Dalton
Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 11382

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# A Sandmeyer type reaction for bromination of 2-mercapto-1-methyl-imidazoline ($N_2C_4H_6S$) into 2-bromo-1-methyl-imidazole ($N_2C_4H_5Br$) in presence of copper(I) bromide†

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*Received 13th July 2011, Accepted 30th August 2011*
**DOI: 10.1039/c1dt11327e**

**2-Mercapto-1-methyl-imidazoline ($N_2C_4H_6S$) is converted at room temperature into 2-bromo-1-methyl-imidazole ($N_2C_4H_5Br$) in presence of copper(I) bromide in acetonitrile-chloroform mixture *via* extrusion of sulfur as sulfate and oxidation of $Cu^I$ into $Cu^{II}$. 2-Bromo-1-methyl-imidazole was isolated as its self assembled tetranuclear $Cu^{II}$ cluster, $[Cu_4(\eta^1\text{-}N\text{-}(N_2C_4H_5Br)_4(\mu_4\text{-}O)(\mu\text{-}Br)_6]$ 1 $\{\eta^1\text{-}N\text{-}(N_2C_4H_5Br)$ = 2-bromo-1-methyl-imidazole$\}$.**

Metal ion-mediated transformation of organic molecules is an important chemical process as it provides facile synthetic routes for the formation of many interesting molecules which are otherwise difficult or even impossible to synthesize by conventional synthetic procedures.[1] For example, in organic chemistry bromination of an aromatic amine occurs *via* preparation of its diazonium salt (eqn (1)) and subsequent displacement of $N_2^+X^-$ with a bromo ion (Sandmeyer reaction).[2] Using this reaction, a variety of five- and six-membered heterocyclic ring amines, such as, aminopyrazoles, aminotriazoles, aminopyridine *etc.* have undergone diazotization followed by halogenation (I–III, Chart 1).[3] Surprisingly, there is no bromination of heterocyclic rings with exocyclic thiones (IV–VI, Chart 2).

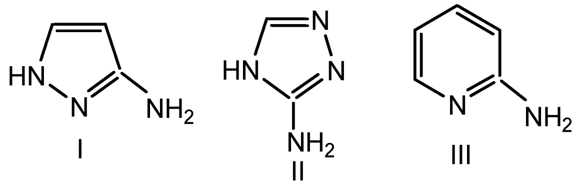


**Chart 1**

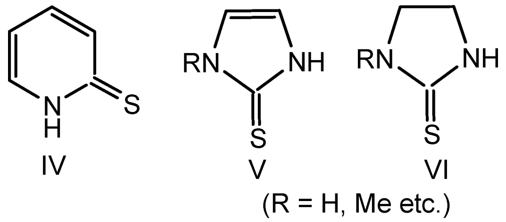
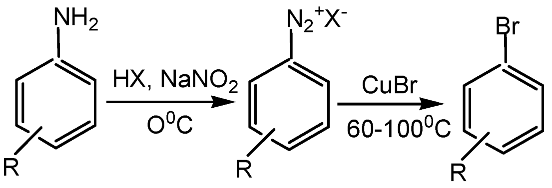


**Chart 2**



(1)

There is keen interest in the interaction of metal ions with heterocyclic thioamides owing to the relevance of their metal complexes in the biological systems.[4–8] From this laboratory, during the course of reactions of copper(I) halides with a series of heterocyclic thioamides, it was observed that solvent and reaction conditions played significant role in altering the nature of the products. For example, reaction of copper(I) halides with 2-mercapto-imidazolidine ($N_2C_3H_6S$, VI, R = H) in acetonitrile/acetonitrile-chloroform mixture formed dinuclear or polynuclear complexes.[6a–c] But when copper(I) chloride/bromide were allowed to react at room temperature in dimethyl sulfoxide or dimethyl formamide, C–S bond rupture along with oxidation of $Cu^I$ to $Cu^{II}$ occurred and formed a sulfate bridged polynuclear complex, $[Cu^{II}\{\eta^2\text{-}N,N\text{-}(N_2C_3H_5)_2S\}(\mu\text{-}O,OSO_2)(\eta^1\text{-}OH_2)]_n$ $\{(N_2C_3H_5)_2S$ = 2,2′-thio-di-2-imidazoline$\}$.[6e] The N-substituted analogous thio-ligand, namely, 2-mercapto-1-methyl-imidazoline ($N_2C_4H_6S$) with copper(I) chloride in acetonitrile or acetonitrile-chloroform mixture yielded a dinuclear complex, $[Cu^{II}_2\{\eta^2\text{-}N,N\text{-}(N_2C_4H_5)_2S\}_2(\mu\text{-}Cl)_2Cl_2]$ $\{(N_2C_4H_5)_2S$ = 1,1′-dimethyl-2,2′-di-imidazolylsulfide$\}$ along with formation of free $CuSO_4{\cdot}5H_2O$.[6e] This reaction involved oxidation of $Cu^I$ to $Cu^{II}$ and *in situ* conversion of 2-mercapto-1-methyl-imidazoline into 1,1′-dimethyl-2,2′-di-imidazolylsulfide (Scheme 1).

The reaction of copper(I) bromide with 2-mercapto-1-methyl-imidazoline ($N_2C_4H_6S$, V, R = Me) in acetonitrile yielded a trinuclear $\{Cu_3(\eta^1\text{-}Br)_3(\mu\text{-}SN_2C_4H_6)_3\}$ complex,[6d] but in dimethyl sulfoxide it formed sulfate chelated mononuclear $Cu^{II}$ complex, $[Cu^{II}\{\eta^2\text{-}N,N\text{-}(N_2C_4H_5)_2S\}(\eta^2\text{-}O,OSO_2)(\eta^1\text{-}OH_2)]$.[6e]

Herein, in this communication we report reaction of copper(I) bromide with 2-mercapto-1-methyl-imidazoline ($N_2C_4H_6S$) in acetonitrile-chloroform which has formed a $Cu^{II}$ tetranuclear

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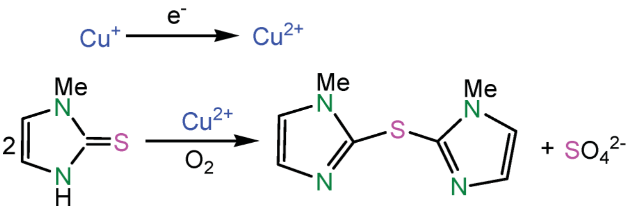
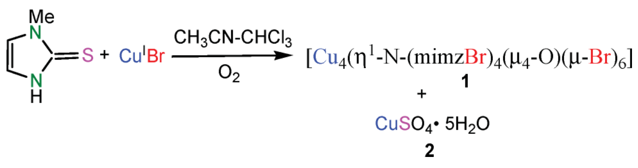
† Electronic supplementary information (ESI) available: Synthesis for **1** and **2**; additional crystallographic details and tables. CCDC reference numbers 820399 (**1**) and 820400 (**2**).



Scheme 1

cluster, $[\mathrm{Cu_4}(\eta^1\text{-}N\text{-}(\mathrm{N_2C_4H_5Br})_4(\mu_4\text{-O})(\mu\text{-Br})_6]$ **1** ($\mathrm{N_2C_4H_5Br}$ = 2-bromo-1-methyl-imidazole) along with free $\mathrm{CuSO_4{\cdot}5H_2O}$ **2**.‡ Copper has tendency to form such cores, for example, $[\mathrm{Cu_4OCl_6(py)_4}]$.[9]

Copper(I) bromide in acetonitrile was added to the solution of 2-mercapto-1-methyl-imidazoline in chloroform in 1 : 1 molar ratio under atmospheric conditions (25–30 °C). The color of the solution changed from colorless to brownish green in 2–3 days and black crystals of composition $\mathrm{C_{16}H_{20}Br_{10}Cu_4N_8O}$ were formed in a week along with blue crystalline product of composition $\mathrm{H_{10}CuSO_9}$. An X-ray study of the black crystals has shown it to be a $\mathrm{Cu^{II}}$ tetranuclear cluster, $[\mathrm{Cu_4}(\eta^1\text{-}N\text{-}(\mathrm{N_2C_4H_5Br})_4(\mu_4\text{-O})(\mu\text{-Br})_6]$ **1** ($\mathrm{N_2C_4H_5Br}$ = 2-bromo-1-methyl-imidazole) and blue crystals were that of $\mathrm{CuSO_4{\cdot}5H_2O}$ **2** (Scheme 2). The magnetic susceptibility measurement of **1** showed the magnetic moment value of 1.972 BM per copper supporting the presence of $\mathrm{Cu^{II}}$. The IR spectrum showed that the diagnostic peak due to ν(C=S) in the free ligand at 930 $\mathrm{cm^{-1}}$ disappears in the spectrum of complex **1**, which indicates that there is extrusion of sulfur atom of the ligand. Further, the electronic absorption spectrum of complex **1** in dmso showed a band in 259 nm ($\varepsilon = 1.268 \times 10^4$ L $\mathrm{mol^{-1}}$ $\mathrm{cm^{-1}}$) region due to charge transfer (O→Cu) transition.[10a] It is weakly fluorescent at $\lambda_{em}$ = 329 nm corresponding to excitation wavelength of 270 nm (Fig. 1).



Scheme 2

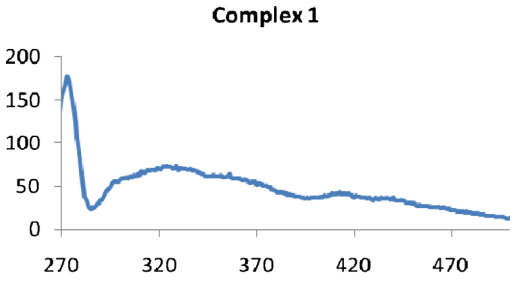


**Fig. 1** Fluorescence spectrum of complex **1**.

Fig. 2 shows molecular structure of complex $[\mathrm{Cu_4^{II}}(\eta^1\text{-}N\text{-}(\mathrm{N_2C_4H_5Br})_4(\mu_4\text{-O})(\mu\text{-Br})_6]$ **1**. Here, each copper is bonded to three μ-Br, one $\mu_4$-O and one nitrogen atom of 2-bromo-1-methyl-imidazole. The Br12, Br13 and Br14 atoms occupy basal plane, while O1 and N1A are the apical donor atoms in the five-coordinated trigonal bipyramidal coordination around Cu(II). The Cu–N bond distances in complex **1** {1.950(7)–1.965(8) Å} are shorter than in complex $[\mathrm{Cu^{II}_2}\{\eta^2\text{-}N,N\text{-}(\mathrm{N_2C_4H_5})_2\mathrm{S}\}_2(\mu\text{-Cl})_2\mathrm{Cl_2}]$ {2.005(3), 2.026(3) Å}.[6e] The Cu–Br bond distances in complex **1** {2.4514(14)–2.6436(14) Å} are longer than in complex $\{\mathrm{Cu_6}(\mu_3\text{-S-}\mathrm{N_2C_3H_6S})_2(\mu\text{-S-}\mathrm{N_2C_3H_6S})_4\mathrm{Br_2}(\mu\text{-Br})_4\}_n$ {2.4839(6)–2.5525(6) Å}.[6c] Molecular structure of complex **2** is given in supplementary. The ESI-mass spectrum of complex **1** did not show molecular ion peak but it has shown peaks which support various components of complex **1**. The important peak at *m/z* value 163.4 corresponds to 2-bromo-1-methyl-imidazole ($\mathrm{N_2C_4H_5Br^{81}}$). Another important peak at *m/z* value 268.3 corresponds to $\mathrm{Cu^{63}{}_4O}$ species. The peak at *m/z* value 385.2 corresponds to ($\mathrm{Cu^{63}Br_2{}^{81}N_2C_4H_5Br^{79}}$). Other peaks at *m/z* values, 225.3 and 243.3 correspond to ($\mathrm{Cu^{63}Br_2{}^{81}}$) and ($\mathrm{Cu^{65}ON_2C_4H_5Br^{81}}$) respectively.

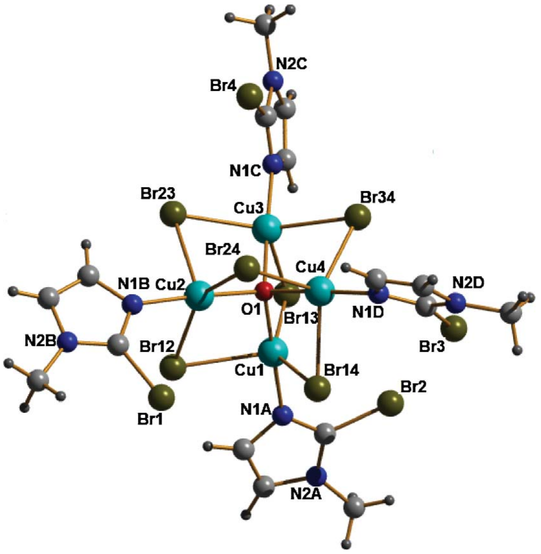
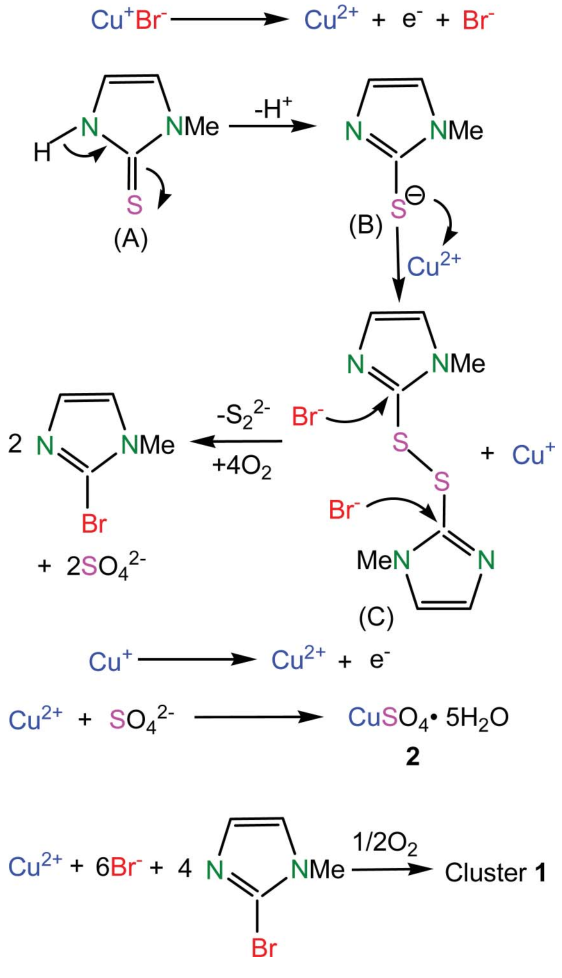


**Fig. 2** Molecular structure of tetranuclear cluster $[\mathrm{Cu_4}(\eta^1\text{-}N\text{-}(\mathrm{N_2C_4H_5Br})_4(\mu_4\text{-O})(\mu\text{-Br})_6]$ **1**. Selected bond lengths (Å) and angles (°): Cu1–O1 1.924(6), Cu1–N1A 1.962(7), Cu1–Br12 2.6436(14), Cu1–Br13 2.4514(14), Cu1–Br14 2.5321(15) and O1–Cu1–N1A 178.1(3), Br13–Cu1–Br14 142.58(6), Br13–Cu1–Br12 110.80(5), Br14–Cu1–Br12 104.83(5).

The formation of **1** and **2** shows that there is oxidation of $\mathrm{Cu^I}$ to $\mathrm{Cu^{II}}$ which in the presence of bromide ion as nucleophile is believed to brominate 2-mercapto-1-methyl-imidazoline ring at C2 carbon with the extrusion of sulfur as sulfate. Scheme 3 shows plausible mechanism of formation of 2-bromo-1-methyl-imidazole and its coordination to $\mathrm{Cu^{II}}$ in the tetranuclear complex **1**. Under the experimental conditions $\mathrm{Cu^I}$ oxidizes to $\mathrm{Cu^{II}}$ which in turn oxidizes the thio moiety (A, B) into its disulfide, namely, 1,1′-dimethyl-2,2′-di-imidazolyl disulphide (C). This disulfide is converted to 2-bromo-1-methyl-imidazole (ring bromination) along with formation of sulfate. Copper(II) in presence of bromide ions coordinates to 2-bromo-1-methyl-imidazole forming tetranuclear complex $[\mathrm{Cu_4}(\eta^1\text{-}N\text{-}(\mathrm{N_2C_4H_5Br})_4(\mu_4\text{-O})(\mu\text{-Br})_6]$ **1**. It is the first example of metal mediated *in situ* bromination of 2-mercapto-1-methyl-imidazoline ($\mathrm{N_2C_4H_6S}$) into 2-bromo-1-methyl-imidazole ($\mathrm{N_2C_4H_5Br}$). In literature this bromo-derivative has been prepared by the metallation of 1-methyl-imidazole with n-butyl lithium at −70 °C followed by treatment of tetrabromomethane.[10b]

It is concluded that 2-mercapto-1-methyl-imidazoline has been converted into 2-bromo-1-methyl-imidazole under ambient



**Scheme 3**

conditions with copper(I) bromide as a brominating agent. The transformation of organic sulfur to inorganic sulfate is a possible approach to a solution of the problem of pollution of organic sulfur compounds.[11a] These reactions also mimic the metabolism of organic sulfur in mammals.[11b]

Financial support (RS) from UGC(SAP) is gratefully acknowledged.

## Notes and references

‡ To a solution of copper(I) bromide (0.025 g, 0.17 mmol) in acetonitrile was added a solution of 2-mercapto-1-methyl-imidazoline (0.020 g, 0.17 mmol) in chloroform. After 2-3 days color of solution changed from colorless to brownish green and black prismatic crystals of complex **1** were formed along with blue crystals of $CuSO_4{\cdot}5H_2O$ **2**. Yield of complex **1**, 0.033 g, 54%, mp. 182–185 °C. Found: C, 14.05; H, 1.65; N, 8.22. Calc. for $C_{16}H_{20}Br_{10}Cu_4N_8O$: C, 13.78; H, 1.44; N, 8.04%. Electronic absorption spectra [dmso, $\lambda_{max}$, nm; ε/L mol$^{-1}$ cm$^{-1}$]: $10^{-4}$M solution: 259 ($1.269 \times 10^4$). Fluorescence spectrum: $10^{-5}$ M, $\lambda_{ex}$ = 270 nm $\lambda_{em}$ = 329 nm. IR absorptions: ($\nu$/cm$^{-1}$) 3121–2960(s), ν(C–H); 1535(sh), 1475(s), ν(C–N) + δ(C–H); 754(s), δ($N{-}CH_3$). Magnetic moment (BM): 1.972 per copper. Mass spectrum (*m/z*): 161.4 (expected, 160, $N_2C_4H_5Br^{79}$), 163.4 (162, $N_2C_4H_5Br^{81}$); 223.3 (223, $Cu^{63}Br^{79}Br^{81}$), 225.3 (225, $Cu^{63}Br_2{}^{81}$), 227.3 (227, $Cu^{65}Br_2{}^{81}$); 241.3 (241, $Cu^{65}ON_2C_4H_5Br^{79}$), 243.3 (243, $Cu^{65}ON_2C_4H_5Br^{81}$); 268.3 (268, $Cu_4{}^{63}0$); 383.2 (383, $Cu^{63}Br_2{}^{79}N_2C_4H_5Br^{81}$), 385.2 (385, $Cu^{63}Br_2{}^{81}N_2C_4H_5Br^{79}$), 387.2 (387, $Cu^{63}Br_2{}^{81}N_2C_4H_5Br^{81}$), 389.2 (389, $Cu^{63}Br_2{}^{81}N_2C_4H_5Br^{81}$).

The single crystals of compounds **1** and **2** were mounted on glass fibers and data were collected using Oxford Gemini diffractometer. The data were processed with *CrysAlisPro*. The structures were solved by direct methods using the program *SHELXS-97* and refined by full-matrix least-squares techniques based on $F^2$ using *SHELXL-97*.[12] *Crystal data* for (**1**); $C_{16}H_{20}Br_{10}Cu_4N_8O$, Mr = 1393.66 g mol$^{-1}$, triclinic, $a$ = 10.7306(7) Å, $b$ = 13.3805(5) Å, $c$ = 13.6898(5) Å, $\alpha$ = 78.199(3), $\beta$ = 75.841(4)°, $\gamma$ = 83.739(4)°, $V$ = 1861.98(16) Å$^3$, $T$ = 200(2)K, space group $P\bar{1}$, $\rho_c$ = 2.486 Mg m$^{-3}$, $Z$ = 2, $\mu$(Mo-Kα) = 13.008 mm$^{-1}$, 24314 reflections measured, unique 11303 [$R_{(int)}$ = 0.0612]. The final $R_1$ was 0.0669 for 6291 reflections [$I > 2.0\sigma(I)$] and w$R_2$ was 0.1410 (24314).

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