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**FULL PAPER** 

# Synthesis and Characterization of Copper Complexes with the N-(2,6-Diisopropylphenyl)-N'-Acylthiourea Ligands

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Dedicated to Professor Ionel Haiduc on the occasion of his 80th birthday

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**Abstract:** Three *N*-(2,6-diisopropylphenyl)-*N*'-acylthiourea ligands (Ar'NHC(S)NHC(O)Ar, Ar' = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; Ar = *p*-*t*BuC<sub>6</sub>H<sub>3</sub> (**1**, **L**<sup>1</sup>), Mes (**2**, **L**<sup>2</sup>), 1-Naph (**3**, **L**<sup>3</sup>)) were synthesized and compared with the homologous ligand **L**<sup>0</sup> (Ar = Ph) in terms of their resultant complexes with copper halides. Reactions of **L**<sup>1</sup> with CuCl<sub>2</sub> led to the formation of mononuclear **L**<sup>1</sup><sub>2</sub>CuCl (**4**), while treatment of **L**<sup>1</sup> with CuX (X = Cl, Br) resulted in the adamantane cage complexes (**L**<sup>1</sup>CuX)<sub>4</sub>(X= Cl, **5**; Br, **6**). These findings are similar to the results shown by its parent ligand **L**<sup>0</sup>. The reaction of **L**<sup>1</sup> with CuI yielded the iodide-bridged dimeric complex [**L**<sup>1</sup><sub>2</sub>Cu(*µ*-1)]<sub>2</sub> (**7**), in contrast to the

#### Introduction

The formation of complexes with transition metal cations is favored in the presence of soft donor atoms such as nitrogen, sulfur or phosphorus containing ligands.<sup>[1]</sup> Acylthiourea, simultaneously bearing O, N, N' and S donor atoms within the C(O)N(H)C(S)N skeleton,<sup>[2]</sup> leads to a huge structural diversity in binding modes of their metal complexes.<sup>[3]</sup> Especially their copper products have found extensive application in analytical, environmental, and medicinal chemistry.<sup>[4]</sup>

According to the type of the substituents on the *N*-site, the acyclic acylthioureas can be generally divided into two main classes: N,N-di-substituted acylthiourea (HL) and N-alkyl/aryl-N'- acylthiourea (H<sub>2</sub>L).

When HL is treated with copper halides, it is readily deprotonated to the monoanionic ligand to yield the *O*,*S*-bis-chelate Cu(II) complexes, which are elusively formed in the *cis* or *trans* conformation.<sup>[5]</sup> In our recent report,<sup>[6]</sup> the trend of formation of *cis* 

ligand-bridged dimer supported by  $L^0$ .  $L^2$  readily afforded the mononuclear copper(I) complexes (8–10) coordinated by two or three ligands.  $L^3$  gave monomeric  $L^3_3$ CuX (X = Cl, 11; Br, 12) and iodide-bridged dimeric  $[L^3_2Cu(\mu-I)]_2$  (13).  $L^3$  can bind with Cu(I) halides in a ratio of 1:1 to give complexes  $L^3$ CuX(PPh<sub>3</sub>)<sub>2</sub> (14–16), when Cu<sub>2</sub>X<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (X = Cl, Br) or CuI(PPh<sub>3</sub>)<sub>3</sub> were used as precursors. Treatment of ( $L^1$ CuCl)<sub>4</sub> (5),  $L^2_2$ CuBr (8), and  $L^3_3$ CuCl (11), respectively, with hot EtOH resulted in the formation of *trans*-CuL<sup>n</sup>'<sub>2</sub> (17–19) compounds. All compounds were characterized by single crystal X-ray diffraction studies.

or *trans* isomer is related to the balance of the flank substituents in size to tune the geometric difference between the *cis* complex and its *trans* isomer. In most of the cases, this complexation can even be carried out by oxidizing the Cu(I) halide precursor. Interestingly HL also was found to be able to act as a neutral, monodentate ligand to bind CuCl through the sulfur site on its own<sup>[7]</sup> or with the support of PPh<sub>3</sub> as an auxiliary donor.<sup>[3, 8]</sup>

In contrast, H<sub>2</sub>L mostly behaves as a neutral sulfur donor without deprotonation in a monodentate or bridging mode in its complexes with Cu(I) salts. Moreover, it was observed that H<sub>2</sub>L can even reduce the Cu(II) halide in solution.<sup>[9]</sup> However, under some circumstances, the CuCl<sub>2</sub> adduct can also be obtained during the redox process.<sup>[10]</sup> Due to the less protective environment of the sulfur site and the highly labile and easily distorted feature of the d<sup>10</sup> Cu(I), the geometry formed during the crystallization of complexes with H<sub>2</sub>L and Cu(I) halide is significantly affected by the hydrogen-bonding, the steric hindrance of the substituents,[11] and the halide type. As such, the H<sub>2</sub>L ligands tend to support Cu(I) halide in a 2:1 stoichiometry in a monomeric or dimeric configuration or in a 3:1 composition. The 2:1 complexes exhibit a butterfly-like structure as the most favorite mode.<sup>[10, 12]</sup> The two ligands adopt a *cis* arrangement relative to the geometry of the halide atom directed by the intramolecular hydrogen bonds N- $H \cdots X$ . Interestingly, the 4:2 dimeric complexes are often bridged through sulfur atoms,<sup>[10, 13]</sup> while only on a few occasions, the chloride bridged isomers were found to coexist in the same unit cell of the crystal.<sup>[14]</sup> Similar to the 2:1 complexes, the structure of mononuclear 3:1 complexes exhibit intramolecular N-H ·· Cl hydrogen bonds<sup>[15]</sup> and show a three-legged piano stool geometry.

Recently, we have reported on the synthesis and structural characterization of the acylthiourea ligand N-(2,6-

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diisopropylphenyl)-*N*'-benzoyl-thiourea ( $\mathbf{L}^{0}$ )<sup>[9, 16]</sup> and its reaction with copper halides.<sup>[9, 17]</sup> The 2,6-diisopropylphenyl substituted ligand  $\mathbf{L}^{0}$  provided unique examples of Cu(I) halide complexes with diversified structures, including the mononuclear  $\mathbf{L}^{0}_{2}$ CuCl, the dimeric binuclear [ $\mathbf{L}^{0}$ XCu( $\mu$ - $\mathbf{L}^{0}$ )]<sub>2</sub> (X= Br, I) and the rare adamantane cage ( $\mathbf{L}^{0}$ CuBr)<sub>4</sub>. Herein, we describe the synthesis of three new ligands *N*-(2,6-diisopropoylphenyl)-*N*'-acylthiourea ( $\mathbf{L}^{1-}$ <sup>3</sup>) and their reactions with copper halides, with the aim of studying their coordination modes and structural features.

### **Results and Discussion**

Three *N*-(2,6-diisopropylphenyl)-*N*-acylthiourea ligands ( $\mathbf{L}^{1-3}$ , Scheme 1) were synthesized using the *in situ* prepared 4-(*tert*-butyl)benzoyl chloride, or the commercial available 2,4,6-trimethylbenzoyl chloride and 1-naphthoyl chloride, respectively. We followed a similar procedure as that reported for *N*-(2,6-diisopropylphenyl)-*N*-benzoylthiourea ( $\mathbf{L}^{0}$ )<sup>[9]</sup> and *N*-(2,6-dimethylphenyl)-*N*-benzoyl thiourea.<sup>[18]</sup>



Scheme 1 Three new acylthioureas L1-3

The melting points of the products  $L^{1-3}$  were found in the range of 202–211 °C. The further characterization of  $L^{1-3}$  ligands is given in the Supporting Material.

The equimolar reaction of  $L^1$  (1) in THF with the ethanol solution of CuCl<sub>2</sub> 2H<sub>2</sub>O led to the formation of  $L^{1}_{2}$ CuCl (4, Scheme 2), where the acylthiourea ligand acts as reducing reagent towards Cu(II) chloride. The melting point of 4 (243 °C) is much higher than that of its ligand  $L^1$  (211 °C).



Scheme 2. Preparation of Cu(I) complexes 4-13

The <sup>1</sup>H NMR spectrum of **4** exhibits two distinct NH protons resonances at 12.39 and 11.25 ppm, showing a downfield shift when compared to those of the ligand  $L^1$  (11.83, 9.17 ppm). These changes are highly related to the complex formation.<sup>[12d]</sup> The composition of  $L^{1}_{2}$ CuCl (**4**) was further confirmed by elementalanalysis. Although the quality of a single crystal of **4** was not adequate enough to accurately determine the molecular geometric parameters,<sup>[19]</sup> it was sufficient to characterize **4** as the 2:1 mononuclear  $L^{1}_{2}CuCl$  complex (Figure S4). This result is principally the same as that of the reaction of the parent ligand  $L^{0}$  with CuCl<sub>2</sub> 2H<sub>2</sub>O.<sup>[9]</sup>

The 1:1 reaction of  $L^1$  (1) with CuCl resulted in product 5 (Scheme 2) with a similar <sup>1</sup>H NMR spectrum to that of  $L^{1}_{2}$ CuCl (4), in view of the chemical shifts of NH protons (12.53 and 11.08 ppm for 5 vs. 12.39 and 11.25 ppm for 4). Elemental analysis of 5 suggests a 1:1 stoichiometric composition of acylthiourea ligand  $L^1$  with CuCl. Single crystal X-ray structural analysis shows the formation of an adamantane cage complex ( $L^{1}$ CuCl)<sub>4</sub> (5), crystallizing in the orthorhombic space group *Pbcn*. The molecular structure of 5 is illustrated in Figure 1 with selected bond lengths and angles in the caption.



Figure 1. Molecular structure of  $(L^1CuCl)_4$  (5). Other hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles / $^{\circ}$  Cu(1)–S(1) 2.3041(9), Cu(1)–Cl(2) 2.3553(9), Cu(1)–S(2) 2.3626(8), Cu(1)–Cl(1) 2.3636(7), Cu(2) ··Cu(2A) 2.6896(9); Cu(1A)–Cl(1)–Cu(1) 115.25(5), Cu(2)–Cl(3)–Cu(2A) 72.07(4).

From the above results, it can be suggested that the use of CuCl<sub>2</sub> or CuCl as a reactant may afford different Cu(I) products.

The similar 1:1 reaction of  $L^1$  (1) with CuBr also produced the adamantane cage complex ( $L^1$ CuBr)<sub>4</sub> (6, Scheme 2) as disclosed by the X-ray structural analysis (Figure S5).

It can be noticed in the cage structure of both **5** and **6** that all halide atoms act as bridging ligands to link the Cu(I) atoms into a puckered eight-membered ring Cu<sub>4</sub>( $\mu$ -X)<sub>4</sub>, while two acylthiourea ligands coordinate the Cu(I) anions in a monodentate mode and the other two in a bridging arrangement. The first adamantane cage complex that contains the unprecedented S<sub>2</sub>Cu<sub>4</sub>Br<sub>4</sub> core was furnished by L<sup>0.[9]</sup> It is obvious that the introduction of the p-*t*Bu substituents at the L<sup>0</sup> ligand created additional chances to produce more 1:1 acylthiourea Cu(I) complexes with an even higher symmetric geometry of the unit cell.

Treatment of  $L^1$  with equivalent amounts of CuBr<sub>2</sub> gave the same cage complex **6**, instead of the expected 2:1 complex  $L^{1}_{2}$ CuBr like  $L^{1}_{2}$ CuCl (**4**) by  $L^{1}$  with CuCl<sub>2</sub>. Interestingly, the 1:1 reaction of  $L^{1}$  with CuI provided an iodide-bridged dimeric  $[L^{1}_{2}$ Cu( $\mu$ -I)]<sub>2</sub> (**7**, Scheme 2). The molecular structure of **7** is depicted in Figure 2.







Previous studies of complexes with Cu(I) and two acylthiourea ligands crystallize either as monomers in a *cis* arrangement<sup>[10, 12]</sup> or as dimers bridged by sulfur atoms.<sup>[10, 13]</sup> So far, only two bridging chloride species with terminal acylthiourea ligands were observed but they coexisted with the ligand-bridged isomers in the crystal structure.<sup>[14]</sup> [L<sup>1</sup><sub>2</sub>Cu( $\mu$ -I)]<sub>2</sub> (7) represents the first of this type to be isolated and structurally characterized. Some complexes of Cu(I) with thiourea ligands contain halide bridges only when PPh<sub>3</sub> was used as an auxiliary ligand.<sup>[20]</sup>



**Figure 2.** Molecular structure of  $[L_{2}^{1}Cu(\mu-I)]_{2}$  (7). Thermal ellipsoids are drawn at 30% level. Other hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /  $^{\circ}$  Cu(1)–S(1) 2.2990(9), Cu(1)–S(2) 2.3450(10), Cu(1)–I(1) 2.5940(4), Cu(1)–I(1A) 2.6851(4), Cu(1) ·· Cu(1A) 2.8781(8); S(1)–Cu(1)–S(2) 103.13(4), Cu(1)–I(1)–Cu(1A) 66.050(15).

The dimeric complex  $[L^{1}_{2}Cu(\mu-I)]_{2}$  (7) crystallizes in the triclinic space group *P*-1, comprising a  $[Cu(\mu-I)]_{2}$  four-membered ring in a crystallographic center of symmetry. The Cu–I bond lengths (2.5940(4) and 2.6853(4) Å), I–Cu–I bond angles (113.953(15) <sup>°</sup>), and Cu(1)–Cu(1A) separation (2.8781(8) Å) fall in the expected range.<sup>[20-21]</sup> A closely related  $[S_{2}Cu(\mu-I)]_{2}$  core stabilized by non-chelating sulfur ligands was found in the heterocyclic 2-thione CuI complex.<sup>[22]</sup> However, it contains longer Cu–I bond lengths (2.713(5) and 2.757(5) Å), narrower I–Cu–I bond angle (98.59(2) °), and a longer Cu(1)–Cu(1A) distance (3.567 Å).

It can be seen that the *p*-tBu substituted  $L^1$  exhibited more Cu(I) halide complexes of interest than its parent ligand  $L^{0.[9]}$  This finding initiated the preparation of Cu(I) products with the Mes and 1-Naph substituted ligands  $L^2$  and  $L^3$ .

Several attempts to isolate pure products from the reaction of  $L^2$  with CuCl or CuCl<sub>2</sub> following the previous procedure failed. Treatment of  $L^2$  with CuBr<sub>2</sub> readily gave a 2:1 monomeric  $L^2_2$ CuBr (8, Scheme 2), as confirmed by X-ray structural analysis (Figure S6).<sup>[19]</sup> Moreover, when CuBr was reacted with  $L^2$ , the same product 8 was obtained instead of the cage complex.

However, the complexation reaction of the  $L^2$  with CuI in a 1:1 ratio afforded the monomeric  $L^2_2$ CuI (9, Scheme 2), which is a colorless solid and crystallizes in the monoclinic space group P2(1)/n (Figure 3).

The X-ray structure of **9** reveals a mononuclear Cu(I) iodide complex where the copper is coordinated by two S atoms of each acylthiourea ligand and one iodide ligand (Figure 3). The two ligands of **9** adopt a *cis* arrangement relative to the iodide anion. The Cu–I and Cu–S bond lengths are each found in the expected range and the sum of the bond angles around the copper is exactly  $360^{\circ}$  exhibiting a trigonal planar geometry.



Figure 3. Molecular structure of  $L^2_2$ CuI (9), 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 /  $^{\circ}$  Cu(1)–S(1) 2.2335(19), Cu(1)–S(2) 2.2373(17), Cu(1)–I(1) 2.4783(9); S(1)–Cu(1)–S(2) 104.19(7).

A comparison of the dimeric products  $[\mathbf{L}^{0}\mathbf{I}\mathbf{Cu}(\mu-\mathbf{L}^{0})]_{2}^{[9]}$  and  $[\mathbf{L}^{1}_{2}\mathbf{Cu}(\mu-\mathbf{I})]_{2}$  (7) with the monomeric  $\mathbf{L}^{2}_{2}\mathbf{CuI}$  (9) leads to an unexpected result. Therefore, a reference reaction in a 2:1 ratio of ligand  $\mathbf{L}^{2}$  with CuI was carried out, aiming at the isolation of a dimeric  $(\mathbf{L}^{2}_{2}\mathbf{CuI})_{2}$ . The resultant product is a bright yellow solid, while its <sup>1</sup>H NMR spectrum is almost the same as that of monomeric  $\mathbf{L}^{2}_{2}\mathbf{CuI}$  (9). The X-ray structural analysis confirmed a 3:1 composition of  $\mathbf{L}^{2}_{3}\mathbf{CuI}$  (10, Scheme 2). Complex 10 crystallizes in the monoclinic space group P2(1)/n (Figure 4).



Figure 4. Molecular structure of  $L^2_3$ CuI (10), 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 /  $\degree$  Cu(1)–S(1) 2.3076(13), Cu(1)–S(2) 2.3084(13), Cu(1)–S(3) 2.3391(13), Cu(1)–I(1) 2.6483(7); S(1)–Cu(1)–S(2) 105.15(5), S(1)–Cu(1)–S(3) 101.93(5), S(2)–Cu(1)–S(3) 101.00(5).



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Similar to the structural feature in  $L^{2}_{2}CuI$  (9), N–H ···I hydrogen bonds were found in  $L^{2}_{3}CuI$  (10), which align the ligands in the same direction. The Cu–I bond length (2.6486(7) Å) in 10 is evidently longer than that in 9 (2.4783(9) Å), while the Cu–S bond lengths share the same trend (av 2.3179 vs 2.2355 Å). Cu(I) halide complexes bearing three acylthiourea molecules coordinated through the sulfur atom and a halide atom in the fourth position are known in literature.<sup>[15]</sup> However, the acylthiourea ligands that can support the CuX core in both 3:1 and 2:1 composition are hardly documented. The potential of this finding needs further research.

When the 1-Naph substituted acylthiourea  $L^3$  was employed, the reaction of  $L^3$  with CuX<sub>2</sub> (X = Cl, Br) afforded the monomeric adduct  $L_{3}^{3}CuX$  (X = Cl, 11; Br, 12) of 3:1 stoichiometry (Scheme 2). The complexes 11 (Figure S7) and 12 (Figure S8) are isomorphous; therefore, the molecular conformation of them is very similar to each other. In contrast, treatment of  $L^3$  with CuCl failed to give the expected product, while the reaction of  $L^3$  with CuBr produced L<sup>3</sup><sub>3</sub>CuBr (12). The X-ray structural investigation of 12 shows that there is additional  $\pi \cdots \pi$  interaction between the 1-Naph rings of neighbor molecules within the packing mode. Interestingly, the reaction of  $L^3$  with CuI led to the formation of another iodide-bridged dimer  $[L^{3}_{2}Cu(\mu-I)]_{2}$  (13, Scheme 2). The molecular structure of 13 is depicted in Figure S9, where the Cu ·· Cu distance (3.076 Å) is found much longer than that in  $[L_{2}^{1}Cu(\mu-I)]_{2}$  (7) (2.8781(8) Å). This increase in bond length may be attributed to the ligand effect caused by the bulky 1-Naph substituents.

As shown in Scheme 2, it can be noticed that the substitution at the acylthiourea ligands has a great effect on the results of the complexation with CuX. The ligands  $L^0$  to  $L^n$  (n = 1, 2, 3) exhibit different properties. The composition and conformation of the resultant products are largely affected by the substituents, the stoichiometry of the precursors, the valency of the copper educt, the kind of halides, the hydrogen bonding, and finally the intermolecular interaction. It is suggested that the *p*-tBu substitued  $L^1$  shared the highest similarity with the parent  $L^0$  and therefore has the best chance to form the adamantane cage complexes (5 and 6), while  $L^2$  and  $L^3$  are prone to give mononuclear or binuclear complexes. In addition, it was realized that the iodide atom is rare to act as bridging ligand (7 and 13) in these systems, and is even harder to be involved in cage complexes.

The bulky P donors function selectively in the formation of CuX complexes with S ligands.<sup>[20, 23]</sup> Especially *N*,*N*-di-substituted acylthiourea ligands have been studied,<sup>[3, 8]</sup> while the *N*-alkyl/aryl-*N*-acylthiourea ligands are less explored. Reactions of L<sup>3</sup> with Cu<sub>2</sub>X<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (X = Cl, Br) or CuI(PPh<sub>3</sub>)<sub>3</sub>, respectively, led to the formation of the mononuclear L<sup>3</sup>CuX(PPh<sub>3</sub>)<sub>2</sub> complexes (X = Cl, 14; Br, 15; I, 16) (Scheme 3).



Scheme 3. Preparation of complexes L<sup>3</sup>CuX(PPh<sub>3</sub>)<sub>2</sub> (14–16).

The <sup>31</sup>P NMR spectra recorded in CDCl<sub>3</sub> solution confirm the presence of triphenylphosphine with a single resonance in the Cu(I) complexes (-4.59 ppm, 14; -5.23 ppm, 15; -5.97 ppm, 16). X-ray single crystal structural analysis further evidenced the composition and structures of complexes 14–16. L<sup>3</sup>CuCl(PPh<sub>3</sub>)<sub>2</sub> (14) crystallizes in the triclinic space group *P*-1 (Figure 5).

In the molecule of **14**, the Cu(I) center is tetra-coordinate by one chlorine, one sulfur, and two phosphorus atoms. The structure of **14** is basically homologous to that of its analogue supported by the *N*,*N*-diphenyl-*N*'-benzoylthiourea ligand.<sup>[8]</sup> In both cases, the O(1)–C(2)–N(1)–C(1) linkage is almost co-planar with the torsion angle of -1.56 ° for **14** and of -8.01 ° for that in literature.<sup>[8]</sup> One striking difference is the deviation of the S atom away from the C(2)–N(1)–C(1) plane by 0.119 Å for **14** and by 1.692 Å for the latter.<sup>[8]</sup> It is suggested that the formation of the intramolecular hydrogen bonding N(2)–H(2A) ···O(1) in **14** keeps the C=O and C=S vectors co-planar in a restricted conformation. The molecular structure of L<sup>3</sup>CuBr(PPh<sub>3</sub>)<sub>2</sub> (**15**) is shown in Figure S10,<sup>[19]</sup> and of L<sup>3</sup>CuI(PPh<sub>3</sub>)<sub>2</sub> (**16**) in Figure S11. They share highly similarity in structure and conformation.



Figure 5. Molecular structure of  $L^3CuCl(PPh_3)_2$  (14). Thermal ellipsoids are drawn at 30% level. Other hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /  $\degree$  Cu(1)–P(1) 2.2769(6), Cu(1)–P(2) 2.2905(5), Cu(1)–Cl(1) 2.3309(6), Cu(1)–S(1) 2.3731(6); P(1)–Cu(1)–P(2) 121.58(2), P(1)–Cu(1)–Cl(1) 103.44(2), P(2)–Cu(1)–Cl(1) 115.16(2), Cl(1)–Cu(1)–S(1) 105.86(2).

Complexes **4–13** are found to be air and moisture stable, while the solids of **14–16** showed a slow color change from clear to opaque when exposed in open air. Even so, complexes **4–13** have shown a facile reactivity towards EtOH. For example, during the recrystallization of complexes **5**, **8** and **11** from hot EtOH, dark colored products of *O*,*N*-bis-chelate Cu(II) compounds of *trans*-CuL<sup>n</sup>'<sub>2</sub> (**17–19**) were formed, with the release of H<sub>2</sub>S and H<sub>2</sub> through redox reactions (Scheme 4).



Scheme 4. Formation of compounds trans-CuL<sup>n</sup>'<sub>2</sub> (17-19).







Single crystals of *trans*-CuL<sup>1</sup>'<sub>2</sub> (17) of X-ray quality are dark purple. 17 crystallizes in the triclinic space group *P*-1, and its molecular structure is shown in Figure 6 with selected bond lengths and angles in the caption. The Cu(II) center is located in a nearly perfect square environment and chelated by two anionic ligands L<sup>1</sup>' in *trans* conformation through O and N sites. The molecular structures of *trans*-CuL<sup>2</sup>'<sub>2</sub> (18) and *trans*-CuL<sup>3</sup>'<sub>2</sub> (19) are depicted in Figures S12 and S13.

By comparison with the structure of the neutral ligand  $L^1(1)$ , the O(1)–C(2) bond length in the complex *trans*-Cu $L^{1\prime_2}(17)$  (1.9026(13) Å) is significantly longer than that in the ligand (1.216(4) Å), while the N–C bond distances in this complex are evidently shorter. This observation essentially reflects the electron delocalization over the chelate ring. In each case of 17–19, the geometry around the Cu atom is a heavily distorted square with the dihedral angle between two OCuN planes ranging from 32.3 to 32.8°. This distortion may be due to the repulsive interaction among the bulky Ar substituents.

It is known that thiourea derivatives are reactive to undergo desulfurization by hydrolysis, amination, and alkoxylation to give the corresponding acylurea,<sup>[2b, 24]</sup> acylguanidine,<sup>[25]</sup> and isoureas respectively.<sup>[26]</sup> The methoxylation or ethoxylation of acylthiourea Cu(II) intermediates has been documented to give *O*,*N*-bis-chelate Cu(II) compounds.<sup>[27]</sup> The current preparation of *trans*-CuL<sup>n'</sup><sub>2</sub> (17–19) further proved that the ethoxylation can occur onto the acylthiourea Cu(I) halides under mild conditions.



**Figure 6**. Molecular structure of *trans*-CuL<sup>11</sup><sub>2</sub> (17). Thermal ellipsoids are drawn at 30% level. Other hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles / $^{\circ}$ . Cu(1)–O(1) 1.9026(13), Cu(1)–N(2) 1.9673(14), N(1)–C(2) 1.312(2), N(1)–C(1) 1.342(2), N(2)–C(1) 1.311(2); O(1A)–Cu(1)–O(1) 180.00(10), O(1A)–Cu(1)–N(2) 89.60(6), O(1)–Cu(1)–N(2) 90.40(6).

In a comparative manner, the 2,6-diisopropylphenyl group was replaced by the imidazole group to prepare N(Him)-N'-(2,4,6-trimethylbenzoyl)thiourea ( $\mathbf{L}^4$ , **20**) (Him = 1*H*-imidazole, Scheme S1).  $\mathbf{L}^4$  was found to be readily transformed into di-(2,4,6-trimethylphenyl)carboxamido disulfide (**21**, Scheme S2) during recrystallization in EtOH. In addition, the reaction of  $\mathbf{L}^4$  with CuBr gave the Cu(II) adduct *trans*-(Him)<sub>2</sub>CuBr<sub>2</sub> (**22**, Scheme S3), due to the facile decomposition of  $\mathbf{L}^4$  by liberating free imidazole.

The Cu(I)/H<sub>2</sub>O<sub>2</sub> catalytic system using N,N-di-substituted acylthiourea copper complexes for the oxidation of alcohols to carbonyl compounds has been known.<sup>[3]</sup> Therefore, the herein prepared Cu(I) complexes were tentatively tried to catalyze the

oxidation of 1-phenylethanol. It was found that at room temperature Cu(I) complexes (4–13) exhibited a conversion of 1-phenylethanol to acetophenone by 17%-46%, and L<sup>n</sup>Cu(PPh<sub>3</sub>)<sub>2</sub> (14–16) gave a conversion of 15%-31%, which were much lower than those catalyzed by *N*,*N*-di-substituted acylthiourea copper complexes (90%-98%).<sup>[3]</sup> When kept at 70 °C, the above conversions were found to be increased marginally, up to 67% and 63%, respectively. Among them, the iodide complexes gave higher conversion than chloride or bromide ones. This low conversion may be due to the substrate dependence, and further optimizations are the next steps in our future studies.

In summary, we have synthesized and characterized three new *N*-(2,6-diisopropylphenyl)-*N*-acylthiourea ligands (Ar'NHC(S) NHC(O)Ar, Ar' =  $2,6-iPr_2C_6H_3$ ; Ar =  $p-tBuC_6H_3$  (1, L<sup>1</sup>), Mes (2,  $L^2$ ), 1-Naph (3,  $L^3$ )) and explored their complexation with Cu(I) halides (4–13). Combined with the previous results of  $L^0$  (Ar = Ph),<sup>[9]</sup> it was found that the adducts of these substituted L and CuX tend to form monomeric adduct L2CuX or L3CuX, dimeric ligandbridged  $[LXCu(\mu-L)]_2$ , halogen bridged  $[L_2Cu(\mu-X)]_2$ , or adamantane cage (LCuX)4 complexes, respectively. Although the adamantane cage structure bearing the S2Cu4Br4 core was for the first time known recently in L<sup>0,[9]</sup> it can be already seen as a common structural type for these complexes. In addition, the new L<sup>n</sup> ligands have created a possibility to isolate the iodide-bridged dimeric complexes  $[L_2Cu(\mu-I)]_2$ . The composition and conformation of the resultant products depend on the substituents, the precursor stoichiometry, the copper valency, the type of halogen, and the short intramolecular distances, respectively. In addition, it was realized that the prepared  $L^n$  ligands can be seen as the typical N-alkyl/aryl-N'-acylthiourea (H<sub>2</sub>L) to play a role as neutral sulfur donor in its complexation with Cu(I) halides, or even by reducing the Cu(II) halides, without giving O,S-bis-chelate Cu(II) complexes. The introduction of PPh3 donors to the complexation of  $L^3$  with CuX led to the formation of mononuclear L<sup>3</sup>CuX(PPh<sub>3</sub>)<sub>2</sub> (14–16). Complexes 4–13 have shown a facile reactivity towards hot EtOH to give dark colored products of O,Nbis-chelate Cu(II) compounds of trans-CuLn'<sub>2</sub> (17-19). The prepared Cu(I) complexes showed moderate catalytic activity for the oxidation of 1-phenylethanol in the presence of H2O2.

**X-ray Crystallography**: Data were collected on a Bruker SMART APEX II CCD diffractometer. 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>[28]</sup> A full-matrix least-squares refinement on  $F^2$  was carried out by using SHELXL-97.<sup>[28]</sup>

Compounds 5, 6, 12, 14, 16 and 18 crystallize with severely disordered solvent molecules in the unit cell. No acceptable connectivity could be established for the embedded solvent molecules. The disordered electron densities were excluded using the SQUEEZE function of the PLATON program.<sup>[29]</sup>

CCDC 1450698 (1), 1450699 (2), 1450700 (3), 1450701 (9), 1450702 (10), 1450703 (11), 1450704 (12), 1450705 (5), 1450706 (6), 1450707 (7), 1450708 (13), 1450709 (14), 1450710 (16), 1450711 (17), 1450712 (18), 1450713 (19), 1450714 (21), and 1450715 (22) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Supporting Information Experimental Section. Molecular structures in Figures S1–S15. Spectroscopic data for 20–22. Structural data in Tables S1.



## FULL PAPER

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**FULL PAPER** 

# Entry for the Table of Contents

## Layout 1:

N-(2,6-diisopropylphenyl)-N'-Three acylthiourea ligands  $(\mathbf{L}^{\mathbf{n}})$ were synthesized and reacted with copper halides to give the corresponding mono-, bi-, and tetranuclear Cu(I) complexes, respectively. The ligand substitution allows the isolation of adamantane cage (LCuX)<sub>4</sub> complexes (X = Cl, Br) with high crystallographic symmetry and unique formation of iodide-bridged dimer of composition  $[L_2Cu(\mu-I)]_2.$ 



**Copper Complexes** 

Dan Wang, Su-Yun Wu, Hai-Pu Li, Ying Yang,\* and Herbert W. Roesky\* ...... Page No. – Page No.

Synthesis and Characterization of Copper Complexes with the *N*-(2,6-Diisopropoyl phenyl)-*N*'-Acylthiourea Ligands

**Keywords:** Acylthiourea / Copper halides / S ligands / Cage compounds