

# CuI-based coordination polymers with 2-thiazolyl sulfide ligands: First examples

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## ABSTRACT

The reaction of CuI with 2-(methylthio)thiazole (MTT) in a 1:1 or 2:1 molar ratio (MeCN, rt, 1 h) leads to the coordination polymer [CuI(MTT)]<sub>n</sub> (**CP1**) or [(CuI)<sub>2</sub>(MTT)]<sub>n</sub> (**CP2**), respectively. **CP1** consists of (–Cu–I–Cu–I–)<sub>n</sub> zigzag chains wherein the adjacent Cu atoms are bridged by the MTT ligand through the thiazole N and sulfide S atoms. 1-D chains of **CP2** are assembled from corner-sharing [Cu<sub>3</sub>N] and [Cu<sub>3</sub>S] tetrahedra, which alternate in a zigzag fashion. By contrast, 2-(methylthio)benzothiazole (MTBT) reacts with CuI, regardless of the reactants ratio, to give the dinuclear complex [Cu<sub>2</sub>I<sub>2</sub>(MTBT)<sub>2</sub>], where the planar [Cu(μ<sub>2</sub>-I)]<sub>2</sub> core is supported by the two ligands in the *N*-monodentate manner. At ambient temperature, **CP1** exhibits a weak yellow luminescence (λ<sub>max</sub> = 570 nm), while **CP2** emits in the deep-red region (λ<sub>max</sub> = 705 nm).

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## 1. Introduction

Over the past decades, neutral copper(I) halide-based coordination polymers (CPs) have attracted increasing attention due to their rich structural diversity and intriguing photophysical properties [1–4]. The Cu<sub>x</sub>I<sub>y</sub> inorganic skeletons in these CPs can contain the most diverse structural motifs, ranging from 1-D zigzag [CuI]<sub>n</sub> chains to more complicated 2-D and 3-D networks [2]. However, it should be noted that the structures of Cu(I) halide CPs are still hardly predictable despite the great body of published data [2]. In terms of the photophysical properties, many of such CPs exhibit intense solid state luminescence as well as thermo- [5–7], mechano- [6,8,9] and vapo-chromic [10] luminescence associated with Cu···Cu interactions. Moreover, CuI-based CPs were demonstrated to show non-linear optical properties [11] as well as luminescent sensing toward O<sub>2</sub> [12] and nitrobenzene [13].

Currently, the most studied neutral Cu(I) halide CPs are those supported by *N*- or *P*-donor ligands, while the *S*-donor ligands are less explored, although they are very promising for the self-assembly of CPs. For instance, the application of organic sulfides as assembling ligands offers exciting possibilities for the construction of unique 1-D, 2-D and even 3-D CPs containing Cu<sub>x</sub>I<sub>y</sub> cluster cores as secondary building units [14,15]. These CPs often feature fascinating emission characteristics and interesting topologies,

which significantly depend on the structure of ligand used and the crystallization conditions [16–26]. In this context, extension of the sulfides scope over essentially new ligands can, firstly, provide access to new original functional CuHal-based CPs and, secondly, gain an insight into the structure-photophysical properties relationship of these compounds.

In this work, to test hetaryl sulfide ligands of the type Het–SR (R = alkyl or aryl; Het = *N*-heterocyclic group) for the synthesis of Cu(I) halide CPs, we have carried out the reaction of CuI with 2-(methylthio)thiazole and its benzene-fused analog. Note, the neutral hetaryl sulfides (Het–SR, where Het = *N*-heterocyclic unit) with a 1,3-disposition of the heterocyclic N and sulfide S donor (–SR) atoms, to our knowledge, have never been used in the coordination chemistry of copper(I) ions.

## 2. Experimental details

### 2.1. General information

2-(Methylthio)thiazole (98%, TCI), 2-(methylthio)benzothiazole (97%, Aldrich), CuI (98%, Alfa Aesar) and MeCN (HPLC grade, Cryochrom) were commercial products. FT-IR spectra were measured on a Bruker Vertex 80 spectrometer. Thermogravimetric analyses were carried out under He at a 10 °C/min<sup>−1</sup> heating rate using a NETZSCH STA 449 F1 Jupiter STA up to 700 °C in a closed Al<sub>2</sub>O<sub>3</sub> pan. The elemental analyses were performed on a MICRO cube analyzer.

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XPRD analyses were performed on a Shimadzu XRD-7000 diffractometer (Cu K $\alpha$  radiation, Ni – filter, 3–35° 2 $\theta$  range, 0.03° 2 $\theta$  step, 5s per point).

## 2.2. X-ray crystallography

Diffraction data for single-crystals of **1–3** were obtained on an automated Agilent Xcalibur diffractometer equipped with an area AtlasS2 detector (graphite monochromator,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å,  $\omega$ -scans) at 130 K. Integration, absorption correction and determination of unit cell parameters were performed using the CrysAlisPro program package [27]. The structures were solved by the dual space algorithm (SHELXT [28]) and refined by the full-matrix least squares technique (SHELXL [28]) in the anisotropic approximation (except for hydrogen atoms). Positions of the hydrogen atoms of the organic ligands were calculated geometrically and refined in the riding model. The crystallographic data and details of the structure refinements are summarized in Table S1.

## 2.3. Photophysical measurements

Photoluminescence and excitation luminescence spectra, and quantum yields were recorded using a Fluorolog-3 (Horiba Jobin Yvon) at room temperature. Fluorolog-3 was equipped with a 450 W ozone-free Xe lamp, an integration sphere, and double grating excitation and emission monochromators. The emission and excitation spectra were corrected for the source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. The luminescence decays (Figs. S11–13) were measured on the same instrument.

## 2.4. Synthesis and characterization data

### 2.4.1. $\{\text{Cu}(\text{MTT})\}_n$ (**1**)

To a solution of 2-(methylthio)thiazole (112 mg, 0.85 mmol) in acetonitrile (3 mL), CuI (147 mg, 0.77 mmol) was added and the mixture was stirred at ambient temperature for 1 h. The formed precipitate was centrifuged, washed with a small amount of MeCN and dried in air. Yield: 216 mg (87%). Colorless powder. *Anal.* Calc. for  $\text{C}_4\text{H}_5\text{CuINS}_2$  (321.67): C, 14.94; H, 1.57; N, 4.35. Found: C, 14.8; H, 1.7; N, 4.4%. FT-IR (KBr,  $\text{cm}^{-1}$ ): 430 (vw), 490 (w), 608 (m), 745 (vs), 770 (w), 872 (w), 968 (s), 978 (m), 1049 (m), 1082 (vs), 1150 (s), 1294 (m), 1373 (s), 1412 (m), 1489 (s), 1578 (w), 1645 (w), 1803 (w), 2735 (vw), 2857 (vw), 2907 (w), 2961 (w), 3069 (s), 3086 (m).

### 2.4.2. $\{(\text{Cu})_2(\text{MTT})\}_n$ (**2**)

To a solution of 2-(methylthio)thiazole (62 mg, 0.47 mmol) in acetonitrile (3 mL), CuI (180 mg, 0.94 mmol) was added and the mixture was stirred at ambient temperature for 1 h. The formed precipitate was centrifuged, washed with a small amount of MeCN and dried in air. Yield: 218 mg (90%). Colorless powder. *Anal.* Calc. for  $\text{C}_4\text{H}_5\text{Cu}_2\text{I}_2\text{NS}_2$  (512.12): C, 9.38; H, 0.98; N, 2.74. Found: C, 9.4; H, 1.1; N, 2.7%. FT-IR (KBr,  $\text{cm}^{-1}$ ): 384 (vw), 494 (w), 608 (m), 733 (vs), 770 (w), 874 (w), 962 (m), 970 (s), 1049 (m), 1080 (vs), 1150 (m), 1294 (m), 1377 (s), 1412 (m), 1420 (m), 1462 (w), 1497 (m), 1614 (vw), 2911 (w), 2988 (w), 3088 (m), 3105 (m).

### 2.4.3. $\{\text{Cu}_2\text{I}_2(\text{MTBT})_2\}$ (**3**)

To a solution of 2-(methylthio)benzothiazole (84 mg, 0.46 mmol) in acetonitrile (3 mL), CuI (88 mg, 0.46 mmol) was added and the mixture was stirred at ambient temperature for 1 h. The formed precipitate was centrifuged, washed with a small amount of MeCN and dried in air. Yield: 161 mg (94%). Colorless powder. *Anal.* Calc. for  $\text{C}_{16}\text{H}_{14}\text{Cu}_2\text{I}_2\text{N}_2\text{S}_4$  (743.46): C, 25.85; H, 1.90; N, 3.77. Found: C, 25.9; H, 2.0; N, 3.7%. FT-IR (KBr,  $\text{cm}^{-1}$ ): 424 (w),

598 (vw), 698 (w), 719 (w), 760 (s), 935 (w), 974 (m), 1013 (w), 1045 (m), 1090 (m), 1107 (w), 1124 (w), 1155 (vw), 1250 (w), 1279 (vw), 1314 (w), 1418 (vs), 1452 (m), 1562 (w), 2909 (w), 2980 (w), 3053 (vw).

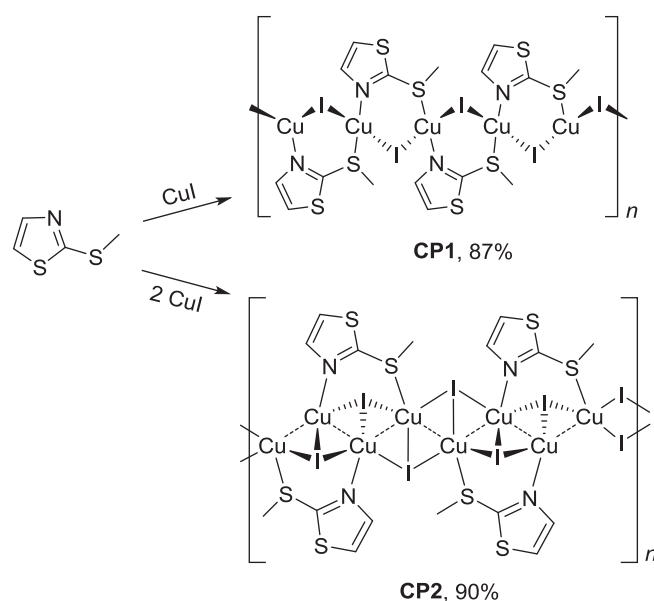
## 3. Results and discussion

### 3.1. Synthesis

After a series of experiments, we have established that treatment of CuI with 2-(methylthio)thiazole (MTT) under mild conditions (rt, acetonitrile, 1 h) affords, depending on the molar ratio of the reactants, either the  $[\text{Cu}(\text{MTT})]_n$  (**CP1**) or  $[(\text{Cu})_2(\text{MTT})]_n$  (**CP2**) 1-D CPs (Scheme 1). At a CuI/MTT molar ratio of 1:1.1, **CP1** with a  $(-\text{Cu}-\text{I}-)_n$  chain is selectively obtained in 87% yield. When the CuI/MTT ratio is 2:1, **CP2** is formed in almost a quantitative yield. As seen from Scheme 1, the MTT ligand in both CPs exhibits the 1,3-N,S bridging mode  $[\mu-\eta^1(\text{N}), \eta^1(\text{S})]$ . As expected, the thiazole sulfur atoms are not involved in coordination with the copper ion.

Our attempts to synthesize CPs using 2-(methylthio)benzothiazole (MTBT) in the reaction with CuI have led to an iodo-bridging dinuclear complex  $[\text{Cu}_2\text{I}_2(\text{MTBT})_2]$  (**3**), containing three-coordinated Cu atoms (Scheme 2). Each MTBT ligand in this complex is coordinated to the metal atom via the thiazole N atom. Apparently, the bulkier structure of the MTBT ligand encumbers the self-assembly of polymeric chains so that the formation of the discrete complex becomes more preferable. Note, the CuI/MTBT ratio (e.g. 1:1 or 2:1) does not affect the structure of the reaction product. Under the best conditions (equimolar CuI/MTBT ratio, r.t., acetonitrile), the yield of complex **3** reaches 94%.

All the compounds obtained are air-stable colorless powders and are soluble in acetonitrile. They have been characterized in the solid state by single crystal X-ray diffraction analysis, FT-IR (Figs. S4–6) and fluorescent spectroscopy. The thermal stability has also been determined using thermogravimetric analysis/differential thermal analysis (TGA/DTA). The phase purity of prepared samples of **1–3** has been confirmed by powder X-ray diffraction determination (Figs. S1–3) and CHN analysis data.



Scheme 1. Synthesis of **CP1** and **CP2**. Conditions: r.t., MeCN, stirring, 1 h.

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