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



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ABSTRACT

The reaction of Cul with 2-(methylthio)thiazole (MTT) in a 1:1 or 2:1 molar ratio (MeCN, rt, 1 h) leads to the coordination polymer $[Cul(MTT)]_n$ (**CP1**) or $[(Cul)_2(MTT)]_n$ (**CP2**), respectively. **CP1** consists of $(-Cu-I-Cu-I)_n$ 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 $[Cul_3N]$ and $[Cul_3S]$ tetrahedra, which alternate in a zigzag fashion. By contrast, 2-(methylthio)benzothiazole (MTBT) reacts with Cul, regardless of the reactants ratio, to give the dinuclear complex $[Cu_2I_2(MTBT)_2]$, where the planar $[Cu(\mu_2-I)]_2$ core is supported by the two ligands in the *N*-monodentate manner. At ambient temperature, **CP1** exhibits a weak yellow luminescence ($\lambda_{max} = 570$ nm), while **CP2** emits in the deep-red region ($\lambda_{max} = 705$ 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_xI_y inorganic skeletons in these CPs can contain the most diverse structural motifs, ranging from 1-D zigzag [CuI]_n 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 vapochromic [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 O₂ [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 selfassembly 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_xI_y cluster cores as secondary building units [14,15]. These CPs often feature fascinating emission characteristics and interesting topologies,

* Corresponding author. E-mail address: chemisufarm@yandex.ru (A.V. Artem'ev). 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⁻¹ heating rate using a NETZSCH STA 449 F1 Jupiter STA up to 700 °C in a closed Al₂O₃ pan. The elemental analyses were performed on a MICRO cube analyzer.







XPRD analyses were performed on a Shimadzu XRD-7000 diffractometer (Cu K α radiation, Ni – filter, 3–35° 2 θ range, 0.03° 2 θ 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, λ (Mo K α) = 0.71073 Å, ω -scans) at 130 K. Integration, absorption correction and determination of unit cell parameters were performed using the CrysA-lisPro 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. {Cul(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 C₄H₅CuINS₂ (321.67): C, 14.94; H, 1.57; N, 4.35. Found: C, 14.8; H, 1.7; N, 4.4%. FT-IR (KBr, 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. {(Cul)₂(MTT)}_n ($\mathbf{2}$)

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 C₄H₅Cu₂I₂NS₂ (512.12): C, 9.38; H, 0.98; N, 2.74. Found: C, 9.4; H, 1.1; N, 2.7%. FT-IR (KBr, 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. $\{Cu_2I_2(MTBT)_2\}$ (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 C₁₆H₁₄Cu₂I₂N₂S₄ (743.46): C, 25.85; H, 1.90; N, 3.77. Found: C, 25.9; H, 2.0; N, 3.7%. FT-IR (KBr, 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 $[CuI(MTT)]_n$ (**CP1**) or $[(CuI)_2(MTT)]_n$ (**CP2**) 1-D CPs (Scheme 1). At a CuI/MTT molar ratio of 1:1.1, **CP1** with a (-Cu-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 [μ - η ¹(N), η ¹(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 Cul have led to an iodo-bridging dinuclear complex $[Cu_2I_2(MTBT)_2]$ (**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 selfassembly of polymeric chains so that the formation of the discrete complex becomes more preferable. Note, the Cul/MTBT ratio (e.g. 1:1 or 2:1) does not affect the structure of the reaction product. Under the best conditions (equimolar Cul/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.



Scheme 2. Synthesis of 3.

3.2. Crystal structures of 1-3

CP1 crystallizes in the $P2_1/c$ space group and its asymmetric motif contains the CuI unit ligated by the 2-methylthiothiazole molecule via the N atom (Fig. 1a). The Cu atoms of **CP1** are linked by μ_2 -bridging I atoms to form 1-D zigzag (CuI)_n chains along the c axis (Fig. 1b). Each Cu atom is also bonded with N and sulfide S atoms from two neighboring ligands, adopting a distorted [I₂NS] tetrahedral geometry ($\tau_4 = 0.94$ [29]). The shortest Cu--Cu distance within these chains is too long [3.8369(13)Å] for any metallophilic interaction. Each MTT ligand simultaneously binds two μ_2 -I-bridged Cu atoms forming a 6-membered chelating "Cu-I-Cu-N-C-S" ring. The latter adopts a boat conformation with the torsion angle between the mean $N^1-C^3-S^2-Cu^1$ and S²–Cu¹–I¹–Cu¹ planes being 54.472(186)°. Both Cu– μ_2 -I bonds have almost the same length. The Cu-I-Cu-I and I-Cu-I-Cu torsion angles in **CP1** are 155.645(39) and 110.544(40)°, respectively. Analysis of CCDC database reveals that the topology of $(-Cu-I-)_n$ chain in CP1 is close to that of the 2-D coordination polymer [CuI $(\text{pyrimidine})]_n$ [30] (see Fig. S14). Note that $(-Cu-I-)_n$ chains with other topologies are also known [31-36].

CP2 crystallizes in the $P\bar{1}$ space group and its asymmetric unit consists of the [Cu₂I₂(MTT)] fragment, as depicted in Fig. 2a. This CP contains a double-stranded (Cu₂I₂)_n chain ligated on both sides by MTT ligands in the 1,3-N,S bridging mode (Fig. 2b). The formed 6-membered chelating "Cu–I–Cu–N–C–S" rings have a boat conformation with the torsion angle between mean N¹–C³–S²–Cu¹ and S²–Cu¹–I¹–Cu¹ planes being 55.894(118)°. The Cu atoms form

an irregular zigzag ($-Cu^1-Cu^2-Cu^1-Cu^2-)_n$ chain [$\angle_{Cu-Cu-Cu}$ are 111.59(4) and 71.29(3)°], formed by the Cu···Cu short contacts of 2.7629(14) and 2.7901(10) Å. Each I atom binds three Cu atoms in a μ_3 -mode. The Cu(1) and Cu(2) atoms are located in a distorted tetrahedral environment ($\tau_4 = 0.83$ and 0.88 [29]) formed by three μ_3 -I atoms and S(2) or N(1) atoms, respectively. The polymeric structure of **CP2** can also be described as alternating [CuI₃N] and [CuI₃S] tetrahedra aggregated in a corner-sharing and edge-sharing manner (Fig. 2c). To our knowledge, a similar structure of a ($Cu_2I_2)_n$ chain was reported only for the CP [$Cu_4I_4(L)_2]_n$ bearing the 1,3,4-thiadiazole-based ligand [37]. The bond lengths and angles around the Cu atoms as well as Cu···Cu distances in **CP2** are comparable with those in the known CP [16–26].

Complex **3** crystallizes in the $P\bar{1}$ space group. Its asymmetric unit consists of one half of a $[Cu_2I_2(MTBT)_2]$ molecule. Its Cu_2I_2 core shows a rhomboid-shaped planar structure (Fig. 3) with the Cu…Cu distance being 2.4981(6)Å, which implies the existence of a cuprophilic interaction. Each Cu atom of **3** is coordinated by two μ_2 -I atoms and the N atom of the ligand, thus adopting a trigonal planar geometry. Each Cu atom deviates from the mean " N^1 - I^1 - I^1 " plane toward the S atom by 0.041 Å. A possible intramolecular Cu(1)-S(2) interaction is hardly probable since this distance [3.3062(7) Å] is longer than the sum of van der Waals radii for these atoms (3.20 Å [38]). The benzothiazole cycle is nearly perpendicular to the Cu₂I₂ plane, with a torsion angle of 75.78°. In the crystal packing of **3**, there are no specific interactions between the molecules except for van der Waals ones. On the whole, the bond lengths and angles in 3 are comparable with those in similar Cu₂I₂ complexes [39].

3.3. Luminescent properties

The luminescent properties of the synthesized compounds were studied for solid samples at room temperature. Upon photoexcitation, compounds **CP1**, **CP2** and **3** exhibit a weak emission with quantum yields of $\ll 1$, 1.2 and 2.5%, respectively. Fig. 4 displays the excitation and emission spectra of the solid powders at 298 K. The emission and excitation maxima, lifetimes and photoluminescence quantum yields at room temperature are summarized in Table 1. The excitation spectra of **CP1**, **CP2** and **3** show quite narrow bands centered at 430, 400 and 360 nm, correspondingly. The emission spectra appear to be broad and unstructured thus



Fig. 1. (a) The asymmetric unit of **CP1**; (b) Fragment of its 1-D chain; (c) polyhedral representation of the Cu(I) coordination environments in the 1-D chains of 1. Selected bond lengths (Å) and angles (°): Cu(1)–Cu(1') 3.8369(13), Cu(1)–I(1) 2.6091(10), Cu(1)–I(1') 2.6120(11), Cu(1)–N(1) 2.033(6), Cu(1)–S(2') 2.336(2), Cu(1)–I(1)–Cu(1') 94.59(3), I(1)–Cu(1)–I(1') 111.36(4), N(1)–Cu(1)–Cu(1) 107.54(17), N(1)–Cu(1)–I(1') 109.46(17).



Fig. 2. (a) The asymmetric unit of **CP2**; (b) Fragment of its1-D chain showing Cu. ··Cu short contacts; (c) polyhedral representation of the Cu(1) coordination environments in the 1-D chains of **CP2**. Selected bond lengths (Å): Cu(1)–Cu(1') 2.7629(14), Cu(2)–Cu(2') 2.7202(16), Cu(1)–Cu(2') 2.7901(10), Cu(1)–I(1) 2.6628(9), Cu(1')–I(1) 2.6792(10), Cu(2')–I(1) 2.7195(8), Cu(2)–N(1) 2.018(4), Cu(1)–S(2) 2.3533(15), Cu(1)–I(2) 2.6173(8), Cu(2)–I(2) 2.6339(8), Cu(2)–I(2') 2.6704(9).



Fig. 3. Molecular structure of **3.** Selected bond lengths (Å) and angles (°): Cu(1)–Cu (1') 2.4981(6), Cu(1)–I(1) 2.5364(3), Cu(1)–I(1') 2.5863(3), Cu(1)–N(1) 1.9651(18), Cu(1)–S(2) 3.3062(7), I(1)–Cu(1)–I(1') 121.636(12), Cu(1)–I(1)–Cu(1') 58.364 (11), N(1)–Cu(1)–Cu(1') 171.99(5), N(1)–Cu(1)–I(1) 125.54(5).

indicating a MLCT character of the emissive state, which is typical for Cu(I) complexes [40]. It ta noteworthy that **CP2** emits in the deep-red region (700 nm) of the spectrum, which is still an uncommon phenomenon for Cu(I) complexes [41]. Thus, the structure of the (CuI)_x chain in **CP1** and **CP2** strongly affects the energies of their emissions and lifetimes. The red-shift of the emission maximum, observed on going from **CP1** to **CP2**, can be tentatively explained by the Cu...Cu interactions in **CP2**, which are known to be responsible for the modulation of emission energies [42].

All the complexes show three-exponential decay dynamics and lifetimes in the microsecond region (Table 1) that indicates the



Fig. 4. Normalized solid state excitation (dashed lines) and emission (solid lines) spectra of **CP1** (λ_{ex} = 430 nm), **CP2** (λ_{ex} = 400 nm) and **3** (λ_{ex} = 360 nm) at 298 K.

triplet origin of the emissions. The observation of three lifetimes is probably due to specific intermolecular interactions in the crystal packing of 1-3. Taking into account the results of recent work [41], the origin of the luminescence in compounds 1-3 may be attributed to ³MLCT state.

Compound	$\lambda_{\rm ex} ({\rm nm})^{\rm a}$	$\lambda_{\rm em} \left({nm} \right)^{\rm a}$	$\tau \left[\mu s\left(A_{n}\right)\right]^{b}$	PLQY (%) ^c
CP1	455	570	0.008(77) 0.142(5) 1.983(18)	<1
CP2	390	700	0.057(13) 0.224(57) 1.169(30)	1.2
3	350	540	0.008(9) 0.070(71) 1.593(20)	2.5

Table 1 Luminescence properties of complexes 1–3 in the solid state at 298 K.

^a Emission or excitation maximum.

^b Emission decays were analyzed with three components $I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$.

^c Photoluminescence quantum yields in the solid state.



3.4. Thermal properties

The thermal stability of the above compounds has been studied by TGA/DTA under a helium atmosphere (for details, see Figs. S7–9). As seen from Fig. 5, **CP2** and complex **3** exhibit similar single-step decomposition trends, losing the ligand molecules at 120–170 and 120–190 °C, correspondingly. The weight losses for **CP2** and **3** (25.1 and 47.5%, correspondingly) well agree with the calculated values (25.6 and 48.8%) for CuI. Above *ca.* 500 °C, the CuI residue begins to vaporize. By contrast, **CP1** demonstrates a two-step decomposition into CuI at *ca.* 90–130 and 130–150 °C. We believe that in the first step, **CP1** eliminates one ligand molecule to form **CP2**, [(CuI)₂(MTT)]_n, which above 130 °C further decomposes into CuI. The calculated values of the weight loss for these stages (23.6 and 17.1%) roughly correspond to the calculated data (27.4 and 20.9%) for the above processes.

4. Conclusions

The first representatives of Cu(I) halide CPs with thiazolyl sulfide ligands have been synthesized by the reaction of CuI with 2-(methylthio)thiazole under mild conditions. The 1-D CP $[CuI(MTT)]_n$ contains $(-Cu-I-)_n$ zigzag chains and 1-D CP $[(CuI)_2(MTT)]_n$ features double-stranded $(Cu_2I_2)_n$ chains. In both CPs, the 2-(methylthio)thiazole ligand binds the adjacent Cu atoms of the chains *via* the thiazole N and sulfide S atoms, thus exhibiting

a 1,3-N,S bridging mode $[\mu-\eta^1(N), \eta^1(S)]$. Meanwhile, 2-(methylthio)benzothiazole in the reaction with CuI affords a dinuclear complex $[Cu_2l_2(MTBT)_2]$, wherein each three-coordinated Cu atom is bonded with the N atom of the MTBT ligand. All the above compounds in the solid state at room temperature show a weak luminescence centered at 570, 705 and 530 nm for $[CuI(MTT)]_n$, $[(CuI)_2(MTT)]_n$ and $[Cu_2l_2(MTBT)_2]$, respectively. It is noteworthy that $[(CuI)_2(MTT)]_n$ displays a deep-red (700 nm) photoluminescence, thus representing a rare example of a Cu(I) complex showing an emission in this region. The results described contribute to the coordination chemistry of both sulfide ligands and Cu(I) halide CPs.

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Appendix A. Supplementary data

CCDC 1815946–1815948 contains the supplementary crystallographic data for **1–3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10. 1016/j.poly.2018.05.045.

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