(5-methyl-4-(*p*-tolyl)pyrimidin-2-yl)disulfide) (**3**). In addition, some Cu(i) thiolates are known to exhibit high reactivity in many organic transformations, including C–X (X = O, N, C, S, B) bond formation.<sup>11</sup> They mainly work as homogeneous catalysts and can be used only once. Thus the development of heterogeneous and recyclable catalysts for such coupling reactions would be of great importance. In this work, the insoluble cluster **1** displayed excellent catalytic performances in the coupling reactions of *N*-heterocycles with arylboronic acids and could be used for several cycles.

The solvothermal reaction of CuI with equimolar mtpmtH in MeCN at 120 °C for one day followed by cooling to 65 °C afforded red prisms of a large Cu–S–I cluster 1·3MeCN (*ca.* 1% yield) coupled with a small amount of black solid Cu<sub>2</sub>S. The filtrate was subsequently cooled to 25 °C to form a yellow crystalline solid of bmtmps (42% yield). Further cooling the filtrate to 0 °C gave several red needles of a Cu–I–bmtmps polymeric complex 2·0.5MeCN coupled with some yellow powder of bmtmps. An X-ray analysis revealed that 1·3MeCN contains one disordered μ<sub>10</sub>-S<sub>4</sub><sup>2–</sup> ion with a rare zigzag conformation that connects eight rhomboid [Cu<sub>3</sub>I] fragments (Fig. S1, ESI†). On each of the two sides of this S<sub>4</sub><sup>2–</sup> ion, four [Cu<sub>3</sub>I] fragments are bridged by two pairs of mtpmt ligands. The resulting two [(Cu<sub>3</sub>I)<sub>4</sub>(mtpmt)<sub>4</sub>] units are further linked by four mtpmt ligands, four iodides and two [Cu<sub>3</sub>I<sub>2</sub>] fragments, forming an oval-shaped structure with a two-fold axis running through the I(6)···I(6A) contact (Fig. 1). The μ<sub>10</sub>-S<sub>4</sub><sup>2–</sup> ion binds to ten Cu atoms, which is different from the chelating or

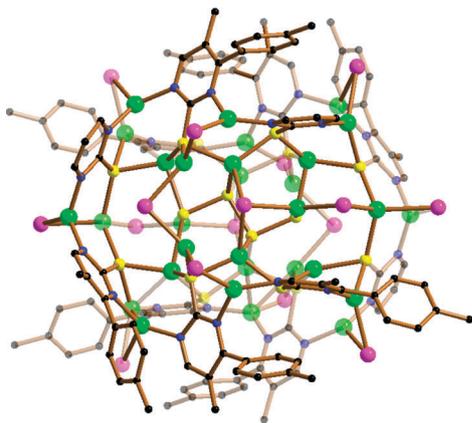
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**Fig. 1** View of the oval-shaped structure of **1**. All H atoms are omitted for clarity. Atom color codes: Cu green, I pink, S yellow, N blue, C black.

chelating/bridging coordination modes found in  $(Et_4N)_2[Ni(S_4)_2]$  and  $[NH_4(CuS_4)]_n$ .<sup>12</sup> Interestingly, each mtpmt acts as a  $\mu-(\kappa_1-N, \kappa_1-N, \kappa_3-S)$  tridentate ligand to bridge five Cu atoms (mode J in Scheme S1, ESI<sup>†</sup>), which is different from other modes. In **1**, some Cu centers are three-coordinated by one I and two N atoms [Cu(1), Cu(1A), Cu(5), Cu(5A), Cu(8), Cu(8A), Cu(11), Cu(11A), Cu(15), Cu(15A)] or by one S and two I atoms [Cu(7), Cu(7A), Cu(10), Cu(10A), Cu(13), Cu(13A)]. Other Cu atoms are tetrahedrally coordinated by one I and three S atoms [Cu(9), Cu(9A), Cu(12), Cu(12A)] or by two S and two I atoms [Cu(14), Cu(14A)]. The Cu...Cu contacts range from 2.545(2) Å to 2.918(2) Å. The strong absorption at  $475\text{ cm}^{-1}$  in the Raman spectrum of **1** (Fig. S11, ESI<sup>†</sup>) could be assigned to the  $\nu(S-S)$  vibration of  $S_4^{2-}$  ions, which is similar to the stretching vibration of elemental  $S_8$  ( $473\text{ cm}^{-1}$ ).<sup>13</sup>

Intriguingly, analogous reactions of CuI with half an equivalent of mtpmtH in MeCN-DMF ( $v/v = 4:1$ ) followed by cooling the solution to ambient temperature produced red prisms of **1**-3MeCN (53% yield). Subsequent diffusion of  $Et_2O$  into the filtrate afforded red plates of **3**-MeCN (9% yield). The liquid chromatography-mass spectrometry (LC-MS) was employed to monitor the possible species of the above-mentioned Cu(I)-mediated C-S cleavage reaction. There were several main peaks in the mass spectra. Two peaks at  $m/z = 431.1$  and  $453.1$  may be ascribed to bmtptmds ( $[M + H]^+ = 431.1$  and  $[M + Na]^+ = 453.1$ ). Another peak at  $m/z = 399.1$  could be assignable to bmtmpms ( $[M + H]^+ = 399.1$ ). Column chromatography on silica was further used to separate bmtmpms (*ca.* 5%) and bmtptmds (*ca.* 5%) ligands from the filtrate. Changing the molar ratios of CuI/mtpmtH or reaction temperatures or other solvent systems did not increase the yield of **1**. The structure of **2** consists of a 1D chain of [(bmtmpms)CuI] units, which extends along the *c* axis (Fig. S2, ESI<sup>†</sup>). The zigzag  $[Cu]_n$  chain is not in one plane. Each Cu(I) atom is tetrahedrally coordinated by two  $\mu$ -I atoms and two N atoms from one bmtmpms ligand. In **3**-MeCN, there is a crystallographic center of inversion located at the mid-point of Cu(2)...Cu(2A) contact. Two Cu atoms on each side in the chairlike  $[Cu_2(\mu-I)(\mu_3-I)]_2$  unit is coordinated by one bmtptmds ligand *via* the N,S,N-tridentate coordination mode (Fig. S3, ESI<sup>†</sup>). All Cu atoms are tetrahedrally coordinated by one  $\mu$ -I, one  $\mu_3$ -I, one N and one S.

It is noteworthy that in such a reductive C-S bond-cleaving reaction,  $O_2$  acted as an oxidant, which is different from the  $Cu^{2+}$  ion as an oxidant in the hydro(solvo)thermal reactions.<sup>7</sup> In our system,  $O_2$  existed since the reactants and solvents were loaded in the Pyrex glass tubes and sealed in open air. While the solvothermal reactions of CuI and two equiv. of mtpmtH in MeCN-DMF were carried out under an argon atmosphere, they did not form **1** but gave rise to one hexanuclear complex  $[Cu_6(mtpmt)_6]$  (**4**) in 67% yield. When the solution of **3** in MeCN-DMF or the solution containing CuI/bmtptmds was heated under solvothermal conditions, **1** could be isolated in medium yields. However, **1** could not be isolated from the similar solvothermal reactions of **2** or **4**. Compounds **2** and **3** could be readily prepared in high yields from the corresponding reactions of CuI with equimolar bmtmpms or bmtptmds in MeCN- $CHCl_3$ . Because of the formation of  $S_4^{2-}$ , bmtmpms and bmtptmds, mtpmtH must partially undergo the desulfurization reaction with the aid of CuI, which activated us to propose the following mechanism for the formation of these species along with **1**-**3**. In the presence of CuI, the homolytic rupture of the C-S bond of mtpmtH or bmtptmds may lead to the formation of three free radical intermediates  $[S^\bullet]$ ,  $[S_2^\bullet]$  and  $[mtpmt^\bullet]$ .<sup>9</sup> With the assistance of  $O_2$ , the self-recombination of  $[S_2^\bullet]$  or  $[S^\bullet]$  radicals may entail the  $S_4^{2-}$  ion while recombination of the  $[mtpmt^\bullet]$  radical with mtpmtH or  $[S_2^\bullet]$  may produce bmtmpms or bmtptmds. Compound **4** has a cage-like structure in which six trigonally-coordinated Cu(I) atoms are connected by six mtpmt ligands. Each mtpmt ligand binds to three Cu(I) atoms in the N,S-bidentate mode (Fig. S4, ESI<sup>†</sup>).

*N*-Arylazoles are ubiquitous in biochemical, biological, and medicinal structures and functions and copper thiolates have been shown to be excellent catalysts for these cross-coupling reactions.<sup>11a</sup> Complex **1** is insoluble in common organic solvents and may work as a heterogeneous catalyst. We found that **1** could display excellent catalytic performances in the coupling reactions of arylboronic acids with *N*-containing heterocycles in the absence of additional bases. As shown in Table 1, the initial reaction was conducted between imidazole and an excess of phenylboronic acid with a loading of 0.17 mol% **1**, in refluxing MeOH for 5 h, affording the *N*-phenylimidazole product in 99% yield. The reaction temperature exerted great impact on this reaction. At lower temperature ( $25\text{ }^\circ\text{C}$  to  $45\text{ }^\circ\text{C}$ ), the reactions gave the product in lower yields (23% and 67%). When the catalyst loading for this reaction was increased from 0.17 to 1 mol%, it did not affect the yields of the products. When the optimized reaction conditions were fixed, we chose a family of arylboronic acids as the substrates in this cross-coupling reaction. When the *m*-, *p*-tolylboronic acids or 3,5-dimethylphenylboronic acid were used, the corresponding *N*-arylation products were obtained in almost quantitative yields. However, this reaction was sensitive to the *o*-substituent of the phenyl group, and the moderate yield was obtained for *o*-tolylboronic acids (35% yield; entry 4), which may be ascribed to the large steric hindrance during the cross-coupling reaction. As shown in entries 6 and 7, electron-donating *p*-substituted arylboronic acids were found to proceed in higher yields than those with electron-deficient substituent groups. The 1- or

**Table 1** Reaction of nitrogen-containing heterocycle compounds with various boronic acids<sup>a</sup>

Entry	Amine	Boronic acid	Product	Yield <sup>b</sup> (%)
1				99
2 <sup>c</sup>				23
3 <sup>d</sup>				67
4 <sup>e</sup>				99
5 <sup>f</sup>				99
6				99
7				99
8				35
9				98
10				99
11				90
12				60
13				72
14				96
15				59
16 <sup>g</sup>				95
17 <sup>h</sup>				88
18 <sup>i</sup>				94
19 <sup>j</sup>				90
20 <sup>k</sup>				87

<sup>a</sup> Reaction conditions: ArB(OH)<sub>2</sub> (1.2 mmol), nitrogen-containing heterocycle compounds (1.0 mmol), MeOH (2.0 mL) and **1** (0.17 mol%) at 64 °C for 5 hours. <sup>b</sup> Isolated yield; the products were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectral analysis. <sup>c</sup> The reaction was carried out at 25 °C. <sup>d</sup> The reaction was carried out at 45 °C. <sup>e</sup> Catalyst loading: 0.5 mol%. <sup>f</sup> Catalyst loading: 1 mol%. <sup>g</sup> Recyclable three times. <sup>h</sup> Recyclable five times. <sup>i</sup> Catalyst: 2 (5 mol%). <sup>j</sup> Catalyst: 3 (5 mol%). <sup>k</sup> Catalyst: 4 (5 mol%).

2-naphthylboronic acids were also coupled with imidazole to obtain *N*-naphthalen-2-yl-imidazole and *N*-naphthalen-1-yl-imidazole in good yields. In addition, we also explored the catalytic reactions by changing imidazole to pyrazole or benzoimidazole derivatives, affording the corresponding products in high (96%) or good (59%) yields. Compound **1** could be recovered from the catalytic system by centrifugation and then reused

for the fresh cross-coupling reaction. The resulting product was formed in 88% yield after reusing **1** five times. Complexes **2–4** could also catalyze such cross-coupling reactions, producing *N*-phenyl-imidazole in 87–94% yields. The catalytic activity of **1** is higher than those of **2–4**, simple copper salts in MeOH,<sup>14a</sup> and [Cu(OH)(TMEDA)]<sub>2</sub>Cl<sub>2</sub> (TMEDA = *N,N,N',N'*-tetramethyl-ethane-1,2-diamine) in CH<sub>2</sub>Cl<sub>2</sub>.<sup>14b</sup>

In summary, we have demonstrated that a unique copper(i)-mediated C–S bond cleavage reaction of mtpmtH under solvothermal conditions resulted in the formation of S<sub>4</sub><sup>2-</sup> and bmtpmS and bmtmds, which were captured by different *in situ*-generated [Cu<sub>x</sub>I<sub>y</sub>] motifs, producing the corresponding coordination complexes **1–3**. The methodology using [Cu<sub>x</sub>I<sub>y</sub>] motifs to trap the cleaved species might be applicable to other biorelevant systems. Compound **1** showed excellent catalytic performances in the coupling reactions of *N*-heterocycles and arylboronic acids, and is anticipated to be used for catalyzing other C–X (X = C, O, S) bond formation.

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