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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Experimental section

Chemical reagents

Copper(I) bromide was prepared by reducing an aqueous solution of $CuSO_4 \cdot 5H_2O$ using SO_2 in the presence of NaBr in water.[S1] The ligand 2-mercapto-1-methyl-imidazoline was procured from Aldrich Chemicals Ltd and used as such.

Techniques Used

Elemental Analysis: Elemental analysis for C, H and N were carried out using Thermoelectron FLASHEA1112 analyzer.

IR: An IR spectrum was recorded using KBr pellets on a Pye–Unicam SP3-300 spectrophotometer.

UV-Visible: A UV-visible spectrum was recorded using UV-1601PC Shimadzu spectrophotometer.

Fluorescence: A Fluorescence spectrum was recorded using RF-1501 Shimadzu spectrophotometer.

Melting point: The melting point was determined with a Gallenkamp electrically heated apparatus.

Magnetic Susceptibility: It was recorded using Magnetic Susceptibility balance by Johnson Matthey, Catalytic Systems Division Equipment.

Mass spectrum: It was recorded using Waters Q-Tof Micromass using ESI as ion source.

Synthesis of complexes

$[Cu_4(\eta^1\text{-}N\text{-}(N_2C_4H_5Br)_4(\mu_4\text{-}O)(\mu\text{-}Br)_6]$ **1**

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 (1.269×10^4). Fluorescence spectra: 10^{-5} M, λ_{ex} = 270 nm λ_{em} = 329 nm. IR absorptions: (ν / 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 spectra (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, $Cu^{63}Br_2{}^{81}N_2C_4H_5Br^{81}$). Analytical data for the formation of $CuSO_4 \cdot 5H_2O$ **2**. Found: H, 4.2; S, 13.07. Calc. for $CuSO_4 \cdot 5H_2O$: H, 4.0; S, 12.8%.

X-ray crystallography

The single crystals of compounds **1** and **2** were mounted on glass fibers and data were collected using Oxford Gemini diffractometer, each equipped with a graphite monochromator and Mo-Kα radiation (λ = 0.71073 Å). The unit cell dimensions and intensity data were measured at 200(2) K. The data were processed (data collection, refinement and reduction) 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*[S2]. All non-hydrogen atoms have been refined anisotropically. The crystallographic data are given in Table 1 and bond lengths and angles in Table 2.

Table 1. Crystallographic data for complexes **1** and **2**.

	1	**2**
Empirical formula	$C_{16}H_{20}Br_{10}Cu_4N_8O$	$H_{10}CuO_9S$
Formula weight	1393.66	249.68
T(K)	200(2)	200(2)
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a(Å)	10.7306(7)	5.9616(6)
b(Å)	13.3805(5)	6.098(3)
c(Å)	13.6898(5)	10.6776(19)
α(°)	78.199(3)	77.27(3)
β(°)	75.841(4)	82.344(11)
γ(°)	83.739(4)	72.52(2)
V ($Å^3$)	1861.98(16)	360.21(19)
Z	2	2
D_{calcd} (Mg m^{-3})	2.486	2.302
μ(mm^{-1})	13.008	3.337
All reflections collected	24314	5132
Unique reflections, R_{int}	11303, 0.0612	2364, 0.0171
Observed reflections (I>2σ(I)	6291	1972
Final R indices		
R1	0.0669	0.0230
wR2 (all)	0.1410	0.0591

Table 2. Bond lengths (Å) and angles (°) for complexes **1** and **2**.

1

Cu1-Br12	2.6436(14)	Cu4-Br24	2.6045(14)
Cu1-Br13	2.4514(14)	Cu4-Br34	2.5209(14)
Cu1-Br14	2.5321(15)	Cu1-O1	1.924(6)
Cu2-Br12	2.5380(14)	Cu1-N1A	1.962(7)
Cu2-Br23	2.6316(15)	Cu2-O1	1.920(6)
Cu2-Br24	2.4837(15)	Cu2-N1B	1.963(8)
Cu3-Br13	2.6174(14)	Cu3-O1	1.923(6)
Cu3-Br23	2.5115(15)	Cu3-N1C	1.950(7)
Cu3-Br34	2.5595(15)	Cu4-O1	1.915(6)
Cu4-Br14	2.5225(14)	Cu4-N1D	1.965(8)

Cu2-Br12-Cu1	74.49(4)	Br23-Cu3-Br34	140.45(6)
Cu1-Br13-Cu3	77.34(4)	Br23-Cu3-Br13	116.96(5)
Cu4-Br14-Cu1	75.09(4)	Br34-Cu3-Br13	101.02(5)
Cu3-Br23-Cu2	75.68(4)	O1-Cu4-N1D	177.8(3)
Cu2-Br24-Cu4	75.93(4)	Br34-Cu4-Br14	134.33(6)
Cu4-Br34-Cu3	76.29(4)	Br34-Cu4-Br24	116.92(5)
O1-Cu1-N1A	178.1(3)	Br14-Cu4-Br24	106.41(5)
Br13-Cu1-Br14	142.58(6)	Cu4-O1-Cu2	109.5(3)
Br13-Cu1-Br12	110.80(5)	Cu4-O1-Cu3	109.7(3)
Br14-Cu1-Br12	104.83(5)	Cu2-O1-Cu3	110.4(3)
O1-Cu2-N1B	176.7(3)	Cu4-O1-Cu1	106.7(3)
Br24-Cu2-Br12	148.87(6)	Cu2-O1-Cu1	109.4(3)
Br14-Cu2-Br23	99.71(5)	Cu3-O1-Cu1	111.0(3)
O1-Cu3-N1C	176.5(3)		

2

Cu1-O12W	1.9635(13)	Cu2-O22W	1.9237(15)
Cu1-O11W	1.9663(14)	Cu2-O21W	1.9578(12)
Cu1-O1	2.3692(12)	Cu2-O2	2.4197(13)
O12W-Cu1-O12W*	180	O22W-Cu2-O21W*	89.54(6)
O12W-Cu1-O11W	91.78(6)	O22W-Cu2-O2	93.47(6)
O12W-Cu1-O11W*	88.22(6)	O22W-Cu2-O2*	86.53(6)
O12W-Cu1-O1	88.00(5)	O21W-Cu2-O2	88.10(5)
O12W-Cu1-O1*	92.00(5)	O21W-Cu2-O2*	91.90(5)
O22W-Cu2-O21W	90.46(6)		

* indicates symmetry transformation

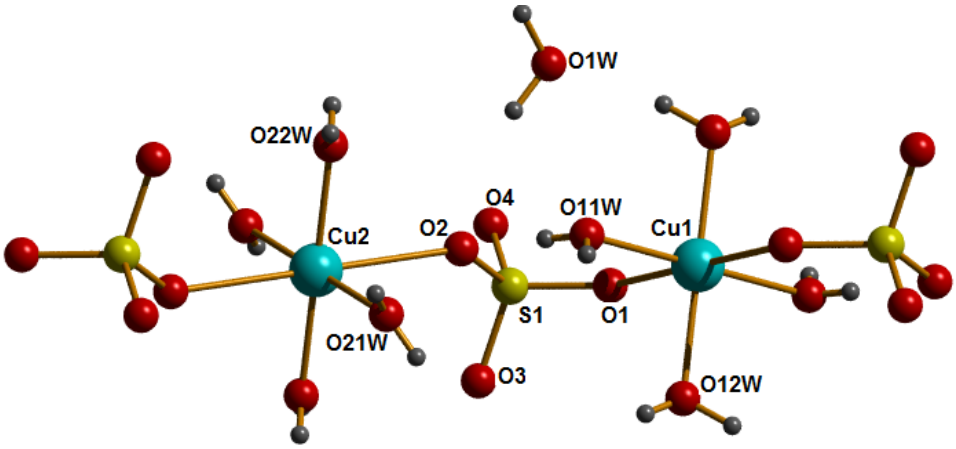

Fig S1. Molecular structure of $CuSO_4 \cdot 5H_2O$ **2**. Selected bond lengths (Å) and angles (°): Cu1-O12W 1.9635(13), Cu1-O11W 1.9663(14), Cu1-O1 2.3692(12) and O12W-Cu1-O12W* 180, O12W-Cu1-O11W 91.78(6), O12W-Cu1-O1 88.00(5), O12W-Cu1-O1* 92.00(5).

References

S1 G. Brauer, Handbook of Preparative Chemistry, 2nd ed., vol. 2, Academic Press, New York, 1965.

S2 G. M. Sheldrick. *Acta Crystallogr*. 2008, **A64**, 112-122.