

Metal mediated C-S rupture of heterocyclic thioamides : in situ generation of 2,2'-thio-di-2-imidazoline, 1,1'-dimethyl-2,2'-diimidazolylsulfide, SO_4^{2-} and their variable coordination to Cu^{II}

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Experimental section

Chemical reagents

Copper(I) halides (chloride and bromide) were prepared by reducing an aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ using SO_2 in the presence of NaX ($X = \text{Cl}, \text{Br}$) in water.^{S1} The ligands imidazolidine-2-thione and 1-methyl-1,3-imidazoline-2-thione were 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 FLASH EA 1112 analyzer.

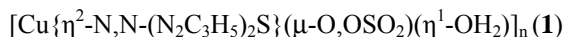
IR: IR spectra were recorded using KBr pellets on a Pye–Unicam SP3-300 spectrophotometer.

UV-Visible: UV-visible spectra were recorded using UV-1601PC Shimadzu spectrophotometer.

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

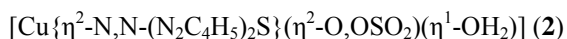
Magnetic Susceptibility: It was recorded using Magnetic Susceptibility balance by Johnson Matthey, Catalytic Systems Division Equipment.

Synthesis of complexes



To a solution of copper(I) chloride (0.025 g, 0.24 mmol) in dimethyl sulfoxide was added a solution of imidazolidine-2-thione (0.025 g, 0.24 mmol) in dimethyl sulfoxide and the solution was kept undisturbed. After 4-5 weeks, the slow evaporation of solution at room temperature formed prismatic blue crystals of polymer **1**. Yield, 0.062 g, 70%, mp. 215-17 °C (melt). Found: C, 20.56; H, 3.4; N, 16.35; S 18.74. Calc. for $\text{C}_6\text{H}_{12}\text{N}_4\text{O}_5\text{S}_2\text{Cu}$: C, 20.7; H, 3.45; N, 16.1; S, 18.4%. Electronic absorption spectra [dmsO, λ_{max} , nm; ϵ / $\text{L mol}^{-1} \text{ cm}^{-1}$]: 10^{-4}M solution: 266 (1.375×10^3); 10^{-3}M solution: very intense absorption in 266 nm region; 676 nm (132). IR absorptions: (ν / cm^{-1}) 3300-3200br (NH + OH), 3020-2900w (C-H), 1100w, 1020m (ν_3); 995m (ν_1) and 608s (ν_4) (SO_4), 930m and 955m (C-S). Magnetic moment (BM): 1.975 per copper.

Copper(I) bromide gave the identical product.



To a solution of copper(I) bromide (0.025 g, 0.17 mmol) in dimethyl sulfoxide was added a solution of 1-methyl-1,3-imidazoline-2-thione (0.020 g, 0.17 mmol) in dimethyl sulfoxide and the solution was kept undisturbed. After 5-6 weeks, the slow evaporation of solution at room temperature formed prismatic blue crystals of complex **2**. Yield, 0.046 g, 71%, mp. 195-97 °C (melt). Found: C, 25.57; H, 3.1; N, 15.2; S

17.42. Calc. for $C_8H_{12}N_4O_5S_2Cu$: C, 25.8; H, 3.2; N, 15.07; S, 17.2%. Electronic absorption spectra [dmsO, λ_{max} , nm; ϵ /L mol⁻¹ cm⁻¹]: 10^{-4} M solution: 265 (1.372×10³); 10^{-3} M solution: very intense absorption in 265 nm region; 675 nm (130). IR absorptions: (ν / cm⁻¹) 3300-3220br (NH + OH), 3015-2910w (C-H), 1105w, 1022m (ν_3); 990m (ν_1) and 610s (ν_4) (SO₄), 940m and 950m (C-S). Magnetic moment (BM): 1.972 per copper.

[Cu₂{ η^2 -N,N-(N₂C₄H₅)₂S}₂}(μ -Cl)₂Cl₂] (**3**)

To a solution of copper(I) chloride (0.025 g, 0.25 mmol) in dimethyl sulfoxide was added a solution of 1-methyl-1, 3-imidazoline-2-thione (0.029 g, 0.25 mmol) in dimethyl sulfoxide and the solution was kept undisturbed. After 2-3 weeks, the slow evaporation of solution at room temperature formed prismatic green crystals of **3** along with blue crystalline product which was identified as CuSO₄·5H₂O. Yield, 0.046 g, 55%, mp. 233-237°C (melt). Found: C, 28.96; H, 3.26; N, 16.9; S, 9.55. Calc. for C₁₆H₂₀N₈S₂Cu₂Cl₄: C, 29.2; H, 3.0; N, 17.0; S, 9.73%. Electronic absorption spectra [dmsO, λ_{max} , nm; ϵ /L mol⁻¹ cm⁻¹]: 10^{-4} M solution: 261 (2.889×10³); 10^{-3} M solution: very intense absorption in 261 nm region; 739 nm (117). IR absorptions: (ν / cm⁻¹) 3157-3109s (N-H), 3026-2948w (C-H), 1525s, 1481s (C-N) + δ (C-H), 948s (C=S), 763s δ (N-CH₃). Magnetic moment (BM): 1.966 per copper. Analytical data for the formation of CuSO₄·5H₂O. Found: H, 4.1; S, 13.17. Calc. for CuSO₄·5H₂O : H, 4.0; S, 12.8%.

Complex **3** can also be synthesized in CH₃CN or CH₃CN-CHCl₃ mixture.

X-ray crystallography

The single crystals of compounds **1** - **3** were mounted on glass fibers and data were collected using Siemens P4 (**1**, **3**) and Xcalibur R (**2**) diffractometers, each equipped with a graphite monochromator and Mo-K α radiation (λ = 0.71073 Å). The unit cell dimensions and intensity data were measured at 295(2) (**1**), 123(2) (**2**) and 296(2) (**3**) K. The data were processed (data collection, refinement and reduction) with XSCANS^{S2} and SHELXTL-PC (**1**, **3**)^{S3} and CrysAlisPro (**2**). The structures were solved by direct methods using the program SIR-92 (**1**, **3**), SHELXS-97 (**2**) and refined by full-matrix least-squares techniques based on F^2 using SHELXL-97^{S3}. 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** - **3**.

	1	2	3
Empirical formula	C ₆ H ₁₂ CuN ₄ O ₅ S ₂	C ₈ H ₁₂ CuN ₄ O ₅ S ₂	C ₁₆ H ₂₀ Cl ₄ Cu ₂ N ₈ S ₂
Formula weight	347.86	371.88	657.44
T(K)	295(2)	123(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2 _{1/n}	P2 _{1/n}	P2 _{1/n}
a(Å)	9.561(5)	7.2777(2)	9.053(1)
b(Å)	7.851(5)	16.8832(4)	8.402(1)
c(Å)	15.768(5)	10.6197(3)	15.754(3)
$\alpha = \gamma(^{\circ})$	90	90	90
$\beta(^{\circ})$	98.490(5)	101.377(2)	94.28(1)
V (Å ³)	1170.6(10)	1279.21(6)	1195.0(3)
Z	4	4	2
D _{calcd} (Mg m ⁻³)	1.974	1.931	1.827
μ (mm ⁻¹)	2.242	2.059	2.425

Reflections collected	2316	8698	2219
Unique reflections, R(int)	2180, 0.0340	4243, 0.0244	1859, 0.0409
Final R indices R1 wR2	0.0334 0.0816	0.0273 0.0721	0.0344 0.0899

Table 2. Bond lengths (Å) and angles (°) for complexes **1** - **3**.

1			
N2-Cu	1.969(3)	O2-Cu	1.983(3)
N3-Cu	1.946(3)	O3-Cu	2.319(3)
O1W-Cu	2.000(3)		
N3-Cu-N2	92.80(11)	O1W-Cu-O3	87.89(11)
N3-Cu-O2	92.80(11)	N2-Cu-O3	101.52(11)
O2-Cu-O1W	89.92(11)	O2-Cu-O3	95.00(12)
N2-Cu-O1W	90.35(11)	N3-Cu-O3	93.26(11)
2			
Cu-N1	1.9520(13)	Cu-O1	2.0241(11)
Cu-N2	1.9638(13)	Cu-O2	2.0067(11)
Cu-O1W	2.1918(12)		
N1-Cu-N2	93.87(5)	N1-Cu-O1W	101.07(5)
N2-Cu-O2	95.05(5)	O1-Cu-O1W	93.93(5)
O2-Cu-O1	71.08(4)	N2-Cu-O1W	103.31(5)
N1-Cu-O1	95.07(5)	O2-Cu-O1W	93.66(5)
3			
Cu-Cl1	2.2931(9)	Cu-N1	2.026(3)
Cu-Cl1#	2.7159(10)	Cu-N3	2.005(3)
Cu-Cl2	2.2624(10)		
Cl1-Cu-Cl1#	86.33(3)	N1-Cu-Cl1#	100.45(8)
Cu-Cl1-Cu#	93.67(3)	Cl2-Cu-Cl1	93.37(3)
N3-Cu-N1	86.94(11)	N3-Cu-Cl2	89.62(8)
N3-Cu-Cl1	175.99(8)	Cl2-Cu-Cl1#	102.87(3)

References

- S1 G. Brauer, Handbook of Preparative Chemistry, 2nd ed., vol. 2, Academic Press, New York, 1965.
 S2 XSCANS, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1994.
 S3 G. M. Sheldrick. *Acta Crystallogr.* 2008, **A64**, 112-122.

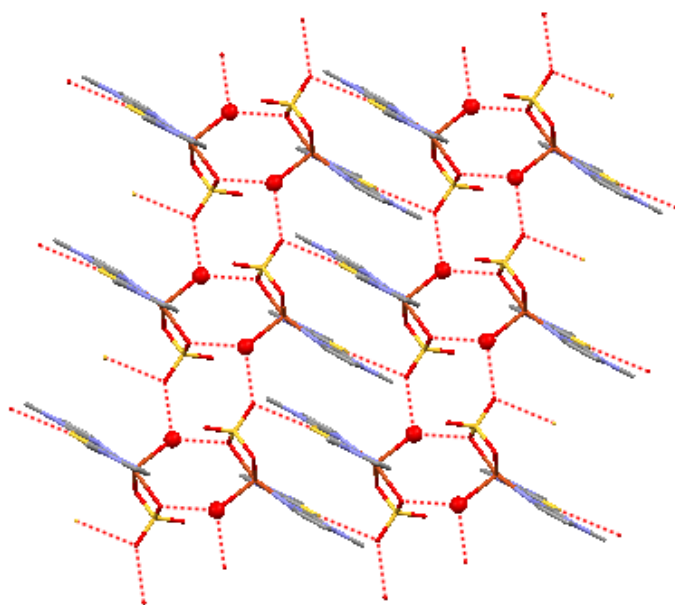


Fig. S1. Showing H-bonding contacts in complex 2. ($O1W-H1W1...O3^i$, 2.743 (2) Å, $H1W1...O3^i$ 1.94 Å, $O1W-H1W1...O3^i$ \angle 167°, $O1W-H1W2...O2^{ii}$, 2.763(3) Å, $H1W2...O2^{ii}$ 1.98 Å, $O1W-H1W2...O2^{ii}$ \angle 174°, $O3...S^{iii}$ 3.219 Å, where $i = -1+x,y,z$; $ii = 1-x,1-y,2-z$; $iii = -x,1-y,1-z$)

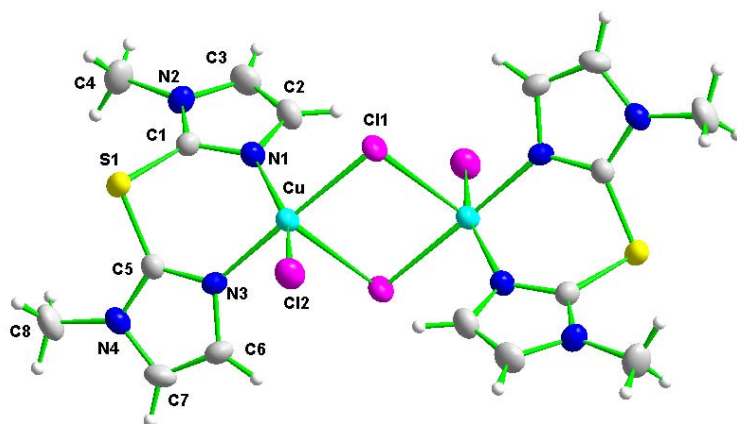


Fig. S2. Molecular structure of complex 3. Selected bond lengths (Å) and angles (°): Cu-Cl1 2.293(1), Cu-Cl1# 2.716(1), Cu-Cl2 2.262(1), Cu-N1 2.026(3) and Cl1-Cu-Cl1# 86.33(3), Cu-Cl1-Cu# 93.67(3), Cl2-Cu-Cl1 93.37(3), N3-Cu-N1 86.94(11).