



Copper(I) complexes of heterocyclic thiourea ligands

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ABSTRACT

The coordination of heterocyclic thiourea ligands (L = *N*-(2-pyridyl)-*N'*-phenylthiourea (**1**), *N*-(2-pyridyl)-*N'*-methylthiourea (**2**), *N*-(3-pyridyl)-*N'*-phenylthiourea (**3**), *N*-(3-pyridyl)-*N'*-methylthiourea (**4**), *N*-(4-pyridyl)-*N'*-phenylthiourea (**5**), *N*-(2-pyrimidyl)-*N'*-phenylthiourea (**6**), *N*-(2-pyrimidyl)-*N'*-methylthiourea (**7**), *N*-(2-thiazolyl)-*N'*-methylthiourea (**8**), *N*-(2-benzothiazolyl)-*N'*-methylthiourea (**9**), *N,N'*-bis(2-pyridyl)thiourea (**10**) and *N,N'*-bis(3-pyridyl)thiourea (**11**)) with CuX (X = Cl, Br, I, NO₃) has been investigated. CuX:L product stoichiometries of 1:1–1:5 were found, with 1:1 being most common. X-ray structures of four 3-coordinate mononuclear CuXL₂ complexes (CuCl(**6**)₂, CuCl(**7**)₂, CuBr(**6**)₂, and CuBr(**9**)₂) are reported. In contrast, CuBr(**1**)₂ is a 1D sulfur-bridged polymer. CuL structures (L = **7**, **8**) are 1D chains with corner-sharing Cu₂(μ-I)₂ and Cu₂(μ-S)₂ units, and CuCl(**10**) is a 2D network having μ-Cl and *N*-*S*-bridging L. Two [CuL₂]NO₃ structures are reported: a mononuclear 4-coordinate copper complex with chelating ligands (L = **10**) and a 1D link-chain with *N*-*S*-bridging L (L = **3**). Two ligand oxidative cyclizations were encountered during crystallization. CuI crystallized with **6** to produce zigzag ladder polymer [(CuI)₂(**12**)]·1/2CH₃CN (**12** = *N*-(pyrimidin-2-yl)benzo[d]thiazol-2-amine) and CuNO₃ crystallized with **10** to form [Cu₂(NO₃)(**13**)₂(MeCN)]NO₃ (**13** = dipyrityltetraazathiapentalene).

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1. Introduction

The self-assembly of transition metals with bridging ligands to produce metal–organic networks (MONs) is currently a very active area of study [1]. Copper(I) centers are especially flexible with respect to coordination environment [2], ranging from 2- to 4-coordinate (see examples in Chart 1 below). However, also important in MON formation are the bonding capabilities of the ligands chosen. A recent review has divided MONs according to dimensionality produced through organic versus inorganic ligand bridging [3]. According to the authors' scheme, the 2D network CuBr(Pyz) (Pyz = pyrazine) [4] would be classified as I¹O¹, since the inorganic ligand bromide links the copper atoms into 1D chains (I¹) and the organic Pyz ligand links them in a perpendicular direction (O¹). The sum of the exponents gives the overall dimensionality of the MON, a 2D sheet in this case.

Halide bridging behavior in MONs such as CuBr(Pyz) may be described as single-atom-bridging (SAB). Unlike conventional organic bridging ligands, such as Pyz or 4,4'-bipyridine, which have two or more widely separated and geometrically constrained lone pair-bearing atoms, SAB ligands have two or more lone pairs residing on a single atom and consequently form short bridges between two or more metal centers. While group 16 or 17 anions are obvious candidates for SAB behavior, organic SAB examples are also

known. One important group of organic SABs is comprised of thio-carbonyl compounds. A remarkable collection of copper(I) networks with thiourea ligands is known, many showing sulfur SAB behavior [5]. The Cu(I) centers bridged by thiocarbonyl sulfur (S) and halide SABs (X) can form rhomboid Cu₂X₂ or Cu₂S₂ dimers, Cu₄X₄ or Cu₄S₄ cubane tetramers, (Cu₂X₂)_n or (Cu₂S₂)_n stair-step polymers, and (CuX)_n or (CuS)_n chains [2]. Examples of SAB complexes are shown in Chart 1. As is suggested by the variety of the products shown in Chart 1, it can be very difficult to predict beforehand when sulfur or halide atoms will act in SAB fashion and when they will remain monodentate. In addition, halide ions can also act as outer sphere anions.

In the following study we have examined the network-forming behavior of thiourea ligands bearing nitrogen heterocycle groups with copper(I) halides and nitrate. The heterocyclic thiourea molecules (HetTu) **1–11** shown in Chart 2 are themselves network-formers through hydrogen-bonding [6]. It was expected that they would show a variety of bridging behaviors involving the sulfur (monodentate or SAB) and nitrogen centers, leading to network formation. Additional network-forming behavior was anticipated from the halide (SAB) and possibly the nitrate ions. To date, a single HetTu complex of copper(I) has been reported [7]. This compound is [Cu(**10**)₂]ClO₄. It is monomeric, with a single 4-coordinate copper coordinated to sulfur and one pyridyl nitrogen from each ligand. The remaining pyridyl nitrogen on each ligand engages in intramolecular hydrogen-bonding with a thiourea N–H. The Zn(II) complex is similar. However, more complicated and highly

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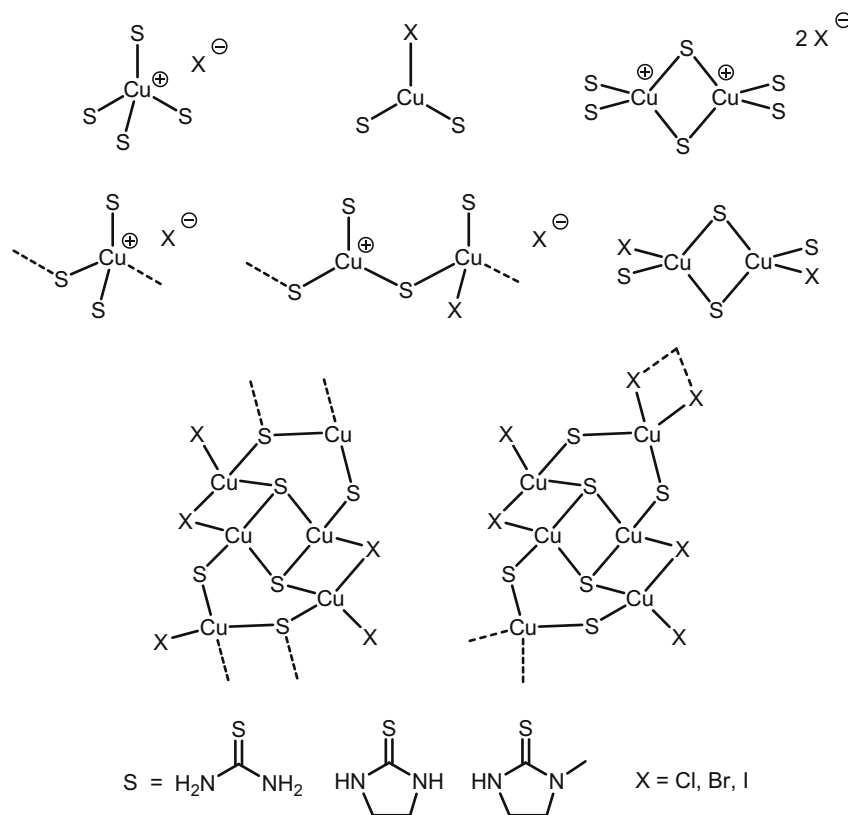


Chart 1. Coordination arrangements in Cu(I) thiourea structures.

networked structures are to be expected when the pyridyl groups and thiocarbonyl sulfur are geometrically prevented from chelating a single metal center.

2. Experimental

2.1. General methods

All syntheses were carried out under nitrogen atmosphere. Microanalyses for C, H, and N were carried out by Atlantic Microlab Inc., Norcross, GA. HetTu ligands, *N*-(2-pyridyl)-*N'*-phenylthiourea (**1**), *N*-(2-pyridyl)-*N'*-methylthiourea (**2**), *N*-(3-pyridyl)-*N'*-phenylthiourea (**3**), *N*-(3-pyridyl)-*N'*-methylthiourea (**4**), *N*-(4-pyridyl)-*N'*-phenylthiourea (**5**), *N*-(2-pyrimidyl)-*N'*-phenylthiourea (**6**), *N*-(2-pyrimidyl)-*N'*-methylthiourea (**7**), *N*-(2-thiazolyl)-*N'*-methylthiourea (**8**), *N*-(2-benzothiazolyl)-*N'*-methylthiourea (**9**), *N,N'*-bis(2-pyridyl)thiourea (**10**) and *N,N'*-bis(3-pyridyl)thiourea (**11**), were synthesized as previously described [6]. Copper(I) chloride and bromide were freshly recrystallized from aqueous HCl or HBr. Copper(I) iodide was used as received from Aldrich. Copper(I) nitrate was prepared *in situ* by comproportionation of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ in MeCN as described below.

2.2. Syntheses

2.2.1. Synthesis of $\text{CuCl}(\mathbf{1})_2$

Copper(I) chloride (99 mg, 1.00 mmol) was dissolved in 25 mL MeCN under N_2 . **1** (229 mg, 1.00 mmol) was added as a solid. The resulting suspension was stirred under nitrogen for 1 h at room temp. The white solid was collected via filtration, and washed with diethyl ether. It was dried under vacuum (184 mg, 68.5% yield). *Anal.* Calc. for $\text{C}_{24}\text{H}_{22}\text{N}_6\text{ClCuS}_2$: C, 51.70; H, 3.98; N, 15.70. Found: C, 52.08; H, 3.97; N, 15.13%.

2.2.2. Synthesis of $[\text{CuBr}(\mathbf{1})]\cdot\text{MeCN}$

The procedure for $\text{CuCl}(\mathbf{1})_2$ was followed using CuBr. A grey-green solid was isolated (77.6%). *Anal.* Calc. for $\text{C}_{14}\text{H}_{14}\text{N}_4\text{BrCuS}$: C, 40.64; H, 3.41; N, 13.54. Found: C, 42.44; H, 3.42; N, 13.53%.

2.2.3. Synthesis of $\text{CuI}(\mathbf{1})$

The procedure for $\text{CuCl}(\mathbf{1})_2$ was followed using CuI. An off-white solid was isolated (94.5%). *Anal.* Calc. for $\text{C}_{12}\text{H}_{11}\text{N}_3\text{CuI}$: C, 34.34; H, 2.64; N, 10.01. Found: C, 34.24; H, 2.63; N, 10.05%.

2.2.4. Synthesis of $\text{CuNO}_3(\mathbf{1})$

$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (116 mg, 0.500 mmol) and excess copper wool were stirred under N_2 in 25 mL MeCN for 30 min. until the blue solution color was discharged. The copper wool was removed and **1** (229 mg, 1.00 mmol) was added as a solid. The resulting suspension was stirred under nitrogen for 1 h at room temp. This resulted in a precipitate. The solid was collected via filtration, and was washed with diethyl ether. The light brown solid was dried under vacuum (226 mg, 63.8% yield). *Anal.* Calc. for $\text{C}_{12}\text{H}_{11}\text{N}_4\text{CuO}_3\text{S}$: C, 40.62; H, 3.12; N, 15.79. Found: C, 42.23; H, 3.06; N, 15.85%.

2.2.5. Synthesis of $(\text{CuCl})_2(\mathbf{2})_3$

The procedure for $\text{CuCl}(\mathbf{1})_2$ was followed using CuCl and **2**. A white solid was isolated (75.1%). *Anal.* Calc. for $\text{C}_{21}\text{H}_{27}\text{N}_9\text{Cl}_2\text{Cu}_2\text{S}_3$: C, 36.05; H, 3.89; N, 18.02. Found: C, 35.88; H, 3.81; N, 17.81%.

2.2.6. Synthesis of $[\text{CuBr}(\mathbf{2})]\cdot\text{MeCN}$

The procedure for $\text{CuCl}(\mathbf{1})_2$ was followed using CuBr and **2**. A white solid was isolated (59.1%). *Anal.* Calc. for $\text{C}_9\text{H}_{12}\text{N}_4\text{CuBrS}$: C, 30.73; H, 3.44; N, 15.93. Found: C, 31.41; H, 3.43; N, 15.62%.

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