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Synthesis and Characterization of *N*,*N*-Di-substituted Acylthiourea Copper(II) Complexes

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Dedicated to Veronique Gouverneur on the Occasion of Receiving the ACS Fluorine Award

Keywords: Acylthiourea; Copper; S ligands; Configuration; X-ray diffraction

Abstract. A series of six *N*,*N*-di-substituted acylthiourea ArC(O)NHC(S)N*RR′* ligands (denoted as HL^n) [Ar = 1-Naph: N*RR′* = NPh_2, HL^1 (**1**); N(*i*Pr)Ph, HL^2 (**2**). Ar = Mes: N*RR′* = NPh_2, HL^4 (**3**); N(*i*Pr)Ph, HL^5 (**4**); NEt_2, HL^6 (**5**). Ar = Ph: N*RR′* = N(*i*Pr)Ph, HL^8 (**6**)] were synthesized and characterized. These ligands were deprotonated to form Cu^{II} complexes through metathesis or combined redox reaction with copper halides. The structures of the complexes were investigated with single-crystal X-ray diffraction. The reaction of the 1-naphthalene derivative HL^1 (**1**) with CuBr in the presence of sodium acetate produced *cis*-CuL^1_2 (**7**), where the deprotonated ligand is bound to the Cu^{II} atom in a bidentate-(O,S) coordination mode. Similarly treatment of HL^2 (**2**) with NaOAc and CuCl resulted in the formation of the *cis*-arranged product [*cis*-CuL^2_2 (**8**)]. The reaction of mesityl derivative HL^4 (**3**) and CuBr with and without the addition of NaOAc gave the *cis*-CuL^4_2 (**9**) and *cis*-$(HL^4)_2CuBr$ (**10**), respectively. In contrast, reaction of HL^5 (**4**) and CuI in the presence of NaOAc resulted in *trans*-CuL^5_2 (**11**). Alternatively *trans*-CuL^6_2 (**12**) was obtained by the reaction of diethyl-substituted HL^6 (**5**) with $CuCl_2$ in the absence of a base.

Introduction

Acylthiourea with the core structure C(O)NHC(S)N contains both hard and soft donor sites. These characteristics favor metal ion complexations and thus have found extensive applications.[1] The ligand properties also depend greatly on the number and nature of the substituents at the terminal nitrogen atoms as well as on the acyl groups.[2] The *N*-alkyl/aryl-*N′*-acylthiourea (H_2L) is prepared from ArNCS and a primary amine H_2NR. This ligand reduces the Cu^{II} halide in solution to give the Cu^{I} adduct and functions as a S donor.[3] However, H_2L was not common to be deprotonated to give the anionic ligand. In contrast, the *N*,*N*-di-substituted acylthiourea (HL), which can be prepared from ArNCS and HN*RR′*, is able to function as a S donor or as a monoanionic ligand by oxidizing the Cu^{I} halide to afford a bis-chelate Cu^{II} complex.

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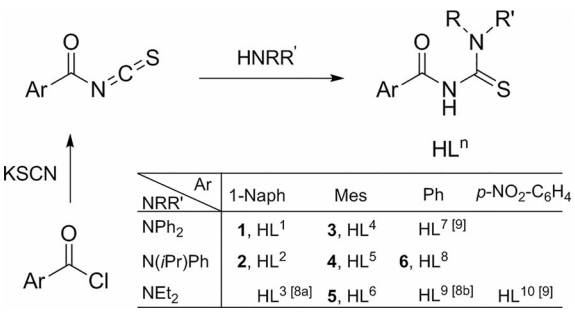
The bis-chelating coordination mode adopted by *N*,*N*-di-substituted acylthiourea ligands always leads to square planar metal complexes, predominantly with *cis* geometrical configuration. For instance, the complexes with Co^{II},[4] Ni^{II},[5] Pd^{II},[6] and Pt^{II}[7] are mostly *cis* products. The Cu^{II} analogues have a similar configuration.[8] Cu^{II} complexes with *trans* arrangement are rarely known. They are unintentionally obtained during the preparation of *cis*/*trans* isomers supported by *N*,*N*-diethyl-*N′*-(*p*-nitrobenzoyl) thiourea.[9] Moreover, the related complexes *trans*-bis(*N*-pyrrolidine-*N′*-(2-chlorobenzoyl) thiourea) copper(II)[10] and bis(*N*-piperidine-*N′*-(2-fluorobenzoyl) thiourea) copper(II) were also reported.[11]

The first example of a bis acylthiourea Pt^{II} complex with a *trans* arrangement can be mainly attributed to the introduction of a sterically demanding naphthyl substituent.[12] This practice likely transmitted an informative message to acquire the *trans*-arranged Cu^{II} product by designing the acylthiourea ligands. In this regard, we used new naphthyl derivatives and related ligands with the intension to isolate *trans* bis-chelate Cu^{II} complexes. Herein, six different *N*,*N*-di-substituted acylthiourea ArC(O)NHC(S)N*RR′* ligands are described with various Ar and N*RR′* groups. Their reactions with copper halides resulted in Cu^{II} complexes, which are reported including their spectroscopic and structural characterization.

Results and Discussion

Six *N*,*N*-di-substituted acylthiourea ligands ArC(O)NHC(S)N*RR′* [Ar = 1-Naph: N*RR′* = NPh_2, HL^1 (**1**); N(*i*Pr)Ph, HL^2 (**2**). Ar = Mes: N*RR′* = NPh_2, HL^4 (**3**);

N(*i*Pr)Ph, HL^5 (**4**); NEt_2, HL^6 (**5**). Ar = Ph: N*RR′* = N(*i*Pr)Ph, HL^8 (**6**)] were prepared according to reported methods. Four related known acylthioureas are also listed in Scheme 1 (Ar = 1-Naph: N*RR′* = NEt_2, HL^3.[8a] Ar = Ph: N*RR′* = NPh_2, HL^7;[9] NEt_2, HL^9.[8b] Ar = *p*-NO_2-C_6H_4, N*RR′* = NEt_2, HL^{10}[9]). The common procedure for the synthesis of ligands HL^n involves the reaction of substituted benzoyl chloride ArC(O)Cl with potassium thiocyanate KSCN in acetone, followed by the condensation of the in-situ formed benzoyl-isothiocyanate ArNCS with the selected secondary amine HN*RR′* (N*RR′* = NPh_2, N(*i*Pr)Ph, NEt_2).[13] The HL^n products (**1**–**6**) were purified by recrystallization and characterized by ^1H and ^{13}C NMR, FT-IR spectroscopy and elemental analysis. The analytical and spectroscopic data are consistent with the proposed structures shown in Scheme 1.



NRR′ \ Ar	1-Naph	Mes	Ph	*p*-NO_2-C_6H_4
NPh_2	**1**, HL^1	**3**, HL^4	HL^7 [9]	
N(*i*Pr)Ph	**2**, HL^2	**4**, HL^5	**6**, HL^8	
NEt_2	HL^3 [8a]	**5**, HL^6	HL^9 [8b]	HL^{10} [9]

Scheme 1. Preparation of *N*,*N*-di-substituted acylthiourea ligands HL^n (**1**–**6**).

The assignments of the ^1H and ^{13}C NMR spectra of HL^n are straightforward with the expected set of ligand protons and carbon resonances, and are further confirmed by ^1H-^{13}C HSQC NMR experiments. In the low-field of each ^1H NMR spectrum of HL^n, the characteristic singlet is assignable to the proton resonance for the NH group. The chemical shifts of the HN functionality recorded in $CDCl_3$ are given in Table 1. The NH absorption bands in the range of 3100–3300 cm^{-1} in the FT-IR spectra are also listed in Table 1.

The solid structures of *N*,*N*-diphenyl-*N′*-(1-naphthoyl) thiourea (HL^1, **1**) and *N*-isopropyl-*N*-phenyl-*N′*-(2,4,6-trimethylbenzoyl)thiourea (HL^5, **4**) were further determined by single-crystal X-ray diffraction. HL^1 (**1**) crystallizes in the orthorhombic space group *Pbca*, as depicted in Figure 1 with selected bond lengths and angles. Crystal data and structure refinements are listed in Table S1 (see Supporting Information). The O(1)–C(2) [1.210(2) Å] and S(1)–C(1) [1.6705(17) Å] bond lengths are found in the range of typical double bonds.[8]

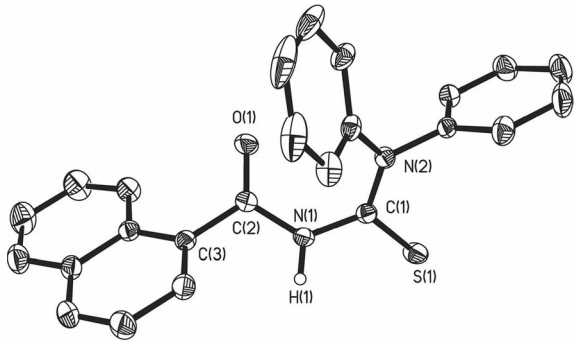
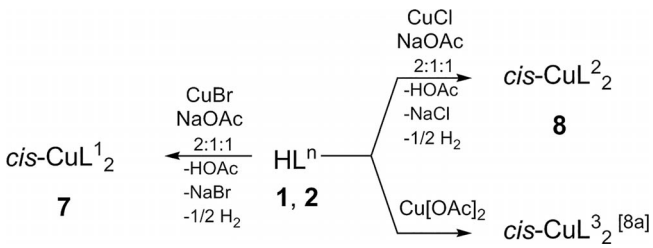


Figure 1. Molecular structure of HL^1 (**1**). Except NH other hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: N(1)–C(2) 1.388(2), N(1)–C(1) 1.389(2), N(2)–C(1) 1.343(2), O(1)–C(2) 1.210(2), S(1)–C(1) 1.6705(17); C(1)–N(1)–C(2) 126.81(14), N(1)–C(1)–N(2) 117.91(14).

It is well known that acylthiourea derivatives are showing hydrogen bonds between N donors and O/S acceptors. In the case of HL^1 (**1**) two neighboring molecules are arranged by a pair of N–H···S hydrogen bonds. Moreover, there are weak intermolecular π–π stacking interactions between naphthalene rings to form a double chain along the *a* axis (Figure S1, Supporting Information).

The overall structure of HL^5 (**4**) is nearly analogous to that of HL^1 (**1**) in view of the arrangement of the ligand skeleton and the substituents. HL^5 crystallizes in the monoclinic space group *Pc* with two symmetry independent molecules in a centrosymmetric unit (Figure S2, Supporting Information). The O(1)–C(2) [1.222(3) Å] and S(1)–C(1) [1.646(3) Å] bond lengths are comparable to those of HL^1 (**1**). The intermolecular arrangement is shown in Figure S3 (see Supporting Information).

The reaction of HL^1 (**1**) with CuBr in the presence of sodium acetate in dichloromethane afforded a dark green solid by eliminating acetic acid and sodium bromide and releasing hydrogen gas (**7**) (Scheme 2), which is in sharp contrast to those from colorless to light yellow Cu^I adducts of acylthiourea with Cu*X* (*X* = Cl, Br, I). The distinct color is indicative for the formation of the Cu^{II} complex.[8,14] In addition, the ^1H



Scheme 2. Preparation of complexes **7** and **8**.

Table 1. Proton chemical shifts in $CDCl_3$ and FT-IR stretching frequency of the NH functionality of HL^n.

NH functionality	HL^1	HL^2	HL^4	HL^5	HL^6	HL^8
^1H NMR /ppm	8.71	8.07	8.06	7.54	7.80	8.09
FT-IR /cm^{-1}	3156	3176	3268	3138	3192	3194

NMR spectrum of **7** displays very broad signals due to its paramagnetic nature. In the FT-IR spectrum the absorption band for NH stretching vibration, observed at 3156 cm^{-1} in the uncomplexed ligand HL^1, has disappeared due to the deprotonation of HL^1. At the same time, the C=O (1627 cm^{-1}) and C=S (1109 cm^{-1}) stretching frequencies of **7** were found to be red shifted upon complexation, relative to those for the free ligand HL^1 (1697 and 1156 cm^{-1}), thus suggesting a bi-chelating behavior of ligand to central metal atom through O and S atoms.[8,15] The elemental analysis of **7** shows a composition in a 2:1 stoichiometric ratio of the anionic ligand to copper.

Single crystals of **7** suitable for X-ray structural analysis were grown from a saturated THF solution. **7**·THF crystallizes in the triclinic space group $P\bar{1}$, and the molecular structure is shown (Figure 2) with relevant bond lengths and angles in the caption of Figure 2. The overall structure of **7** can be described as a *cis*-CuL^1_2 and it is analogous to those of the diphenyl derivative *cis*-CuL^7_2 and other related complexes with *cis* configuration.[8,9] Compared with the structure of the free ligand HL^1 (**1**), the bond lengths of the carbonyl [O(1)–C(2) 1.262(3), O(2)–C(26) 1.253(3) Å] and thiocarbonyl [S(1)–C(1) 1.728(3), S(2)–C(25) 1.719(3) Å] moieties in the complex *cis*-CuL^1_2 (**7**) are longer than those in the ligand [O(1)–C(2) 1.210(2), S(1)–C(1) 1.6705(17) Å], while the N–C bond lengths in this complex are evidently shorter. This observation essentially reflects the electron delocalization over the chelate ring.[8c] During the complexation, the C(S)NPh_2 moiety has rotated half a turn along the N(1)–C(1) bond to complete the chelate ring. The arrangement around the Cu atom is a slightly distorted square with the sum of bond angles at the copper atom of 362.47°. Correspondingly, the dihedral angle between two OCuS planes is 19.38°, due to the repulsive interaction among the bulky 1-Naph substituents. From the packing diagram of **7**, it is found that there is significant intermolecular π–π interaction between the naphthalene rings of two discrete molecules in the crystal (Figure S4, Supporting Information).

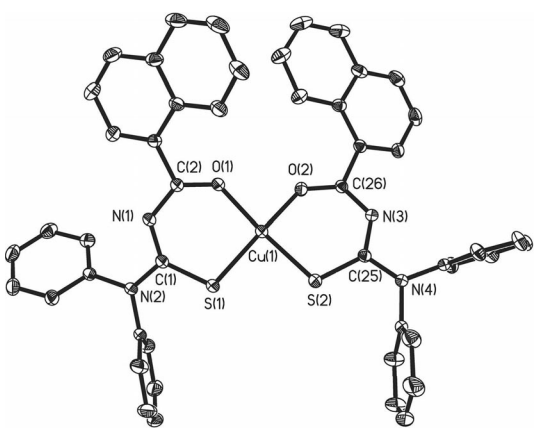


Figure 2. Molecular structure of *cis*-CuL^1_2 (**7**). Hydrogen atoms and solvent molecule are omitted for clarity. Selected bond lengths /Å and angles /°: Cu(1)–O(1) 1.9334(18), Cu(1)–O(2) 1.9388(18), Cu(1)–S(1) 2.2267(8), Cu(1)–S(2) 2.2273(8), N(1)–C(1) 1.331(3), N(1)–C(2) 1.333(3), N(3)–C(26) 1.325(3), N(3)–C(25) 1.332(3), O(1)–C(2) 1.262(3), O(2)–C(26) 1.253(3), S(1)–C(1) 1.728(3), S(2)–C(25) 1.719(3); O(1)–Cu(1)–S(1) 94.43(6), O(2)–Cu(1)–S(2) 93.63(6).

Compared with literature data it is shown that both diphenyl derivatives, HL^1 (**1**) and HL^7, gave the *cis* bis-chelate Cu^{II} complexes. It is of interest to know whether a phenyl-*i*Pr substituent at the terminal nitrogen atom of the acylthiourea ligand changes the properties in such a way that the formation of *trans* product is favored. Following this idea, the reaction of *N*-isopropyl-*N*-phenyl-*N*′-(1-naphthoyl)thiourea (HL^2, **2**) and CuCl in the presence of NaOAc was performed to isolate a dark green solid (**8**) (Scheme 2). The single-crystal X-ray analysis revealed that complex **8** crystallizes in the monoclinic space group *I2/a* as a *cis* arranged complex (*cis*-CuL^2_2, Figure S5, Supporting Information). The sum of bond angles at the central copper atom (365.19°) and the dihedral angle between OCuS planes (23.56°) was found to be larger than that in *cis*-CuL^1_2 (**7**).

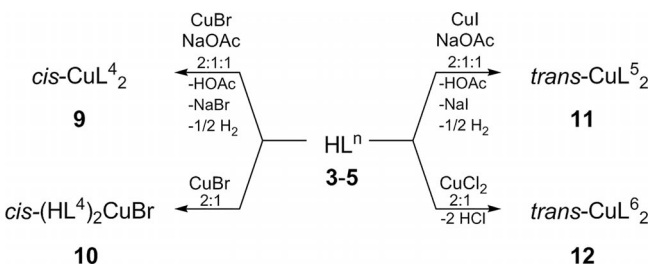
Previously *N*,*N*-diethyl-*N*′-(1-naphthoyl)thiourea (HL^3) has been used to form a Cu^{II} complex (*cis*-CuL^3_2).[8a] Inspection of the molecular structure of *cis*-CuL^3_2 revealed that the angle at the copper atom (359.82°) and the dihedral angle (11.05°) are appreciably smaller than those of *cis*-CuL^1_2 (**7**) and *cis*-CuL^2_2 (**8**). A comparison of the three dihedral angles of 23.56° (*cis*-CuL^2_2, **8**), 19.38° (*cis*-CuL^1_2, **7**), and 11.05° (*cis*-CuL^3_2) of the *cis* bis-chelate naphthalene Cu^{II} complexes shows a plausible sequence of the three N*RR*' substituents N(*i*Pr)Ph > NPh_2 > NEt_2. In this order the distortion of the square environment is enhanced.

All three naphthalene derivatives ($HL^{1–3}$) correspond to the *cis* bis-chelate Cu^{II} complexes, although the naphthyl ring should have a stronger influence due to its bigger size when compared with those of the investigated N*RR*′ groups [N(*i*Pr)Ph, NPh_2, NEt_2]. The fine tuning of the N*RR*′ substituents did not change the results in the scope of the current investigation.

It is well known that the *cis* product is thermodynamically favored, as found in a number of examples.[4–8] The *cis*/*trans* isomers of Cu^{II} complex with HL^{10} (Scheme 1) provide a good example to compare the structural difference between *cis* and *trans* products.[9] In the *cis*-CuL^{10}_2, the angle at the central copper atom (360.05°) is considerably close to the ideal angle of 360°, while the dihedral angle (2.51°) is very small. This observation is close to those in *trans*-CuL^{10}_2 (exactly 360° and 0°, respectively). The right combination of Ar and N*RR*′ groups may help to reduce the distortion of the coordination square in the *cis* configuration and promotes the formation of the *trans* product.

When the steric hindrance of the Ar group of the *N*,*N*-disubstituted acylthiourea is decreased from naphthyl to phenyl ring, all four diethyl and diphenyl acylthioureas are known to form the *cis* bis-chelate Cu^{II} products [*cis*-CuL^1_2 (**7**), *cis*-CuL^3_2,[8a] *cis*-CuL^7_2,[9] and *cis*-CuL^9_2[8b]]. It can therefore be postulated that an intermediate size Ar group may trigger a change between a naphthyl group and an unsubstituted phenyl ring. An in-between adjustment of the size of the substituents at the phenyl group might be a compromise (see Ref. [7a]). Based on this assumption the Mes group was chosen as the new ligand for further investigations.

The reaction of *N*,*N*-diphenyl-*N*′-(2,4,6-trimethylbenzoyl) thiourea (HL^4, **3**) with CuBr was carried in dichloromethane in the presence of sodium acetate to afford a light green solid (**9**) (Scheme 3). Complex **9** was established by X-ray structural analysis. **9** crystallizes in the monoclinic space group $P2_1/c$ and was determined as a *cis* product, *cis*-CuL^4_2 (Figure S6, Supporting Information). The dihedral angle between two OCuS planes was additional useful information. When compared to the respective data of Cu^{II} analogues *cis*-CuL^1_2 (19.38°) and *cis*-CuL^7_2 (12.36°), it was noticed that *cis*-CuL^4_2 (**9**) gave an intermediate value of 16.77°, indicating that the Mes group plays an expected and reasonable role in mediating the OCuS dihedral angle.



Scheme 3. Preparation of complexes **9**–**12**.

It has been known that in the Cu^I adducts $(H_2L)_2CuX$ or $(HL)_2CuX$ (X = Cl, Br, I), the acylthiourea ligands always are arranged in *cis* position, driven by the orientation of intramolecular N–H···*X* hydrogen bond interaction.[3] For example, the same reaction of HL^4 with CuBr in the absence of NaOAc gave a bright yellow solid, which turned out to be the 2:1 adduct *cis*-$(HL^4)_2CuBr$ (**10**) (Scheme 3), as revealed by the X-ray diffraction study (Figure S7, Supporting Information).

Actually, during the formation of the Cu^{II} complex supported by deprotonated acylthiourea ligand, the *trans* product might be formed, as long as the Ar and N*RR*′ couple match to each other. The structural results of *cis*-CuL^4_2 (**9**) initiated the idea of products with N(*i*Pr)Ph and NEt_2 substituents to compare these results with that of the known NPh_2 derivative.

The reaction of *N*-isopropyl-*N*-phenyl-*N*′-(2,4,6-trimethylbenzoyl)thiourea (HL^5, **4**) and CuI in the presence of NaOAc, gave a yellow-green solid (**11**) (Scheme 3). The color suggested the formation of the Cu^{II} complex, which was further confirmed by analytical and spectroscopic data. Recrystallization, however, gave piles of pale green hexagonal flakes. The quality of single crystals of **11** did not allow to obtain the molecular geometric parameters with sufficient accuracy, but they were adequate to characterize complex **11** as *trans*-CuL^5_2 (Figure S8, Supporting Information).[16]

Encouraged by this result, we further tried the preparation of *N*,*N*-diethyl-*N*′-(2,4,6-trimethylbenzoyl)thiourea (HL^6, **5**), where the former NPh_2 moiety in HL^4 is replaced by NEt_2. In the literature the *N*,*N*-diethyl acylthiourea complexes with an extensive range of Ar groups have been known to form *cis* bis-chelate Cu^{II} complexes (Table S2, Supporting Information). One known exception was the Cu^{II} complex supported by HL^{10} (Scheme 1), with both *cis* and *trans* isomers.[9] In the current work, HL^6 (**5**) was tentatively treated with $CuCl_2$ in acetone without the addition of any base, and this reaction was found to proceed smoothly to give a blue-green solid (**12**) (Scheme 3). It is suggested that the molecular elimination of HCl between HL^6 and $CuCl_2$ is highly spontaneous to result in complex formation. Parallel experiments using HL^6 with Cu*X* (*X* = Br, I) revealed that the presence of NaOAc is still necessary to afford the same Cu^{II} product.

Complex **12** crystallizes in the monoclinic space group $P2_1/n$. The X-ray crystal dada of **12** confirm that the Cu^{II} atom is chelated by two anionic ligands L^6 in *trans* conformation (Figure 3).

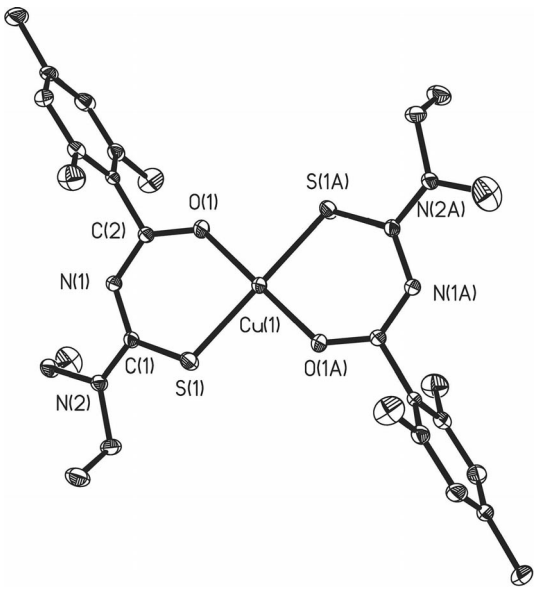


Figure 3. Molecular structure of *trans*-CuL^6_2 (**12**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% level. Selected bond lengths /Å and angles /°: Cu(1)–O(1) 1.925(2), Cu(1)–S(1) 2.2529(9), N(1)–C(2) 1.311(4), N(1)–C(1) 1.351(4), O(1)–C(2) 1.264(3), S(1)–C(1) 1.729(3); O(1)–Cu(1)–S(1) 93.79(7).

The Cu–S [2.2529(9) Å] and Cu–O [1.925(2) Å] bond lengths in *trans*-CuL^6_2 (**12**) are comparable to or slightly longer than those of *trans*-CuL^9_2 [2.253(1) and 1.901(2) Å],[9] as well as *trans*-bis(*N*-pyrrolidine-*N*′-(2-chlorobenzoyl) thiourea)copper(II)[10] [2.2417(6) and 1.9078(15) Å] and *trans*-bis(*N*-piperidine-*N*′-(2-fluorobenzoyl)thiourea) copper(II) [2.249 and 1.896 Å].[11] It is noticeable that, for each of the four cases in *trans* configuration, the Cu^{II} atom lies in a crystallographic inversion center and the dihedral angle of OCuS planes was exactly 0° to present a strictly square-planar arrangement.

The products of *N*-isopropyl-*N*-phenyl-*N*′-(benzoyl) thiourea (HL^8, **6**) with copper halides in a variety of solvents failed to yield X-ray quality crystals.

Conclusions

Six *N*,*N*-di-substituted acylthiourea ligands were synthesized and deprotonated to support the bis-chelate Cu^{II} complexes. Single crystal X-ray structural analysis revealed that when Ar is the steric demanding 1-naphthalene ring, the result-

ant Cu^{II} complexes are always in *cis* arrangement [like *cis*-$CuL^1{}_2$ (**7**), *cis*-$CuL^2{}_2$ (**8**), and *cis*-$CuL^3{}_2$[8a]] regardless of the tuning of the N*RR′* substituents. The phenyl ring (Ar) exhibits a similar situation to give *cis*-$CuL^7{}_2$[9] and *cis*-$CuL^9{}_2$.[8b] Examination of the structural data suggested that Ar and N*RR′* have to match each other and one of the two should not be exceedingly more bulky than the other one in order to obtain the *trans* product. By following this assumption, the Mes group was introduced to comprise the size between naphthalene and substituted phenyl rings. Starting from *cis*-$CuL^4{}_2$ (**9**) two *trans* bis-chelate Cu^{II} complexes were obtained, *trans*-$CuL^5{}_2$ (**11**) and *trans*-$CuL^6{}_2$ (**12**), by enlarging or diminishing the N*RR′* groups of the *N*,*N*-di-substituted acylthioureas. They represent the first examples of such a *trans* system by design with acyclic N*RR′* substituents and without being accompanied by their *cis* isomers. These results show the importance of balancing the Ar and N*RR′* flanks in size to obtain a matchable couple, where the dihedral angle of the OCuS planes can shrink. This allows that the geometric difference of the core structure between a *cis* and a *trans* isomer can be minimized to reach a transition state. Under such a condition, also the formation of a *trans* product is even more favorable during complexation. Nevertheless, this should be carefully applied because there are additional factors, like intermolecular interaction, accounting for the variation of molecules.[9] It is implied that, although the *trans* product was solely observed in our work and those of reported examples,[10,11] it is still possible that the *cis* isomer could exist due to its thermodynamic favored formation.

Experimental Section

All chemicals commercially available used in the synthesis were of analytical grade and used as received. Melting points were measured in a sealed glass tubes with 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 ^1H and ^{13}C NMR spectra were recorded with 5 mm tubes in $CDCl_3$ 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.

The ligands were prepared according to the method of *Douglass* and *Dains*.[13] The syntheses of *N*,*N*-diethyl-*N′*-(1-naphthoyl)thiourea HL^3, *N*,*N*-diphenyl-*N′*-(benzoyl)thiourea HL^7, *N*,*N*-diethyl-*N′*-(benzoyl)-thiourea HL^9, *N*,*N*-diethyl-*N′*-(*p*-nitrobenzoyl) thiourea HL^{10}, and their Cu^{II} complexes have been reported elsewhere. The analytical and FT-IR data for the new ligands and their respective complexes are given below.

***N*,*N*-Diphenyl-*N′*-(1-naphthoyl)thiourea (HL^1) (1):** Pale yellow solid. Yield 80 %. M.p. 151–152 °C. **^1H NMR** (500 MHz, $CDCl_3$): δ = 8.71 (s, 1 H, N*H*), 7.98 (d, 1 H, Naph-*H*), 7.93(d, 1 H, Naph-*H*), 7.84 (d, 1 H, Naph-*H*), 7.51 (m, 3 H, Naph-*H*), 7.42 (m, 10 H, Ph-*H*), 7.30 (m, 2 H, Naph-*H*) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 182.26 (*C*=S), 163.41 (*C*=O), 132.21 (Naph-*C*), 129.31 (Ph-*C*), 128.34 (Naph-*C*), 127.62 (Naph-*C*), 127.52 (Naph-*C*), 126.99 (Ph-*C*), 126.71 (Naph-*C*), 125.86 (Naph-*C*), 125.05 (Naph-*C*), 124.37 (Ph-*C*) ppm. **FT-IR** (KBr): $\tilde{\nu}$ = 3156 (w, NH), 1697 (s, C=O), 1592 (w), 1492 (s), 1376 (s), 1264 (m), 1236 (s), 1215 (s), 1156 (m, C=S), 1119 (s), 865 (m), 806 (m), 778 (s), 758 (s), 693 (s), 630 (s), 583 (m) cm^{-1}. $C_{24}H_{18}N_2OS$ (382.5): calcd. C, 75.37; H, 4.74; N, 7.32; S, 8.38 %; found C, 75.33; H, 4.77; N, 7.23; S, 8.35 %. Colorless X-ray quality single crystals of **1** were obtained from a concentrated THF solution.

***N*-Isopropyl-*N*-phenyl-*N′*-(1-naphthoyl)thiourea (HL^2) (2):** White solid. Yield 80 %. M.p. 155–156 °C. **^1H NMR** (500 MHz, $CDCl_3$): δ = 8.07 (s, 1 H, N*H*), 7.90 (d, 1 H, Naph-*H*), 7.84 (d, 1 H, Naph-*H*), 7.79 (d, 1 H, Naph-*H*), 7.44 (m, 5 H, Ph-*H*), 7.40 (d, 1 H, Naph-*H*), 7.29 (m, 3 H, Naph-*H*), 7.15 (d, 1 H, Naph-*H*), 5.77 (sept, 1 H, C*H*$(CH_3)_2$), 1.24 (d, 6 H, CH(C*H*$_3)_2$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 179.64 (*C*=S), 165.25 (*C*=O), 133.57, 131.73, 129.99, 129.05, 128.88, 128.29, 127.42, 126.58, 125.49, 125.07, 124.40 (Naph/Ph-*C*), 54.28 (*C*H$(CH_3)_2$), 20.50 (CH(*C*H$_3)_2$) ppm. **FT-IR** (KBr): $\tilde{\nu}$ = 3176 (w, NH), 2980 (w), 1696 (s, C=O), 1504 (s), 1400 (s), 1348 (m), 1248 (m), 1233 (s), 1184 (m), 1152 (s), 1134 (s, C=S), 1104 (s), 908 (w), 854 (w), 813 (m), 781 (s), 734 (m), 710 (m), 624 (m), 595 (m), 522 (m) cm^{-1}. $C_{21}H_{20}N_2OS$ (348.5): calcd. C, 72.38; H, 5.79; N, 8.04; S, 9.20 %; found C, 72.15; H, 5.70; N, 7.88; S, 9.33 %.

***N*,*N*-Diphenyl-*N′*-(2,4,6-trimethylbenzoyl)thiourea (HL^4) (3):** Bright yellow solid. Yield 53 %. M.p. 199–200 °C. **^1H NMR** (500 MHz, $CDCl_3$): δ = 8.06 (s, 1 H, N*H*), 7.38 (m, 8 H, Ph-*H*), 7.28(m, 2 H, Ph-*H*), 6.75 (s, 2 H, Mes-*H*), 2.23 (s, 3 H, *p*-*Me*-Mes), 1.98 (s, 6 H, *o*-*Me*-Mes) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 181.90 (*C*=S), 165.26 (*C*=O), 145.82, 139.36, 134.37, 133.01, 129.33, 128.38, 127.62, 127.29 (Ar-*C*), 21.09, 18.91 (Ar-*C*H$_3$) ppm. **FT-IR** (KBr): $\tilde{\nu}$ = 3268 (w, NH), 1669 (s, C=O), 1610 (w), 1490 (vs), 1453 (m), 1374 (s), 1263 (s), 1199 (s, C=S), 1152 (m), 1085 (w), 848 (w), 758 (m), 691 (m), 633 (w), 600 (m) cm^{-1}. $C_{23}H_{22}N_2OS$ (374.5): calcd. C, 73.76; H, 5.92; N, 7.48; S, 8.56 %; found C, 73.85; H, 5.88; N, 7.36; S, 8.67 %.

***N*-Isopropyl-*N*-phenyl-*N′*-(2,4,6-trimethylbenzoyl)thiourea (HL^5) (4):** White solid. Yield 91 %. M.p. 197–198 °C. **^1H NMR** (500 MHz, $CDCl_3$): δ = 7.54 (s, 1 H, N*H*), 7.43 (m, 3 H, Ph-*H*), 7.23 (m, 2 H, Ph-*H*), 6.71 (s, 2 H, Mes-*H*), 5.69 (sept, 1 H, C*H*$(CH_3)_2$), 2.21 (s, 3 H, *p*-*Me*-Mes), 1.90 (s, 6 H, *o*-*Me*-Mes), 1.19 (d, 6 H, CH(C*H*$_3)_2$) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 179.30 (*C*=S), 167.05 (*C*=O), 138.97, 138.76, 134.18, 133.44 (Mes-*C*), 129.12, 129.00, 128.90 (Ph-*C*), 128.17 (Mes-*C*), 54.45 (*C*H$(CH_3)_2$), 21.07 (*p*-*Me*-Mes), 20.42 (CH(*C*H$_3)_2$), 18.73 (*o*-*Me*-Mes) ppm. **FT-IR** (KBr): $\tilde{\nu}$ = 3138 (m, NH), 2972 (s), 1659 (vs, C=O), 1611 (m), 1501 (vs), 1404 (vs), 1348 (s), 1283 (m), 1244 (vs), 1167 (s, C=S), 1116 (m), 1088 (s), 909 (m), 844 (m), 758 (m), 702 (s), 683 (m), 592 (m) cm^{-1}. $C_{20}H_{24}N_2OS$ (340.5): calcd. C, 70.55; H, 7.10; N, 8.23; S, 9.42 %; found C, 70.43; H, 7.01; N, 8.17; S, 9.57 %. Colorless X-ray quality single crystals of **4** were obtained from a concentrated THF solution.

***N*,*N*-Diethyl-*N′*-(2,4,6-trimethylbenzoyl)thiourea (HL^6) (5):** White solid. Yield 20 %. M.p. 113–114 °C. **^1H NMR** (500 MHz, $CDCl_3$): δ = 7.80 (s, 1 H, N*H*), 6.85 (s, 2 H, Mes-*H*), 4.00 (s, 2 H, C*H*$_2$CH$_3$), 3.77 (s, 2 H, C*H*$_2$CH$_3$), 2.33 (s, 6 H, *o*–*Me*–Mes), 2.28 (s, 3H *p*–*Me*–Mes), 1.35 (t, 6 H, CH$_2$C*H*$_3$) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 178.51 (*C*=S), 167.14 (*C*=O), 139.43, 134.31, 133.46, 128.48 (Mes-*C*), 48.26, 47.95 (*C*H$_2$CH$_3$), 21.13 (*p*-*Me*-Mes), 19.24 (*o*-*Me*-Mes), 13.40, 11.54 (CH$_2$*C*H$_3$) ppm. **FT-IR** (KBr): $\tilde{\nu}$ = 3192 (w, NH), 2974 (w), 1696 (s, C=O), 1542 (s), 1444 (s), 1425 (s), 1374 (m), 1354 (w),1286 (m), 1257 (m), 1227 (s), 1174 (m), 1131 (m, C=S), 1074 (m), 1056 (w), 852 (m), 687 (w) cm^{-1}. $C_{15}H_{22}N_2OS$ (278.4): calcd. C, 64.71; H, 7.96; N, 10.06; S, 11.52 %; found C, 64.66; H, 7.85; N, 10.00; S, 11.67 %.

***N*-Isopropyl-*N*-phenyl-*N′*-(benzoyl)thiourea (HL^8) (6):** White solid. Yield 90 %. M.p. 152–154 °C. **^1H NMR** (500 MHz, $CDCl_3$): δ = 8.09

(s, 1 H, N*H*), 7.45 (m, 3 H, Ph-*H*), 7.40 (m, 1 H, Ph-*H*), 7.31–7.35 (m, 4 H, Ph-*H*), 7.25 (m, 2 H, Ph-*H*), 5.81 (m, 1 H, C*H*$(CH_3)_2$), 1.22 (d, 6 H, CH(CH_3)$_2$) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 179.17 (*C*=S), 163.62 (*C*=O), 138.40, 133.48, 132.45, 129.30, 129.02, 128.99, 128.83, 128.66, 127.23 (Ph-*C*), 53.49 (*C*H$(CH_3)_2$), 20.51 (CH(CH_3)$_2$) ppm. **FT-IR** (KBr): $\tilde{\nu}$ = 3194 (w, NH), 2976 (w), 1700 (m, C=O), 1641 (m), 1582 (w), 1513 (s), 1407 (m), 1366 (w), 1350 (m), 1233 (s), 1171 (m), 1153 (m, C=S), 1072 (m), 915 (w), 828 (w), 793 (w), 763 (w), 703 (s), 669 (w), 628 (w), 566 (w) cm^{-1}. $C_{17}H_{18}N_2OS$ (298.4): calcd. C, 68.42; H, 6.08; N, 9.39; S, 10.75 %; found C, 68.33; H, 6.06; N, 9.35; S, 10.86 %.

***cis*-CuL$^1_2$ (7):** To a solution of HL^1 (**1**) (0.3825 g, 1.0 mmol) in dichloromethane (15 mL) at room temperature was added an aqueous sodium acetate solution (0.0836 g, 1.0 mmol) under intense stirring within 1 h. A suspension of CuBr (0.1415 g, 1.0 mmol) in ethanol was added to the reaction mixture drop by drop. An additional 12 h was allowed to insure the completion of complexation. The resultant precipitates were filtered, washed with ethanol repeatedly, and dried at 80 °C to obtain deep green powders (0.3088 g, 0.37 mmol, 37.4 %). M.p. 210–212 °C. **FT-IR** (KBr): $\tilde{\nu}$ = 3433.06 (w), 3052.4 (w), 1590.55 (vw, C=O), 1488.76 (m), 1428.04 (m), 1393.05 (m), 1287.28 (w), 1238.8 (w), 1149.31 (vw, C=S), 1074.37 (vw), 1032.83 (vw), 884.92 (vw), 780.73 (w), 754.9 (vw), 696.98 (vw), 624.45 (vw) cm^{-1}. $C_{48}H_{34}CuN_4O_2S_2$ (826.5): calcd. C, 69.75; H, 4.15; N, 7.69; S, 7.76 %; found C, 69.49; H, 4.10; N, 7.57; S, 7.90 %. X-ray quality single crystals of **7** were obtained from a concentrated dichloromethane solution.

***cis*-CuL$^2_2$ (8):** The procedure was similar to that for *cis*-CuL$^1_2$ (**7**), using HL^2 (**2**) (0. 3485 g, 1.0 mmol), sodium acetate (0.0836 g, 1.0 mmol), and CuCl (0.1032 g, 1.0 mmol). Dark green solid (0.33 g, 0.44 mmol, 44 %). M.p. 186–189 °C. **FT-IR** (KBr): $\tilde{\nu}$ = 3436 (w), 3050 (vw), 2976 (vw), 2928 (vw), 1627 (vw, C=O), 1508 (vw), 1487 (vw), 1431 (w), 1407 (w), 1274 (vw), 1237 (vw), 1109 (vw, C=S), 780 (vw), 696 (vw) cm^{-1}. $C_{42}H_{38}CuN_4O_2S_2$ (758.5): calcd. C, 66.51; H, 5.05; N, 7.39; S, 8.46 %; found C, 66.19; H, 5.07; N, 7.23; S, 8.48 %. X-ray quality single crystals of **8** were obtained from a concentrated dichloromethane solution.

***cis*-CuL$^4_2$ (9):** The procedure was similar to that for *cis*-CuL$^1_2$ (**7**), using HL^4 (**3**) (0.3745 g, 1.0 mmol), sodium acetate (0.0836 g, 1.0 mmol), and CuBr (0.1441 g, 1.0 mmol). Deep green solid (0.4278 g, 0.53 mmol, 52.9 %). M.p. 233–235 °C. **FT-IR** (KBr): $\tilde{\nu}$ = 3441.22 (w), 2961.35 (vw), 2917.97 (vw), 1609.50 (vw, C=O), 1475.38 (m), 1427.92 (m), 1371.26 (m), 1288.36 (w), 1254.98 (vw), 1153.77 (vw, C=S), 1073.90 (vw), 1027.99 (vw), 874.84 (vw), 756.01 (vw), 696.74 (vw), 627.19 (vw) cm^{-1}. $C_{46}H_{42}CuN_4O_2S_2$ (810.5): calcd. C, 68.16; H, 5.22; N, 6.91; S, 7.91 %; found C, 68.11; H, 5.22; N, 6.80; S, 7.94 %. X-ray quality single crystals of **9** were obtained from a concentrated dichloromethane solution.

***trans*-CuL$^5_2$ (11):** The procedure was similar to that for *cis*-CuL$^1_2$ (**7**), using HL^5 (**4**) (0.8575 g, 2.5 mmol), sodium acetate (0.2062 g, 2.5 mmol), and CuI (0.4835 g, 2.5 mmol). Deep green solid (1.12 g, 1.5 mmol, 61 %). M.p. 210–212 °C. **FT-IR** (KBr): $\tilde{\nu}$ = 2969 (vw), 2921 (vw), 2870 (vw), 1631 (vw, C=O), 1504 (vw), 1481 (vw), 1414 (vw), 1262 (vw), 1166 (vw), 1119 (vw), 1092 (vw, C=S) cm^{-1}. $C_{40}H_{46}CuN_4O_2S_2$ (742.5): calcd. C, 64.70; H, 6.24; N, 7.55; S, 8.64 %; found C, 64.38; H, 6.16; N, 7.44; S, 8.67 %.

***trans*-CuL$^6_2$ (12)**: A solution of mixture of HL^6 (**5**) (0.2824 g, 1 mmol) and $CuCl_2{\cdot}2H_2O$ (0.1801 g, 1 mmol) in ethanol (30 mL) was stirred at room temperature for 12 h. The resultant precipitates were filtered, washed with ethanol repeatedly, and dried at 50 °C in vacuo to obtain off-white powders (0.45 g, 0.73 mmol, 73 %). M.p. 178–179 °C. **FT-IR** (KBr): $\tilde{\nu}$ = 3105 (s), 2975 (m), 2934 (m), 2863 (m), 1698 (s), 1610 (w, C=O), 1549 (m), 1439 (s), 1381 (w), 1295 (w), 1256 (m), 1223 (s), 1169 (w), 1122 (m, C=S), 1057 (w), 845 (w) cm^{-1}. $C_{30}H_{42}CuN_4O_2S_2$ (618.4): calcd. C, 58.27; H, 6.85; N, 9.06; S, 10.37 %; found C, 57.99; H, 6.86; N, 8.85; S, 10.22 %. Dark green X-ray quality single crystals of **12** were obtained from a concentrated THF solution.

X-ray Crystallography: Data were collected with a Bruker SMART APEX II CCD diffractometer. The diffraction data were obtained by using graphite monochromated Mo-K_α radiation with a ω-2θ scan technique at room temperature. The structure was solved by direct methods with SHELX-97.[17] A full-matrix least-squares refinement on F^2 was carried out by using SHELXL-97.[17]

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-1037321 (**1**), CCDC-1037322 (**4**), CCDC-1037323 (**7·THF**), CCDC-1037324 (**8**), CCDC-1037325 (**9**), CCDC-1037326 (**10**), and CCDC-1037327 (**12**) (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): Molecular structures and packing diagrams in Figures S1–S8. Structural data in Tables S1 for **1**, **4**, **7·THF**, **8–10**, and **12**. Spectroscopic data for **10**.

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