

## Coordination Polymers of Copper(I) Halides and Neutral Heterocyclic Thiones with New Coordination Modes

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Reaction of copper(I) chloride or bromide with equimolar amounts of the neutral pyrimidine-2-thione ligand (pymtH) afforded linear chain polymers  $[\text{Cu}(\text{pymtH})\text{X}]_n$  ( $\text{X} = \text{Cl}, \text{Br}$ ) with the pymtH ligand acting as a bridging N, S donor. In contrast, copper(I) iodide under the same conditions gave the dimeric complex  $[\text{Cu}(\text{pymtH})_2]_2$  with the pymtH ligand adopting monodentate coordination mode through the exocyclic sulfur atom in terminal and bridging modes. Reactions of the heterocyclic thione ligand 2,4,6-trimercaptotriazine ( $\text{H}_3\text{TMT}$ ) with copper(I) halides afforded novel three-dimensional polymers, which crystallized in the cubic space group  $Pa\bar{3}$ . Each copper(I) ion is coordinated by three S atoms of three distinct  $\text{H}_3\text{TMT}$  ligands, and each  $\text{H}_3\text{TMT}$  acts as a tridentate bridging ligand linking three copper(I) ions through its sulfur atoms, thus forming two independent three-dimensional (3D) networks. The network belongs to a three-connected (10, 3)-a topology, which is enantiometric and interpenetrating. In all complexes the ligands are present in the thione form, and all halides are terminally coordinated to copper(I) ions. The photoluminescent and thermal properties of the complexes have also been investigated.

### Introduction

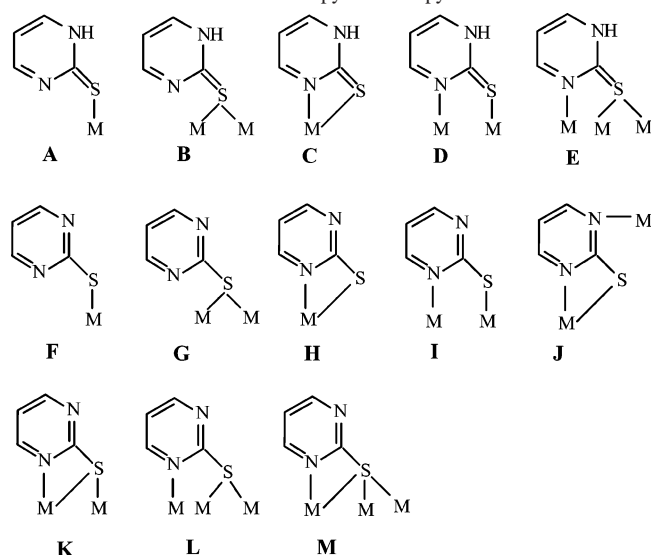
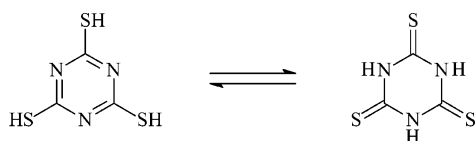
Heterocyclic thiones have attracted considerable interest as ligands in metal complexes because of their relevance in biological systems.<sup>1,2</sup> The chemical interest of heterocyclic thiones is due to the fact that they are potentially ambidentate or multifunctional donors with either the exocyclic sulfur or heterocyclic nitrogen atom available for coordination. They are often used for studying binding properties with a soft Lewis acid like Cu(I), and this interaction is highly flexible; thus, a variety of stereochemistries have been formed.<sup>3–7</sup> On the other hand, self-assembly processes involving multidend-

tate ligands and metal ions with appropriate stereoelectronic preferences can lead to different fantastic polynuclear complexes, especially coordination polymers. It is possible that diverse polymers with interesting structures may be isolated through reactions of Cu(I) ions with heterocyclic thiones. Pyrimidine-2-thione (pymtH) and the corresponding thiolate (pymt<sup>−</sup>) can adopt different coordination modes (Chart 1) to yield a variety of coordination complexes. Complexes of pyrimidine-2-thiolate have been found to coordinate to metals with coordination modes **F**,<sup>8</sup> **G**,<sup>9</sup> **H**,<sup>10</sup> **I**,<sup>11</sup> **J**,<sup>12</sup> **K**,<sup>12</sup> **L**,<sup>13</sup> and **M**.<sup>14</sup> Neutral pyrimidine-2-thione, however, always bind to the metal center exclusively via the monodentate coordination mode using the exocyclic sulfur in either terminal (**A**)<sup>15</sup> or bridging mode (**B**).<sup>16</sup>

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**Chart 1.** Coordination Modes of pymtH and pymt<sup>-</sup>**Scheme 1**

Complexes with coordinated pyrimidine nitrogen are scarce, and as far as we are aware, only one example (**C**)<sup>17</sup> is known. No structural work has been reported so far on the coordination polymer of pymtH because of not only the difficulty to attain single crystals for structural characterization due to the very poor solubility but also the difficulty of binding of heterocyclic nitrogen.

Our recent studies revealed that the reaction of pymtH with CuCl in a 1:1 molar ratio formed an insoluble product which reacted with triphenylphosphine to yield a monomer.<sup>18</sup> To further understand the complexity of the interaction of copper(I) halides with pymtH, in this paper, we report our extraordinary preparation and characterization of three new copper(I) complexes: [Cu(pymtH)Cl]<sub>n</sub> (**1**) and [Cu(pymtH)Br]<sub>n</sub> (**2**) with a chain polymeric structure; [Cu(pymtH)<sub>2</sub>I]<sub>2</sub> (**3**) with a dinuclear structure. It is noteworthy that neutral pymtH in **1** and **2** adopts two kinds of unprecedented bidentate binding modes through the exocyclic S and heterocyclic N atoms, acting as a bridging ligand (**D** and **E** in Chart 1). As a comparative study, self-assembly reactions of 2,4,6-trimercaptotriazine (H<sub>3</sub>TMT, referred to as trithiocyanuric acid), potentially existing in either thiol or thione form (Scheme 1), with copper(I) halides have been carried out. Three isostructural polymers, [Cu(μ<sub>3</sub>-H<sub>3</sub>TMT)Cl]<sub>n</sub> (**4**), [Cu(μ<sub>3</sub>-H<sub>3</sub>TMT)Br]<sub>n</sub> (**5**), and [Cu(μ<sub>3</sub>-H<sub>3</sub>TMT)I]<sub>n</sub> (**6**), with a 2-fold interpenetrating 3-D network were obtained. Despite structures of H<sub>3</sub>TMT as a potentially multifunctional bridging ligand, as deprotonated forms L<sup>3-</sup>, HL<sup>2-</sup>, and H<sub>2</sub>L<sup>-</sup> with metals are known,<sup>19–26</sup> no transition metal complexes of the neutral H<sub>3</sub>TMT ligand have been structurally characterized.

## Experimental Section

All reagents were commercially available and used as received. Solvents CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> were analytical grade and used without further purification. Infrared spectra were obtained in KBr disks on a Nicolet Avatar 360 FTIR spectrometer in the range of 4000–400 cm<sup>-1</sup>. Photoluminescence analyses were performed on a Perkin-Elmer LS 55 luminescence spectrometer. Elemental analyses of C, H, and N were determined with a Perkin-Elmer 2400C elemental analyzer. Thermal analysis (TG) was carried out in a nitrogen stream using Seiko Extar 6000 TG/DTA equipment with a heating rate of 10 °C/min.

**[Cu(pymtH)Cl]<sub>n</sub> (1).** Equimolar quantities (0.05 mmol) of solid CuCl (0.0067 g) and solid pymtH (0.0055 g) were carefully placed on opposite sides of the bottom of a small beaker (25 cm<sup>3</sup>) filled with the mixed solvents of CH<sub>2</sub>Cl<sub>2</sub> (4 cm<sup>3</sup>) and CH<sub>3</sub>CN (3 cm<sup>3</sup>). The beaker was sealed with kitchen film and left standing at room temperature. Dark red block crystals were obtained after 2 days. Yield: 24%. Anal. Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>8</sub>S<sub>4</sub>Cu<sub>4</sub>Cl<sub>4</sub>: C, 22.75; H, 1.91; N, 13.27. Found: C, 22.77; H, 1.89; N, 13.30. IR (ν/cm<sup>-1</sup>): 3101 w, 1573 vs, 1491 s, 1319 vs, 1172 vs, 1001 m, 792 m.

**[Cu(pymtH)Br]<sub>n</sub> (2).** The procedure was the same as that for **1** using CuBr instead of CuCl. Dark red block crystals of **2** were obtained in 2 days. Yield: 80%. Anal. Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>8</sub>S<sub>4</sub>Cu<sub>4</sub>Br<sub>4</sub>: C, 18.80; H, 1.58; N, 10.96. Found: C, 18.82; H, 1.60; N, 10.98. IR (ν/cm<sup>-1</sup>): 3096 w, 1569 vs, 1483 s, 1311 vs, 1176 vs, 1001 m, 776 m.

**[Cu(pymtH)<sub>2</sub>I]<sub>2</sub> (3).** The procedure was the same as that for **1** using CuI instead of CuCl. Ruby red block crystals of **2** were obtained in 2 days. Yield: 80%. Anal. Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>8</sub>S<sub>4</sub>Cu<sub>2</sub>I<sub>2</sub>: C, 23.17; H, 1.94; N, 13.51. Found: C, 23.20; H, 1.91; N, 13.50. IR (ν/cm<sup>-1</sup>): 3117 w, 1556 vs, 1479 s, 1315 s, 1168 vs, 972 m, 780 m.

**[Cu(μ<sub>3</sub>-H<sub>3</sub>TMT)Cl]<sub>n</sub> (4).** Solid CuCl (0.0116 g, 0.075 mmol) and H<sub>3</sub>TMT (0.0052 g, 0.025 mmol) were carefully placed on opposite sides of the bottom of a small beaker (25 cm<sup>3</sup>) filled with the mixed solvents of CH<sub>2</sub>Cl<sub>2</sub> (4 cm<sup>3</sup>) and CH<sub>3</sub>CN (3 cm<sup>3</sup>). The beaker was sealed with kitchen film and left in room temperature. Orange block crystals were obtained after 2 days. Yield: 15% based on CuCl. Anal. Calcd for C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>S<sub>3</sub>CuCl: C, 13.04; H, 1.09; N, 15.21. Found: C, 13.06; H, 1.12; N, 15.20. IR (ν/cm<sup>-1</sup>): 3052 w, 2855 w, 1527 s, 1384 s, 1245 v, 1127 s, 890 w, 804 m, 596 w.

**[Cu(μ<sub>3</sub>-H<sub>3</sub>TMT)Br]<sub>n</sub> (5).** The procedure was the same as that for **4** using CuBr instead of CuCl. Orange block crystals of **5** were obtained in 2 days. Yield: 18% based on CuBr. Anal. Calcd for C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>S<sub>3</sub>CuBr: C, 11.24; H, 0.94; N, 13.10. Found: C, 11.27; H, 0.91; N, 13.08. IR (ν/cm<sup>-1</sup>): 3092 w, 2998 w, 2847 w, 1715 w, 1523 s, 1380 s, 1237 w, 1123 s, 886 w, 784 m, 592 w.

**[Cu(μ<sub>3</sub>-H<sub>3</sub>TMT)I]<sub>n</sub> (6).** The procedure was the same as that for **4** using CuI instead of CuCl. Orange block crystals of **6** were obtained in 2 days. Yield: 20% based on CuI. Anal. Calcd for

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**Table 1.** Summary of the Crystal Data and Structure Refinement Parameters for **1–6**

param	1	2	3	4	5	6
empirical formula	C <sub>16</sub> H <sub>16</sub> N <sub>8</sub> S <sub>4</sub> Cu <sub>4</sub> Cl <sub>4</sub>	C <sub>16</sub> H <sub>16</sub> N <sub>8</sub> S <sub>4</sub> Cu <sub>4</sub> Br <sub>4</sub>	C <sub>16</sub> H <sub>16</sub> N <sub>8</sub> S <sub>4</sub> Cu <sub>2</sub> I <sub>2</sub>	C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> S <sub>3</sub> CuCl	C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> S <sub>3</sub> CuBr	C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> S <sub>3</sub> CuI
fw	844.57	1022.41	829.49	276.25	320.71	367.70
temp (K)	293 (2)	293 (2)	293 (2)	293 (2)	293 (2)	293 (2)
cryst system	triclinic	triclinic	orthorhombic	cubic	cubic	cubic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Fdd2</i>	<i>Pa</i> $\bar{3}$	<i>Pa</i> $\bar{3}$	<i>Pa</i> $\bar{3}$
<i>a</i> (Å)	7.4760(6)	7.4238(8)	12.8302(10)	11.7472(4)	11.8847(3)	12.0266(4)
<i>b</i> (Å)	7.5128(6)	7.5749(8)	38.855(3)	11.7472(4)	11.8847(3)	12.0266(4)
<i>c</i> (Å)	12.9983(11)	13.4896(15)	9.9562(8)	11.7472(4)	11.8847(3)	12.0266(4)
$\alpha$ (deg)	83.0860(10)	83.579(2)	90.00	90.00	90.00	90.00
$\beta$ (deg)	81.8930(10)	81.452(2)	90.00	90.00	90.00	90.00
$\gamma$ (deg)	62.8890(10)	63.055(2)	90.00	90.00	90.00	90.00
<i>V</i> (Å <sup>3</sup> )	642.04(9)	667.87(13)	4963.3(7)	1621.07(10)	1678.67(7)	1739.52(10)
<i>Z</i>	1	1	8	8	8	8
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	2.184	2.542	2.220	2.264	2.538	2.808
$\mu$ (mm <sup>-1</sup> )	4.036	9.463	4.561	3.726	8.040	6.715
reflens colld	5614	5860	7650	9510	9865	9933
indep reflens	2906	3031	2816	651	671	698
<i>R</i> <sub>int</sub>	0.0154	0.0217	0.0222	0.0263	0.0360	0.0423
final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	<i>R</i> <sub>1</sub> = 0.0282 w <i>R</i> <sub>2</sub> = 0.0740	<i>R</i> <sub>1</sub> = 0.0352 w <i>R</i> <sub>2</sub> = 0.0702	<i>R</i> <sub>1</sub> = 0.0258 w <i>R</i> <sub>2</sub> = 0.0527	<i>R</i> <sub>1</sub> = 0.0223 w <i>R</i> <sub>2</sub> = 0.0568	<i>R</i> <sub>1</sub> = 0.0392 w <i>R</i> <sub>2</sub> = 0.0866	<i>R</i> <sub>1</sub> = 0.0836 w <i>R</i> <sub>2</sub> = 0.1880
final <i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0331 w <i>R</i> <sub>2</sub> = 0.0893	<i>R</i> <sub>1</sub> = 0.0448 w <i>R</i> <sub>2</sub> = 0.0799	<i>R</i> <sub>1</sub> = 0.0270 w <i>R</i> <sub>2</sub> = 0.0532	<i>R</i> <sub>1</sub> = 0.0237 w <i>R</i> <sub>2</sub> = 0.0574	<i>R</i> <sub>1</sub> = 0.0411 w <i>R</i> <sub>2</sub> = 0.0872	<i>R</i> <sub>1</sub> = 0.0865 w <i>R</i> <sub>2</sub> = 0.1894
$\rho_{\text{min}}$ (max/min) (e Å <sup>-3</sup> )	0.457/−0.450	0.674/−0.467	0.842/−0.368	0.281/−0.264	0.943/−0.300	1.647/−2.549

<sup>a</sup> *R*<sub>1</sub> =  $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ ; w*R*<sub>2</sub> =  $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$ .

C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>S<sub>3</sub>CuI: C, 9.80; H, 0.82; N, 11.43. Found: C, 9.82; H, 0.81; N, 11.45. IR ( $\nu/\text{cm}^{-1}$ ): 3060 w, 3007 w, 2859 w, 1715 w, 1531 s, 1384 s, 1241 w, 1131 s, 886 w, 804 m, 600 w.

**Crystal Structure Determination.** Suitable crystals of **1–6** were mounted with glue at the end of a glass fiber, respectively. Data collections were performed on a Bruker-AXS SMART CCD area detector diffractometer at 293(2) K using  $\omega$  rotation scans with a scan width of 0.3° and Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The crystal parameters and experimental details of the data collection are summarized in Table 1. Empirical absorption corrections were carried out utilizing SADABS routine. The structures were solved by direct methods and refined by full-matrix least-squares refinements based on *F*<sup>2</sup>. All non-hydrogen atoms were anisotropically refined. All hydrogen atoms were found from difference electron density maps and refined isotropically. Structure solutions, refinements, and graphics were performed with the SHELXL-97 package.<sup>27</sup> Selected bond lengths and angles for the complexes are given in Tables 2 and 3.

## Results and Discussion

**Synthesis.** Reaction rates between CuX (X = halides) and pymtH were so fast that precipitates were formed immediately when the suspension of two reactants met. Structures of these insoluble products of composition [CuX-(pymtH)]<sub>*n*</sub> were unknown because of the difficulty to prepare single crystals suitable for X-ray diffraction analysis.<sup>5,6</sup> To pursue the binding properties of pymtH to CuX, much work has focused on the depolymerization of the precipitates by using triphenylphosphine,<sup>15,18,28</sup> tri-*p*-tolylphosphine,<sup>16</sup> or other diphosphanes such as 1,3-propanebis(diphenylphosphine) (dppp)<sup>29</sup> and *cis*-1,2-bis(diphenylphosphino)ethylene (dppet).<sup>30</sup> The depolymerized products have been structurally

**Table 2.** Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes **1–3**

Complex 1			
Cu1–S1	2.2420(8)	S1–Cu1–N1	121.28(7)
Cu1–S2	2.4279(8)	S1–Cu1–Cl1	117.32(3)
Cu1–N1	2.115(2)	S2–Cu1–N1	96.70(6)
Cu1–Cl1	2.3506(8)	S2–Cu1–Cl1	102.43(3)
Cu2B–S2A	2.2131(8)	Cl1–Cu1–N1	100.65(6)
Cu2B–N3	2.014(2)	S2A–Cu2B–N3	137.58(7)
Cu2B–Cl2	2.3194(9)	S2A–Cu2B–Cl2	117.42(3)
Cl1···H4	2.346	Cl1···H4–N4	164.9
Cl2···H6	2.179	Cl2···H6–N6	172.0
Complex 2			
Cu1–S1	2.2508(12)	S1–Cu1–N1	122.64(10)
Cu1–S2	2.4528(12)	S1–Cu1–Br1	118.29(4)
Cu1–N1	2.119(3)	S2–Cu1–N1	95.63(10)
Cu1–Br1	2.4877(7)	S2–Cu1–Br1	101.20(3)
Cu2B–S2A	2.2271(12)	Br1–Cu1–N1	100.31(9)
Cu2B–N3	2.032(3)	S2A–Cu2B–N3	137.78(11)
Cu2B–Br2	2.4644(8)	S2A–Cu2B–Br2	118.29(4)
Br1···H4	2.559	Br1···H4–N4	160.4
Br2···H6	2.364	Br2···H6–N6	168.0
Complex 3			
Cu1–S1	2.2508(11)	S1–Cu1–S2A	104.81(5)
Cu1–S2A	2.6572(13)	S1–Cu1–S2	105.66(5)
Cu1–S2	2.3009(13)	S2–Cu1–S2A	94.95(4)
Cu1–I1	2.6178(6)	S2A–Cu1–I1	104.50(3)
I1···H1	2.725	I1···H1–N1	168.6
I1···H3	2.987	I1···H3–N3	167.7

characterized as phosphane–thione mixed-ligand complexes, thione-free halide-bridging dicopper phosphane complexes, or phosphane-free thione-*S*-bridging dicopper halide complexes (Scheme 2). In all the pymtH-containing complexes, pymtH binds to copper(I) via exocyclic sulfur atom, whereas the pyrimidine nitrogen atom remains free.

Our strategy to obtain polymers in crystalline form is to control the formation speed of the insoluble product. Taking into consideration that pymtH is insoluble or sparingly soluble in common solvent (e.g. CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub>) and

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**Table 3.** Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes 4–6

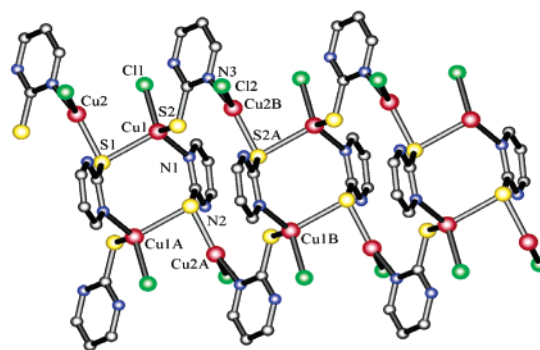
Complex 4			
Cu1–S1	2.3104(5)	S1–Cu1–S2	106.709(17)
Cu1–Cl1	2.3568(9)	S1–Cu1–Cl1	112.109(15)
S1–C1	1.6564(19)	C1–S1–Cu1	103.80(6)
Cl1···H1B	2.568	Cl1···H1B–N1B	172.1
Complex 5			
Cu1–S1	2.3150(10)	S1–Cu1–S2	104.62(4)
Cu1–Br1	2.4777(11)	S1–Cu1–Br1	113.97(3)
S1–C1	1.656(4)	C1–S1–Cu1	105.02(13)
Br1···H1B	2.615	Br1···H1B–N1B	176.2
Complex 6			
Cu1–S1	2.321(3)	S1–Cu1–S2	103.03(11)
Cu1–I1	2.630(3)	S1–Cu1–I1	115.33(9)
S1–C1	1.657(10)	C1–S1–Cu1	106.8(4)
I1···H1B	2.679	I1···H1B–N1B	176.1

copper(I) halides are soluble or sparingly soluble in CH<sub>3</sub>CN, we chose CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> as mixed solvents. Both copper(I) halides and neutral pymtH diffused slowly in such a mixed-solvent system and reacted with each other at a very slow rate. Accordingly, single crystals were obtained.

X-ray diffraction determination revealed that pymtH in [CuX(pymtH)]<sub>n</sub> (X = Cl, Br) acts as bridging ligand with two different coordination modes (see Structure Description for details). We noticed that when the polymer was further treated with triphenylphosphine, the coordination nitrogen was dissociated from copper and gave a mononuclear complex CuX(PPh<sub>3</sub>)<sub>2</sub>(pymtH). This may be due to the tendency that copper(I) favors “soft” sulfur and phosphorus rather than “hard” nitrogen.<sup>31</sup>

Unlike in pymtH, we expected heterocyclic nitrogen atoms in H<sub>3</sub>TMT may be protonated and cannot provide N-donors for further coordination. Therefore, three exocyclic sulfur atoms make H<sub>3</sub>TMT a good candidate as a rigid ligand to construct three-connected polymeric networks. As that for pymtH, reaction rates of H<sub>3</sub>TMT and copper(I) halides are also very fast. Fortunately, we obtained three isostructural polymers by using the above-mentioned diffusion strategy.

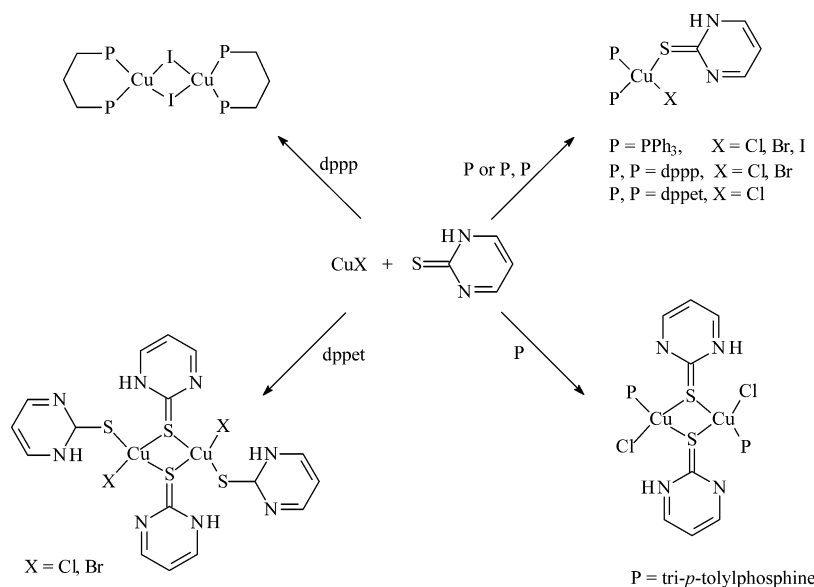
The characteristic NH stretching vibrations (3050–3160 cm<sup>-1</sup>) appear in the infrared spectra of complexes 1–6

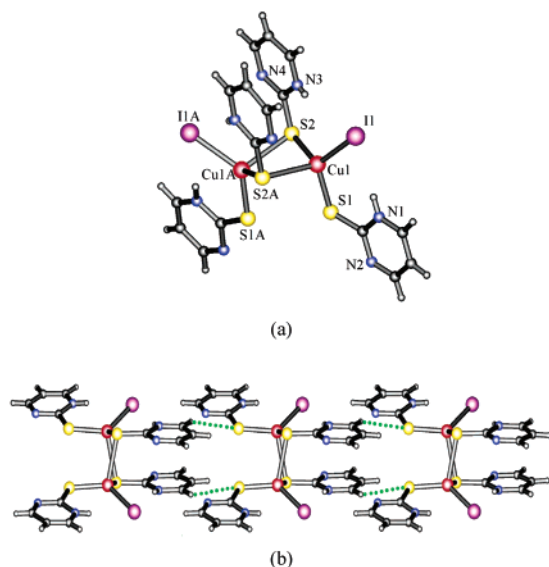
**Figure 1.** Linear chain structure of **1**. All hydrogen atoms are omitted for clarity.

recorded in the region 4000–400 cm<sup>-1</sup>.<sup>32</sup> The four usual “thioamide bands” in the regions ~1510, 1320, 1000, and 750 cm<sup>-1</sup> were also observed.<sup>33</sup>

**Structure Description. Complexes of Copper(I) Halides and pymtH.** Self-assembly reaction of pymtH with CuCl gave complex [Cu(pymtH)Cl]<sub>n</sub> (**1**), as shown in Figure 1, a polymer with a centrosymmetric tetranuclear [Cu<sub>4</sub>(pymtH)<sub>4</sub>-Cl<sub>4</sub>] unit as a building-block unit. In each unit, four copper atoms are ideally coplanar and form a parallelogram plane [Cu1···Cu2 (3.049 Å), Cu1A···Cu2 (5.542 Å), Cu1–Cu2–Cu1A (53.9°)]. The two pymtH ligands locating on both sides of the Cu<sub>4</sub> parallelogram plane are ideally parallel to each other, and each of them bridges copper(I) ions in coordination mode **E** (Chart 1) giving a centrosymmetric eight-membered (CuSCN)<sub>2</sub> ring with Cu1···Cu1A separation of 4.481 Å. Two pymtH ligands adopting bridging mode **D** (Chart 1) bridge two adjacent Cu<sub>4</sub> building-block unit to form a centrosymmetric 16-membered (CuSCN)<sub>4</sub> ring. The 8-membered ring and 16-membered ring arrange alternately along the crystallographic *a*-direction to construct a 1D linear chain polymer. According to the search results of the latest version CCDC database and to the best of our knowledge, coordination modes **D** and **E** of neutral pymtH have not been reported.

It is interesting that Cu centers have two different coordination environments in this complex, that is, CuNSCl





**Figure 2.** (a) Crystal structure of **3** with the labeling scheme. (b) Formation of a 1D chain through C–H···S intermolecular interactions in **3**.

in a distorted planar trigonal geometry and  $\text{CuNS}_2\text{Cl}$  in a distorted tetrahedral geometry. In the tetrahedral  $\text{CuNS}_2\text{Cl}$  core, the largest deviation from the ideal geometry is reflected in the  $\text{S1–Cu1–N1}$  bond angles, whose values of  $121.28(7)^\circ$  are markedly higher than the tetrahedral value of  $109.4^\circ$ . The  $\text{Cu2B–N3}$  and  $\text{Cu2B–Cl2}$  bond distances of  $2.014(2)$  and  $2.3194(9)$  Å in trigonal  $\text{CuNSCl}$  geometry are somewhat shorter than those in tetrahedral  $\text{CuNS}_2\text{Cl}$  [ $\text{Cu1–N1}$ ,  $2.115(2)$  Å;  $\text{Cu1–Cl1}$ ,  $2.3506(8)$  Å], showing that an increase in the coordination number lengthens the bond distances.

The similar reaction of  $\text{CuBr}$  with  $\text{pymtH}$  gave complex **2** (Figure S1 in the Supporting Information). Complexes **1** and **2** are isostructural. Corresponding bond distances and angles are listed in Table 2.

On the contrary, self-assembly reaction of  $\text{CuI}$  with  $\text{pymtH}$  in the same condition proceeded in a different way to give complex  $[\text{Cu}(\text{pymtH})_2\text{I}]_2$  (**3**), which was structurally characterized as a dimer shown in Figure 2a. The structure is markedly different from polymers **1** and **2**. In **3**, the neutral  $\text{pymtH}$  with both nitrogen and sulfur as potential donating atoms adopted the monodentate coordination mode, binding the metal centers exclusively through the exocyclic sulfur atom in terminal ( $\text{S1}$ ,  $\text{S1A}$ ; **A** in Chart 1) and bridging ( $\text{S2}$ ,  $\text{S2A}$ ; **B**) modes. The two copper atoms are doubly bridged by two S atoms of  $\text{pymtH}$  ligands to form an asymmetric nonplanar  $\text{Cu}_2\text{S}_2$  core. The distorted tetrahedral coordination forms by a terminal sulfur atom from  $\text{pymtH}$  and a terminal I atom. The  $\text{Cu}\cdots\text{Cu}$  separation distance is  $3.181$  Å, which is comparable to those in complexes with a  $\text{Cu}_2\text{S}_2$  core, such as  $[\text{Cu}_2(\text{py}2\text{tH})_4\text{I}_2]$  with a separation  $\text{Cu}\cdots\text{Cu}$  of  $3.139$  Å ( $\text{py}2\text{tH} = 1H\text{-pyridine-2-thione}$ ).<sup>34</sup> Reasonably, the terminal

$\text{Cu1–S1}$  distance ( $2.2508(11)$  Å) is invariably shorter than the bridging distances of  $2.3009(13)$  Å ( $\text{Cu1–S2}$ ) and  $2.6572(13)$  Å ( $\text{Cu1–S2A}$ ). The  $\text{S–Cu–S}$  and  $\text{Cu–S–Cu}$  bridging angles ( $94.95(4)$  and  $79.45(4)^\circ$ ) are close to those of  $[\text{Cu}(\text{py}2\text{tH})(p\text{-Tol}_3\text{P})_2]$  ( $94.8$  and  $85.3^\circ$ ).<sup>35</sup> Unexpectedly, the *cis*- $\text{Cu}_2\text{S}_2$  core arrangement makes two bridging  $\text{pymtH}$  ligands almost parallel and approximately  $3.34$  Å apart, showing a  $\pi\text{–}\pi$  stacking interaction. These two  $\text{pymtH}$  ligands are nearly perpendicular to the least-squares plane of the  $\text{Cu}_2\text{S}_2$  core ( $89.6^\circ$ ). Noteworthy is that intermolecular weak interactions ( $\text{H}\cdots\text{S}$   $2.94$  Å,  $\text{C–H}\cdots\text{S}$   $133.8^\circ$ ) exist between adjacent dimers to form a one-dimensional chain (Figure 2b). An isomorphous complex  $[\text{Cu}(\text{pymtH})_2\text{Br}]_2$  was recently reported.<sup>29</sup> Unlike **3**,  $[\text{Cu}(\text{pymtH})_2\text{Br}]_2$  has a *trans*- $\text{Cu}_2\text{S}_2$  core (See Figure S2 in the Supporting Information for comparison) with both terminal S atoms and both Br atoms in *trans* positions, respectively. No  $\pi\text{–}\pi$  stacking interaction or intermolecular hydrogen bond was found.

**Complexes of Copper(I) Halides and  $\text{H}_3\text{TMT}$ .** Reaction of  $\text{H}_3\text{TMT}$  with  $\text{CuCl}$  yielded complex  $[\text{Cu}(\mu_3\text{-H}_3\text{TMT})\text{Cl}]_n$  (**4**). A single-crystal X-ray diffraction study revealed that complex **4** is a 3-D polymer; the ORTEP view of the coordination geometry around central  $\text{Cu(I)}$  ion is shown in Figure 3a. As expected, the protonated heterocyclic nitrogen atoms cannot bind to metals. Each copper(I) has a  $\text{CuS}_3\text{Cl}$  core completed by three sulfur atoms ( $\text{S1}$ ,  $\text{S2}$ ,  $\text{S3}$ ) of three separate thione  $\text{H}_3\text{TMT}$  ligands and one Cl atom. The copper-centered angles of the tetrahedron vary between  $106.709(17)$  and  $112.109(15)^\circ$ , indicating a slightly distorted geometry around the copper atom. The dihedral angle between the three  $\text{H}_3\text{TMT}$  rings coordinated to the same copper(I) ion are  $70.5$ ,  $70.5$ ,  $109.5^\circ$ , respectively. The equal  $\text{Cu–S}$  bond lengths of  $2.3104(5)$  Å in complex **4** are usually found for tetrahedrally coordinated copper(I) complexes with thione-sulfur donors.<sup>36,37</sup> The  $\text{C–S}$  bond distances of  $1.6564(19)$  Å can be comparable to those in a cocrystal structure  $[(\text{H}_3\text{TMT})_2:4,4'\text{-bipy}:\text{C}_6\text{H}_6]$ .<sup>38</sup> The nitrogen-bonded hydrogen atom ( $\text{H1B}$ ,  $\text{H1E}$ ,  $\text{H1F}$ ) participates in an intramolecular  $\text{Cl}\cdots\text{H–N}$  hydrogen bond [ $\text{Cl}\cdots\text{N} = 3.256$  Å,  $\text{H}\cdots\text{Cl} = 2.568$  Å,  $\text{N–H}\cdots\text{Cl} = 172.1^\circ$ ].

Interestingly, each copper(I) atom in **4** is coordinated by three different  $\text{H}_3\text{TMT}$  ligands and, in turn, each  $\text{H}_3\text{TMT}$  ligand, which is essentially planar with the maximum deviation from S of  $0.0717$  Å, acts as a  $\mu_3$  bridge linking three copper(I) ions through its sulfur atom. Such a coordination mode generates an infinite 3D structure (Figure 3b). If either a copper(I) atom or the midpoint of a  $\text{H}_3\text{TMT}$  ligand is defined as a trigonal node, the shortest closed circuits in the network contain five Cu atoms and five moieties of  $\text{H}_3\text{TMT}$ ; thus, 10-membered rings are formed (Figure 3b). In these rings, the lengths of the neighboring Cu atoms are equivalent with  $\text{Cu}\cdots\text{Cu}$   $7.213$  Å, whereas the lengths of

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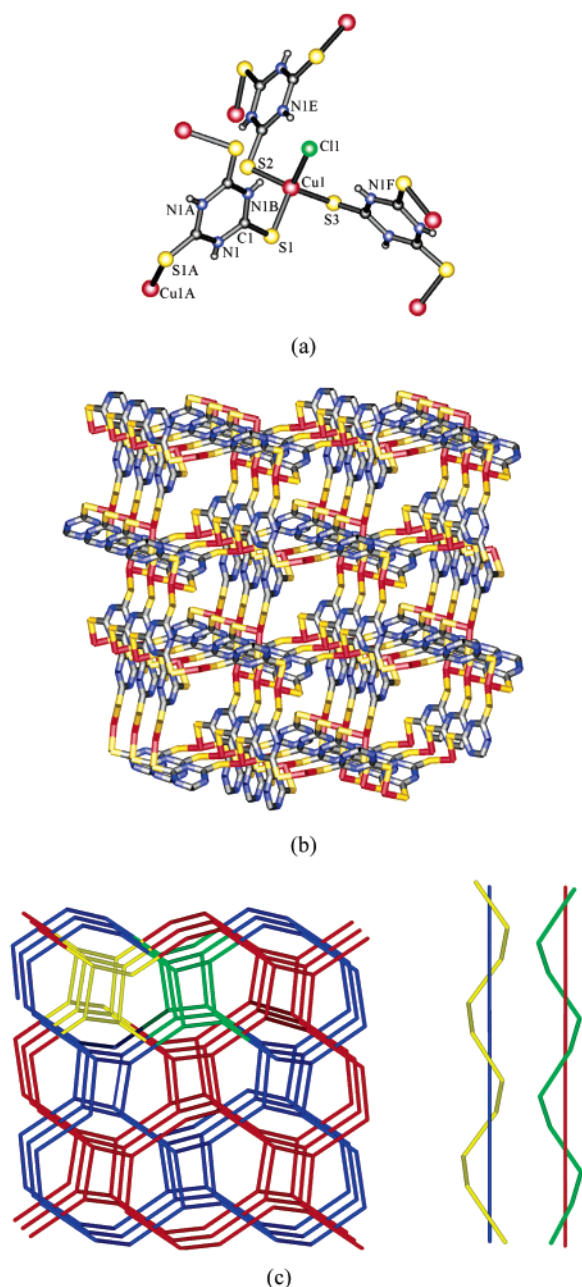
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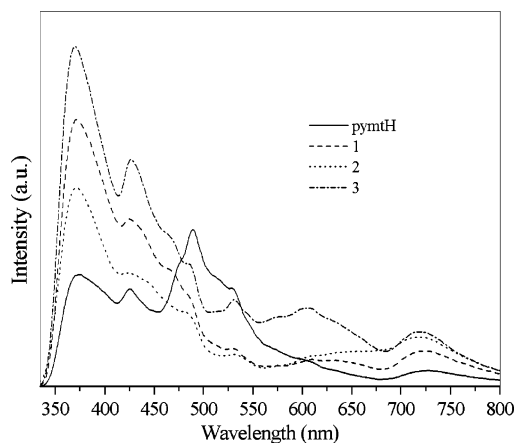


**Figure 3.** Schematic view of **4**: (a) Cu(I) coordination environment; (b) 3-D network with all chlorine and hydrogen atoms omitted for clarity; (c) interpenetrating networks (left) containing two different helices with opposite handedness (right).

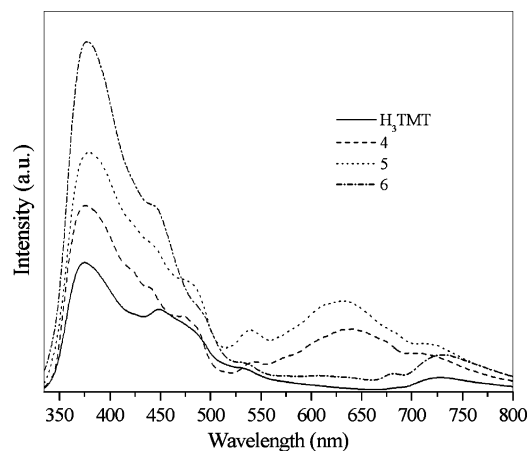
the neighboring S atoms from different thione ligands are 3.707 Å. The extended 3D network can therefore be rationalized as a (10,3)-a net topology, the most symmetrical of all the three-connected nets, which in its geometrically most regular form is cubic with strictly trigonal planar nodes and exactly 120° angles<sup>39</sup> as depicted in Figure 3c. An intermolecular S...S distance of 3.442 Å shows interactions between the two interpenetrating networks since a van der Waals interaction of S...S is 3.8 Å on the basis of the data derived from Me<sub>2</sub>S.<sup>40</sup>

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**Figure 4.** Emission spectra of complexes **1–3** and free thione ligand pymtH ( $\lambda_{\text{ex}} = 320$  nm) in the solid state at room temperature.



**Figure 5.** Emission spectra of complexes **4–6** and free thione ligand H<sub>3</sub>TMT ( $\lambda_{\text{ex}} = 330$  nm) in the solid-state at room temperature.

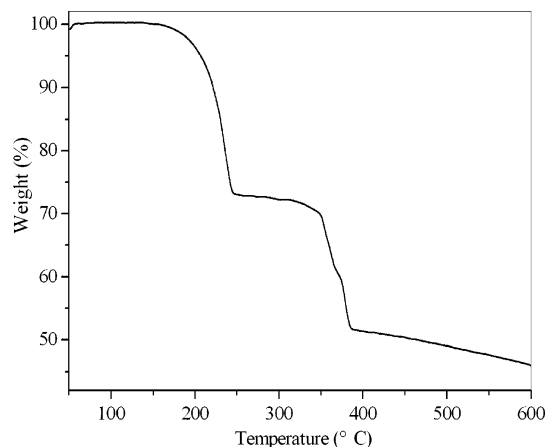
To examine the role of halide atoms in the formation of interpenetrated (10,3)-net, CuBr and CuI are used instead of CuCl to produce complexes **5** and **6**, respectively. Single-crystal X-ray diffraction analysis has proved that complexes **4–6** are isomorphous (see Figures S3 and S4 in the Supporting Information). They all have (10,3)-a net topology. Selected bond lengths and angles are given in Table 3.

**Photoluminescence.** The emission spectra of complexes **1–3** and **4–6** are illustrated in Figures 4 and 5, respectively. The free ligands pymtH and H<sub>3</sub>TMT display very weak emission in the solid state with a high-energy band around 350–550 nm and a low-energy band around 700–780 nm (Figures 4 and 5). On the basis of the comparison to other organic luminescence,<sup>41</sup> we suggest that the bands come from the fluorescence of ( $\pi, \pi^*$ )<sup>1</sup> and phosphorescence of ( $\pi, \pi^*$ )<sup>3</sup> excited states, respectively. The patterns of the emission curves of the complexes are similar to those of their corresponding ligands except the region from 550 to 680 nm. Polynuclear nuclear copper(I) complexes with chalcogen ligands show emissions in this region and have been ascribed to be dominated by a LMCT (S → Cu) character.<sup>42,43</sup>

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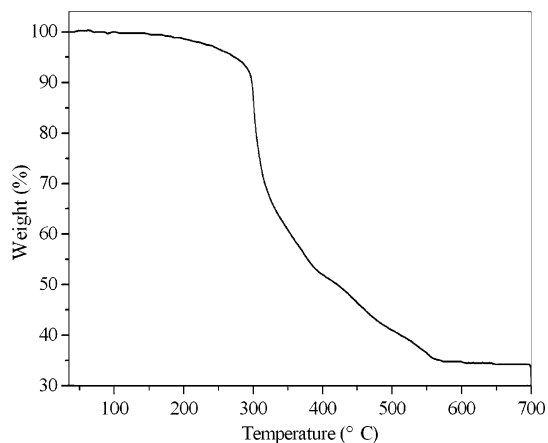
**Figure 6.** Thermogravimetry curve of complex **1**.

**Thermogravimetric Characterization.** The thermal degradation behavior of complex **1** shows that the structural skeleton of polymer **1** remains stable until 170 °C (Figure 6). The thermogravimetric curve gives two abrupt weight losses of 27.6% from 170 to 250 °C and 25.5% from 330 to 380 °C; each corresponds to the removal of two pymtH ligands in one building-block unit (calculated 26.6%). When the temperature exceeds 380 °C, the complex loses all pymtH ligands and remains cuprous chloride.

Figure 7 depicts the thermal behavior of complex **4**. The complex began to lose weight at around 250 °C, and then there is a weight loss of 65.1% from 250 to 570 °C, which corresponds to the removal of the ligands H<sub>3</sub>TMT (calculated 64.2%) to yield cuprous chloride.

## Conclusions

In this work we demonstrate a synthetic strategy to obtain suitable crystals of complexes formed by the reactions of copper(I) halides and neutral heterocyclic thione pymtH and H<sub>3</sub>TMT. Reactions of CuX with pymtH give an unprec-



**Figure 7.** Thermogravimetry curve of complex **4**.

edented linear chain polymer (X = Cl, Br) or a dimer (X = I). Two new coordination modes of pymtH as a bridging ligand via heterocyclic nitrogen and exocyclic sulfur were observed. Isostructural polymers of CuX (X = Cl, Br and I) with H<sub>3</sub>TMT are three-dimensional with a (10, 3)-a topology network. The complexes show intraligand emission in the solid state at room temperature. This work broadens the potential for synthesizing polymers on the basis of neutral heterocyclic thione ligands.

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**Supporting Information Available:** Figures showing the structures of complexes and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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