

# Versatile coordination patterns in the reaction system of *N*-benzoyl-*N'*-(2-pyridyl)thiourea with CuCl<sub>2</sub>. Their reaction conditions, systematic isolation and crystal structures

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A versatile reaction system; *N*-benzoyl-*N'*-(2-pyridyl)thiourea (L) with CuCl<sub>2</sub>, has been studied under conditions of control of the relative concentration of the components (L or CuCl<sub>2</sub>). Therefore, both converse approaches were employed: one is dropwise addition of L to CuCl<sub>2</sub> in ethanol solution, from which a dark-brown needle-like crystal,  $\infty^1$  {[CuCIL'] [Cl]} **1**, was obtained, which is a chloride-bridged one-dimensional Cu(II) polynuclear complex coordinated by the oxidative cyclization product L' generated from L (L' = 2-benzoylimino-[1,2,4]thiadiazolo-[2,3-*a*]pyridine), and the second approach is conversely dropping CuCl<sub>2</sub> into L in acetone solution; at first, a pale-yellow reduced copper(I) mononuclear complex, [CuL<sub>2</sub>Cl] **2**, was formed, which exhibits a planar molecular configuration with a regular three coordination geometry, and then a red bis-sulfur-bridged copper(II) dinuclear complex, {[CuLCl<sub>2</sub>]<sub>2</sub>} **3**, appeared subsequently. The crystal structures of these three products have been determined by X-ray diffraction. From the presented results the coordination and redox reaction pathways in the L–CuCl<sub>2</sub> system have been clearly revealed.

It has been shown that the reaction systems of thiourea and its derivatives with the Cu(II) ion are complicated and versatile as a result of the ready redox between them in combination with the flexible coordination of copper and the bridging capability of thioureas. Therefore, there have been a number of reports on such systems in which a variety of Cu(I) and Cu(II) mononuclear and polynuclear complexes with one or more coordination geometries usually coexist within a system.<sup>1–3</sup> However, as far as we are aware, systematic isolation and structural studies of various products in a particular system are still very limited.

Even though extensive research has been undertaken over the past decades, even now many interesting works continue to be published on studies of the equilibrium and redox kinetics of copper(II)–thiourea complexes,<sup>3</sup> of the crystal structures of a family of new copper(I) cyanide complexes of thiourea and substituted thioureas,<sup>4</sup> and of a copper(II) complex on a thiourea-functionalized silica gel.<sup>5</sup> However, what is worthy of special mention is their biological importance as models of the copper-sulfur interaction in many biomolecules such as copper metallothioneins.<sup>6</sup>

In regard to such versatile reaction systems, we believe that control of the relative concentration between reaction components may be crucial. Therefore, a “dropping method” was adopted, namely drop-by-drop addition of a ligand to a metal solution, or reversely adding metal to ligand solution, such that the reactions proceed under the condition of one component (ligand or metal) in excess, and the other under control. By this means, we investigated the complex system of *N*-benzoyl-*N'*-(2-pyridyl)thiourea (L) with copper(II) chloride in ethanol or acetone solution. From this system three Cu(II) and Cu(I) coordination compounds: a chloride-bridged one-dimensional polynuclear copper(II) coordination complex,  $\infty^1$  {[CuCIL'] [Cl]} **1**, a bis-sulfur-bridged copper(II) dinuclear complex, {[CuLCl<sub>2</sub>]<sub>2</sub>} **3**, and a reduced copper(I)–L complex,

[CuL<sub>2</sub>Cl] **2**, were isolated systematically. In particular, we reported the synthesis and partial characterization of the polymer **1** in a preliminary communication.<sup>7</sup> Here we present a more complete characterization of these complexes, reveal the nature of Cu(II)–thioureas interactions and demonstrate the redox and coordination pathways in the system.

## Experimental

### General details

All reagents and solvents used in this study were commercially available and were used as received. Solvents were dried by conventional procedures prior to use. The C, H and N analyses were carried out on a MOD 1106 analyzer. Infrared spectra in the range 400–4000 cm<sup>–1</sup> were recorded on a Shimadzu IR-435 instrument using KBr pellets. Proton NMR spectra were obtained with a Brüker DPX-400 spectrometer and calibrated against the solvent signals (CD<sub>3</sub>CN,  $\delta_{\text{H}}$  1.95).

### Synthesis of *N*-benzoyl-*N'*-(2-pyridyl)thiourea (L)

L was prepared using a similar procedure described in the literature<sup>8</sup> by the reaction of benzoyl chloride with KSCN in anhydrous acetone to produce benzoyl isothiocyanate, followed by condensation with 2-aminopyridine. The product was recrystallized from acetone. Yield: about 83%, m.p. 149 °C. Found: C, 60.94; H, 4.22; N, 16.12. Calcd for C<sub>13</sub>H<sub>11</sub>N<sub>3</sub>OS: C, 60.7; H, 4.28; N, 16.34%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  7.2–7.7 (m, 4H, 2, 3, 4 & 5 pyridyl protons), 7.8–8.8 (m, 5H, 2', 3', 4', 5' & 6' phenyl protons), 9.8 (br, NH). IR (KBr, cm<sup>–1</sup>) 3000–3300 (N–H); 1680 [–C(O)–NH–carbonyl]; 1500–1600 (pyridine C=N, C=C); 1430–1490 (–N–C=S); 1330 (amide-II); 1260 (N=C=S); 1150 (C=S).

## Reaction of CuCl<sub>2</sub> with L

The reaction products in the CuCl<sub>2</sub>–L system were synthesized and isolated by the “dropping method” under two sets of conditions.

Route A: To CuCl<sub>2</sub> in ethanol was added dropwise an ethanol solution of L at a speed of about one drop per 2 h at room temperature for several days until a dark-brown needle-like crystal of  $\infty^1\{[\text{CuCIL}]/[\text{Cl}]\}$ , **1**, was formed. Details of the synthesis and the characterization of complex **1** have been described previously.<sup>7</sup>

Route B: To an acetone solution (50 ml) of L (0.02 mmol), CuCl<sub>2</sub> (0.01 mmol) in acetone (20 ml) was added dropwise at the same speed as above. At first, a pale-yellow prismatic crystal, [CuL<sub>2</sub>Cl] **2**, began to appear within several days, isolated in 23% yield based on CuCl<sub>2</sub>. Anal. found: C, 50.78; H, 3.50; N, 13.65. Calcd for CuC<sub>26</sub>H<sub>22</sub>O<sub>2</sub>N<sub>6</sub>ClS<sub>2</sub>: C, 50.89; H, 3.59; N, 13.70%. IR (KBr, cm<sup>−1</sup>): 3070–3217 (N–H); 1716 [–C(O)–NH–carbonyl]; 1526–1606 (pyridine C=N, C=C); 1431 (phen ring); 1328 (amide-II); 1265 (C=S); 1150 (N=C=S). After two or more weeks, a second red prismatic crystal,  $\{[\text{CuLCl}_2]\}_2$  **3**, formed simultaneously, isolated in 34% yield based on CuCl<sub>2</sub>. Anal. found: C, 40.07; H, 3.12; N, 10.69. Calcd for CuC<sub>13</sub>H<sub>11</sub>OSN<sub>3</sub>Cl<sub>2</sub>: C, 39.84; H, 2.81; N, 10.73%. IR (KBr, cm<sup>−1</sup>): 3439–3037 (N–H); 1667 (carbonyl C=O); 1187 (N=C=S). Both crystals were of adequate size and quality for X-ray studies and easily separated manually.

## X-Ray crystallography

Crystal data and experimental details are given in Table 1. Data were collected on a RAXIS-IV area detector diffractometer with graphite monochromated Mo–K $\alpha$  radiation ( $\lambda = 0.7101$  Å). The structures were solved by direct methods and expanded using Fourier techniques. The data were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included but not refined. All calculations were performed by using the teXsan crystallographic software package of Molecular Structure Corporation.<sup>9</sup>

For crystal  $\infty^1\{[\text{CuCIL}]/[\text{Cl}]\}$  **1**, a dark-brown prismatic crystal with dimensions of  $0.60 \times 0.10 \times 0.10$  mm<sup>3</sup> was used for data collection. A total of 28 3.00° oscillation frames with an exposure time of 20.0 min. per frame were collected.

For crystal [CuL<sub>2</sub>Cl] **2**, a pale-yellow prismatic crystal with dimensions of  $0.4 \times 0.3 \times 0.10$  mm<sup>3</sup> was used for data

collection. A total of 40 4.00° oscillation frames with an exposure time of 30.0 min. per frame were collected.

For crystal  $\{[\text{CuLCl}_2]\}_2$  **3**, a red prismatic crystal with dimensions of  $0.40 \times 0.15 \times 0.10$  mm<sup>3</sup> was used for data collection. A total of 18 10.00° oscillation frames with an exposure time of 45.0 min. per frame were collected.

CCDC reference numbers 182319–182321 for compounds **1**–**3**, respectively. See <http://www.rsc.org/suppdata/nj/b2/b206257g/> for crystallographic files in CIF or other electronic format.

## Results and discussion

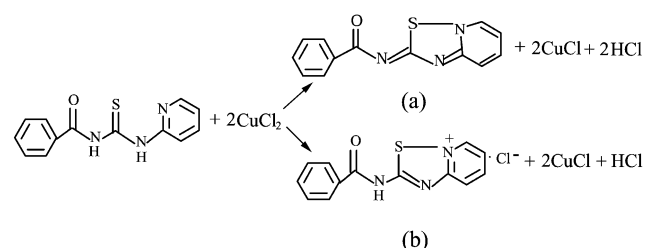
### Syntheses by the “dropping method”

Despite the complexity and versatility of the copper(II)–thiourea reaction systems, we think that the key to the investigation of such systems lies in control of the relative concentration between the reaction components. Therefore, both converse approaches were employed: one is dropwise addition of L to copper(II) chloride in ethanol or acetone solution, and the other is conversely dropping copper(II) chloride into L in the same solvent. In the first approach a sufficient amount of CuCl<sub>2</sub> exists in the solution to oxidize the additive ligand L and further coordinate to the *in situ* generated oxidative product L', forming a dark-brown needle-like compound,  $\infty^1\{[\text{CuCIL}]/[\text{Cl}]\}$  **1**, which is a chloride-bridged one-dimensional polynuclear copper(II) complex coordinated by the oxidative cyclization product L' (Schemes 1, 2 and Fig. 1). In the second approach additive CuCl<sub>2</sub> is almost completely reduced to Cu(I), which can be coordinated further to the excess L in the solution, yielding a pale-yellow reduced copper(I) mononuclear complex, [CuL<sub>2</sub>Cl] **2** (Scheme 2 and Fig. 2), and only in the presence of a lower concentration of L can the additive CuCl<sub>2</sub> be not completely reduced; in this case, the ligand L can effectively bridge the CuCl<sub>2</sub> to form a red bis-sulfur-bridged copper(II) dinuclear complex,  $\{[\text{CuLCl}_2]\}_2$  **3** (Scheme 2 and Fig. 3).

It follows that by using the dropping method to control the relative concentrations of the components (namely stoichiometric control), the reactions take place in a regular sequence and the different products are formed under different concentration conditions; consequently, the reaction pathways are revealed in more detail and in this system we see that the thiourea L plays a triple role: acting as a reductant for Cu(II) and complexing agent for reduced copper(I) and forming a polynuclear complex through its oxidized derivative L'. In addition, the dropping method allowed the reactions to proceed under mild conditions favoring of the formation of single crystals suitable for X-ray studies. The selection of the solvents was made for the sake of the growth of quality crystals; the X-ray quality crystals of **1** were grown in ethanol solution, and in acetone for **2**.

### Molecular structures

**One-dimensional polynuclear Cu(II) complex,  $\infty^1\{[\text{CuCIL}]/[\text{Cl}]\}$  **1**.** As can be seen in Fig. 1, compound **1** is a

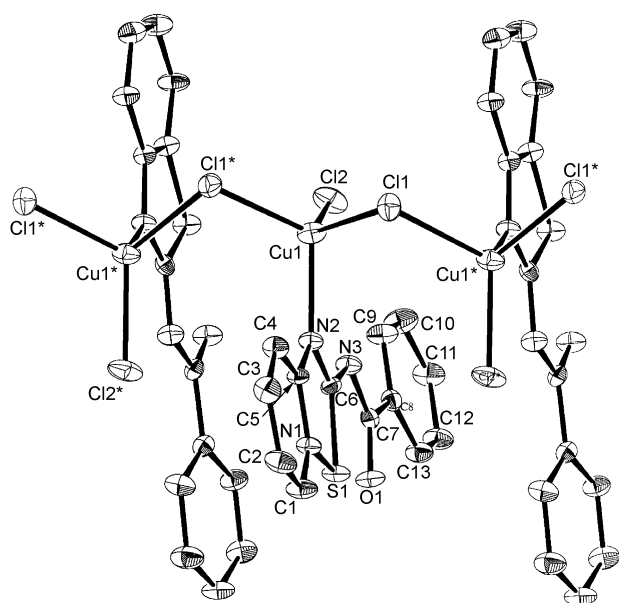


Scheme 1 Oxidative cyclization of L.

Table 1 Crystallographic data for **1**–**3**

|                                    | <b>1</b>   | <b>2</b>  | <b>3</b>  |
|------------------------------------|--|---|---|
| Formula                            | C <sub>13</sub> H <sub>9</sub> ON <sub>3</sub> SCl <sub>2</sub> Cu | C <sub>26</sub> H <sub>22</sub> N <sub>6</sub> O <sub>2</sub> ClS <sub>2</sub> Cu | C <sub>13</sub> H <sub>11</sub> N <sub>3</sub> OCl <sub>2</sub> SCu |
| <i>M</i>                           | 389.55   | 613.62  | 391.76  |
| Crystal system                     | Orthorhombic   | Monoclinic  | Triclinic   |
| Space group                        | <i>Pbca</i> (#61)  | <i>Cc</i> (#9)  | <i>P</i> <sub>1</sub> (#2)  |
| <i>a</i> /Å                        | 16.801(3)  | 10.761(3)   | 9.674(4)  |
| <i>b</i> /Å                        | 6.951(1)   | 36.62(1)  | 11.085(6)   |
| <i>c</i> /Å                        | 24.335(6)  | 7.511(9)  | 7.751(3)  |
| $\alpha$ /°                        |  |   | 97.63(3)  |
| $\beta$ /°                         |  | 116.186(6)  | 102.76(3)   |
| $\gamma$ /°                        |  |   | 108.18(2)   |
| <i>U</i> /Å <sup>3</sup>           | 2841.86  | 2556.18   | 751.81  |
| <i>Z</i>                           | 8  | 4   | 2   |
| <i>T</i> /K                        | 291(1)   | 293(1)  | 293(1)  |
| $\mu$ /cm <sup>−1</sup>            | 20.59  | 11.17   | 19.46   |
| No. reflect.                       | 2523   | 2100  | 2022  |
| No. obsd reflect.                  | 2033 [ <i>I</i> > 2.00 $\sigma$ ( <i>I</i> )]                      | 2075 [ <i>I</i> > 1.00 $\sigma$ ( <i>I</i> )]                                     | 2001 [ <i>I</i> > 1.00 $\sigma$ ( <i>I</i> )]                       |
| <i>R</i> <sub>int</sub>            | 0.00   | 0.00  | 0.00  |
| <i>R</i> <sup>2</sup>              | 0.062  | 0.055   | 0.073   |
| <i>R</i> <sub>w</sub> <sup>b</sup> | 0.097  | 0.050   | 0.066   |

<sup>a</sup>  $R = \Sigma [|F_o| - |F_c|] / \Sigma |F_o|$ . <sup>b</sup>  $R_w = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^3]^{1/2}$ .



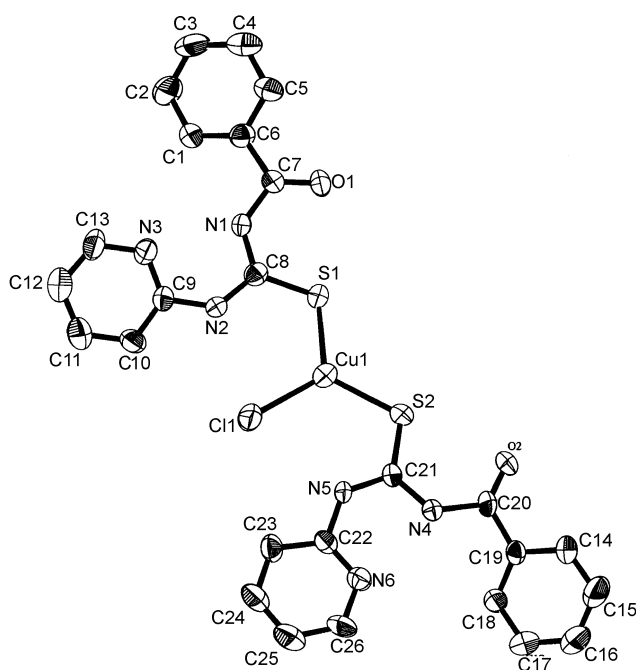
**Fig. 1** Perspective view of the zigzag chain structure of the polynuclear complex  $\infty^1\{[\text{CuClL}]/[\text{Cl}]\}$  **1** with atom labeling scheme.

one-dimensional copper(II) coordination compound, consisting of an infinite zigzag  $(\text{Cu}-\text{Cl})_n$  chain linked by single  $\text{Cu}-\text{Cl}-\text{Cu}'$  bridges. Each copper(II) center is coordinated to two bridging and one terminal chloride ions, as well as a heterocyclic thiadiazole nitrogen atom, displaying a distorted tetrahedral geometry. The resulting chain unit has symmetrical  $\text{Cl}-\text{Cu}-\text{Cl}'$  bridging distances of 2.313 Å, a  $\text{Cu}\cdots\text{Cu}$  separation of 3.52 Å and a bridging  $\text{Cu}(1)-\text{Cl}-\text{Cu}(1')$  angle of  $99.07(7)^\circ$  (Table 2).<sup>10</sup> The terminal  $\text{Cu}-\text{Cl}(2)$  distance [2.247(2) Å] is shorter than the bridging one (2.313 Å), as expected. The ligand  $L'$  coordinated to the copper center in the chain is the oxidative cyclization product formed *via* the elimination of both protons from the precursor  $\text{H}_2\text{L}$  at the amide nitrogen (N3) and thioamide nitrogen (N2); its complete hydrogen molecular structure and coordination mode are unequivocally displayed in Fig. 1. The chains run along the crystallographic  $b$  axis and the ligands are near planar (mean deviation 0.094), being disposed parallel and alternate to each other both in the intra- and inter-chains, forming continuous  $\pi$  stacks throughout the crystal (Fig. 1).

**Reduced Cu(I) mononuclear complex,  $[\text{CuL}_2\text{Cl}]$  **2**.** The molecular structure of **2** is illustrated in Fig. 2. Selected bond distances and angles are listed in Table 3. **2** is a complex of the reduced copper(I) ion with the ligand  $L$ , exhibiting a planar molecular configuration with a butterfly geometry. The copper(I) center displays a regular three-coordination with similar bond distances [ $\text{Cu}-\text{S}(1)$ , 2.223(2);  $\text{Cu}-\text{S}(2)$ , 2.225(2) and  $\text{Cu}-\text{Cl}$ , 2.296(2) Å], and approximately the same bond

**Table 2** Selected bond distances (Å) and angles (deg) for **1**

|   |           |   |          |
|---|-----------|---|----------|
| $\text{Cu}(1)-\text{Cl}(1)$               | 2.313(2)  | $\text{S}(1)-\text{N}(1)$                 | 1.758(6) |
| $\text{Cu}(1)-\text{Cl}(1')$              | 2.319(2)  | $\text{S}(1)-\text{C}(6)$                 | 1.744(7) |
| $\text{Cu}(1)-\text{Cl}(2)$               | 2.247(2)  | $\text{O}(1)-\text{C}(7)$                 | 1.241(9) |
| $\text{Cu}(1)-\text{N}(2)$                | 2.083(5)  | $\text{C}(7)-\text{C}(8)$                 | 1.476(9) |
| $\text{N}(3)-\text{C}(6)$                 | 1.356(8)  | $\text{N}(2)-\text{C}(6)$                 | 1.334(8) |
| $\text{N}(3)-\text{C}(7)$                 | 1.381(8)  | $\text{N}(2)-\text{C}(5)$                 | 1.368(8) |
| $\text{N}(1)-\text{C}(5)$                 | 1.350(8)  |   |          |
| $\text{Cl}(1)-\text{Cu}(1)-\text{Cl}(1')$ | 98.37(7)  | $\text{Cl}(1')-\text{Cu}(1)-\text{N}(2)$  | 110.8(2) |
| $\text{Cl}(1)-\text{Cu}(1)-\text{Cl}(2)$  | 122.87(8) | $\text{Cl}(2)-\text{Cu}(1)-\text{N}(2)$   | 110.4(2) |
| $\text{Cl}(1')-\text{Cu}(1)-\text{Cl}(2)$ | 113.39(8) | $\text{Cu}(1)-\text{Cl}(1)-\text{Cu}(1')$ | 99.07(7) |
| $\text{Cl}(1)-\text{Cu}(1)-\text{N}(2)$   | 99.8(2)   |   |          |



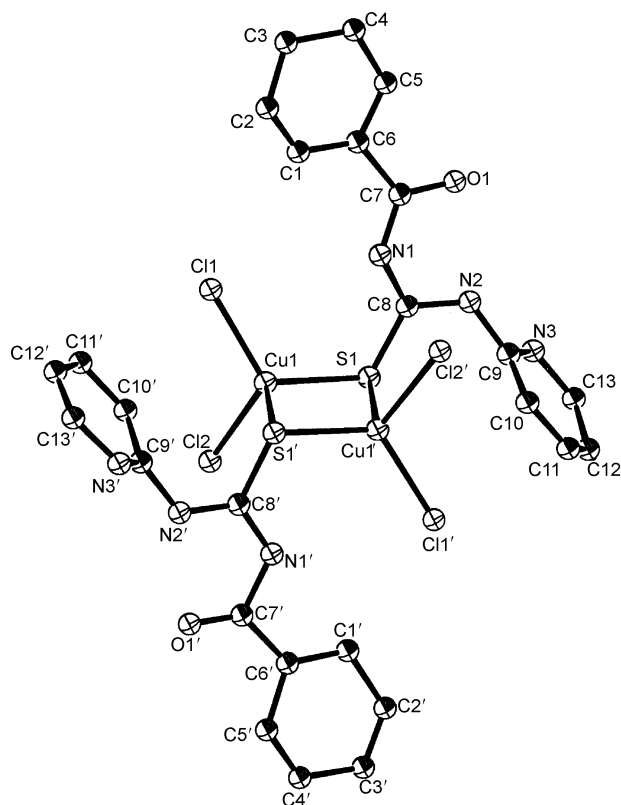
**Fig. 2** Perspective view of compound  $[\text{CuL}_2\text{Cl}]$  **2** with atom labeling scheme. The hydrogen atoms are omitted for clarity.

angles [ $\text{Cl}(1)-\text{Cu}-\text{S}(1)$ ,  $117.83(7)^\circ$ ;  $\text{Cl}(1)-\text{Cu}-\text{S}(2)$ ,  $119.42(7)^\circ$  and  $\text{S}(1)-\text{Cu}-\text{S}(2)$ ,  $122.74(6)^\circ$ ]. The three donor atoms together with the central copper(I) ion are perfectly coplanar. The  $\text{Cu}-\text{S}(1)-\text{C}(8)$  angle of  $111.3^\circ$  indicates that the thiourea sulfur is bound to  $\text{Cu}(I)$  primarily *via* a lone pair of electrons in a non-bonding  $\text{sp}^2$  sulfur orbital, probably containing some contribution of the  $\pi$  electrons of the  $\text{S}-\text{C}$  bond as well, since the  $\text{S}(1)-\text{C}(8)$  distance of 1.696(6) Å agrees very well with those in related compounds,<sup>11</sup> being intermediate between 1.82 Å for a  $\text{C}-\text{S}$  single bond and 1.56 Å for a  $\text{C}=\text{S}$  double bond.<sup>12</sup> The use of the  $\text{sp}^2$  orbital and electron pair is the most common bonding mode of thiourea to  $\text{Cu}(I)$  ion.<sup>13</sup> The bond distances in  $L$  are normal as in other similar thioureas.<sup>11</sup>

**Bis-sulfur-bridged Cu(II) dinuclear complex,  $\{[\text{CuLCl}_2]\}_2$  **3**.** The molecular structure of **3** shows the complex to be a bis-sulfur-bridged copper(II) compound (Fig. 3). Selected geometrical details are listed in Table 4. Each copper(II) ion is four-coordinate with bonds from two terminal chloride ions and two bridging sulfur atoms originating from ligands  $L$ , displaying a distorted tetrahedral geometry. The two copper(II) ions and the bridging sulfur atoms form a strictly planar  $\text{Cu}_2\text{S}_2$  core with two short [2.257(2) Å] and two longer  $\text{Cu}-\text{S}$  [2.595(2) Å] distances. The core also contains a short  $\text{Cu}\cdots\text{Cu}$  separation of 2.95 Å, a narrow bridging  $\text{Cu}(1)-\text{S}-\text{Cu}(1')$  angle of  $74.4(6)^\circ$ , and a wide  $\text{S}(1)-\text{Cu}-\text{S}(1')$  angle of  $105.59(6)^\circ$ . Both terminal chloride ions are coordinated to the copper(II) ion at different distances:  $\text{Cu}(1)-\text{Cl}(1)$ , 2.257(2) Å and  $\text{Cu}(1)-\text{Cl}(2)$ , 2.337(2) Å.

**Table 3** Selected bond distances (Å) and angles (deg) for **2**

|   |           |                                       |          |
|---|-----------|---------------------------------------|----------|
| $\text{Cu}(1)-\text{Cl}(1)$             | 2.296(2)  | $\text{N}(1)-\text{C}(8)$             | 1.352(7) |
| $\text{Cu}(1)-\text{S}(1)$              | 2.223(2)  | $\text{N}(2)-\text{C}(8)$             | 1.371(6) |
| $\text{Cu}(1)-\text{S}(2)$              | 2.225(2)  | $\text{N}(1)-\text{C}(7)$             | 1.423(6) |
| $\text{S}(1)-\text{C}(8)$               | 1.696(6)  | $\text{O}(1)-\text{C}(7)$             | 1.213(6) |
| $\text{Cl}(1)-\text{Cu}(1)-\text{S}(1)$ | 117.83(7) | $\text{C}(7)-\text{N}(1)-\text{C}(8)$ | 129.4(4) |
| $\text{Cl}(1)-\text{Cu}(1)-\text{S}(2)$ | 119.42(7) | $\text{O}(1)-\text{C}(7)-\text{N}(1)$ | 122.5(5) |
| $\text{S}(1)-\text{Cu}(1)-\text{S}(2)$  | 122.74(6) | $\text{S}(1)-\text{C}(8)-\text{N}(1)$ | 124.2(4) |
| $\text{Cu}(1)-\text{S}(1)-\text{C}(8)$  | 111.3(2)  | $\text{S}(1)-\text{C}(8)-\text{N}(2)$ | 120.2(4) |



**Fig. 3** Perspective view of dinuclear complex  $\{[\text{CuLCl}_2]_2\}$  **3** with atom labeling scheme. The hydrogen atoms are omitted for clarity.

### IR and $^1\text{H}$ NMR spectroscopy

IR spectra data are summarized in Table 5. The vibrational stretches of the  $\text{--NH}$  groups in the ligand **L** give rise to a multiple absorption band around  $3300\text{ cm}^{-1}$ , which disappears in complex **1**, giving evidence of the loss of the  $\text{N--H}$  proton upon oxidative cyclization (Scheme 1). The vibrational bands at  $1340$ ,  $1250$  and  $860\text{ cm}^{-1}$  observed in the free ligand **L** can be attributed to the  $\nu(\text{C}=\text{S})$  vibration;<sup>14</sup> two frequencies ( $1340$ ,  $1250\text{ cm}^{-1}$ ) show a slightly negative shift in complexes **2** and **3**. The frequency of  $860\text{ cm}^{-1}$  is absent in **1** and weak in **2** and **3**. These observations indicate the involvement of the  $\text{C}=\text{S}$  group in the cyclization and coordination, which are in reasonable agreement with the structure results.

In the  $^1\text{H}$  NMR spectrum of the free ligand **L** four signals for the protons on the pyridyl ring were observed clearly at  $\delta$  7.2–7.7 and five signals for the protons on the phenyl ring at  $\delta$  7.8–8.8, while the  $\text{NH}$  resonances ( $\text{D}_2\text{O}$ , exchangeable) were observed at  $\delta$  9.8 as a broad singlet.<sup>15,16</sup> For the complex **1** the  $^1\text{H}$  NMR signals arising from pyrido ( $\delta$  7.5–7.7) and phenyl ( $\delta$  8.0–8.9) protons show similar patterns to those assigned to the corresponding protons of **L**. However, it is worth noting that no coupling between  $^1\text{H}$  and  $\text{N}$  nuclei could be detected in **1**, as a consequence of the deprotonation of the  $\text{N--H}$  bonds upon the oxidative cyclization (Scheme 1).

**Table 4** Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **3**

|                              |           |                             |          |
|------------------------------|-----------|-----------------------------|----------|
| $\text{Cu(1)--Cl(1)}$        | 2.257(2)  | $\text{N(1)--C(7)}$         | 1.397(8) |
| $\text{Cu(1)--Cl(2)}$        | 2.337(2)  | $\text{N(1)--C(8)}$         | 1.371(7) |
| $\text{Cu(1)--S(1)}$         | 2.257(2)  | $\text{N(2)--C(8)}$         | 1.333(7) |
| $\text{Cu(1)--S(1')}$        | 2.595(2)  | $\text{N(2)--C(9)}$         | 1.405(7) |
| $\text{S(1)--C(8)}$          | 1.692(6)  | $\text{O(1)--C(7)}$         | 1.225(7) |
| $\text{C(6)--C(7)}$          | 1.486(8)  |                             |          |
| $\text{Cl(1)--Cu(1)--Cl(2)}$ | 113.70(7) | $\text{Cu(1)--S(1)--C(8)}$  | 100.6(2) |
| $\text{Cl(1)--Cu(1)--S(1)}$  | 105.03(7) | $\text{Cu(1')--S(1)--C(8)}$ | 115.0(2) |
| $\text{Cl(2)--Cu(1)--S(1)}$  | 102.36(6) | $\text{S(1)--C(8)--N(2)}$   | 120.1(5) |
| $\text{Cl(1')--Cu(1)--S(1)}$ | 118.47(7) | $\text{N(1)--C(8)--N(2)}$   | 117.8(5) |
| $\text{Cu(2')--Cu(1)--S(1)}$ | 109.90(7) | $\text{N(1)--C(8)--S(1)}$   | 122.0(5) |
| $\text{S(1)--Cu(1)--S(1')}$  | 105.59(6) | $\text{O(1)--C(7)--N(1)}$   | 120.4(6) |
| $\text{Cu(1)--S(1)--Cu(1')}$ | 74.41(6)  | $\text{O(1)--C(7)--C(6)}$   | 121.5(6) |
| $\text{N(2)--C(9)--N(3)}$    | 115.6(5)  | $\text{N(1)--C(7)--C(6)}$   | 118.2(6) |

### Interpretation on the reaction pathways

Of particular interest is that four kinds of reactions occur in the system, including oxidative cyclization, chloride-bridging coordination, bis-sulfur-bridging coordination and reduced copper(i) coordination.

In the redox process, the  $\text{Cu(II)}$  was reduced to  $\text{Cu(I)}$  by **L** and **L** was oxidized to an unexpected cyclization product, 2-benzoylimino-[1,2,4]thiadiazolo[2,3-*a*]pyridine (labeled as **L'**); its molecular structure was clearly revealed in **1** (Fig. 1).

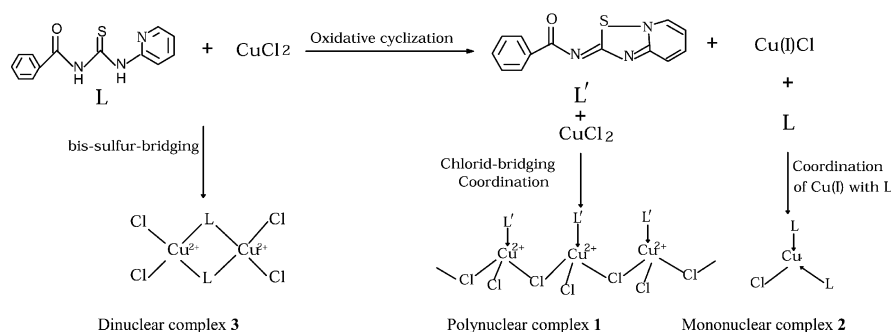
The oxidative cyclization of *N*-(2-pyridyl) thioureas by  $\text{Br}_2$  in  $\text{CH}_3\text{COOH}$  or  $\text{PCl}_5$  in  $\text{POCl}_3$ <sup>16</sup> has been reported. The oxidative cyclization of *N*-(2-pyridinyl)benzenecarbothiamide and *N*-(2-pyridinyl)ketothioacetamide by copper(II) ions, as well as the coordination of the oxidized products with copper(II) or copper(I) ions, have also been investigated by Fuller<sup>17</sup> and Iliopoulos<sup>18</sup> and their colleagues, but no definite products have been isolated and characterized.

By analogy with previous reports the reaction of **L** with a large excess of copper(II) chloride in acetone or alcohol solution may result in the formation of two forms of the oxidative cyclization products **L'**: 2-benzoylimino-[1,2,4]thiadiazolo[2,3-*a*]pyridine (**a**), or its thiadiazolo[2,3-*a*]pyridinium (**b**), as shown in Scheme 1. If **L'** is coordinated in its neutral form (**a**), the copper center would be in the divalent state, if in the cation form (**b**), the copper would be coordinated in its monovalent state, therefore, it is necessary to determine the coordinated form of **L'** in **1**. The main difference between both forms lies in the elimination of one or two protons from the precursor **L**, namely, deciding on the presence or absence of a proton on the amide nitrogen atom  $\text{N(3)}$  in **L'**. On the basis of our experiments **L'** should be thiadiazolo[2,3-*a*]pyridine rather than its pyridinium ion: in the molecular structure of **L'** the amide nitrogen atom  $\text{N(3)}$  is deprotonated (Fig. 1), and thus the  $\text{N(3)--C(6)}$  bond length ( $1.356\text{ \AA}$ ) approaches that of a double bond,<sup>19</sup> in the IR spectrum the  $\nu(\text{N--H})$  vibration, observed at  $3300\text{ cm}^{-1}$  in its precursor **L**, is absent, and the  $\text{NH}$  resonances at  $\delta$  9.8 in the  $^1\text{H}$  NMR spectrum cannot be detected in **L'**. Consequently, these results allow us to establish the coordination of the thiadiazolo[2,3-*a*]pyridine to the copper(II) ion in **1**.

In order to confirm the reaction pathways we have further examined the reaction directly between copper(II) chloride

**Table 5** Major IR bands ( $\text{cm}^{-1}$ ) of **L** and complexes

| Complex          | $\nu(\text{CH})$ , $\delta(\text{NH})$ | $\nu(\text{C}=\text{O})$ | $\nu(\text{C}=\text{N})$ , $\nu(\text{C}=\text{C})$ | $\nu(\text{phen, ring})$ | $\nu(\text{C}=\text{S})$ | $\nu(\text{N}=\text{C}=\text{S})$ |
|------------------|--|--------------------------|---|--------------------------|--------------------------|-----------------------------------|
| <b>L</b>         | 3000, 3300                             | 1680                     | 1500–1600   | 1440                     | 1340, 1250, 860          | 1160                              |
| Polymer <b>1</b> | 3000                                   | 1620                     | 1500–1600   | 1460                     | 1680, 1320–1280          | 1160                              |
| Complex <b>2</b> | 3070, 3217                             | 1716                     | 1606  | 1431                     | 1328, 1265, 807          | 1150                              |
| Dimer <b>3</b>   | 3000–3480                              | 1667                     | 1614  | 1448                     | 1314, 1245, 856          | 1158                              |



Scheme 2 Reaction pathways in  $\text{CuCl}_2\text{-L}$  system.

and  $\text{L}'$ , the latter was synthesized from the oxidation of  $\text{L}$  by  $\text{Br}_2$  in  $\text{CH}_3\text{COOH}$ , or  $\text{PCl}_5$  in  $\text{POCl}_3$ , using the previous methods.<sup>16</sup> However, in such a direct reaction system we have not yet unambiguously observed the formation of **1**, which was easily formed by the dropping method as described above; this suggests that the reaction may not proceed firstly in the oxidation of  $\text{L}$  to  $\text{L}'$  and then coordination of  $\text{L}'$  to copper(II), the mechanism may be more complicated and still remains to be explored.

But it seems of interest that the oxidative cyclization product  $\text{L}'$ , as its precursor  $\text{H}_2\text{L}$ , still acts as a ligand to participate in the copper(II) coordination through its thiadiazole nitrogen atom. Such heterocyclic nitrogen coordinated compounds are comparatively rare.

In addition to undergoing oxidative cyclization, the ligand  $\text{L}$  may monodentately bridge two copper(II) ions *via* sulfur donor atoms to form a bis-sulfur-bridged copper(II) complex **3** (Fig. 3), and also monodentately coordinate to reduced copper(I) ion through sulfur atoms to yield a planar three-coordinated copper(I) complex **2** (Fig. 2).

The overall reaction scheme for the complexes formed in the system can be summarized as shown in Scheme 2.

## Conclusion

By means of the “dropping method” we have successfully isolated three crystal products from the reaction of *N*-benzoyl-*N'*-(2-pyridyl)thiourea with  $\text{CuCl}_2$  and clearly demonstrated four types of reactions occur in the system. On the basis of the present results, we found that control of the relative concentration between the reaction components may be an excellent method to make the reaction proceed towards a certain direction and under mild conditions. According to the molecular structures of the products and conditions of the formation reactions, the reaction pathways in the system were revealed.

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