

# Reactivity of thiazolidine-2-thione towards Cu<sup>I</sup>/Cu<sup>II</sup>: Synthesis and structures of [3-(2-thiazolin-2-yl)thiazolidine-2-thione]copper(I) bromide and [bis(2,2'-bipyridine)nitratocopper(II)] nitrate

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**Abstract.** Thiazolidine-2-thione (L<sup>1</sup>, NC<sub>3</sub>H<sub>5</sub>S<sub>2</sub>) reacted with copper(I) bromide in CH<sub>3</sub>CN under aerobic conditions and transformed through C–S bond cleavage into 3-(2-thiazolin-2-yl)thiazolidine-2-thione (L<sup>2</sup>, C<sub>3</sub>H<sub>4</sub>S<sub>2</sub>N–C<sub>3</sub>H<sub>4</sub>SN). This thio-ligand L<sup>2</sup> with Cu<sup>I</sup> ion yielded a three coordinate complex, [3-(2-Thiazolin-2-yl)thiazolidine-2-thione]copper(I)bromide **1a** which crystallized in the triclinic system with the space group P1 as reported earlier. Treatment of **1a** with bis(diphenylphosphino)methane (dppm) in dichloromethane also formed [3-(2-thiazolin-2-yl)thiazolidine-2-thione]copper(I) bromide **1b** but it crystallized into the triclinic system with a new space group, P-1: 296(2) K, a, 7.3890(19); b, 8.473(2); c, 9.491(2) Å; α, 70.273(5); β, 67.170(5); γ, 84.949(5)°; R, 6.79%. Reactions of copper(II) nitrate with thiazolidine-2-thione followed by the addition of 2,2'-bipyridine or with 2,2'-bipyridine first followed by the addition of thiazolidine-2-thione, gave blue crystals in both the cases. The x-ray crystallography revealed stoichiometry of the complex formed as: [Cu(κ<sup>2</sup>-N,N'-bipy)<sub>2</sub>(κ<sup>1</sup>-ONO<sub>2</sub>)](NO<sub>3</sub>) **2**, which crystallized in monoclinic crystal system with space group, P2<sub>1</sub>/n(14). Crystal data: 173(2) K, a, 11.318(1), b, 12.160(1), c, 14.967(1) Å; β = 98.01(1)°, R, 3.99%; 296(2) K, a, 11.340(5), b, 12.249(5), c, 15.065(6) Å; β = 98.04(2)°, R, 4.09%.

**Keywords.** Thiazolidine-2-thione; 3-(2-thiazolin-2-yl)thiazolidine-2-thione; 2,2'-bipyridine; copper(I) bromide; copper(II) nitrate.

## 1. Introduction

In literature, it was recently reported that reactions of heterocyclic thioamides with copper(I) salts in acetonitrile have shown C–S rupture, formation of new thio-ligands (*in situ* formed) and their subsequent coordination to Cu<sup>I</sup> or Cu<sup>II</sup>.<sup>1–3</sup> Further, it is known that C–S bond activation, cleavage and transformations using transition metal compounds have found wide interest in synthetic chemistry, shown relevance in the biological reactions,<sup>4–6</sup> as well as has found importance in petroleum industry.<sup>7</sup> We investigated that the reactions of thiazolidine-2-thione (L<sup>1</sup>) with copper(I) chloride/bromide or with [Cu(NCCH<sub>3</sub>)<sub>4</sub>](BF<sub>4</sub>) under aerobic conditions generated a new ligand, 3-(2-thiazolin-2-yl)thiazolidine-2-thione (L<sup>2</sup>), which *in situ* coordinated to Cu<sup>I</sup> ions and gave complexes (**1a**, **3**, **4**) as shown in scheme 1.<sup>3</sup> In this paper, reactions of thio-ligand L<sup>1</sup> with copper(I) bromide under aerobic conditions followed by the treatment with bis(diphenylphosphino)methane (dppm) as well as that with copper(II) nitrate in the presence

of 2,2'-bipyridine are described. Compound **1b** with a new crystal modification as well as the product **2** are reported in this paper.

## 2. Experimental

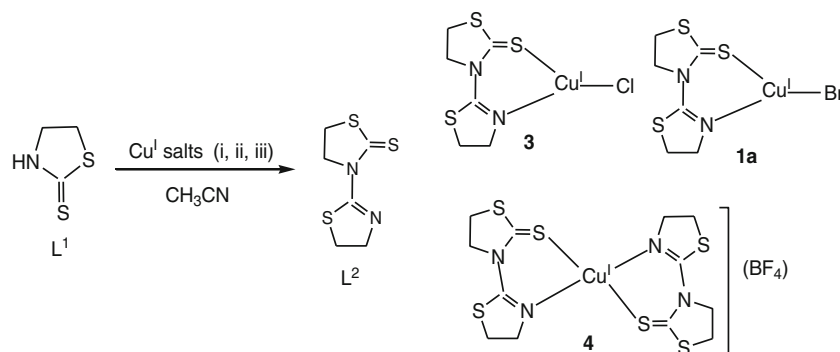
### 2.1 Materials

Copper(I) bromide was prepared by reducing an aqueous solution of CuSO<sub>4</sub>·5H<sub>2</sub>O using SO<sub>2</sub> in the presence of NaBr in water. Copper(II) nitrate, thiazolidine-2-thione and 2,2'-bipyridine were purchased from Sigma–Aldrich Ltd. Solvents were of Analytical Research grade and used as such.

### 2.2 Synthesis of [Cu(κ<sup>2</sup>-N, S - C<sub>3</sub>H<sub>4</sub>S<sub>2</sub>N - C<sub>3</sub>H<sub>4</sub>SN)Br] (**1b**)

Copper(I) bromide (0.025 g, 0.17 mmol) was dissolved in acetonitrile and to it solid thiazolidine-2-thione (0.022 g, 0.25 mmol) was added. The reaction mixture was kept undisturbed. After several days, red violet (or red brown) crystals along with the light blue crystals

\*For correspondence



**Scheme 1.** Reactions with products: i. CuCl, ii. CuBr, iii.  $[Cu(NCCH_3)_4](BF_4)$  in  $CH_3CN$ .

of  $CuSO_4 \cdot 5H_2O$  were formed. The mother liquor was removed and to the solid left behind was added a solution of dppm in dichloromethane. The red violet compound rapidly dissolved in dichloromethane solution of dppm leaving behind blue crystals of  $CuSO_4 \cdot 5H_2O$ . This solution was left at room temperature in a culture tube which gave red brown crystals of  $[Cu(\kappa^2-N,S-C_3H_4S_2N-C_3H_4SN)Br]$  (**1b**) studied using x-ray crystallography. Yield 60%.

### 2.3 Synthesis of $[Cu(\kappa^2-N,N'-bipy)_2(\kappa^1-ONO_2)](NO_3)$ (**2**)

To a blue solution of copper(II) nitrate (0.025 g, 0.10 mmol) in ethanol (2 mL) was added a solution of thiazolidine-2-thione (0.11g, 0.10 mmol) in ethanol (2 mL). To the mixture was added two drops of dimethyl formamide. The colour of the solution becomes light blue and blue precipitates were formed. The contents were left undisturbed at room temperature ( $25^\circ C$ ) until the colour changed to green after 24 h. To this solution, 2,2'-bipyridine (0.038 g, 0.24 mmol) was added and allowed the solution undisturbed. This led to the formation of bluish green crystals. Same product was formed when order of addition was reversed. The crystals were studied by using x-ray crystallography at 176(2) K and 296(2) K. Yield: 55%.

### 2.4 X-ray crystallography

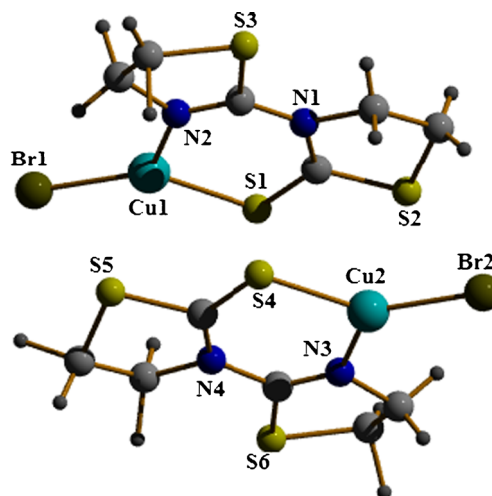
A single crystal was mounted on a glass fiber and used for data collection with a Xcalibur, Eos, Gemini (**2a** and 173(2) K) equipped with graphite monochromated  $Cu-K\alpha$  ( $\lambda = 1.54184 \text{ \AA}$ ) as well as with a Bruker Kapa – Apex (II) CCD diffractometer (**1b** and **2b**; 296(2) K) equipped with graphite monochromated  $Mo-K\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ). The data recorded at low temperature was processed with CrysAlisPro CCD (data collection), CrysAlisPro RED (cell refinement, data reduction).<sup>8</sup> The structure was solved by direct

methods using the program SHELXS-97, refined by full-matrix least-squares techniques against  $F^2$  using SHELX-97 and molecular graphics from SHELXL.<sup>9</sup> The data collected at room temperature was also processed with Bruker Kapa – Apex(II) CCD and corrected for absorption using SADABS.<sup>10</sup> The structures were solved by direct methods using SIR-92 software<sup>10</sup> and refined by full-matrix least-squares method based on  $F^2$  using the program using SHELX-97.<sup>9</sup> Atomic scattering factors taken from “International Tables for Crystallography”.<sup>11</sup>

## 3. Results and Discussion

### 3.1 Synthesis and general comments

Reaction of copper(I) bromide with the thio-ligand  $L^1$  is reported to form the compound  $[3-(2-thiazolin-2-yl)thiazolidine-2-thione]copper(I) bromide$  **1a**, whose x-ray crystallography suggested that it has triclinic crystal with the space group P1 as shown in figure 1.<sup>3</sup> Compound **1a** was reacted with bis(diphenylphosphino)



**Figure 1.** Molecular structure of compound **1a**.<sup>3</sup>

methane (dppm) for preparing a P-coordinated mononuclear or P,P-coordinated dinuclear complex. However, x-ray crystallography of red brown crystals showed that the new compound formed is [3-(2-thiazolin-2-yl)thiazolidine-2-thione]copper(I) bromide **1b** which is shown in figure 2. Scheme 2 depicts transformation of **1a** into **1b**. Compound **1a** is insoluble in dichloromethane, but addition of dppm assisted the compound **1a** to become soluble and then it de-ligated during crystallization giving rise to the formation of compound **1b**.

In the reactions of copper(II) nitrate with thiazolidine-2-thione and 2,2'-bipyridine, it was believed that the C-S rupture similar to that shown by CuCl/CuBr (scheme 1) might occur and product of the type **A** as shown in scheme 3 was expected. However, the single

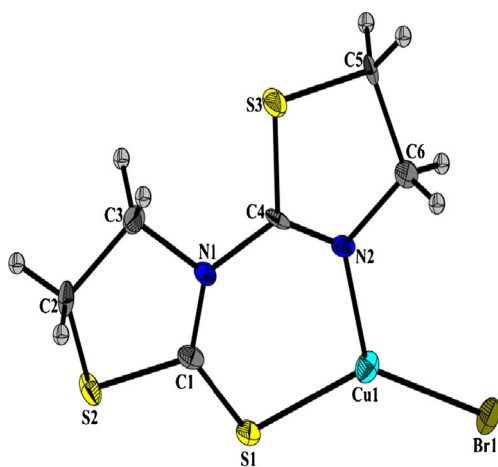
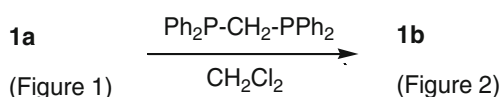


Figure 2. Molecular structure of compound **1b**.

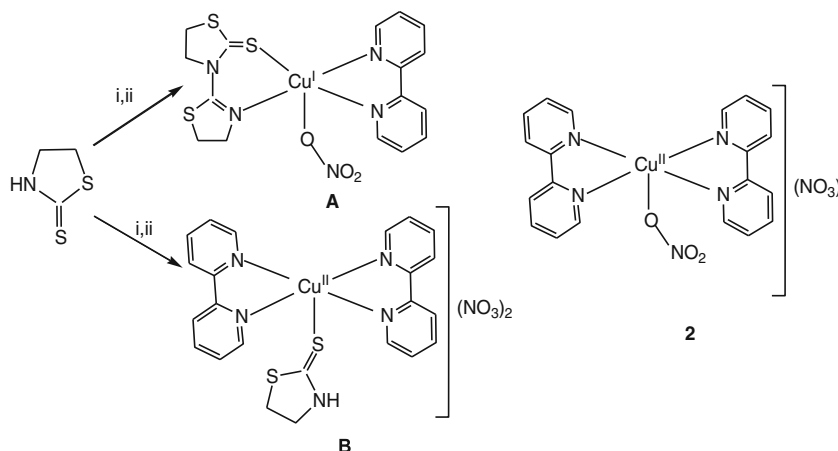


Scheme 2. Change of **1a** into **1b**.

crystal x-ray crystallography has shown the product as,  $[\text{Cu}(\kappa^2\text{-N,N'-bipy})_2(\kappa^1\text{-ONO}_2)](\text{NO}_3)$  **2** (scheme 3). It means there is no C-S rupture under the experimental conditions and the product of type **A** is not formed in the presence of 2,2'-bipyridine. Likewise, the product **B** is also not formed and the only preferred product was compound **2**. Due to the strong coordinating ability of 2,2'-bipyridine neither C-S rupture nor coordination of thiazolidine-2-thione to copper are observed under experimental conditions.

### 3.2 Molecular structures (**1b**, **2**)

The x-ray crystal data are given in table 1 and the bond parameters for compounds **1b** and **2** are placed in table 2. The *in situ* generated thio-ligand, 3-(2-thiazolin-2-yl)thiazolidine-2-thione  $\text{L}^2$  chelates to  $\text{Cu}^{\text{I}}$  of complex **1b** through its N, S donor atoms {Cu-S, 2.190(4); Cu-N, 1.970(11) Å} with N-Cu-S bite angle of  $99.3(4)^\circ$ . The third position is occupied by bromide ion {Cu-Br, 2.287(2)} giving rise to a three coordinate complex. The angles, N-Cu-Br and S-Cu-Br { $127.1(3)$  and  $133.55(13)^\circ$  respectively} and the N-Cu-S bite angle suggest a distorted trigonal planar geometry (figure 2). The bond distances/angles are comparable to those in compound **1a**<sup>3</sup>. Compound **2** crystallized in monoclinic crystal system with  $\text{P}2_1/\text{n}(14)$  space group. The x-ray data at low temperature is labelled as **2a**, and that at room temperature is labelled as **2b**. Low temperature data was obtained to check if more than one oxygen atom of  $\text{NO}_3^-$  is coordinating to  $\text{Cu}^{\text{II}}$  which it was not. The quality of data at low temperature is better with low R factor of 3.99%. Copper(II) is bonded to two bipy ligands through its nitrogen donor atoms at Cu-N distances in the range 1.9776(18)–2.1215(18) Å (figure 3). The fifth site is occupied by one O atom of one nitrate group at Cu-O distance of 2.0828(18) Å.



Scheme 3. Synthetic products expected: (i)  $\text{Cu}(\text{NO}_3)_2$ , (ii) bipy.

**Table 1.** Crystal data for compounds **1b** and **2**.

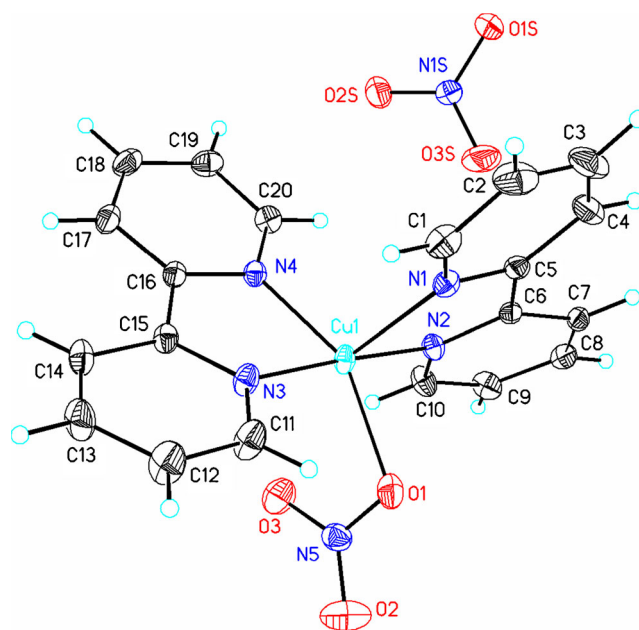
T(K)	<b>1b</b> , 296(2) K	T(K)	<b>2a</b> , 173(2) K,	<b>2b</b> , 296(2) K
Empirical formula	C <sub>6</sub> H <sub>8</sub> BrCuN <sub>2</sub> S <sub>3</sub>	Empirical formula	C <sub>20</sub> H <sub>16</sub> CuN <sub>5</sub> O <sub>3</sub> .N O <sub>3</sub>	
M	347.80	M	499.93;	499.94
λ(Å)	0.71069	λ(Å)	1.54184;	0.71073
Crystal system	Triclinic	Crystal system	Monoclinic	Monoclinic
Space group	P-1	Space group	P2 <sub>1</sub> /n(14);	P2 <sub>1</sub> /n(14);
Unit cell dimensions		Unit cell dimensions		
a(Å)	7.3890(19)	a(Å)	11.31848(19);	11.340(5)
b(Å)	8.473(2)	b(Å)	12.1599(2);	12.249(5)
c(Å)	9.491(2)	c(Å)	14.9672(3);	15.065(6)
α(°)	70.273(5)	α(°)	-	-
β(°)	67.170(5)	β(°)	98.0053(16);	98.043(16)
γ(°)	84.949(5)	γ(°)	-	-
V(Å <sup>3</sup> )	514.9(2)	V(Å <sup>3</sup> )	2039.88(6);	2072.0(15)
Z	2	Z	4;	4
D <sub>calcd</sub> (g cm <sup>-3</sup> )	2.243	D <sub>calcd</sub> (g cm <sup>-3</sup> )	1.628;	1.603
μ(mm <sup>-1</sup> )	6.560	μ(mm <sup>-1</sup> )	1.988;	1.107
F(000)	340	F(000)	1020;	1020
Reflections collected	6655	Reflections collected	13344;	15176
Unique reflections	1888	Unique reflections	3912	4114
	(R <sub>int</sub> = 0.0395)		(R <sub>int</sub> = 0.041);	(R <sub>int</sub> = 0.061)
Data/restraints/ parameters	1888/0/118	Data/restraints/ parameters	3912/0/299;	4114/0/298
Reflns. with [I > 2σ(I)]	1742	Reflns. with [I > 2σ(I)]	3577;	2408
R Indices		R Indices		
R <sub>1</sub>	0.0679	R <sub>1</sub>	0.0399;	0.0409
wR <sub>2</sub>	0.2195	wR <sub>2</sub>	0.1088;	0.0785
R indices (all data)		R indices (all data)		
R <sub>1</sub>	0.0709	R <sub>1</sub>	0.0428;	0.0912
wR <sub>2</sub>	0.2204	wR <sub>2</sub>	0.1116;	0.0939
Largest diff.	1.954 e. Å <sup>-3</sup> ,	Largest diff. Peak	0.48 e. Å <sup>-3</sup> ,	0.355 e. Å <sup>-3</sup>
Peak and hole	-1.217 e. Å <sup>-3</sup>	and hole	-0.44 e. Å <sup>-3</sup> ,	-0.268 e. Å <sup>-3</sup>

The coordination of nitrate lengthens O1-N5 distance {1.280(3) Å} vis-à-vis uncoordinated O2-N5 {1.199(3) Å} and O3-N5 {1.241(3) Å} bond distances. The angles around copper metal centre vary in the wide range,

**Table 2.** Bond lengths (Å) and angles (°) of compounds **1b** and **2a**\*.

<b>1b</b>			
Cu1 – Br1	2.287(2)	C1 – S2	1.749(14)
Cu1 – N2	1.970(11)	N2 – Cu1 – S1	99.3(4)
Cu1 – S1	2.190(4)	N2 – Cu1 – Br1	127.1(3)
C1 – S1	1.665(15)	S1 – Cu1 – Br1	133.55(13)
<b>2a</b>			
Cu1 – O1	2.0828(18)	Cu1 – N3	1.9776(18)
Cu1 – N1	2.1215(18)	Cu1 – N4	2.0228(17)
Cu1 – N2	1.9875(17)		
N1 – Cu1 – N2	79.93(7)	N2 – Cu1 – O1	87.61(7)
N1 – Cu1 – O1	101.10(7)	N2 – Cu1 – N4	99.05(7)
N1 – Cu1 – N3	103.30(7)	N3 – Cu1 – O1	90.31(7)
N1 – Cu1 – N4	108.36(7)	N3 – Cu1 – N4	81.40(7)
N2 – Cu1 – N3	176.46(7)	N4 – Cu1 – O1	150.49(7)

\*See [supplementary](#) for more details

**Figure 3.** Molecular structure of [Cu(κ<sup>2</sup>-N,N'-bipy)<sub>2</sub>(κ<sup>1</sup>-ONO<sub>2</sub>)](NO<sub>3</sub>) **2a**.

80–177°, the shortest being the bite angles (ca. 80°) of bipy ligands. The  $\tau$  parameter of 0.43 suggests significant deviation from a square pyramid and the structure is in between a trigonal bipyramid-square pyramid. The nitrate has shown a variety of coordination trends (see [supplementary data](#)).<sup>12–22</sup>

#### 4. Conclusions

Conversion of three coordinated complex, [3-(2-Thiazolin-2-yl)thiazolidine-2-thione]copper(I) bromide **1a**, crystallized in triclinic system with a space group P1, using dppm in dichloromethane, into [3-(2-thiazolin-2-yl)thiazolidine-2-thione]copper(I) bromide **1b**, crystallized into triclinic system with a new space group, P-1, is an interesting observation involving change in crystal modification. The lack of C-S rupture in reaction of copper(II) nitrate with thiazolidine-2-thione in presence of bipyridine is attributed to the strong coordinating ability of bipyridine to Cu<sup>II</sup> which has prevented this rupture under the experimental conditions.

#### Supplementary Information

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC 1006272 for **1b**, 988896 for **2a** and 988897 for **2b** (Fax: +44-1223-336-033; E-Mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk), <http://www.ccdc.cam.ac.uk>). (See Tables S1 and S2 for more details about nitrate coordination, complete bond lengths/angles for **2** as well as for bonding trends of nitrate in presence of 2,2'-bipyridines).

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