Journal of Inorganic and General Chemistry

ZAAC

Zeitschrift für anorganische und allgemeine Chemie

Accepted Article

Title: Self-Assembly of Discrete Copper(I)-Halide Complexes with Diacylthioureas

Authors: Herbert W. Roesky, Xianhui Hou, Fanfan Wang, Li Han, Xia Pan, Haipu Li, and Ying Yang

To be cited as: *Z. anorg. allg. Chem.* 10.1002/zaac.201700430

Link to VoR: http://dx.doi.org/10.1002/zaac.201700430

WILEY-VCH

www.zaac.wiley-vch.de

Self-Assembly of Discrete Copper(I)-Halide Complexes with Diacylthioureas

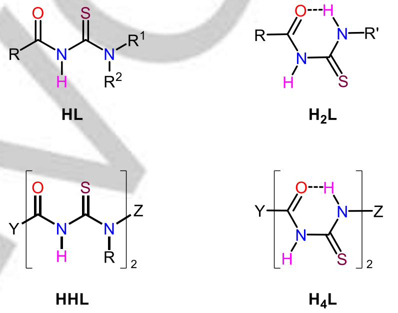
Xianhui Hou,[a] Fanfan Wang,[a] Li Han,[a] Xia Pan,[a] Haipu Li,[a] Ying Yang,*[a] and Herbert W. Roesky*[b]

Abstract: Three diacylthioureas 1,4-$C_6H_4[C(O)NHC(S)NHAr]_2$ (Ar = 2,6-$i$$Pr_2C_6H_3$) (**L^1**, **1**), 1,3-$C_6H_4[C(O)NHC(S)NHAr]_2$ (**L^2**, **2**) and 1,3-$C_6H_4[C(O)NHC(S)NHAr']_2$ (Ar′ = 2,6-$Me_2C_6H_3$) (**L^3**, **3**) were synthesized and characterized. The Cu^I complexes from the reactions of bipodal ligands **L^n** with CuX (X = Cl, Br, I) were structurally investigated by single crystal X-ray diffraction methods. Treatment of **L^1** with CuX gave the metallamacrocyclic complexes $(\mathbf{L^1}CuX)_2$ (X = Cl, **4**; Br, **5**; I, **6**) with the ligand to metal in a ratio of 2:2, where both sulfur and halide anions function as terminal substituents. In contrast, when **L^2** or **L^3** was reacted with CuBr, the two **L^n** ligands coordinate to four copper atoms each in a bridging and terminal fashion to yield $[\mathbf{L^n}(CuBr)_2]_2$ (n = 2, **7**; 3, **8**). The obtained $S_4Cu_4Br_4$ core contains all four bromide anions in bridging positions. The reaction of **L^3** with CuX (X = Cl, I) gave the 3:3 trinuclear complexes $(\mathbf{L^3}CuX)_3$ (X = Cl, **9**; I, **10**), interconnected by halide bridges. The obtained diacylthioureas (**1-3**) and their Cu^I complexes (**4-10**) were also characterized by elemental analysis, FT-IR, ^1H- and ^{13}C NMR spectroscopy.

Introduction

Acylthiourea derivatives containing the C(O)NHC(S)N core fragment have been well recognized due to their biological,[1] optical,[2] analytical,[3] and catalytic properties.[4] Their Cu^I complexes are also attractive in view of the metal-based drugs.[5] As addressed before,[6] the acyclic mono-acylthioureas can be generally divided into two main classes (Scheme 1): *N*,*N*-disubstituted acylthiourea (**HL**) and *N*-alkyl/aryl-*N*′-acylthiourea (**H$_2$L**). When treated with metal reagents, **HL** is readily deprotonated into the monoanionic ligand to give *O*,*S*-bis(chelate)-M^{II} complexes in most of the cases.[7] In contrast **H$_2$L** behaves always as a neutral sulfur donor in terminal or bridging mode to support a variety of coordination complexes[6, 8] due to the ligand specificity.

Under similar conditions, the bipodal diacylthioureas that contain two C(O)NHC(S)N fragments in each molecule also can be classified into 3,3′-disubstituted diacylthiourea (**HHL**, Scheme 1) and 3,3′-monosubstituted diacylthiourea (**H$_4$L**). The role of Y and Z substituents acting as either spacer or end group depends on the properties of the used diamines[9] (Z spacer and Y end group) or diacyl chlorides[10] (Y spacer and Z end group). In the complexation reactions, the bipodal **HHL** tends to be deprotonated into the dianionic ligand and generates the 2:2 or 3:3 metallamacrocycles, using the κ-*O*,*S* mode to chelate metal centers like Co^{II},[11] Ni^{II},[12] Cu^{II},[12a, 13] Zn^{II}, Cd^{II},[13b, 14] Hg^{II},[15] Pt^{II},[16] Pt^{IV},[17] Pd^{II},[18] Ru^{II},[19] and Re^V.[20] In rare cases, **HHL** was also found to support polymeric compounds of Pb^{II}[13a] or Ag^I[21] with or without deprotonation, respectively.



Scheme 1. Monoacylthioureas (**HL** and **H$_2$L**) and diacylthioureas (**HHL** and **H$_4$L**). Among the Y and Z substituents, one of them represents the spacer group and the other is the end group.

In contrast, the investigation of coordination complexes with the diacylthiourea **H$_4$L** is largely unexplored. When considering the performance of the mono-acylthiourea **H$_2$L**,[6, 8] the bipodal **H$_4$L** can be expected to bring abundant structural variety in the complexation with CuX (X = Cl, Br, I). The two sulfur and the involved halides could play an alternative role in terminal or bridging positions. The only previous related report revealed that **H$_4$L** can form a coordination polymer with CuCl (**H$_4$L** = $Fe[C_5H_4C(O)NHC(S)NH$$i$$Pr]_2$),[22] where the isopropyl substituents were less bulky and the relative position of the sulfur pair was disordered. Based on this finding, we propose the synthesis of new **H$_4$L** diacylthioureas: 1,4-$C_6H_4[C(O)NHC(S)NHAr]_2$ (Ar = 2,6-$i$$Pr_2C_6H_3$) (denoted as **L^1**, **1**), 1,3-$C_6H_4[C(O)NHC(S)NHAr]_2$ (**L^2**, **2**) and 1,3-$C_6H_4[C(O)NHC(S)NHAr']_2$ (Ar′ = 2,6-$Me_2C_6H_3$) (**L^3**, **3**), starting from isophthaloyl dichloride or terephthaloyl dichloride. Each of **L^n** is armed with bulky aryl flanks and shows a large separation between two sulfur atoms to support the self-assembly with Cu^I halides. Complexation reactions of **L^n** with CuX were carried out in a comparative manner to investigate the possible formation of discrete or infinite supramolecular species by coordination-driven self-assembly.[23]

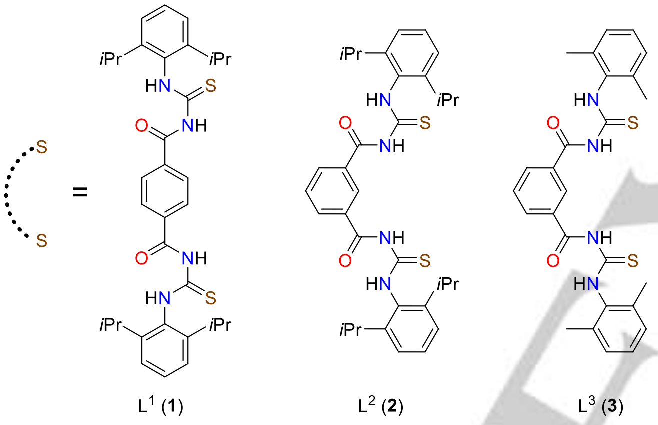
Results and Discussion

The diacylthiourea 1,4-$C_6H_4[C(O)NHC(S)NHAr]_2$ (Ar = 2,6-$i$$Pr_2C_6H_3$) (**L^1**, **1**) (Scheme 2) was isolated as a yellow solid in moderate yield (74%) from the successive reaction of terephthaloyl dichloride with potassium thiocyanate and then 2,6-diisopropyl aniline, by following the previous procedure.[10d,

---

[a] School of Chemistry and Chemical Engineering
Centre for Environment and Water Resource
Central South University
Lushannan Road 932, 410083 Changsha, P. R. China
Fax: +86-731-88879616
E-mail: yangy@csu.edu.cn
[b] Institut für Anorganische Chemie
Universität Göttingen
Tammannstrasse 4, 37077 Göttingen, Germany
Fax: +49-551-39-33373
E-mail: hroesky@gwdg.de
Supporting information for this article is given via a link at the end of the document.

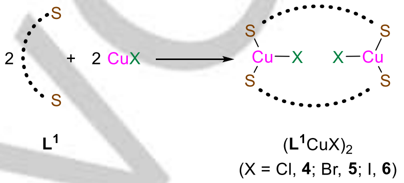
24] The melting point of $\mathbf{L^1}$ (259-260°C) is much higher than its phenyl analogue $1,4\text{-}C_6H_4[C(O)NHC(S)NHPh]_2$ (215-220°C).[10d] In the FT-IR spectrum, the NH absorption bands were observed at 3432 and 3248 cm^{-1}, and the ^{1}H NMR spectrum recorded in $CDCl_3$ confirmed the presence of N*H* groups (δ 11.76 and 9.43 ppm) as well as the characteristic isopropyl groups (δ 3.13 ppm for the tertiary H atoms and δ 1.24-1.35 ppm for the Me groups). Furthermore, the ^{13}C NMR spectrum showed the featured resonances of *C*=S (δ 179.84 ppm) and *C*=O (δ 164.52 ppm). The structure of $\mathbf{L^1}$ was elucidated by single crystal X-ray diffraction. As shown in Figure S1 (see Supporting Information), there are two independent molecules of $\mathbf{L^1}$ in one unit cell, with totally different S-C-C-S torsions (4.35° for **1a** and -76.29° for **1b**, Figure S2). The packing diagram of $\mathbf{L^1}$ (Figure S3) and the topological analysis (Figure S4) by TOPOS[25] indicated that the neighboring **1b** molecules are connected by each other through N–H···O intermolecular hydrogen bonds to form the zigzag chains along the *b* axis. These chains are weaved into an infinite network through N–H···S intermolecular hydrogen bonds by molecular pairs of **1a.**



Scheme 2. Diacylthioureas $\mathbf{L^n}$ (**1**-**3**) in study

Likewise, $1,3\text{-}C_6H_4[C(O)NHC(S)NHAr]_2$ ($\mathbf{L^2}$, **2**) and $1,3\text{-}C_6H_4[C(O)NHC(S)NHAr']_2$ ($Ar' = 2,6\text{-}Me_2C_6H_3$) ($\mathbf{L^3}$, **3**) were synthesized (Scheme 2) and characterized by spectroscopic techniques. The molecular structure of $\mathbf{L^3}$ is shown in Figure S5, and the simplified topological network (Figure S6) and packing diagram (Figure S7) suggest that the $\mathbf{L^3}$ molecules are connected into double chains through N–H···O intermolecular hydrogen bonds in three alternate directions. These chains are further cross-linked through N–H···S intermolecular hydrogen bonds.

Treatment of $\mathbf{L^1}$ (**1**) in ethanol with an equivalent of CuCl in acetonitrile afforded a yellow solid **4** (Scheme 3). Its melting point (304-305°C) was found considerably higher than that of its parent ligand $\mathbf{L^1}$ (259-260°C). The NH adsorption bands are red-shifted to 3213 and 3151 cm^{-1}, suggesting a general effect during coordination of the acylthiourea ligand to the metal atom of the *v*(NH) frequencies.[5a, 22] The elemental analysis of **4** indicated a composition of 1:1 stoichiometric ratio of the ligand $\mathbf{L^1}$ to copper chloride, and its structure and composition were further confirmed as a dimeric binuclear Cu^I complex ($\mathbf{L^1}$CuCl)$_2$ (**4**) by single crystal X-ray diffraction. **4**·$2CH_2Cl_2$ crystallizes in the triclinic space group *P*-1, and its molecular structure is shown in Figure 1. The two $\mathbf{L^1}$ ligands are each adopting a *cis* configuration and they act like a pair of tweezers to the CuCl molecules. The two CuCl moieties are arranged opposite to each other with a Cl(1)···Cl(1A) distance of 4.563 Å. It is interesting to note that the $\mathbf{L^1}$ ligands represent a ring system with two CuCl molecules, instead of forming a zipper-like polymeric chain in interlace mode. It was suggested that under given conditions the self-assembly of discrete supramolecules are more thermodynamically favored than oligomeric or polymeric products.[26]



Scheme 3. Preparation of ($\mathbf{L^1}$CuCl)$_2$ (**4**), ($\mathbf{L^1}$CuBr)$_2$ (**5**) and ($\mathbf{L^1}$CuI)$_2$ (**6**)

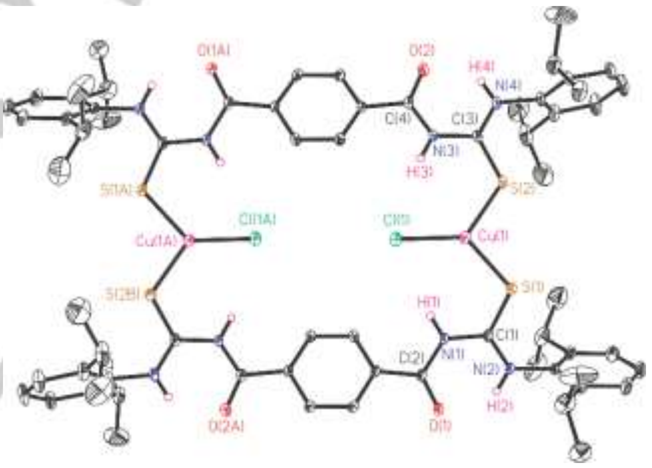


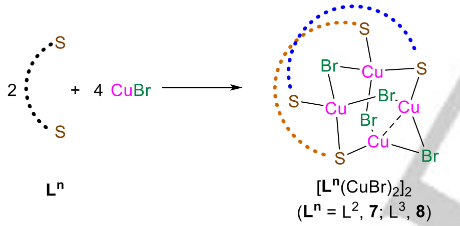
Figure 1. Molecular structure of complex ($\mathbf{L^1}$CuCl)$_2$ (**4**). Solvent molecules and all hydrogen atoms except for NH groups were omitted for clarity. Selected bond lengths /Å and angles /°: Cu(1)–S(1) 2.2176(2), Cu(1)–S(2) 2.132(9), Cu(1)–Cl(1) 2.1865(12), Cl(1)···Cl(1A) 4.563; S(1)–Cu(1)–S(2) 102.4(3), Cl(1)–Cu(1)–S(1) 129.88(4), Cl(1)–Cu(1)–S(2) 125.2(3).

In ($\mathbf{L^1}$CuCl)$_2$ (**4**) the chlorides function as terminal ligands. No comparable example of **4** was found in the literature, where neutral diacylthiourea ligands operate as building block for an empty metallamacrocycle. Previously we have reported on a Cu^I chloride complex ($\mathbf{H_2L}$)$_2$CuCl supported by the bulky mono-acylthiourea ($\mathbf{H_2L}$ = PhC(O)NHC(S)NHAr),[8] whose molecule exhibited a butterfly-like structure (Figure S8). In comparison, the S-Cu-S bond angle of **4** (102.4(3)°) is much more acute than that in ($\mathbf{H_2L}$)$_2$CuCl (115.71(2)°),[8] indicating the structural constrain imposed by the formed macrocycle. In the crystal structure the neighboring molecules of **4** are connected through a pair of N–H···O intermolecular hydrogen bonds resulting in a chain-of-rings (Figure S9).

The reaction of **L^{1}** (**1**) with CuBr afforded an analogous metallamacrocyclic complex (**L^{1}**CuBr)$_2$ (**5**), as revealed by spectroscopic characterizations and single crystal X-ray structural analysis (Figure S10). The Br(1)···Br(1A) separation is 4.313 Å, indicating a large cavity within the macrocycle. The packing style of **5** (Figure S11) is almost the same to that of **4**. Furthermore, the unit cell parameters[27] indicate that complex (**L^{1}**CuI)$_2$ (**6**) is isostructural to (**L^{1}**CuX)$_2$ (X = Cl **4**, Br, **5**).

It turned out that the diacylthiourea **L^{1}** (**1**) resulted in the formation of discrete supramolecular Cu^{I} complex (**L^{1}**CuX)$_2$, although the halide has been changed. Therefore it is of interest to examine whether moving the acylthiourea substituents from the para to the meta position on the benzene ring (as from **L^{1}** to **L^{2}** in Scheme 2) or decreasing the steric hindrance of the aryl groups (as from **L^{2}** to **L^{3}**) would show different complexation mode in the products.

The reaction of the 1:1 molar ratio of **L^{2}** (**2**) with CuBr resulted in the formation of **7** (Scheme 4) as the direct (separable) product in relatively low yield, which could be improved by doubling the amount of CuBr. The elemental analysis suggested a 1:2 composition of ligand to metal. Due to the low quality of single crystals, the molecular structure of **7** could not been solved with a high level of accuracy.[28] However, the data obtained allowed unambiguously to determine the structure as the discrete tetranuclear complex [**L^{2}**(CuBr)$_2$]$_2$ (Figure S12) with the characteristic S$_4$Cu$_4$Br$_4$ cores as enantiomeric pairs.



Scheme 4. Preparation of [**L^{2}**(CuBr)$_2$]$_2$ (**7**) and [**L^{3}**(CuBr)$_2$]$_2$ (**8**)

Similarly, the 1:2 reaction of **L^{3}** (**3**) with CuBr led to the production of [**L^{3}**(CuBr)$_2$]$_2$ (**8**, Scheme 4) in moderate yield (60%). The single crystal X-ray diffraction analysis revealed that **8** (Figure 2) is isostructural to **7** in view of the tetranuclear composition and the resulting S$_4$Cu$_4$Br$_4$ core. The four bromide atoms function as bridging species while each **L^{3}** ligand provides one bridging and one terminal sulfur atom. Previously, under the support of mono-acylthioureas (**H$_2$L**), we reported on the formation of the adamantanoid cage (**H$_2$L**CuBr)$_4$,[6, 8] which shares the same S$_4$Cu$_4$Br$_4$ core with that of **7** and of **8**. In this respect, each diacylthiourea ligand in **7** or **8** simply mimics a pair of mono-acylthioureas. The S···S separation (6.980-7.035 Å) of each diacylthiourea ligand in **8** was found much larger than that in the free **L^{3}** ligand (6.579 Å) or those in the counterparts of (**H$_2$L**CuBr)$_4$ (6.593-6.655 Å).[6, 8] This observation suggests that both the diacylthiourea ligand and the S$_4$Cu$_4$Br$_4$ core can adjust the constraint by more or less transformation in the geometry.

In the packing diagram, the molecule of **7** was arranged in a tetrahedral center and connected with four neighbors by four intermolecular N–H···O hydrogen bonds (Figure S13). In the molecules of **8** stage-like nets are formed by three intermolecular N–H···O hydrogen bonds (Figure S14).

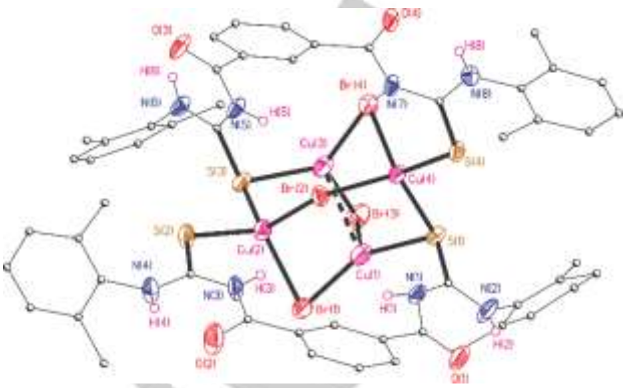
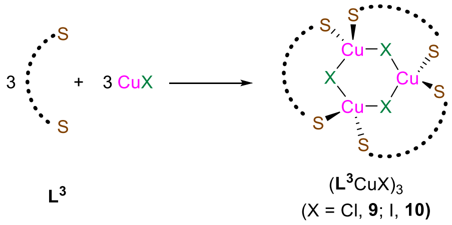


Figure 2. Molecular structure of [**L^{3}**(CuBr)$_2$]$_2$ (**8**). All hydrogen atoms except for NH groups were omitted for clarity. Selected bond lengths /Å and angles /°: Cu(1)–Br(1) 2.3378(19), Cu(1)–Br(3) 2.3651(18), Cu(1)···Cu(3) 2.6482(18), Cu(2)–Br(1) 2.4617(16), Cu(2)–Br(2) 2.5681(16), Cu(3)–Br(4) 2.3343(18), Cu(3)–Br(3) 2.3665(17), Cu(4)–Br(4) 2.4688(16), Cu(4)–Br(2) 2.5380(15); Cu(1)–Br(3)–Cu(3) 68.07(5), Cu(2)–Br(2)–Cu(4) 102.67(5).

The resulting powders from reaction of **L^{2}** with CuCl or CuI could not be obtained in a crystalline form, while the products of **L^{3}** with the copper salts (Scheme 5) were easily recrystallized in good shaped crystals. However, the single crystals of **9** became fragile and quickly decayed after being removed from the solvent. Therefore they could only be used for the determination of the unit cell parameters,[29] which were found to be totally different from those of [**L^{3}**(CuBr)$_2$]$_2$ (**8**) but almost the same to those of **10**. Crystals of the latter were stable during X-ray data collection.



Scheme 5. Preparation of (**L^{3}**CuCl)$_3$ (**9**) and (**L^{3}**CuI)$_3$ (**10**)

The molecular structure of **10** is depicted in Figure 3 with selected bond lengths and angles. (**L^{3}**CuI)$_3$ (**10**) crystallized in the orthorhombic space group $P2_12_12_1$, with a puckered six-membered Cu$_3$I$_3$ ring centered in the molecular domain, where all iodine atoms act as the bridging ligands and sulfur atoms are arranged in terminal positions. The copper atoms in **10** are all located in the tetragonal environment completed by two sulfur and two iodine atoms. In addition, each ligand plane of **L^{3}** (represented by the C$_6$H$_4$ ring plane) intersects with the Cu$_3$ plane by about 28.5° and thus provides three blades of a chiral propeller-like structure (Figure S15).

A similar Cu$_3$I$_3$ ring was furnished by triazacyclohexane (R$_3$TAC) bearing three thioether functionalities (R),[30] where each copper atom is bound to two bromide bridges, one nitrogen and one sulfur atom. In the current case, benefiting from the

10.1002/zaac.201700430

large S···S separation in $\mathbf{L^3}$, the Cu_3I_3 ring in **10** is more stretched and spread, as indicated by the wider Cu–I–Cu angles (about 102°) and longer Cu···Cu distances (about 4.1 Å), when compared to those counterparts in $R_3TAC(CuI)_3$ (about 68° and 2.9 Å).[30] In the packing diagram, each molecule of **10** has four direct neighbors to construct the three-dimensional grids by four intermolecular N–H···O hydrogen bonds (Figure S16).

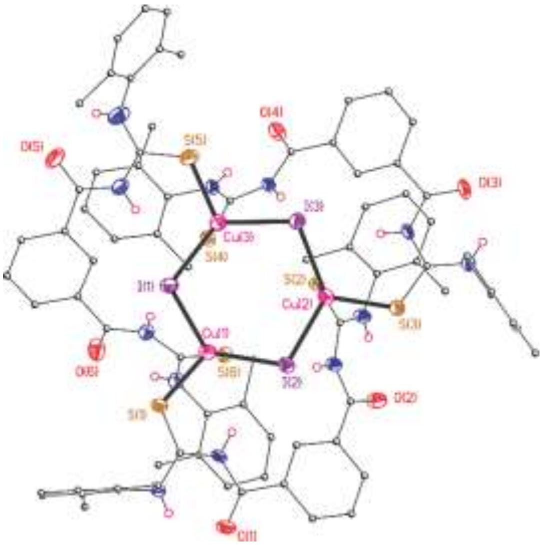


Figure 3. Molecular structure of $(\mathbf{L^3}CuI)_3$ (**10**). Solvent molecules and all hydrogen atoms except for NH groups were omitted for clarity. Selected bond lengths /Å and angles /°: Cu(1)-S(1) 2.3118(13), Cu(1)-S(6) 2.3429(13), Cu(1)–I(1) 2.5944(6), Cu(1)–I(2) 2.6537(7), Cu(2)–S(2) 2.3435(13), Cu(2)–I(2) 2.6164(6), Cu(3)–S(4) 2.3394(13), Cu(3)–I(1) 2.6388(7); Cu(1)–I(1)–Cu(3) 101.99(2), Cu(2)–I(2)–Cu(1) 102.14(2), Cu(3)–I(3)–Cu(2) 102.72(2).

Complex $(\mathbf{L^3}CuI)_3$ (**10**) was found be sensitive to moisture and then tended to slowly transform into a binuclear complex $[\mathbf{L^{3'}}Cu(\mu\text{-}I)]_2$ (**11**, Scheme S1) by partially hydrolyzing one of the acylthiourea groups of $\mathbf{L^3}$ into the acylurea functionality. This hydrolysis undergoing desulfurization has been known for monoacylthioureas.[1d, 31] In this way, $\mathbf{L^{3'}}$ can be considered as a bulky monoacylthiourea. Cu^I complexes of Cu_2X_2 with halide bridges and terminal acylthioureas are so far rare, and the first one of this type that was isolated and characterized as the 4:2 binuclear $[(\mathbf{H_2L})_2Cu(\mu\text{-}I)]_2$.[6] In compound **11**, the more bulky $\mathbf{L^{3'}}$ has caused a 2:2 dimeric complex formation (Figure S17). A related $[\mathbf{L}Cu(\mu\text{-}I)]_2$ complex was previously prepared using thioamidoguanidine (**L**),[32] where the copper atoms were additionally coordinated by morpholine-O atoms to give a 1D coordination polymer. In contrast, the copper atoms in **11** are three-coordinate and the adjacent molecules are connected through two intermolecular N–H···O hydrogen bonds (Figure S18).

For further comparison the assembly of Cu^I complexes with a less bulky $1,4\text{-}C_6H_4[C(O)NHC(S)NHAr']_2$ ($\mathbf{L^4}$, Figure S19) was also investigated. However $\mathbf{L^4}$ was sparingly soluble in common organic solvents and was also found to be easily hydrolyzed to give the diacylurea (Figure S20). The latter prevented the separation of the resulting products.

Conclusions

Three diacylthioureas ($\mathbf{L^n}$) were synthesized, each supported by bulky aryl flanks, which are showing a large S···S separation. Their self-assemblies with Cu^I halides were investigated and examined in view of the ligand effect. The single crystal structural analysis revealed that the complexation products of $\mathbf{L^n}$ with CuX (X = Cl, Br, I) turned out to be the discrete supramolecular Cu^I complexes, instead of an infinite coordination polymer. Reactions of $\mathbf{L^1}$ (**1**) with CuX gave the binuclear metallamacrocyclic complexes $(\mathbf{L^1}CuX)_2$ (X=Cl, **4**; Br, **5**; I, **6**), while the complexation of $\mathbf{L^2}$ (**2**) or $\mathbf{L^3}$ (**3**) with CuBr produced the tetranuclear copper clusters $[\mathbf{L^n}(CuBr)_2]_2$ (n = 2, **7**; 3, **8**). Interestingly, $\mathbf{L^3}$ (**3**) supported the formation of trinuclear complexes $(\mathbf{L^2}CuX)_3$ (X= Cl, **9**; I, **10**) with a three-blade propeller structure. The reported results show that the mono-acylthiourea $\mathbf{H_2L}$ ligands are less competent in self-assembly with Cu^I halide in a 2:1 stoichiometry, in a monomeric or dimeric configuration or in a 3:1 composition, respectively to give mononuclear or binuclear complexes.[6] In contrast the bipodal diacylthioureas $\mathbf{L^n}$ proved to be the ligand of choice to design and synthesize the discrete supramolecular complexes by self-assembly.

Experimental Section

All reagents and solvents used in the synthesis were purchased from commercial sources and used as received. Melting points were determined with a sealed capillary tube using an X-4B apparatus. Elemental analyses for carbon, hydrogen, nitrogen, and sulfur were carried out with a Thermo Quest Italia SPA EA1110 instrument. The ^1H and ^{13}C NMR spectra were recorded in 5 mm tubes in a DMSO-d_6 or $CDCl_3$ solution using AVANCE III 400 or AVANCE III HD 500 spectrometers. Infrared spectra were recorded by using KBr pellets with a Nicolet iS 50 (Thermo Nicolet Corporation) FT-IR spectrometer.

$1,4\text{-}C_6H_4[C(O)NHC(S)NHAr]_2$ (Ar = 2,6-*i*$Pr_2C_6H_3$) ($\mathbf{L^1}$, **1**): To an acetone solution (300 mL) of potassium thiocyanate (4.85 g, 50.0 mmol) was added terephthaloyl dichloride (5.08 g, 25 mmol) at ambient temperature under rigorous stirring. Then the reaction mixture was further stirred for 1 h under 50°C, forming the terephthaloyl diisothiocyanate. Finally to this mixture was added 2,6-diisopropyl aniline (9.4 mL, 50 mmol) drop by drop, followed by another 2 h stirring to complete the reaction. Then the obtained mixture was poured into a beaker containing water (500 mL). The colored precipitates were filtered off, washed thoroughly with ethanol (100 mL), and dried in air at 80°C to give a yellow solid. Yield: 10.87 g, 18.1 mmol, 72.4%. M.p.: 259.1-260.3°C. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 11.76 (s, 2H, N*H*), 9.43 (s, 2H, N*H*), 8.14 (s, 4H, Ph-*H*), 7.43 (t, *J* = 7.7 Hz, 2H, Ar-*H*), 7.29 (d, *J* = 7.2 Hz, 4H, Ar-*H*), 3.13 (sept, *J* = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 1.35 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.24 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$). **^{1}H NMR** (500 MHz, DMSO-d_6, ppm): δ 11.87 (s, 4H, N*H*), 8.16 (s, 4H, Ph-*H*), 7.32-7.36 (m, 2H, Ar-*H*), 7.22-7.24 (m, 4H, Ar-*H*), 3.06 (sept, *J* = 6.9 Hz, 4H, C*H*$(CH_3)_2$), 1.23 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.15 (d, *J* = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 179.84 (*C*=S), 164.52 (*C*=O), 144.47, 135.15, 131.55, 128.26, 127.46, 122.92 (Ar/Ph-*C*), 27.92, (*C*H$(CH_3)_2$), 23.38, 22.12 (CH(*C*H$_3$)$_2$). **FT-IR** (KBr, cm^{-1}): ṽ 3432.16 (vs, NH), 3248.29 (w, NH), 2960.73 (m), 2866.88 (m), 1674.05 (w, C=O), 1529.69 (s), 1484.12 (s), 1380.99 (vs), 1321.81 (w), 1257.49 (m), 1152.06 (w, C=S), 1122.77 (m), 804.38 (w), 726.75 (w), 610.06 (w). Anal. Calcd. for $C_{34}H_{42}N_4O_2S_2$ (602.86): C, 67.74; H, 7.02; N, 9.29; S, 10.64%. Found: C, 67.83; H, 7.30;

N, 9.54; S, 10.61%. X-ray quality single crystals of **1** were obtained from a concentrated dichloromethane solution.

1,3-C_6H_4[C(O)NHC(S)NHAr]$_2$ (**L^2**, **2**): The procedure was similar to that for **L^1**(**1**) using isophthaloyl dichloride (5.08 g, 25 mmol), potassium thiocyanate (4.85 g, 50.0 mmol) and 2,6-diisopropyl aniline (9.4 mL, 50 mmol) to obtain a white solid. Yield: 13.6 g, 22.6 mmol, 90.4%. M.p.: 235.0°C. **^{1}H NMR** (400 MHz, CDCl$_3$, ppm): δ 11.80 (s, 2H, N*H*), 9.65 (s, 2H, N*H*), 8.67 (s, 1H, Ph-*H*), 8.26 (dd, *J* = 7.8, 1.7 Hz, 2H, Ph-*H*), 7.79 (t, *J* = 7.8 Hz, 1H, Ph-*H*), 7.41-7.45 (m, 2H, Ar-*H*), 7.28-7.30 (m, 4H, Ar-*H*), 3.13 (sept, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 1.34 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.24 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$). **^{13}C NMR** (126 MHz, CDCl$_3$, ppm) δ 181.11 (*C*=S), 165.73 (*C*=O), 145.31, 132.91-132.48, 129.26, 123.93 (Ar/Ph-*C*), 28.95 (*C*H(CH$_3$)$_2$), 24.41, 23.13 (CH(*C*H$_3$)$_2$). **FT-IR** (KBr, cm^{-1}): ṽ 3225.38 (vw, NH), 2963.67 (w), 1676.19 (w, C=O), 1513.97 (m), 1324.59 (vw), 1229.6 (vw), 1155.59 (w, C=S), 803.53 (vw), 736.86 (vw), 690.99 (vw). Anal. Calcd. for $C_{34}H_{42}N_4O_2S_2$ (602.86): C, 67.74; H, 7.02; N, 9.29; S, 10.64%. Found: C, 67.92; H, 6.96; N, 9.44; S, 10.59%.

1,3-C_6H_4[C(O)NHC(S)NHAr′]$_2$ (Ar′ = 2,6-$Me_2C_6H_3$) (**L^3**, **3**): The procedure was similar to that for **L^1** (**1**) using isophthaloyl dichloride (5.08 g, 25 mmol), potassium thiocyanate (4.85 g, 50.0 mmol) and 2,6-dimethyl aniline (6.16 mL, 50 mmol) to obtain a yellow solid. Yield: 11.4 g, 23.3 mmol, 93.2%. M.p.: 217°C. **^{1}H NMR** (500 MHz, DMSO-*d*$_6$, ppm) δ 11.88 (s, 2H, N*H*), 11.67 (s, 2H, N*H*), 8.68 (s, 1H, Ph-*H*), 8.22 (d, *J* = 7.8 Hz, 2H, Ph-*H*), 7.73 (t, *J* = 7.8 Hz, 1H, Ph-*H*), 7.14-7.19 (m, 6H, Ar-*H*), 2.24 (s, 12H, C*H*$_3$). **^{13}C NMR** (126 MHz, DMSO-*d*$_6$, ppm) δ 180.56 (*C*=S), 167.49 (*C*=O), 136.74, 135.55, 133.77, 132.33, 129.57, 129.38, 128.40, 127.99 (Ar/Ph-*C*), 18.35 (*C*H$_3$). **FT-IR** (KBr, cm^{-1}): ṽ 3336.68 (s, NH), 3186.12 (s, NH), 3070.05 (m), 3038.07 (m), 2981.54 (m, CH$_3$), 2918.66 (m), 2855 (w), 1676.55 (vs, C=O), 1601.57 (w), 1529.82 (vs), 1512.54 (vs), 1442.43 (m), 1376.48 (w), 1325.8 (m), 1275.31 (m), 1235.49 (m), 1215.79 (m), 1159.35 (s, C=S), 1108.8 (w), 1091.75 (w), 764.18 (w), 731.58 (w), 682.76 (w). Anal. Calcd. for $C_{26}H_{26}N_4O_2S_2$ (490.64): C, 63.65; H, 5.34; N, 11.42; S, 13.07%. Found: C, 63.45; H, 5.25; N, 10.91; S, 13.24%. Yellow X-ray quality single crystals of **3** were obtained from a concentrated acetone solution.

(L^{1}CuCl)$_2$ (**4**): To a solution of **L^1** (0.602 g, 1 mmol) in ethyl alcohol (40 mL) at ambient temperature was added a suspension of CuCl (0.105 g, 1 mmol) in acetonitrile (10 mL) drop by drop under rigorous stirring. Then stirring was continued for 4 h to insure the completion of complexation. The resultant precipitate was filtered, washed with ethanol repeatedly, and dried at 80°C to obtain a yellow powder. Yield: 0.365 g, 0.26 mmol, 51.6%. M.p. 303.5-304.8°C.**^{1}H NMR** (400 MHz, DMSO-*d*$_6$, ppm) δ 11.87 (s, 4H, N*H*), 8.17 (s, 4H, Ph*H*), 7.32-7.37 (m, 2H, Ar-*H*), 7.23-7.25 (m, 4H, Ar-*H*), 3.06 (sept, *J* = 6.7 Hz, 4H, C*H*(CH$_3$)$_2$), 1.23 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.15 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$). **^{13}C NMR** (126 MHz, CDCl$_3$, ppm) δ 181.19 (*C*=S), 168.34 (*C*=O), 145.13, 135.24, 131.73, 129.77, 129.51, 124.02 (Ar/Ph-*C*), 28.90 (*C*H(CH$_3$)$_2$), 24.43, 23.07 (CH(*C*H$_3$)$_2$). **FT-IR** (KBr, cm^{-1}): ṽ 3211.76 (w, NH), 3146.94 (m, NH), 2963.96 (s), 2930.38 (m), 1675.17 (s, C=O), 1520.09 (vs), 1363.21 (w), 1319.33 (m), 1262.58 (s), 1202.61 (m), 1151.29 (s, C=S), 1120.55 (m), 1088.97 (w), 800.08 (m), 745.61 (m), 682.42 (m). Anal. Calcd. for $C_{68}H_{84}Cl_2Cu_2N_8O_4S_4$ (1403.70): C, 58.19; H, 6.03; N, 7.98; S, 9.14%. Found: C, 57.99; H, 6.16; N, 7.80; S, 8.85%. Yellow X-ray quality single crystals of **4** were obtained from a concentrated dichloromethane solution.

(L^{1}CuBr)$_2$ (**5**): The procedure was similar to that for **4** using **L^1** (**1**) (0.602 g, 1 mmol), and CuBr (0.145 g, 1 mmol) to obtain a yellow solid. Yield: 0.45 g, 0.30 mmol, 60.2%. M.p. 289.7-290.9°C. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$, ppm) δ 11.88 (s, 2H, N*H*), 11.82 (s, 2H, N*H*), 8.19 (s, 4H, Ph-*H*), 7.32-7.37 (m, 2H, Ar-*H*), 7.23-7.25 (m, 4H, Ar-*H*), 3.05 (sept, *J* = 6.7 Hz, 4H, C*H*(CH$_3$)$_2$), 1.23 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.15 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$). **^{13}C NMR** (126 MHz, CDCl$_3$, ppm): δ 179.76 (*C*=S), 167.34 (*C*=O), 144.10, 134.27, 130.67, 128.80, 128.47, 122.99 (Ar/Ph-*C*), 27.86 (*C*H(CH$_3$)$_2$), 23.40, 22.04 (CH(*C*H$_3$)$_2$). **FT-IR** (KBr, cm^{-1}): ṽ 3213.65 (vs, NH), 3151.58 (vs, NH), 2964.23 (vw), 2363.2 (vw), 1676.26 (vw, C=O), 1518.82 (vw), 1319.89 (w), 1261.47 (vw), 1203.79 (vw), 1152.6 (vw, C=S), 1087.56 (vw), 1016.13 (vw), 862.04 (vw), 800.34 (vw), 749.46 (vw), 684.39 (vw), 621.89 (vw), 454.17 (vw). Anal. Calcd. for $C_{68}H_{84}Br_2Cu_2N_8O_4S_4$ (1492.61): C, 54.72; H, 5.67; N, 7.51; S, 8.59%. Found: C, 54.81; H, 5.97; N, 7.77; S, 8.80%. Yellow X-ray quality single crystals of **5** were obtained from a concentrated dichloromethane solution.

(L^{1}CuI)$_2$ (**6**): The procedure was similar to that for **4** using **L^1** (**1**) (0.602 g, 1 mmol), and CuI (0.19 g, 1 mmol) to obtain a yellow solid. Yield: 0.435 g, 0.27 mmol, 54.9%. M.p. 282.7-283.9°C. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$, ppm): δ 11.91 (s, 2H, N*H*), 11.64 (s, 2H, N*H*), 8.25 (s, 4H, Ph-*H*), 7.34-7.37 (m, 2H, Ar-*H*), 7.24-7.25 (m, 4H, Ar-*H*), 3.04 (sept, *J* = 6.9Hz, 4H, C*H*(CH$_3$)$_2$), 1.22 (d, *J* = 6.5 Hz, 12H, CH(C*H*$_3$)$_2$), 1.15 (d, *J* = 6.6 Hz, 12H, CH(C*H*$_3$)$_2$). **^{13}C NMR** (126 MHz, CDCl$_3$, ppm): δ 180.35 (*C*=S), 168.37 (*C*=O), 145.14, 135.18, 131.55, 129.95, 129.56, 124.02 (Ar/Ph-*C*), 28.91 (*C*H(CH$_3$)$_2$), 24.42, 23.07 (CH(*C*H$_3$)$_2$). **FT-IR** (KBr, cm^{-1}): ṽ 3215.40 (vs, NH), 3163.69 (vs, NH), 2963.49 (w), 2869.01 (m), 1676.41 (w, C=O), 1516.27 (s), 1321.19 (vs), 1259.5 (m), 1202.35 (m), 1153.48 (w, C=S), 1120.32 (m), 1086.46 (w), 801.18 (w), 747.5 (w), 683.83 (w), 608.6 (w). Anal. Calcd. for $C_{68}H_{84}I_2Cu_2N_8O_4S_4$ (1586.61): C, 51.48; H, 5.34; N, 7.06; S, 8.08%. Found: C, 51.67; H, 5.45; N, 6.75; S, 7.72%.

[L^2(CuBr)$_2$]$_2$ (**7**): The procedure was similar to that for **4** using **L^2** (**2**) (0.605 g, 1 mmol), and CuBr (0.29 g, 2 mmol) to obtain a yellow solid. Yield: 0.605 g, 0.34 mmol, 67.6%. M.p. 320°C. **^{1}H NMR** (400 MHz, CDCl$_3$, ppm) δ 12.07 (s, 2H, N*H*), 11.05 (s, 2H, N*H*), 8.85 (s, 1H, Ph-*H*), 8.46 (d, J = 7.5 Hz, 2H, Ph-*H*), 7.69 (t, *J* = 7.8 Hz, 1H, Ph-*H*), 7.38 (t, *J* = 7.7 Hz, 2H, Ar-*H*), 7.22 (d, J = 7.8 Hz, 4H, Ar-*H*), 2.99 (sept, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 1.20 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.15 (d, *J* = 6.8 Hz, 15H, CH(C*H*$_3$)$_2$). **^{13}C NMR** (126 MHz, CDCl$_3$, ppm) δ 180.82 (*C*=S), 167.67 (*C*=O), 145.31, 134.10, 131.91, 129.34, 123.92 (Ar/Ph-*C*), 28.86 (*C*H(CH$_3$)$_2$), 24.36, 23.08 (CH(*C*H$_3$)$_2$). **FT-IR** (KBr, cm^{-1}): ṽ 3226.57 (w, NH), 2963.65 (w), 1679.15 (w, C=O), 1533.13 (m), 1322.06 (w), 1231.36 (w), 1207.05 (w), 1158.43 (w, C=S), 801.48 (w), 742.85 (w), 679.66 (w). Anal. Calcd. for $C_{68}H_{84}Br_8Cu_8N_8O_4S_4$ (1779.51): C, 45.90; H, 4.76; N, 6.30; S, 7.21%. Found: C, 45.97; H, 4.74; N, 6.44; S, 7.50%. Yellow X-ray quality single crystals of **7** were obtained from a concentrated filtered reaction solution.

[L^3(CuBr)$_2$]$_2$ (**8**) : The procedure was similar to that for **4** using **L^3** (**3**) (0.49 g, 1 mmol), and CuBr (0.29 g, 2 mmol) to obtain a yellow solid. Yield: 0.467 g, 0.3 mmol, 60%. M.p. 224°C. **^{1}H NMR** (500 MHz, DMSO-*d*$_6$, ppm) δ 11.90 (s, 2H, N*H*), 11.47 (s, 2H, N*H*), 8.89 (s, 1H, Ph-*H*), 8.28 (d, *J* = 7.6 Hz, 2H, Ph-*H*), 7.76 (t, *J* = 7.8 Hz, 1H, Ph-*H*), 7.14-7.21 (m, 6H, Ar-*H*), 2.21 (s, 12H, C*H*$_3$). **^{13}C NMR** (126 MHz, DMSO-*d*$_6$, ppm) δ 179.70 (*C*=S), 168.25 (*C*=O), 136.48, 135.40, 134.08, 132.07, 128.47, 128.30, 127.20 (Ar/Ph-*C*), 18.27 (*C*H$_3$). **FT-IR** (KBr, cm^{-1}): ṽ 3219.08 (m, NH), 3163.06 (m, NH), 3066.03 (w), 3032.7 (w), 2981.35 (w), 2919.22 (w), 2872.2 (vw), 2854.34 (vw), 1678.62 (m, C=O), 1602.53 (w), 1582.93 (vw), 1525.07 (s), 1518.21 (s), 1443.27 (w), 1397.45 (vw), 1376.32 (vw), 1335.07 (w), 1283.56 (vw), 1263.04 (vw), 1230.33 (w), 1157.32 (m, C=S), 1114.22 (vw), 1090.4 (vw), 1068.1 (vw), 1033.36 (vw), 771.01 (vw), 751.11 (vw), 738.27 (vw), 728.73 (vw), 687.87 (vw), 677.23 (vw). Anal. Calcd. for $C_{52}H_{52}Br_4Cu_4N_8O_4S_4$ (1555.08): C, 40.16; H, 3.37; N, 7.21; S, 8.25%. Found: C, 40.33; H, 3.53; N, 6.85; S, 8.25%. Yellow X-ray quality single crystals of **8** were obtained from a concentrated acetone-dichloromethane solution.

(L^{3}CuCl)$_3$ (**9**): The procedure was similar to that for **4** using **L^3** (**3**) (0.49 g, 1 mmol) and CuCl (0.105 g, 1 mmol) to obtain a yellow powder. Yield: 0.465 g, 0.263 mmol, 78.2%. M.p.: 217°C. **^{1}H NMR** (500 MHz, DMSO-*d*$_6$, ppm) δ 11.89 (s, 2H, N*H*), 11.59 (s, 2H, N*H*), 8.78 (s, 1H, Ph-*H*), 8.26 (d, *J* = 7.2 Hz, 2H, Ph-*H*), 7.76 (t, *J* = 7.2 Hz, 1H, Ph-*H*), 7.14-7.20 (m, 6H, Ar-*H*), 2.21 (s, 12H, C*H*$_3$). **^{13}C NMR** (126 MHz, DMSO-*d*$_6$, ppm) δ 180.37 (*C*=S), 167.40 (*C*=O), 136.67, 135.51, 133.82, 132.32, 129.43, 128.41, 128.03 (Ar/Ph-*C*), 18.31 (*C*H$_3$). **FT-IR** (KBr, cm^{-1}): $\tilde{\nu}$ 3212.61 (m, NH), 3156.78 (m, NH), 3027.39 (w), 2980.76 (w), 2919.34 (w), 2855.54 (vw), 1677.33 (m, C=O), 1601.19 (vw), 1528.65 (s), 1442.64 (w), 1376.99 (vw), 1332.38 (w), 1285.21 (vw), 1231.41 (w), 1157.61 (w, C=S), 1114.3 (vw), 1089.41 (vw), 1033.64 (vw), 752.85 (vw), 732.91 (vw), 678.51 (vw). Anal. Calcd. for $C_{78}H_{78}Cl_3Cu_3N_{12}O_6S_6$ (1768.91): C, 52.96; H, 4.44; N, 9.50; S, 10.87%. Found: C, 52.99; H, 4.21; N, 9.22; S, 10.40%. Yellow X-ray quality single crystals of **9** were obtained from a concentrated acetone solution.

(L^{3}CuI)$_3$ (**10**): The procedure was similar to that for **4** using **L^3** (**3**) (0. 49g, 1 mmol) and CuI (0.19 g, 1 mmol) to obtain a yellow solid. Yield: 0.51 g, 0.25 mmol, 75%. M.p. 281°C. **^{1}H NMR** (500 MHz, DMSO-*d*$_6$, ppm) δ 11.98 (s, 2H, N*H*), 11.19-11.28 (br, 2H, N*H*), 9.12-21 (br, 1H, Ph-*H*), 8.32 (m, 2H, Ph-*H*), 7.84 (m, 1H, Ph-*H*), 7.14-7.27 (m, 6H, Ar-*H*), 2.24 (s, 12H, C*H*$_3$). **^{13}C NMR** (126 MHz, DMSO-*d*$_6$, ppm) δ 179.14 (*C*=S), 166.21 (*C*=O), 136.36, 135.21, 134.69, 131.37, 130.47, 129.71, 128.56 (Ar/Ph-*C*), 18.33 (*C*H$_3$). **IR** (KBr, cm^{-1}): $\tilde{\nu}$ 3247.78 (s, NH), 3167.19 (m), 3027.16 (w), 2974.53 (w), 2917.84 (w), 2854.56 (vw), 1680.59 (s, C=O), 1600.3 (w), 1527.6 (vs), 1508.75 (vs), 1442.11 (w), 1376.13 (w), 1335.69 (w), 1281.26 (w), 1215.51 (m), 1157.83 (m, C=S), 1117.83 (vw), 1083.8 (vw), 1034.37 (vw), 755.75 (vw), 743.2 (vw), 676.08 (vw). Anal. Calcd. For $C_{78}H_{78}I_3Cu_3N_{12}O_6S_6$ (2043.27): C, 45.85; H, 3.85; N, 8.23; S, 9.41%. Found: C, 45.85; H, 4.04; N, 7.82; S, 9.76%. Yellow X-ray quality single crystals of **10** were obtained from a concentrated acetone solution.

X-ray Crystallography: Data were collected with a Bruker SMART APEX II CCD diffractometer. The diffraction data were obtained using graphite monochromated Mo-K$_\alpha$ radiation with a ω-2θ scan technique at room temperature. The structure was solved by direct methods with SHELX-97.[33] A full-matrix least-squares refinement on F^2 was carried out by using SHELXL-97.[33] Crystallographic data with 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-1576583 ((**1**·CH_2Cl_2)$_2$·H_2O), CCDC-1576584 (**2**), CCDC-1576585 (**4**·2CH_2Cl_2), CCDC-1576586 (**5**·2CH_2Cl_2), CCDC-1576588 (**8**), CCDC-1576587 (**10**), CCDC-1576590 (**11**), CCDC-1576589 (**12**·2THF), and CCDC-1576591 (**13**·2DMSO) (Fax: +44-1223-336-033;E-Mail:deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21771194), and the Special Fund for Agro-scientific Research in the Public Interest (201503108). Support of the Deutsche Forschungsgemeinschaft (RO 224/68-1) is gratefully acknowledged.

Keywords: Diacylthiourea • Copper(I) complex • Self-assembly • Bipodal ligand

[1] a) M. Fizer, S. Sukharev, M. Slivka, R. Mariychuk, V. Lendel, *J. Organomet. Chem.* **2016**, *804*, 6-12; b) S. Hussain, A. Badshah, B. Lal, R. A. Hussain, S. Ali, M. N. Tahir, A. A. Altaf, *J. Coord. Chem.* **2014**, *67*, 2148-2159; c) B. Lal, A. Badshah, A. A. Altaf, M. N. Tahir, S. Ullah, F. Huq, *Aust. J. Chem.* **2013**, *66*, 1352-1360; d) A. Saeed, U. Flörke, M. F. Erben, *J. Sulfur Chem.* **2013**, *35*, 318-355.

[2] A. S. Al-Kady, M. Gaber, M. M. Hussein, E.-Z. M. Ebeid, *J. Phys. Chem. A* **2009**, *113*, 9474-9484.

[3] K. R. Koch, *Coord. Chem. Rev.* **2001**, *216*, 473-488.

[4] a) M. K. Barman, A. K. Sinha, S. Nembenna, *Green Chem.* **2016**, *18*, 2534-2541; b) S. B. Tsogoeva, D. A. Yalalov, M. J. Hateley, C. Weckbecker, K. Huthmacher, *Eur. J. Org. Chem.* **2005**, *2005*, 4995-5000.

[5] a) M. K. Rauf, D. Imtiaz ud, A. Badshah, M. Gielen, M. Ebihara, D. d. Vos, S. Ahmed, *J. Inorg. Biochem.* **2009**, *103*, 1135-1144; b) N. Selvakumaran, L. Sandhiya, N. S. P. Bhuvanesh, K. Senthilkumar, R. Karvembu, *New J. Chem.* **2016**, *40*, 5401-5413.

[6] D. Wang, S.-Y. Wu, H.-P. Li, Y. Yang, H. W. Roesky, *Eur. J. Inorg. Chem.* **2017**, 1406-1413.

[7] a) J. A. Cornejo, K. Ayala, R. Richter, H. Böhlig, L. Hennig, L. Beyer, *Z. Anorg. Allg. Chem.* **2005**, *631*, 3040-3045; b) G. Binzet, H. Arslan, U. Flörke, N. Külcü, N. Duran, *J. Coord. Chem.* **2006**, *59*, 1395-1406; c) G. Binzet, N. Külcü, U. Flörke, H. Arslan, *J. Coord. Chem.* **2009**, *62*, 3454-3462; d) S. Saeed, N. Rashid, M. Ali, R. Hussain, *Eur. J. Chem.* **2010**, *1*, 200-205; e) G. Binzet, U. Flörke, N. Külcü, H. Arslan, *Eur. J. Chem.* **2012**, *3*, 211-213; f) S. Saeed, N. Rashid, R. Hussain, M. A. Malik, P. O'Brien, W.-T. Wong, *New J. Chem.* **2013**, *37*, 3214-3221; g) S.-Y. Wu, X.-Y. Zhao, H.-P. Li, Y. Yang, H. W. Roesky, *Z. Anorg. Allg. Chem.* **2015**, *641*, 883-889.

[8] X.-Y. Zhao, C.-B. Zhu, H.-P. Li, Y. Yang, H. W. Roesky, *Z. Anorg. Allg. Chem.* **2014**, *640*, 1614-1621.

[9] a) R. Richter, O. Seidelmann, L. Beyer, H. Plenio, *J. Organomet. Chem.* **1996**, *525*, 199-205; b) F. Aydın, D. Aykaç, H. Ünver, N. O. İskeleli, *J. Chem. Crystallogr.* **2012**, *42*, 381-387; c) A. Okuniewski, J. Chojnacki, B. Becker, *Acta Crystallogr. E* **2012**, *68*, o619-o620.

[10] a) A. Rodenstein, R. Richter, R. Kirmse, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1713-1717; b) N. Selvakumaran, R. Karvembu, S. W. Ng, E. R. T. Tiekink, *Acta Crystallogr. Sect. Sect. E: Struct. Rep. Online* **2013**, *69*, o1368-o1368; c) L.-Y. Zhang, Y.-F. Yuan, A.-G. Hu, J.-T. Wang, J. Sun, *J. Organomet. Chem.* **2001**, *637–639*, 204-208; d) W. S. H. Wan Zullkiplee, A. N. Abd Halim, Z. Ngaini, M. A. Mohd Ariff, H. Hussain, *Phosphorus, Sulfur Silicon Relat. Elem.* **2014**, *189*, 832-838.

[11] A. Rodenstein, R. Richter, R. Kirmse, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1713-1717.

[12] a) N. Selvakumaran, N. S. Bhuvanesh, R. Karvembu, *Dalton Trans.* **2014**, *43*, 16395-16410; b) O. Hallale, S. A. Bourne, K. R. Koch, *New J. Chem.* **2005**, *29*, 1416-1423; c) O. Hallale, S. A. Bourne, K. R. Koch, *CrystEngComm* **2005**, *7*, 161-166; d) S. A. Bourne, O. Hallale, K. R. Koch, *Cryst. Growth Des.* **2005**, *5*, 307-312.

[13] a) V. D. Schwade, L. Kirsten, A. Hagenbach, E. Schulz Lang, U. Abram, *Polyhedron* **2013**, *55*, 155-161; b) A. Rodenstein, J. Griebel, R. Richter, R. Kirmse, *Z. Anorg. Allg. Chem.* **2008**, *634*, 867-874; c) H. Arslan, N. Külcü, *Transition Met. Chem.* **2003**, *28*, 816-819.

[14] F. A. Saad, J. C. Knight, B. M. Kariuki, A. J. Amoroso, *Dalton Trans.* **2016**, *45*, 10280-10288.

[15] R. Richter, J. Sieler, R. Köhler, E. Hoyer, L. Beyer, I. Leban, L. Golič, *Z. Anorg. Allg. Chem.* **1989**, *578*, 198-204.

[16] K. R. Koch, S. A. Bourne, A. Coetzee, J. Miller, *J. Chem. Soc., Dalton Trans.* **1999**, 3157-3161.

[17] A. N. Westra, S. A. Bourne, K. R. Koch, *Dalton Trans.* **2005**, 2916-2924.

[18] K. R. Koch, O. Hallale, S. A. Bourne, J. Miller, J. Bacsa, *J. Mol. Struct.* **2001**, *561*, 185-196.

[19] A. I. Matesanz, C. Hernández, J. Perles, P. Souza, *J. Organomet. Chem.* **2016**, *804*, 13-17.

[20] H. H. Nguyen, P. C. Thang, A. Rodenstein, R. Kirmse, U. Abram, *Inorg. Chem.* **2011**, *50*, 590-596.

[21] U. Schröder, L. Beyer, J. Sieler, *Inorg. Chem. Commun.* **2000**, *3*, 630-633.

[22] Y.-F. Yuan, S.-M. Ye, L.-Y. Zhang, J.-T. Wang, H.-G. Wang, *Transition Met. Chem.* **1997**, *22*, 561-564.

[23] a) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853-908; b) G. F. Swiegers, T. J. Malefetse, *Chem. Rev.* **2000**, *100*, 3483-3538.

[24] I. B. Douglass, F. B. Dains, *J. Am. Chem. Soc.* **1934**, *56*, 719-721.

[25] V. A. Blatov, L. Carlucci, G. Ciani, D. M. Proserpio, *CrystEngComm* **2004**, *6*, 377-395.

[26] a) V. M. Cangelosi, T. G. Carter, L. N. Zakharov, D. W. Johnson, *Chem. Commun.* **2009**, 5606-5608; b) W. J. Vickaryous, E. R. Healey, O. B. Berryman, D. W. Johnson, *Inorg. Chem.* **2005**, *44*, 9247-9252.

[27] Unit cell parameters for ($\mathbf{L^1}$CuI)$_2$·2CH$_2$Cl$_2$ (**6**). Triclinic, *P*-1. a = 8.543(2), b = 14.920(4), c = 18.450(5) Å; α = 74.226(12), β = 76.882(13), γ = 79.760(12)º; V = 2187.0(10) Å^3.

[28] Unit cell parameters for ($\mathbf{L^2}$(CuBr)$_2$]$_2$ (**7**). Monoclinic, *C*2/*c*. a =37.032(10), b = 13.568(3), c = 25.418(7) Å; β = 132.220(14)º; V = 9458(4) Å^3.

[29] Unit cell parameters for ($\mathbf{L^3}$CuCl)$_3$ (**9**). Orthorhombic. a =19.45, b = 19.72, c = 28.07 Å; V = 10766 Å^3.

[30] R. D. Kohn, L. Tomas Laudo, Z. Pan, F. Speiser, G. Kociok-Kohn, *Dalton Trans.* **2009**, 4556-4568.

[31] A. Solinas, H. Faure, H. Roudaut, E. Traiffort, A. Schoenfelder, A. Mann, F. Manetti, M. Taddei, M. Ruat, *J. Med. Chem.* **2012**, *55*, 1559-1571.

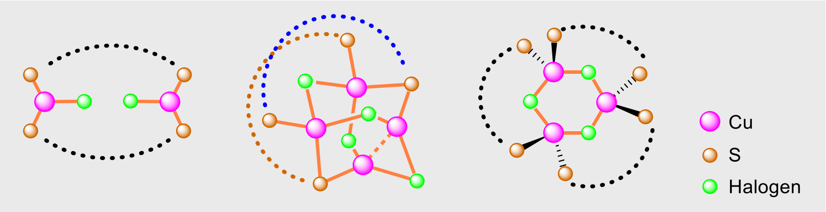
[32] S. K. Sahoo, N. Khatun, H. S. Jena, B. K. Patel, *Inorg. Chem.* **2012**, *51*, 10800-10807.

[33] G. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112-122.

Entry for the Table of Contents

Layout 2: (11.5cm*2.5cm)

FULL PAPER



The self-assemblies of three different diacylthioureas (**L**) with CuX (X = Cl, Br, I) led to the formation of discrete copper(I) complexes, including the binuclear (**L**CuX)$_2$, tetranuclear [**L**(CuX)$_2$]$_2$, and trinuclear (**L**CuX)$_3$ species.

X. H. Hou, F. F. Wang, L. Han, X. Pan, H. P. Li, Y. Yang, and H. W. Roesky**

Page No. – Page No.

Self-Assembly of Discrete Copper(I)-Halide Complexes with Diacylthioureas