

Note

# Synthesis of a novel copper(II) complex and its crystal structure

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## Abstract

One novel chiral copper(II) complex was successfully synthesized from the reaction of chiral 1,3-thiazolidine-2-thione ligand with  $\text{CuCl}_2$  in dichloromethane in the presence of  $\text{Et}_3\text{N}$  and DMAP at room temperature. Its unique crystal structure was unambiguously disclosed by X-ray analysis. The crystal is tetragonal, space group  $I4(1)$ , space group  $a = 15.0875(11)$ ,  $b = 15.0875(11)$ ,  $c = 19.362(3)$  Å,  $\alpha = 90$ ,  $\beta = 90$ ,  $\gamma = 90^\circ$ ,  $V = 4407.4(8)$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_{\text{calc}} = 1.639$  mg cm<sup>-3</sup>. © 2002 Published by Elsevier Science B.V.

*Keywords:* Chiral copper(II) complex; 1,3-Thiazolidine-2-thione; Bidentate chiral ligand; Crystal structure; X-ray analysis

## 1. Introduction

Historically, metal–sulfur cluster complexes is a very active field for organometallic chemists because of the novelty and versatility of structures and reactivities of such clusters, as well as their potential applications as models for the active site in non-heme proteins such as the ferredoxins [1]. In the preparation of chiral auxiliaries for catalytic asymmetric Baylis–Hillman reaction, we incidentally found that, in the reaction of 1,3-thiazolidine-2-thione **1** with acryloyl chloride in the presence of  $\text{Et}_3\text{N}$ , DMAP and  $\text{CuCl}_2$ , the reaction product is a novel Cu(II) complex **3** rather than compound **2** (Scheme 1). Further examination of this reaction disclosed that acryloyl chloride did not effect the reaction at all because, in the absence of acryloyl chloride, the Cu(II) complex **3** was formed in similar yields as well (Scheme 2). We believe that this is caused by the fact that 1,3-thiazolidine-2-thione **1** was in an equilibrium with its tautomer which directly reacted with  $\text{CuCl}_2$  to give the corresponding novel Cu(II) complex **3** (Scheme 3) [2]. The crystal structure of this novel copper(II) complex was unambiguously disclosed by X-ray analysis. We wish to report the experimental details and the crystal structure of **3** in this paper.

## 2. Results and discussion

### 2.1. Synthesis of chiral ligand **1** and its copper(II) complex **3**

The chiral auxiliary **1** was synthesized according to the literature [3] and the copper(II) complex **3** was isolated by silica gel ( $\text{SiO}_2$ ) column chromatography from the reaction of **1** with  $\text{CuCl}_2$  in the presence of  $\text{Et}_3\text{N}$  and DMAP at room temperature (Scheme 2) (eluent: ethyl acetate/petroleum ether = 1/4). The metal complex **3** was obtained as a colorless solid. We first confirmed its structure by microanalysis because Cu(II) complex **3** is a paramagnetic complex, therefore, its fine structure cannot be determined by <sup>1</sup>H-NMR spectroscopic analysis.

### 2.2. Molecular structure of complex **3**

After tremendous efforts, the single crystal of novel copper(II) complex **3** was obtained by careful recrystallization from dichloromethane and petroleum ether (1:10). Thus, finally, its structure was unambiguously disclosed by X-ray analysis (Fig. 1). The crystal data are shown in Table 1. The bond lengths and bond angles are elucidated in Tables 2 and 3, respectively.

From Fig. 1, it is very clear that the chiral auxiliary 1,3-thiazolidine-2-thione **1** is a bidentate ligand because both the nitrogen atom and the sulfur atom of thiocar-

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bonyl group coordinate to the metal center to form the metal complex. The adjacent two ligands take anti-parallel direction using S and N atoms to coordinate with the Cu center forming the Cu/S, N core network. The sulfur atom in fact coordinates to two Cu(II) atoms with bond lengths 2.2383(18) and 2.2938(15) Å, respectively. The bond length of N–Cu is 1.984(4) Å. In addition, the distances of Cu(1)–Cu(2), Cu(1)–Cu(2A) and Cu(2)–Cu(1A) are 2.6511(8), 2.5779(8), and 2.5779(8) Å, respectively. These distances are within the sum of the van der Waals separation of 2.8 Å (Cu = 1.4 Å [4]). In general, this copper(II) metal cluster **3** is quite stable.

As can be seen from Fig. 1, four ligands **1** and four copper(II) atoms form a novel metal cluster. The four copper atoms present in complex **3** are connected with S and N atoms with bond angles: N(2A)–Cu(1)–S(2) 121.08(14)°, N(2A)–Cu(1)–S(3) 111.55(14)°, S(2)–Cu(1)–S(3) 127.15(8)°, S(3)–Cu(1)–Cu(2A) 118.68(5)°, S(2)–Cu(1)–Cu(2A) 57.02(4)°, N(1)–Cu(2)–Cu(1) 93.95(14)°, N(2A)–Cu(1)–Cu(2) 134.69(14)°, Cu(1)–S(2)–Cu(2A) 68.88(5)°, N(1)–Cu(2)–S(3) 120.85(14)°, and Cu(2)–S(3)–Cu(1) 71.74(5)°. The Cu/S, N core apparently takes an irregular network structure. The cluster forms a butterfly-type structure.

Concerning Cu/S,N metal complex, Raper in 1998 reported the crystal structure of a [cyclo{tetrakis- $\mu_3(\eta^2$ -S,  $\eta^1$ -N)-(1,3-thiazolidine-2-thionato)-bis-( $\eta^1$ -S)-(1,3-

thiazolidine-2-thione)tetracopper(I)}] from the electrochemical synthesis using 2-mercaptothiazoline **4** and AR grade metallic copper [5]. Its crystal structure is very different from that of **3** having an “open-butterfly” configuration with Cu–Cu distances and angles in the range 2.8887(15)–3.8357(16) Å and 47.51(3)–78.27(4)°, respectively. We also confirmed that, under the normal organic reaction conditions mentioned above, none of the corresponding metal complex could be formed by the reaction of 1,3-thiazolidine-2-thione **4** with CuCl<sub>2</sub> (Scheme 4). In general, many Cu/S metal complexes were formed from the reaction of CuCl<sub>2</sub> or CuBr<sub>2</sub> with sulfur ligands to give the corresponding CuL<sub>2</sub> complexes [6]. Thus, it is very interesting that a novel butterfly-type metal cluster could be formed via a very simple organic reaction under mild reaction conditions.

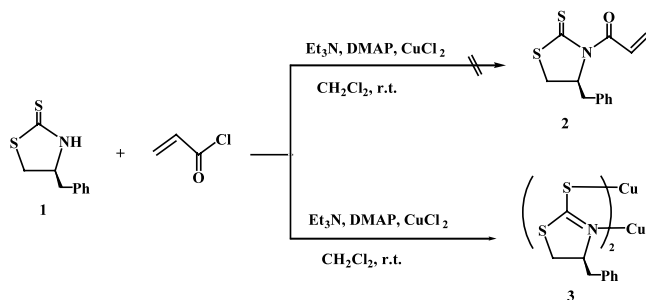
### 3. Conclusion

In conclusion, we have explored a novel Cu(II)/S,N metal cluster from the reaction of 1,3-thiazolidine-2-thione **3** with CuCl<sub>2</sub> and disclosed its interesting structure by X-ray analysis. We expect that our results will develop a new strategy on the design of chiral ligands and the synthesis of chiral metal complexes. Further studies in this area are in progress in our laboratory.

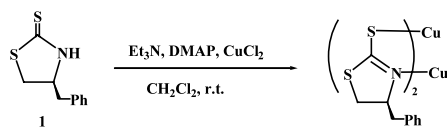
### 4. Experimental

#### 4.1. General procedures

MPs were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were determined for solution in MeOH at 20 °C by using a Perkin–Elmer-241 MC polarimeter;  $[\alpha]_D$  values are given in units of 10<sup>-1</sup> ° cm<sup>2</sup> g<sup>-1</sup>. <sup>1</sup>H-NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in CDCl<sub>3</sub> with TMS as internal standard; *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA + mass spectrometer. Organic solvents used were dried by standard methods when necessary. All solid compounds reported in this paper gave satisfactory CHN microanalyses with an Italian Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions



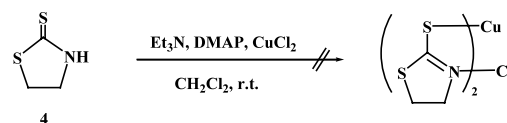
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

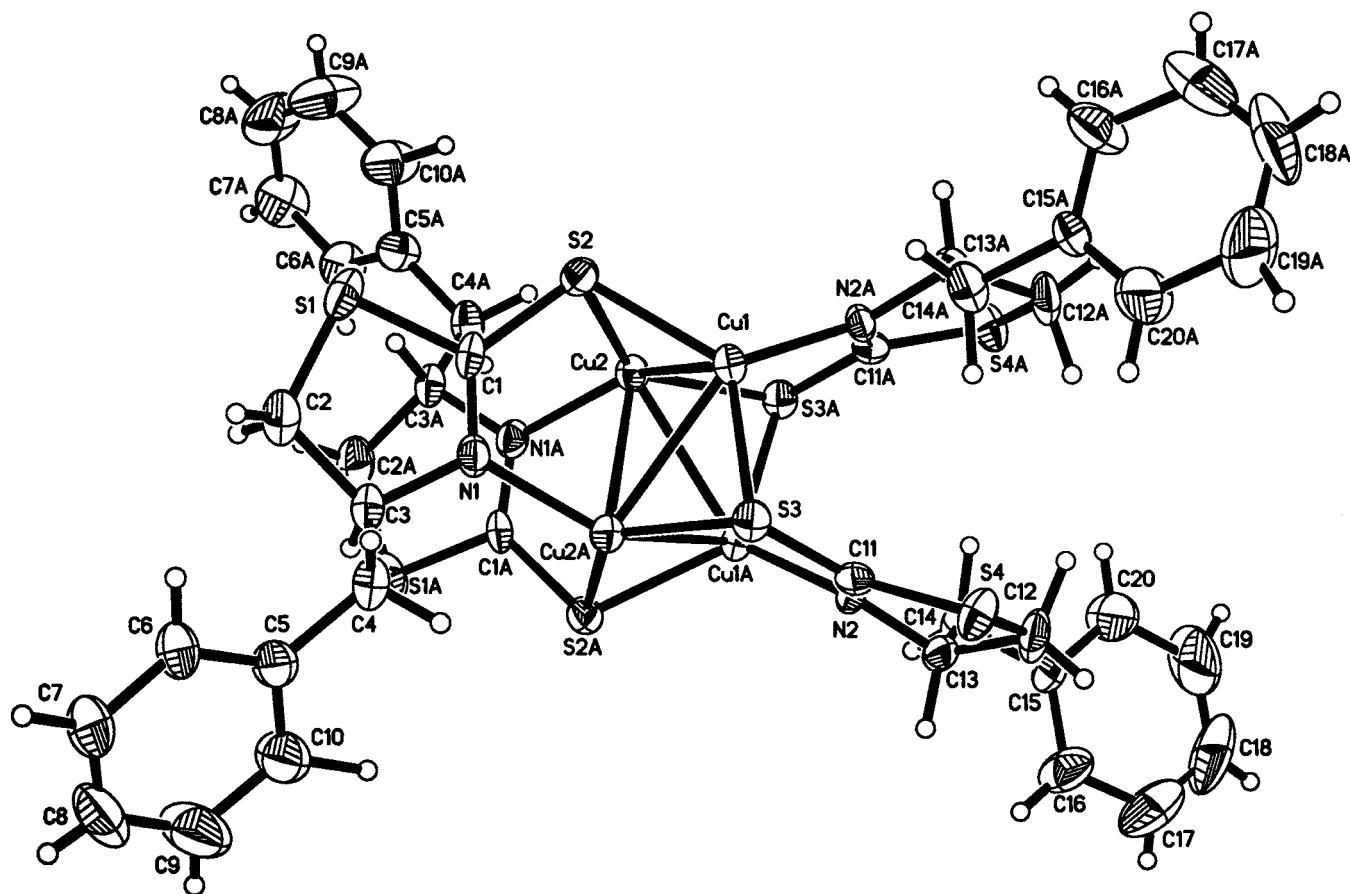


Fig. 1. The crystal structure of **3**.

were monitored by TLC with Huanghai GF<sub>254</sub> silica gel coated plates. Flash Column Chromatography was carried out using 300–400 mesh silica gel at increased pressure. The chiral starting material 1,3-thiazolidine-2-thione **1** and 2-mercaptothiazoline **4** were prepared according to the literature [3].

#### 4.2. Preparation of 1,3-thiazolidine-2-thione **1** and **4**

These compounds were prepared according to the literature [3].

Compound **1**:  $[\alpha]_D^{20} -123.7$  (c 1.64, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, TMS)  $\delta$  2.90–3.10 (2H, m, CH<sub>2</sub>), 3.23 (1H, dd,  $J=11.2, 6.8$  Hz, CH), 3.59 (1H, dd,  $J=11.2, 6.8$  Hz, CH), 4.40–4.54 (1H, m, CH), 7.13–7.45 (5H, m, Ar), 7.65 (1H, s, NH). The <sup>1</sup>H-NMR data are consistent with those reported in the literature [3].

Compound **4**: <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, TMS)  $\delta$  3.58 (2H, t,  $J=7.6$  Hz, CH<sub>2</sub>), 4.01 (2H, t,  $J=7.6$  Hz, CH<sub>2</sub>), 8.27 (1H, s, NH). The <sup>1</sup>H-NMR data are consistent with those reported in the literature [3].

#### 4.3. Preparation of chiral copper(II) complex **3**

To a Schlenk tube was added compound **1** (105 mg,

0.5 mmol), CuCl<sub>2</sub>·H<sub>2</sub>O (257 mg, 1.5 mmol) and DMAP (5.6 mg, 0.05 mmol) under Ar atmosphere. Solvent CH<sub>2</sub>Cl<sub>2</sub> (5.0 ml) and Et<sub>3</sub>N (61 mg, 0.6 mmol) was added successively and the reaction mixture was stirred at room temperature for 24 h. After filtration, the filtrate was washed with water (10 ml) and the organic layer was dried over anhydrous MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (length: 20 cm,  $\phi$ : 2 cm) to give the compound **3** as a colorless solid (eluent: EtOAc–petroleum ether = 1/4). 42 mg, 31%; m.p. 242–244 °C;  $[\alpha]_D^{20} +29$  (c 0.26, CHCl<sub>3</sub>); IR(KBr)  $\nu$  1495, 1520, 1539 cm<sup>-1</sup>; Anal. Found: C, 44.12; H, 3.71; N, 4.98. Calc. for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>S<sub>4</sub>Cu<sub>2</sub> requires: C, 44.18; H, 3.71; N, 5.15%.

#### 4.4. Crystallography

A suitable crystal was mounted on the top of a glass capillary. Crystal data and details of data collection and structure refinement are given in Table 1. Data were collected on a CCD area detector with graphite-monochromated Mo–K $\alpha$  radiation  $\lambda = 0.71069$  Å using the  $\omega$ – $2\theta$  technique at 20 °C. A total of 3887 unique reflection was collected. The data were collected for Lorentz polarization effects. The structure was solved

by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares. All hydrogen

Table 1  
Crystal data and structure refinement of **3**

Empirical formula	C <sub>20</sub> H <sub>20</sub> Cu <sub>2</sub> N <sub>2</sub> S <sub>4</sub>
Formula weight	543.70
Temperature (K)	293(2)
Crystal system	Tetragonal
Lattice type	Primitive
Unit cell dimension	
<i>a</i> (Å)	15.0875(11)
<i>b</i> (Å)	15.0875(11)
<i>c</i> (Å)	19.362(3)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	4407.4(8)
Space group	14(1)
<i>Z</i>	8
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.639
<i>F</i> (000)	2208
Theta range for data collection (°)	1.71–28.32
Reflections collected/unique	13 631/3887 [ <i>R</i> <sub>int</sub> = 0.0645]
Completeness to theta = 28.32	96.6 (%)
Absorption correction	SADABS
Max/min transmission	1.0000, 0.3902
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	3887/1/260
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.831
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0322, <i>wR</i> <sub>2</sub> = 0.0573
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0486, <i>wR</i> <sub>2</sub> = 0.0605
Absolute structure parameter	−0.016(15)
Extinction coefficient	0.00020(4)
Largest difference peak and hole (e Å <sup>-3</sup> )	0.372 and −0.269

Table 2  
The selected bond lengths of **3** (Å)

Cu(1)–N(2) # 1	1.984(4)	N(2)–C(13)	1.478(6)
Cu(1)–S(2)	2.2383(18)	N(2)–Cu(1) # 1	1.984(4)
Cu(1)–S(3)	2.2938(15)	C(2)–C(3)	1.553(7)
Cu(1)–Cu(2) # 1	2.5779(9)	C(3)–C(4)	1.521(7)
Cu(1)–Cu(2)	2.6511(8)	C(4)–C(5)	1.498(6)
Cu(2)–N(1)	1.969(5)	C(5)–C(6)	1.347(7)
Cu(2)–S(3)	2.2301(17)	C(5)–C(10)	1.384(7)
Cu(2)–S(2) # 1	2.3182(16)	C(6)–C(7)	1.363(9)
Cu(2)–Cu(1) # 1	2.5779(9)	C(7)–C(8)	1.349(9)
Cu(2)–Cu(2) # 1	2.9837(13)	C(8)–C(9)	1.336(9)
S(1)–C(1)	1.751(6)	C(9)–C(10)	1.385(8)
S(1)–C(2)	1.765(6)	C(12)–C(13)	1.514(8)
S(2)–C(1)	1.757(6)	C(13)–C(14)	1.518(6)
S(2)–Cu(2) # 1	2.3182(16)	C(14)–C(15)	1.512(6)
S(3)–C(11)	1.748(6)	C(15)–C(20)	1.343(7)
S(4)–C(11)	1.764(7)	C(15)–C(16)	1.344(7)
S(4)–C(12)	1.837(6)	C(16)–C(17)	1.388(8)
N(1)–C(1)	1.273(6)	C(17)–C(18)	1.343(11)
N(1)–C(3)	1.472(7)	C(18)–C(19)	1.306(11)
N(2)–C(11)	1.262(6)	C(19)–C(20)	1.386(10)

Table 3  
Selected bond angle of **3** (°)

N(2) # 1–Cu(1)–S(2)	121.08(14)
N(2) # 1–Cu(1)–S(3)	111.55(14)
S(2)–Cu(1)–S(3)	127.15(8)
N(2) # 1–Cu(1)–Cu(2) # 1	92.79(14)
S(2)–Cu(1)–Cu(2) # 1	57.02(4)
S(3)–Cu(1)–Cu(2) # 1	118.68(5)
N(2) # 1–Cu(1)–Cu(2)	134.69(14)
S(2)–Cu(1)–Cu(2)	84.65(4)
S(3)–Cu(1)–Cu(2)	53.02(4)
Cu(2) # 1–Cu(1)–Cu(2)	69.57(3)
N(1)–Cu(2)–S(3)	120.85(14)
N(1)–Cu(2)–S(2) # 1	107.31(14)
S(3)–Cu(2)–S(2) # 1	131.74(8)
N(1)–Cu(2)–Cu(1) # 1	136.59(14)
S(3)–Cu(2)–Cu(1) # 1	86.22(4)
S(2) # 1–Cu(2)–Cu(1) # 1	54.09(5)
N(1)–Cu(2)–Cu(1)	93.95(14)
S(3)–Cu(2)–Cu(1)	55.25(4)
S(2) # 1–Cu(2)–Cu(1)	122.27(5)
Cu(1) # 1–Cu(2)–Cu(1)	73.43(3)
N(1)–Cu(2)–Cu(2) # 1	82.30(14)
S(3)–Cu(2)–Cu(2) # 1	106.18(4)
S(2) # 1–Cu(2)–Cu(2) # 1	76.01(4)
Cu(1) # 1–Cu(2)–Cu(2) # 1	56.37(3)
Cu(1)–Cu(2)–Cu(2) # 1	54.06(3)
C(1)–S(2)–Cu(1)	108.3(2)
C(1)–S(2)–Cu(2) # 1	97.6(2)
Cu(1)–S(2)–Cu(2) # 1	68.88(5)
C(11)–S(3)–Cu(2)	105.7(2)
C(11)–S(3)–Cu(1)	100.98(19)
Cu(2)–S(3)–Cu(1)	71.74(5)
C(11)–S(4)–C(12)	89.6(3)
C(1)–N(1)–Cu(2)	120.8(4)
C(3)–N(1)–Cu(2)	123.7(4)
C(11)–N(2)–Cu(1) # 1	119.3(4)
C(13)–N(2)–Cu(1) # 1	126.9(4)

atoms were included in calculated position. All calculations were performed using the SHELXS-97 (Sheldrick, 1990) crystallographic software package. Final *R* and *R*<sub>w</sub> values were 0.032 and 0.057.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 174127. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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