DOI: 10.1002/zaac.201400079

# Synthesis and Characterization of Copper(I) Halide Complexes with N-(2,6-Diisopropylphenyl)-N'-benzoylthiourea: Monomeric, Dimeric, and Cage Structures

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Dedicated to Professor Helmut Werner on the Occasion of His 80th Birthday

Keywords: Acylthiourea; Copper(I) halides; S ligands; Cage compounds

Abstract. The N-(2,6-diisopropylphenyl)-N'-benzoylthiourea ligand (shown as L) (1) was synthesized and characterized. Reactions of 1 with CuCl<sub>2</sub> and CuBr<sub>2</sub> afforded the monomeric L<sub>2</sub>CuCl (2) and dimeric [LBrCu( $\mu$ -L)]<sub>2</sub> (3), respectively, due to the reduction of Cu<sup>II</sup>. The reaction of 1 and CuCl gave the same product L<sub>2</sub>CuCl (2), while the treatment of 1 with CuBr led to the formation of a rare example

Introduction

Copper complexes with sulfur donors have attracted renewed interest for their pharmaceutical activity and potential applicability as metal-based drugs,<sup>[1]</sup> especially in the exploration of the role of Cu<sup>I</sup> system as antioxidant for preventing oxidative DNA damage.<sup>[2]</sup> Among these sulfur containing ligands, thiourea and its derivatives have been frequently reported to support Cu<sup>I</sup> complexes.<sup>[3]</sup> The acylthiourea derivatives represent one of the popular members in the family of thiourea and are attracting much research attention due to their easy availability,<sup>[4]</sup> facile reactivity and widespread application in analytical and heterocyclic chemistry.<sup>[5]</sup> The basic C(O)N(H)C(S)N unit that is shared by acylthiourea ligands is also regarded as the core segment of special drugs with high scores according to visual and structural criteria.<sup>[6]</sup> Another appealing feature of acylthioureas is the structural diversity of

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/zaac.201400079 or from the author.

of adamantanoid cage  $(LCu)_2(\mu-L)_2Cu_2(\mu-Br)_4$  (4) containing enantiomeric couple. The product of 1 and CuI was found to be dimeric  $[LICu(\mu-L)]_2$  (5), which is isomorphous to 3. All compounds obtained were fully characterized by elemental analysis, IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy, and single-crystal X-ray diffraction.

their complexes with "elusive" properties of binding modes, beneficial in the presence of O, N, N', and S donor atoms.<sup>[7]</sup> On the one hand, the *N*,*N*-dialkyl-*N'*-acylthiourea is able to coordinate only through sulfur as the neutral, monodentate ligand,<sup>[8]</sup> while it is also possible to act as a chelating bidentate O,S-monoanionic ligand to form a six-membered ring with the metal ion in *cis/trans* arrangement.<sup>[9]</sup> On the other hand, *N*alkyl/aryl-*N'*-acylthiourea mostly behaves as a soft ligand with the sulfur donor in unidentate or diverse bridging modes in its complexes with Cu<sup>1</sup> salts,<sup>[10]</sup> favored by the formation of intramolecular hydrogen bond (N–H•••O). In a few cases, an O,N-mode was observed.<sup>[11]</sup> Moreover, acylthiourea ligands have developed a wide variety of supramolecular synthons by the intermolecular hydrogen bonds to generate 1D or 2D coordination polymers.<sup>[12]</sup>

The crystallization of acylthiourea complexes may be relevant to the solvents, the strong hydrogen-bonding characteristics, modification by substitution,<sup>[13]</sup> or the relative concentration between reactants.<sup>[14]</sup> Starting from the basic molecule of N-aryl-N'-benzoylthiourea, a number of derivatives have been synthesized and structurally characterized with varying aryl rings typically modified by methyl,<sup>[15]</sup> carboxyl,<sup>[16]</sup> phenyl,<sup>[17]</sup> hydroxyl,<sup>[18]</sup> trifluoromethyl,<sup>[19]</sup> ferrocenoyl,<sup>[10,20]</sup> and halide<sup>[21]</sup> substituents. However, the isopropyl group, which has been used as a bulky group in a number of ligand systems,<sup>[22]</sup> was not so common in acylthiourea derivatives.<sup>[12]</sup> Previous work with β-diketiminato ligands has shown that the substituent effect on the synthesis of dialuminoxanes is of principal importance.<sup>[23]</sup> In this study the synthesis of a new ligand N-(2,6-diisopropylphenyl)-N'-benzoylthiourea, as well as its reactions with copper halides and the spectroscopic characteri-



zation and structural determination of new copper(I) halide acylthiourea complexes are reported.

#### **Results and Discussion**

The N-(2,6-diisopropylphenyl)-N'-benzoylthiourea ligand (1, shown as L) was readily prepared in moderate yield based on the general procedure described in the literature for its methyl analogue N-(2,6-dimethylphenyl)-N'-benzoylthiourea (1', donated as L').<sup>[15]</sup> In the <sup>1</sup>H NMR spectrum of 1, the presence of one characteristic septet ( $\delta = 3.11$  ppm) and two doublet signal (1.32, 1.20 ppm) indicate the isopropyl group, appearing relatively rotation-free of aryl flank in solution. Two singlet signals were found at low field (11.87, 9.25 ppm). which are assignable to the proton signals for thioamide aryl-NH and amide acyl-NH groups, respectively. This is consistent with the observation of two distinctive absorption bands at 3211 and 3232 cm<sup>-1</sup> in the FT-IR spectra due to the N-H stretching vibrations. X-ray quality single crystals were obtained from a saturated THF solution. Room-temperature Xray diffraction data of 1. THF indicate that the structure belongs to the monoclinic space group  $P2_1/c$  with two symmetry independent molecules in a centrosymmetric unit. One of them is depicted in Figure S1 (Supporting Information) with selected bond lengths and angles, and crystal data and structure refinements are listed in Table S1 (Supporting Information). The C(2)-O(1) bond length [1.219(2) Å] of 1.THF is found to be exactly the same as that of its methyl analogue,<sup>[15]</sup> whereas the C(1)-S(1) separation [1.676(2) Å] is slightly longer than that of 1' [1.6599(19) Å]. As expected, an intramolecular hydrogen bonding interaction N(1)-H(1A)····O(1) [D···A, 2.664(2) Å; D-H···A, 134.2°] is present and helps to form a pseudo-sixmembered ring. Closer examination reveals that the two independent molecules in the crystal structure of 1.THF form a twelve-membered cyclic dimer<sup>[12,24]</sup> mediated by intramolecular N-H-O hydrogen bonds (Figure S2) and thus construct molecular chains by intramolecular N-H···S contacts along the a axis.

Furthermore, the single crystals of the ligand **L** without solvent molecules present in the structure were obtained from *n*-hexane solution. **1** crystallizes in the triclinic space group  $P\bar{1}$  with a small cell volume [927.50(18) Å<sup>3</sup>]. In contrast to its THF solvate, **1** contains a single ligand molecule in the centro-symmetric unit. Yet similarly, ligand molecules are connected by intermolecular hydrogen bonds to produce the molecular chain along the diagonal of *a* and *b* crystallographic axes (Figure S3, Supporting Information). Instead, its methyl analogue **1**' showed a weak intermolecular C–H···S interaction in the solid state.<sup>[15]</sup>

It is well known that the preparation of complexes of Cu<sup>I</sup> with thiourea derivatives can be simply achieved by mixing the solution of ligand and the corresponding Cu<sup>II</sup> salt,<sup>[13]</sup> where Cu<sup>II</sup> is reduced to Cu<sup>I</sup> with concomitant oxidation of a portion of the thiourea ligand. In some cases, the chemical composition or structures of final products depend on the thiourea ligand involved and also on the reaction conditions.<sup>[13,14]</sup>

The treatment of **1** in CH<sub>2</sub>Cl<sub>2</sub> with the ethanol solution of CuCl<sub>2</sub> and CuBr<sub>2</sub> lead to the formation of L<sub>2</sub>CuCl (**2**) and [LBrCu( $\mu$ -L)]<sub>2</sub> (**3**), respectively, as shown in Scheme 1. The <sup>1</sup>H NMR spectrum of **2** exhibits that the NH protons resonate at  $\delta = 12.45$  and 11.37 ppm, presenting a downfield shift when compared to those of the free acylthiourea ligand (11.87, 9.25 ppm).



Scheme 1. Preparation of compounds 2 and 3.

Similarly, signals of the NH protons of **3** are observed at comparable positions (12.41 and 11.07 ppm). The single septet siganl is upfield shifted in both cases (2.99–3.00 ppm). These changes are indicative for the complex formation.<sup>[10]</sup> The composition of **2** and **3** was further confirmed by elemental analysis and single-crystal X-ray diffraction.

Compound  $L_2$ CuCl (2) crystallizes in the triclinic space group  $P\bar{1}$  with one severely disordered molecule of *n*-hexane in the unit cell. No acceptable connectivity could be established for the embedded solvent molecule. The disordered electron density was excluded using the SQUEEZE function of the PLATON program.<sup>[25]</sup> The X-ray structure reveals 2 as a mono nuclear copper(I) chloride complex coordinated by two sulfur atoms of each acylthiourea ligand and one chlorine atom (Figure 1).



**Figure 1.** Molecular structure of **2**, showing intramolecular hydrogen bonds as dotted lines. Thermal ellipsoids are drawn at 30% level. Other hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: Cu(1)–S(1) 2.2026(6), Cu(1)–S(2) 2.2114(7), Cu(1)–Cl(1) 2.2236(7); S(1)–Cu(1)–S(2) 115.71(2). Hydrogen bonds D···A distances /Å and D–H···A angles /°: N(2)–H(1A)···O(1) [2.621(3), 137], N(3)–H(1B)···Cl(1) [3.277(2), 166], N(4)–H(2A)···O(2) [2.618(3), 141], N(1)–H(2B)···Cl(1) [3.454(2), 157].

The two ligands of **2** adopt a *cis* arrangement relative to the chlorine atom. This butterfly-like structure with a less conformational flexibility is common in literature.<sup>[10,26]</sup> One of the

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main driving factors for the structural feature are the intramolecular hydrogen bonds between Cl(1) and N(1)/N(3) atoms to form pseudo-six-membered rings. The Cu-Cl and Cu-S bond lengths are each found in the reasonable range,<sup>[10,26]</sup> and the sum of the bond angles around the copper is exactly 360° to exhibit a trigonal planar arrangement. Aromatic rings fundamentally occupy the opposite sides of the CuS<sub>2</sub>Cl plane when compared to their counterparts. There are no intermolecular hydrogen bonds evident in the structure. Instead, the crystal packing structure of 2 (Figure 2) shows the significant stabilization by intermolecular  $\pi - \pi$  stacking interactions between two neighboring phenyl rings (I)...(I) in the cell, centroidcentroid distance 3.8041(14) Å, face-to-face, with a dihedral angle of 0°. Additionally, similar but much weaker intermolecular  $\pi$ - $\pi$  stacking interactions are found between their sibling phenyl rings (II)...(II) [centroid-centroid distance 4.2553(16) Å].



**Figure 2.** Structure diagram of **2**, showing the intermolecular  $\pi$ – $\pi$  stacking interactions between phenyl rings: (I)···(I), centroid–centroid distance 3.8041(14) Å, dihedral angle 0°, slip angle 22°, perpendicular distance between the rings 3.5274(9) Å, slippage 1.424 Å; (II)···(II), centroid–centroid distance 4.2553(16) Å, dihedral angle 0°, slip angle 36.8°, perpendicular distance between the rings 3.4069(11) Å, slippage 2.55 Å.

The two short contacts in zigzag arrangement form the teeth of adjacent molecular arrays and interlock them into a coordination chain in the c axis direction (Figure S4).

In contrast, from the concentrated toluene solution, 2-tol was obtained, which crystallizes with a toluene molecule in the orthorhombic space group  $P2_12_12_1$ . The observation that the crystal contains solvent molecules and gives rise to a different space group is commonly seen in practice.<sup>[27]</sup> The crystal structures of 2 and 2 tol (Figure S5) are essentially similar with respect to the cis arrangement of two ligands and bond angles around the copper atom (360°). However, the torsion angles of Cl(1)-Cu(1)-S(1)-C(1) [-29.90(19)°] and Cl(1)-Cu(1)-S(2)-C(21) [19.42(19)°] of 2·tol are significantly different from, and wider than, those of 2 [11.85(9),  $8.93(9)^{\circ}$ ]. The aromatic rings of 2·tol are almost located on the same sides of the CuS<sub>2</sub>Cl plane. The packing diagram of 2-tol gives a plausible explanation that the molecular skeleton bends slightly to embrace the cocrystallized molecule of toluene (Figure S6). Consequently, an interesting wave-shape molecular chain along the c axis is

formed by combining  $L_2$ CuCl molecules with the single intramolecular hydrogen bonding interaction of N(3)–H(3)···O(1A) [D···A, 3.273(4) Å, D–H···A, 132.5°, [–x+3/2, –y+2, z+1/2]] (Figure S7). Interestingly, **2**-tol crystallizes in a chiral space group. The possible axial chirality could be induced by restricted rotation of the ligand framework along the molecule axis in the case of using an achiral ligand.<sup>[28]</sup>

The structure of **3** (Figure 3) of composition  $[LBrCu(\mu-L)]_2$ cocrystallizes with two toluene solvent molecules in the triclinic space group  $P\overline{1}$ . The dimer is located in a crystallographic center of symmetry, comprising a  $[Cu(\mu-S)]_2$  fourmembered ring. One striking feature is that the Cu···Cu separation [2.6121(6) Å] is obviously the shortest thus far observed in the analogous systems bearing the  $[SBrCu(\mu-S)]_2$ core involving heterocyclic thiones<sup>[13,29]</sup> or acyclic thiourea derivative,<sup>[30]</sup> and similar to but still slightly shorter than that of a related compound containing a  $[PBrCu(\mu-S)]_2$ core [2.6906(1) Å].<sup>[31]</sup> Comparable Cu···Cu separations [2.619(2) Å,<sup>[32a]</sup> 2.6316(13)<sup>[32b]</sup>] were previously reported on copper(II) compounds containing the  $[SClCu(\mu-S)]_2$  core.



**Figure 3.** Molecular structure of **3**, showing intramolecular hydrogen bonds as dotted lines. Other hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: Cu(1)–S(1) 2.3863(7), Cu(1)–S(2) 2.2829(7), Cu(1)–Br(1) 2.4207(4), Cu(1)–Cu(1A) 2.6121(6); Cu(1)–S(1)–Cu(1A) 66.29(2). Hydrogen bonds *D*···A distances /Å and *D*–H···A angles /°: N(2)–H(2A)···O(1) [2.605(3), 133], N(4)–H(4A) ···O(2) [2.658(3), 130], N(3)–H(3A)–Br(1) [3.527(2); 172.0], N(1)–H(1A)–Br(1A) [3.399(2), 149.9; (–x+2, –y+1, –z+1)].

The closed-shell interactions between the central d<sup>10</sup> metal atoms are generally designated as metallophilic interactions. For example, aurophilicity has long been recognized and plays a dominant role in gold chemistry, while cuprophilic interactions are still controversial.<sup>[33]</sup> Metallophilic Cu<sup>I</sup>–Cu<sup>I</sup> interactions are frequently evidenced between 2.60 and 3.50 Å in ligand-unsupported systems.<sup>[33f]</sup> In an alternative view, the van der Waals radius (Cu<sup>I</sup>–Cu<sup>I</sup> 2.80 Å) is often used as reference data to draw a comparison to the cuprophilicity before extensive calculations or spectroscopic characterizations are carried out.<sup>[34]</sup> However, metallophilic effects concerning bridging ligands should be treated with caution, because the effects are easily blurred by the architecture of the ligand. The short Cu-··Cu contact [2.6121(6) Å] in **3**, together with the compressed Cu–S–Cu angle  $[66.29(2)^{\circ}]$ , might suggest the presence of weak attractive metallophilic interactions between the central copper atoms. However, the close proximity of copper atoms could be caused by the ring constraint and ligand effect.<sup>[34g]</sup>

Another feature in **3** is that a 2D molecular sheet is assembled by intermolecular hydrogen bonding interaction of N(4)–H(4A)···O(2A) [D···A, 3.104(3) Å, D–H···A, 142°, [–x+2, –y+1, –z]] along the *c* axis and by intermolecular  $\pi$ – $\pi$ stacking interactions between two neighboring phenyl rings (I)···(I) along the *b* axis [centroid–centroid distance 3.7630(19) Å, face-to-face, with a dihedral angle of 0°, slip angle 25°, perpendicular distance between the rings 3.4110(12) Å, slippage 1.589 Å] (Figure S8, Supporting Information).

At the same time, reactions of the acylthiourea ligand 1 and copper(I) halides were conducted for comparison (Scheme 2). The product of 1 and CuCl was found to be identical to  $L_2$ CuCl (2) according to spectroscopic and structural characterization. However, treatment of 1 with CuBr gave product 4 with slightly different chemical shifts of NH protons (12.47, 10.95 ppm) compared to those of 3 (12.41, 11.07 ppm). Elemental analysis of 4 suggests a 1:1 stoichiometry copper(I) bromide of acylthiourea ligand.



Scheme 2. Reaction of 1 with copper(I) halides.

X-ray structural analysis confirmed the 1:1 composition of **4** and further indicated the formation of a cage-like compound  $(LCu)_2(\mu-L)_2Cu_2(\mu-Br)_4$ . Complex **4** crystallizes in the triclinic space group  $P\bar{1}$ . There are two inequivalent molecules in the asymmetric unit. They have the same overall structure, but their conformations are distinctly different by forming an enantiomeric couple. The different core structures are illustrated in Figure 4.

Each molecule contains an unprecedented central  $S_2Cu_4Br_4$  framework of an adamantane-like structure that comprises four annealed six-membered SCu<sub>3</sub>Br<sub>2</sub> rings in a chair conformation.

In each molecule, four CuBr units form a puckered  $Cu_4(\mu$ -Br)<sub>4</sub> eight-membered ring, which is rarely reported in literature.<sup>[35]</sup> Taking **4a** for example, the four bromide anions almost lie in a common plane, as indicated by the tiny deviation of the Br(1) atom from the Br(2)Br(3)Br(4) plane (0.086 Å). The four copper atoms create a highly distorted tetrahedron with Cu-Cu distances ranging from 2.622 to 3.739 Å, and they can be divided into two special Cu-Cu pairs (Cu<sub>1,2</sub> and Cu<sub>3,4</sub>) by the Br<sub>4</sub> quasi-plane, each bridged by one sulfur donor of the acylthiourea ligand. The sulfur atoms of the other two ligands additionally coordinate to one copper atom of the pairs above [Cu(2) in Cu<sub>1,2</sub> and Cu(4) in Cu<sub>3,4</sub>] in a terminal fashion. Thus



Figure 4. Core structure of 4. Thermal ellipsoids are drawn at 30% level. Other atoms are omitted for clarity. Selected bond lengths /Å and angles /°: for 4a: S(1)–Cu(1) 2.2687(18), S(4)–Cu(4) 2.3208(18), Br(4)–Cu(1) 2.3273(11), Br(4)–Cu(4) 2.5392(9), Cu(1)–Cu(3) 2.6223(10); Cu(1)–Br(1)–Cu(3) 67.60(3); for 4b: S(7)–Cu(7) 2.2792(16), S(7)–Cu(8) 2.3208(17), Br(7)–Cu(7) 2.3314(11), Br(7)–Cu(6) 2.5267(10), Cu(5)–Cu(7) 2.6140(12); Cu(5)–Br(5)–Cu(7) 67.39(3).

**4** exhibits  $Cu^{I}$  ions both in tricoordinate [Cu(1) and Cu(3)] and tetracoordinate [Cu(2) and Cu(4)] mode with distorted trigonal planar and tetrahedral coordination, respectively. As expected, the Cu–S and Cu–Br bond lengths of the tricoordinate copper ions are distinctly shorter than those of the tetracoordinate ones.<sup>[36]</sup> For instance in **4a**, the bond lengths of Cu(1) and Cu(3) with respective bridging atoms S(1), S(3), Br(2), or Br(4) (if available) are shorter than those involving Cu(2) and Cu(4) atoms.

It has been shown that reactions between copper(I) halides and thiourea or its derivatives frequently generate a variety of complexes, which have unpredictable stoichiometry and stereochemistry.<sup>[37]</sup> This structural diversity originates from the propensity of the halide to act as terminal or bridging ligand and of the thiourea ligand to coordinate in a monodentate or a bridging mode.<sup>[36]</sup> In the known tetranuclear Cu<sup>I</sup> systems with sulfur donor, the adamantanoid cages often contain the Cu<sub>4</sub>S<sub>6</sub> core,<sup>[38]</sup> in which simply the soft anions like halides have the chance to bind with the copper site in a terminal fashion (Cl,<sup>[39]</sup> I<sup>[13,37]</sup>). Only one comparable example involving edge-bridging bromine atoms in the P<sub>4</sub>Cu<sub>4</sub>Br<sub>4</sub> core with adamantane-like topology was established by treatment of 1,1'-diphosphaferrocene with CuBr, but with single conformation.<sup>[36]</sup> In solution, the core structures of 4a to 4b might undergo a similar "windshield-wiper" sliding movement<sup>[36]</sup> of the ligands along each Cu--Cu pair vector (Cu<sub>1,2</sub> and Cu<sub>3,4</sub>) by simultaneously changing the role of terminal and bridging mode, so as to refold the Cu<sub>4</sub>Br<sub>4</sub> ring and then interconverse to each other. Compound 4 is relatively stable under ambient condition. In contrast to some cases, Cu<sup>II</sup> compound was possibly formed in air to introduce a  $\mu_4$ -O into the cage.<sup>[40]</sup>

A detailed investigation of the molecular structure of **4** leads to the finding that the terminal sulfur donors nearly lie on the plane defined by two tetracoordinate copper atoms and their bridging bromide atom. This plane could describe the characteristic position of each molecule. Such two planes of **4a** and **4b** are roughly perpendicular (86.09°) to each other. In addition, exemplified by **4a** (Figure 5), the top apex bromide

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atom Br(3), which connects two tetracoordinate copper atoms, exhibits potentially weak intramolecular hydrogen bonding with two nitrogen atoms from the bridging ligands, while the shoulder bromide atoms Br(2) and Br(4) form weak intramolecular hydrogen interaction each with the nitrogen donor from the terminal ligand. Restrictions imposed by those interactions together with steric strain of the ligand render short Cu(1)···Cu(3) distance of 2.6223(10) Å. Also the inward bending of the copper atoms Cu(1) and Cu(3) in 4a results in a somewhat acute Cu(1)-Br(1)-Cu(3) angle of 67.60(3)°, which is very close to that in the P<sub>4</sub>Cu<sub>4</sub>Br<sub>4</sub> complex [66.61(5)°].<sup>[36]</sup> The root tip bromide atom Br(1) is found to be innocent in any hydrogen bonding interaction. According to the vector moving from the top Br(3) to the Br(1), both 4a and 4b show the same direction in the cell. The ligands residing on the opposite sides of the  $S_2Cu_4Br_4$  core adopt the *cis* arrangement relative to each other, while each ligand is in the trans arrangement with respect to its nearest neighbors. It is interesting to note that all ligand planes (defined by N<sub>2</sub>O) tilt relative to the top bromide vector by 11-23° in anti-clock wise in 4a and in clock wise in 4b, when looking inwards the molecule.



Figure 5. Molecular structure of 4a with intramolecular hydrogen bonds as dotted lines. Other hydrogen atoms are omitted for clarity. Hydrogen bonds D···A distances /Å and D-H···A angles /°: N(2)-H(2A)···Br(3) [3.631(4), 172.5], N(6)-H(6A)···Br(3) [3.717(4), 167.5], N(4)-H(4A)···Br(2) [3.556(5), 145.2], N(8)-H(8A)···Br(4) [3.509(4), 151.6].

Intermolecular N–H···O hydrogen bonding interactions of **4** give rise to an infinite 2D grid in the *ac* plane of the unit cell. Each molecule is interconnected to its four enantiomers (Figure S9), so as to define **4** a racemic compound.

In a comparative manner, the complexation reaction of the methyl derivative *N*-(2,6-dimethylphenyl)-*N'*-benzoylthiourea (**1**') with CuBr in a 1:1 ratio (Scheme S1) was carried out. Instead of cage structure, the product turned out to be the dimer [**L**'BrCu( $\mu$ -**L**')]<sub>2</sub> (**2**'), which crystallizes also with two toluene molecules in the triclinic space group  $P\overline{1}$  (Figure S10, Supporting Information) and is isostructural with **3** and contains the [SBrCu( $\mu$ -S)]<sub>2</sub> core. The Cu-Cu separation of **2**' [2.6235(6) Å] is slightly longer than that of **3** but still shorter than those of other analogues.<sup>[13,29,30]</sup> No evident intermo-

lecular hydrogen bonding interaction is detected in 2'. The molecules are connected by intermolecular  $\pi$ - $\pi$  stacking interactions between two neighboring 2,6-dimethylphenyl rings, face-to-face, in a direction parallel to each other, resulting in one type of 1D strand along the *c* axis (Figure S11).

The reaction of 1 with CuI afforded the dimeric adduct  $[LICu(\mu-L)]_2$  (5) of 1:2 stoichiometry (Scheme 2). In the <sup>1</sup>H NMR spectrum of 5, there are two singlet signals found at low field (12.17, 10.34 ppm) responsible for NH proton resonances, which are shifted slightly upfield relative to those of 2-4. The iodide (5) and bromide (3) complexes are isomorphous, therefore, the molecular conformation of them is very similar. The dimer 5 is located around a crystallographic center of symmetry, one half comprising the asymmetric unit of the structure (Figure S12). The Cu-Cu distance [2.7378(8) Å] falls in the expected range. As in the form of 3 and the parent ligand, it appears that hydrogen bonding is an important contributor to the stability of 5, and each iodide is involved in intramolecular hydrogen bonds with nitrogen donors from two adjacent terminal and bridging ligands. Molecules of 5 are connected by intermolecular N(2)-H(2A)···O(1A) [D···A, 3.260(3) Å, D-H···A,  $132.9^{\circ}$ , [-x, 1-y, 1-z] hydrogen bonds forming chains running along the b axis (Figure S13, Supporting Information).

#### Conclusions

The new acylthiourea ligand N-(2,6-diisopropylphenyl)-N'benzoylthiourea (1, shown as L) and its derivatives with copper(I) halides (2-5) were synthesized and characterized. In the solid state of 1. THF, molecular dimeric chains are formed by intermolecular hydrogen bonding along the *a* axis, which is totally different with its methyl analogue by a weak intermolecular C-H···S interaction. The reaction of 1 with CuCl<sub>2</sub> and CuBr<sub>2</sub> afforded mononuclear L<sub>2</sub>CuCl (2) and dimeric dinuclear  $[LBrCu(\mu-L)]_2$  (3), respectively. Complex 3 exhibits the shortest Cu-Cu separation [2.6121(6) Å] so far known of this type. A molecular chain is also formed in 3 by intermolecular N-H···O hydrogen bonding along the c axis. Treatment of 1 with CuCl gave the same complex  $L_2$ CuCl (2), while the product of 1 and CuI turned out to be the dimeric adduct [LICu( $\mu$ -**L**)]<sub>2</sub> (5) with a structure resembling to that of [LBrCu( $\mu$ -L)]<sub>2</sub> (3). Instead, the direct reaction of 1 with CuBr led to the formation of the adamantanoid cage  $(LCu)_2(\mu-L)_2Cu_2(\mu-Br)_4$  (4) with two inequivalent molecules as enantiomeric couple. Intermolecular N-H···O hydrogen bonding of cages 4 give rise to an infinite 2D grid in the ac plane of the unit. In sharp contrast, treatment of its methyl analogue with CuBr resulted in the formation of dimeric  $[L'BrCu(\mu - L')]_2$  (2'). These results suggest that the ligand effect plays an important role in thiourea derivatives. The isopropyl-substituted ligand L provided unique examples of copper(I) halide complexes with structural diversity feature of monomeric, dimeric, and cage conformations.



### **Experimental Section**

All chemicals commercially available used in the synthesis were of analytical grade and used as received. Melting points were measured in sealed glass tubes using a Büchi B-540 instrument without correction. Elemental analyses for carbon, hydrogen, and nitrogen were performed with a Thermo Quest Italia SPA EA1110 instrument. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with 5 mm tubes in CDCl<sub>3</sub> solution using AVANCE III 400 and AVANCE III HD 500 spectrometers. Infrared spectra were recorded by using KBr pellets with a NEXUS670 (Thermo Fisher Scientific) FT-IR spectrometer.

N-(2,6-diisopropylphenyl)-N'-benzoylthiourea (L) (1): Ligand (L) was prepared using a similar procedure to that described for N-(2,6-dimethylphenyl)-N'-benzovlthiourea<sup>[15]</sup> by the reaction of benzovl chloride with KSCN in acetone to produce benzovl isothiocyanate, followed by the condensation with 2,6-diisopropylaniline. The product in 50 mmol scale synthesis was recrystallized from acetone to give a moderate yield (13.79 g, 40.50 mmol, 81%). M.p. 195-197 °C. <sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 11.87$  (s, 1 H, NH), 9.25 (s, 1 H, NH), 7.94, 7.68, 7.57 (m, 5 H, Ph), 7.40, 7.25 (m, 3 H, Ar), 3.11 [sept,  ${}^{3}J_{\text{HH}}$  = 7.0 Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.32 [d,  ${}^{3}J_{\text{HH}}$  = 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.20 [d,  ${}^{3}J_{\text{HH}}$  = 6.9 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>] ppm.  ${}^{13}$ C NMR  $(101 \text{ MHz}, \text{CDCl}_3): \delta = 181.39 (C = S), 167.04 (C=O), 145.59, 133.81,$ 129.25, 129.12, 127.67, 123.86 (Ar/Ph), 28.92 [CH(CH<sub>3</sub>)<sub>2</sub>], 24.41, 23.13 [CH(*C*H<sub>3</sub>)<sub>2</sub>] ppm. **IR** (KBr):  $\tilde{v} = 3232$  (m), 3122 (m), 2962 (s), 2868 (m), 1667 (s), 1600 (w), 1527 (vs), 1383 (m), 1362 (m), 1326 (m), 1259 (s), 1204 (m), 1156 (s), 1058 (w), 1025 (w), 999 (w), 931 (w), 802 (m), 752 (w), 701 (m), 686 (m), 665 (m), 621 (w), 531 (w) cm<sup>-1</sup>. C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>OS (340.5): calcd. C 70.55, H 7.10, N 8.23%; found C 70.63, H 7.38, N 8.40%. X-ray quality single crystals of 1.THF were obtained from a concentrated THF solution.

L<sub>2</sub>CuCl (2): To a solution of 1 (3.40 g, 10 mmol) in dichloromethane (30 mL) at room temperature was added drop by drop a solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.85 g, 5 mmol) in ethanol (30 mL) in 15 min under intense stirring. An additional 6 h was allowed to insure completion of complexation. The precipitate was separated by filtration, washed with distilled water repeatedly, and dried at 80 °C to obtain a white solid (1.60 g, 2.05 mmol, 41%). Complex 2 was alternatively accomplished by using 1 (1.70 g, 5 mmol) in THF and CuCl (0.25 g, 2.5 mmol) in ethanol (30 mL) in moderately higher yield (1.35 g, 1.73 mmol, 69 %). M.p. 239–241 °C. <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 12.45 (br., 1 H, NH), 11.37 (s, 1 H, NH), 8.31, 7.64, 7.52, 7.36, 7.21 (m, 8 H, Ar/Ph), 3.00 [sept,  ${}^{3}J_{HH} = 6.5$  Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.27 [d,  ${}^{3}J_{HH} = 6.4$  Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.16 [d,  ${}^{3}J_{\text{HH}}$  = 6.4 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>] ppm. <sup>13</sup>C **NMR** (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 181.36 (C = S), 169.80 (C=O), 145.22, 133.96, 131.78, 131.07, 129.52, 129.42, 128.64, 123.96 (Ar/Ph), 28.85  $[CH(CH_3)_2]$ , 24.43, 23.04  $[CH(CH_3)_2]$  ppm. **IR** (KBr):  $\tilde{v} = 3440$  (w), 3357 (w), 3187 (w), 2963 (w), 2868 (vw), 1672 (m), 1514 (s), 1465 (w), 1396 (vw), 1363 (vw), 1315 (w), 1261 (m), 1205 (w), 1157 (m), 1103 (vw), 1084 (vw), 1025 (vw), 936 (vw), 852 (vw), 800 (w), 732 (w), 711 (w), 687 (w), 662 (w) cm<sup>-1</sup>.  $C_{40}H_{48}ClCuN_4O_2S_2$  (779.96): calcd. C 61.60, H 6.20, N 7.18%; found C 61.85, H 5.93, N 6.97%. X-ray quality single crystals of 2 were obtained from a mixture of nhexane and diethyl ether (1:1). From a concentrated toluene solution of 2, X-ray quality single crystals of 2-tol were obtained.

[LBrCu( $\mu$ -L)]<sub>2</sub> (3): The procedure for the preparation of 3 was similar to that described for compound 2 using 1 (3.40 g, 10 mmol) and CuBr<sub>2</sub> (1.12 g, 5 mmol) to afford a yellow green solid (0.99 g, 0.60 mmol, 24%). M.p. 241–243 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 12.41 (s, 1 H, NH), 11.07 (s, 1 H, NH), 8.28, 7.63, 7.51, 7.37, 7.22 (m, 8 H,

Ar/Ph), 2.99 [sept,  ${}^{3}J_{\rm HH} = 6.5$  Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.26 [d,  ${}^{3}J_{\rm HH} = 6.8$  Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.16 [d,  ${}^{3}J_{\rm HH} = 6.9$  Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>] ppm.  ${}^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 182.58$  (C = S), 169.77 (C=O), 145.13, 134.12, 130.88, 129.99, 129.55, 128.73, 124.00, 123.54 (Ar/ Ph), 28.89 [CH(CH<sub>3</sub>)<sub>2</sub>], 24.43, 23.06 [CH(CH<sub>3</sub>)<sub>2</sub>] ppm. IR (KBr):  $\tilde{v} = 3518$  (w), 3424 (w), 3187 (m), 2963 (m), 2868 (w), 1675 (s), 1599 (w), 1510 (vs), 1384 (w), 1362 (w), 1317 (m), 1260 (s), 1205 (m), 1158 (s), 1104 (w), 1084 (w), 1024 (w), 852 (w), 799 (m), 752 (m), 732 (m), 712 (m), 687 (m), 661 (m) cm<sup>-1</sup>. C<sub>80</sub>H<sub>96</sub>Br<sub>2</sub>Cu<sub>2</sub>N<sub>8</sub>O<sub>4</sub>S<sub>4</sub> (1648.83): calcd. C 58.28, H 5.87, N 6.80%; found C 58.40, H 5.53, N 6.58%. X-ray quality single crystals of **3**-2tol were obtained from a concentrated toluene solution.

 $(LCu)_2(\mu-L)_2Cu_2(\mu-Br)_4$  (4): The procedure for the preparation of 4 was similar to that described for compound **2** using **1** (1.70 g, 5 mmol) in THF (30 mL) and CuBr (0.72 g, 5 mmol) in ethanol (30 mL) to afford a yellow solid, which was recrystallized from ethanol (1.06 g, 0.55 mmol, 44%). M.p. 238–240 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.47 (s, 1 H, NH), 10.95 (s, 1 H, NH), 8.28, 7.62, 7.51, 7.38, 7.21 (m, 8 H, Ar/Ph), 2.98 [sept,  ${}^{3}J_{HH} = 6.5$  Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.27 [d,  ${}^{3}J_{\text{HH}} = 6.7 \text{ Hz}, 6 \text{ H}, \text{CH}(\text{CH}_{3})_{2}], 1.16 \text{ [d, }{}^{3}J_{\text{HH}} = 6.7 \text{ Hz}, 6 \text{ H},$ CH(CH<sub>3</sub>)<sub>2</sub>] ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 179.77 (C = S), 169.84 (C=O), 145.12, 134.13, 131.56, 130.69, 129.59, 128.74, 124.02 (Ar/Ph), 28.91 [CH(CH<sub>3</sub>)<sub>2</sub>), 24.45, 23.08 (CH(CH<sub>3</sub>)<sub>2</sub>] ppm. IR (KBr):  $\tilde{v} = 3150.96$  (w), 2962.96 (m), 2867.51 (w), 1672.45 (m), 1596.04 (vw), 1508.32 (s), 1489.02 (m), 1383.85 (vw), 1362.48 (w), 1311.86 (w), 1257.56 (m), 1204.29 (w), 1154.31 (m), 1102.71 (vw), 1067.16 (w), 1023.98 (vw), 799.39 (w), 750.99 (w), 704.57 (w), 685.29 (w), 661.86 (w) cm  $^{-1}$ . C $_{80}H_{96}Br_4Cu_4N_8O_4S_4$  (1935.73): calcd. C 49.64, H 5.00, N 5.79%; found C 49.34, H 5.15, N 5.63%. X-ray quality single crystals of 4 were obtained from a concentrated THF solution.

 $[LICu(\mu-L)]_2$  (5): The procedure for the preparation of 5 was similar to that described for compound 2 using 1 (0.85g, 2.5 mmol) in THF (20 mL) and CuI (0.25 g, 1.3 mmol) in ethanol (20 mL) to afford a yellow precipitate. The solid was separated by filtration and washed with *n*-hexane (0.4 g, 0.23 mmol, 37 %). <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 12.17$  (s, 1 H, NH), 10.34 (s, 1 H, NH), 8.17, 7.64, 7.53, 7.37, 7.22 (m, 8 H, Ar/Ph), 3.01 [sept,  ${}^{3}J_{HH} = 6.5$  Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.26  $[d, {}^{3}J_{HH} = 6.7 \text{ Hz}, 6 \text{ H}, CH(CH_{3})_{2}], 1.17 [d, {}^{3}J_{HH} = 6.7 \text{ Hz}, 6 \text{ H},$ CH(CH<sub>3</sub>)<sub>2</sub>] ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  = 180.49 (C = S), 168.96 (C=O), 145.34, 133.96, 131.91, 130.70, 129.34, 129.24, 128.86, 123.91 (Ar/Ph), 28.85 [CH(CH<sub>3</sub>)<sub>2</sub>], 24.38, 23.08 [CH(CH<sub>3</sub>)<sub>2</sub>] ppm. **IR** (KBr):  $\tilde{v} = 3210$  (w), 2961 (w), 2926 (vw), 2866 (vw), 1672 (w), 1528 (m), 1507 (m), 1488 (w), 1363 (vw), 1317 (vw), 1257 (w), 1200 (vw), 1152 (w), 800 (vw), 752 (vw), 702 (vw), 685 (vw), 664 (w) cm<sup>-1</sup>. C<sub>80</sub>H<sub>96</sub>Cu<sub>2</sub>I<sub>2</sub>N<sub>8</sub>O<sub>4</sub>S<sub>4</sub> (1742.83): calcd. C 55.13, H 5.55, N 6.43%; found C 55.25, H 5.42, N 6.35%. X-ray quality single crystals of 5 were obtained from a concentrated toluene solution.

**X-ray Crystallography**: Data were collected with a Bruker SMART APEX II CCD diffractometer for 1·THF, 2–5, and 2'·2tol and an Oxford Gemini S Ultra system for 1. The diffraction data were obtained by using graphite monochromated Mo-K<sub>a</sub> radiation with a  $\omega$ -2 $\theta$  scan technique at room temperature. The structure was solved by direct methods with SHELX-97.<sup>[41]</sup> A full-matrix least-squares refinement on  $F^2$  was carried out by using SHELXL-97.<sup>[41]</sup>

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-968855 (1•THF), CCDC-979429 (1), CCDC-968856 (2), CCDC-974673 (2•tol), CCDC-968857 (3•2tol), CCDC-968858 (4),

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CCDC-968859 (**5**), and CCDC-968860 (**2**'·2tol) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

**Supporting Information** (see footnote on the first page of this article): Figures S1–S13: Molecular structures and packing diagrams. Tables S1a and S1b: Structural data for 1–5 and 2'·2tol. Spectroscopic data for 1' and 2'.

#### Acknowledgements

This work was supported by the Research Fund for Teachers of Central South University (2013JSJJ007), and the Science and Technology Planning Project of Hunan Province of China (2013FJ2003). Support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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Received: February 20, 2014 Published Online: May 2, 2014