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# 2,2'-Ethylenebis(1,3-dithiane) as polydentate μ<sub>2</sub>-, μ<sub>4</sub>- and μ<sub>5</sub>- assembling ligand for the construction of sulphur-rich Cu(I), Hg(II) and heterometallic Cu(I)/Hg(II) coordination polymers featuring uncommon network architectures

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#### ABSTRACT

With the aim to elaborate novel and inexpensive sulphur-rich materials featuring unusual network architectures, the coordination chemistry of the tetradentate thiaheterocycle 1,2-di(1,3dithian-2-yl)ethane L1 ligand toward CuX and HgX2 salts was investigated. When L1 is reacted with CuI in a 1:1 ratio, a two-dimensional CP [ $\{Cu(\mu_2-I)_2Cu\}(\mu_2-L1)\}_n$  (CP1) is formed, in which two out of four S atoms of L1 remain non-coordinated. A particularity is the occurrence of three different type of  $[Cu(\mu_2-I)_2Cu]$  rhomboids as SBU (Secondary Building Unit), which differ in the Cu···Cu distances. Upon treatment of L1 with CuI in a 1:2 ratio,  $[{Cu(\mu_2-I)_2Cu}(\mu_4-L1)]_n$ (CP2) is obtained, in which each S atom of L1 coordinates to one copper centre forming a 2D layer. Contrary to **CP1**, **CP2** contains a single type of  $[Cu(\mu_2-I)_2Cu]$  SBU, but with a particular short Cu...Cu bond length of 2.6132(9) Å. Raising the ligand-to-CuI ratio to 1:4 affords the 2D material  $[{Cu(\mu_4-I)(\mu_2-I)Cu}_2(\mu_4-L1)]_n$  (CP3), in which  $[Cu(\mu_4-I)(\mu_2-I)Cu]_n$  ribbons are interconnected through µ4-bridging L1 ligands. Upon reaction of L1 with CuBr in a 1:2 ratio, a 2D CP [{Cu( $\mu_2$ -Br)}<sub>2</sub>( $\mu_4$ -L1)]<sub>n</sub> (CP4) is formed, in which the Cu atoms are bridged by a single  $\mu_2$ -Br ligand giving rise to  $[Cu(\mu_2-Br)Cu]_n$  ribbons. Employing a 1:3 ratio, a 1D ribbon  $[{Cu(\mu_2-Br)Cu}_n ribbons]$ Br)}<sub>3</sub>(MeCN)( $\mu_4$ -L1)]<sub>n</sub> (CP5) is generated, which five out of the six different copper atoms present a tetrahedral geometry, while the sixth one is only three-coordinated. **CP5** also presents two different L1 ligands that differ by the coordination mode of the sulphur atoms (S acting as 2 or as 4 electron-donor). With CuCl, a 2D network  $[{Cu(\mu_2-Cl)_2Cu}(\mu_4-L1)]_n(CP6)$  is generated.

L1 coordinates also on HgX<sub>2</sub> salts to yield CPs whose architecture depends on the ligand-tometal ratio. The meander-shaped 1D CP  $[(HgI_2)(\mu_2-L1)]_n$  (CP7) and the linear 1D ribbons of CP8 and CP11  $[(HgX_2)(\mu_2-L1)]_n$  (X = Br, Cl) result from treatment with L1 in a 1:1 ratio. In the case of HgBr<sub>2</sub>, using a 2:1 metal-to-ligand ratio, 1D polymeric  $[{BrHg}(\mu_2-Br)_2HgBr}(\mu_2-L1)]$ (CP9) is produced. HgI<sub>2</sub> and HgBr<sub>2</sub> have also been reacted with 2-methyl-1,3-dithiane L2 yielding the molecular complexes  $[{IHg}(\mu_2-I)_2HgI}(\kappa^1-L2)_2]$  (D1) and  $[HgBr_2(\kappa^1-L2)_2]$  (M1). A heterometallic 1D material  $[{IHg}(\mu_2-I)_2HgI(\mu_2-I)_2{Cu(MeCN)_2}_2(\mu_2-L1)]_n$  (CP12) results from treatment of CP1 with HgI<sub>2</sub>.

#### Introduction

Coordination polymers (CPs), especially those formed by assembly of inexpensive copper(I) salts with organosulphur ligands such as thioether R-S-R and thiolates R-S<sup>-</sup> present interesting structural and photophysical properties.<sup>1</sup> Complexes, CPs and even MOFs with different dimensionality (0D to 3D) and secondary building units (SBUs) could be constructed depending on the nature of the ligands, the metal-to-ligand ratio and the experimental conditions (solvent, temperature etc..). Beside their interest in crystal engineering, these materials have also found applications in sensing, optoelectronics<sup>2</sup> and catalysis.<sup>3</sup> They have also been used as precursors to prepare materials *i.e.*  $\gamma$ -CuI nanocrystals<sup>4</sup> or as a precursor for CuI-based thermoelectric composites, exhibiting a moderate to high Seebeck coefficient (543–1308  $\mu$ V K<sup>-1</sup>) at elevated temperature.<sup>5</sup> Stretchable, luminescent and self-healing hybrid films were obtained using polymers bearing thioethers functions allowing further coordination to copper iodide.<sup>6</sup>

Several research groups, including ours, have been interested in the formation of various CPs by reacting copper(I) salts with different mono or dithioether ligands. Though the results of the self-assembly process are difficult to predict, Schlachter *et al* have recently reviewed on networks built upon chalcogenoether and chalcogenone assemblies, providing some very interesting trends based on the architecture of the assembling ligands and the nature of the halide.<sup>7</sup> In particular, for sensing applications, the design of porous 3D CP materials plays a crucial role. One may expect that the construction of highdimensional CPs and MOFs is favoured using tridentate or tetradentate ligands. Different polydentate phosphine- and amine-based ligands have been used for the assembly of Cu(I) complexes and CPs, however examples of Cu(I)-based CPs obtained using polydentate organosulfur ligands are much scarce. One of the first example is the coordination of the tridentate thioether ligand MeSi(CH<sub>2</sub>SMe)<sub>3</sub> with CuX salts that led to the formation of 1D CPs.<sup>8</sup> In 2001, Brooks et al. reported the coordination of [12]aneS4 (1,4,7,10tetrathiacyclododecane) or [16]aneS4(1,5,9,13-tetrathiacyclohexadecane) with CuBr or CuI leading to the formation of either discrete molecular entities or CPs with 2D or 3D structures containing rhomboid dimers as SBU when the metal to ligand ratio is increased.<sup>9</sup> 3D CuI-based CPs containing the calix[4]-bis-thiacrown were reported by Lee et al. in 2008<sup>10</sup> and 2D CPs were obtained by assembly of CuI with p-tertbutylthiacalix[4]-arene.<sup>11</sup> The cyclophane derivative 2,11,20,29-tetrathiadodecahydro[3.3.3.3]cyclophane reacts with CuI in MeCN in a 1:1 molar ratio to generate a 3D CP built upon rhomboid dimers as SBUs.<sup>12</sup> In a collaborative work, our group has reported on the network assembly of octadentate thioether-decorated octasilsesquioxanes with CuI salts under mild conditions yielding 3D POSS-based CPs incorporating dinuclear or close-cubanes SBUs.<sup>13</sup> The tetradentate thioether functionalized silanes Si(CH<sub>2</sub>SR)<sub>4</sub> (R = Me or Ph) was found to react with HgBr<sub>2</sub> yielding 1D CPs, where HgBr<sub>2</sub> moieties are connected by doubly bidentate chelating thioether ligands.<sup>14</sup>

Five-, six- and seven-membered dithiaheterocycles have been used in the past by several groups as ligand in coordination chemistry.<sup>15, 16</sup> In the case of 1,3-dithianes, it has been demonstrated that the parent compound 1,3-dithiacyclohexane may be coordinated as mono- and bidentate ligand to a series of early and late transition metal complexes. Several CPs have been built up by treatment of 1,3-dithiane with AgNO<sub>3</sub>, AgBF<sub>4</sub> and AgPF<sub>6</sub>, respectively.<sup>17</sup> Keller and Knaust reacted [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> with that dithiaheterocycle and obtained four coordination networks depending on metal-to-ligand ratio and solvent conditions used.<sup>18</sup> In the context of our research work on the coordination chemistry of dithiolanes and dithianes with Cu(I) salts, we have recently investigated in an exhaustive manner the possibility to construct coordination polymers using both parent 1,3-dithiane and a series of derivates substituted at the 2-position such as such as 2-isobutyl-1,3dithiane, 2-Me<sub>3</sub>Si-1,3-dithiane, 2-phenyl-1,3-dithiane, 2-ferrocenyl-1,3-dithiane and 2methyl-1,3-dithiane.<sup>19-23</sup> Notably with the latter ligand, we demonstrated that CPs with uncommon architectures and dimensionalities ranging from discrete 0D to 3D can be obtained, in function of the nature of CuX (X = Cl, Br, I, CN) and the metal-to-ligand ratio. We highlighted furthermore that with CuI an original 3D network  $[{Cu_8(\mu_3-I)_8}(\mu_2-2$ methyl-1,3-dithiane)<sub>4</sub>]<sup>*n*</sup> can be constructed, which incorporates strongly luminescent and unprecedented octanuclear Cu<sub>8</sub>I<sub>8</sub>S<sub>8</sub> clusters as SBUs (Secondary Building Units).<sup>21</sup> The original idea of the present work was to try to obtain 3D CPs showing interesting structural and photophysical properties. For this, we raised the number of available S-donor sites from two to four using 2,2'-ethylenebis(1,3-dithiane) L1 ligand. We herein present our results on the coordination of L1 vis-à-vis CuX salts under varying reaction conditions. This cyclic bisdithioacetal, which has hitherto never been explored as ligand system, was chosen due to its structural resemblance with 2-methyl-1,3-dithiane L2, since it combines formally two C<sub>4</sub>H<sub>7</sub>S<sub>2</sub>CH<sub>2</sub>·moieties (Chart 1). This investigation on the coordination chemistry of L1 has been extended towards other soft metal salts, namely HgBr<sub>2</sub> and HgI<sub>2</sub> and we present the crystal structures of all novel CPs including that of L1. For comparison, HgI<sub>2</sub> and HgBr<sub>2</sub> were also treated with L2 and the resulting materials were characterized by means of single-crystal X-ray diffraction studies. Exploiting the presence of numerous uncoordinated *S*-donor sites in some of our sulphur-rich CuX materials presented in this work, we also succeed to use one example as precursor for a heterometallic HgI<sub>2</sub>CuI array and present here the crystal structure of the of the unique 1D ribbon of [{IHg( $\mu_2$ --I)<sub>2</sub>HgI( $\mu_2$ -I)<sub>2</sub>{Cu(MeCN)<sub>2</sub>}<sub>2</sub>( $\mu_2$ -L1)]<sub>n</sub> (CP12).

Chart 1. Overview of the investigated dithiane ligands and CPs including those previously published

Ligand	Metal	Х	CPs	SBU	Ligand L1/L2	Dimensi
		(Ligand:Metal			hapticity	onality
		Ratio)				
	Cu	<b>I</b> (1:1)	CP1	$Cu(\mu_2-I)_2Cu$	μ2	2D
$\frown$		<b>I</b> (1:2)	CP2	$Cu(\mu_2-I)_2Cu$	μ4	2D
 S. S		<b>I</b> (1:4)	CP3	$Cu_2(\mu_4-I)(\mu_2-I)$	μ4	2D
		<b>Br</b> (1:2)	CP4	Cu(µ2-Br)2Cu	μ4	2D
~~~		<b>Br</b> (1:3)	CP5	Cu(µ2-Br)3(MeCN)	μ4 and μ5	1D
s		<b>Cl</b> (1:2)	CP6	$Cu(\mu_2$ - $Cl)_2Cu$	μ4	2D
Ĺ	Hg	<b>I</b> (1:1)	CP7	Hgl <sub>2</sub>	μ2	1D
$\sim$		<b>Br</b> (1:1)	CP8	Hg <mark>Br</mark> 2	μ2	1D
L1		<b>Br</b> (1:2)	CP9	$Br_2Hg_2(\mu_2-Br)_2$	μ2	1D
		<b>Cl</b> (1:1)	CP11	HgCl <sub>2</sub>	μ2	1D
	Cu+Hg	<b>I</b> (1:1:1)	<b>CP12</b>	IHg(µ2-I)(µ2-	μ2	1D
				I){Cu(MeCN) <sub>2</sub>		
	Cu	<b>I</b> (1:1)	Ref <sup>21</sup>	Cu(µ2-I)2Cu	μ2	1D or
		<b>I</b> (1:2)	Ref <sup>21</sup>	Cu <sub>8</sub> (µ <sub>3</sub> -1) <sub>8</sub>	μ2	2D
$\bigcap$		<b>Br</b> (1:1)	Ref <sup>22</sup>	$Cu(\mu_2-Br)_2Cu$	$\mu_2$	3D
Ś, Ś		<b>Cl</b> (1:1)	Ref <sup>22</sup>	$Cu(\mu_2-Cl)_2Cu$	μ2	1D
						1D
L2	Hg	<b>I</b> (1:1)	D1	IHg(µ2-I)	$\kappa^1$	0D
		<b>Br</b> (1:1)	M1	Hg <mark>Br</mark> 2	$\kappa^1$	0D
		<b>Br</b> (1:2)	<b>CP10</b>	HgBr <sub>2</sub>	μ2	1D

#### **Results and discussion**

#### Structural Characterization of L1

The ethylene-bridged compound 2,2'-ethylenebis(1,3-dithiane) L1 was first synthesized in 1968 by Seebach et al. via treatment of 2,5-dimethoxytetrahydrofuran with 1,3propanethiol.<sup>24</sup> L1 is also an interesting ligand in organic chemistry and is used as starting material for the preparation of *cis*-jasmone or the preparation of  $\gamma$ -diketones, 2,5bis(trialkylsilyl)furans and 2,6-bis(trialkylsilyl)-4*H*-pyrans.<sup>25</sup> Except for the parent compound 1,3-dithiane and 2-phenyl-1,3-dithiane, most other 1,3-dithiane are liquids at ambient temperature. Therefore, the structural database is quite limited. Since L1 is also a solid, we recrystallized a commercial sample from hot EtOH and obtained a crystalline product suitable for an X-ray analysis. The molecular structure of this sulphur-rich compound is shown in Fig. 1, the crystallographic refinement data are gathered in Table S1. The six-membered dithiane-heterocycle of L1 adopts the chair conformation encountered also in 2-phenyl-1,3-dithiane.<sup>26</sup> Like the phenyl group in the latter thiaheterocycle, the C2 atom of methylene group linking the two six-membered rings occupies the equatorial position. The mid-point of the C2-C2# bond constitutes the symmetry centre of the two identical moieties. The bond lengths and angles in L1 are normal for this kind of molecules and deserve no further comments.



**Figure 1**. Molecular structure of **L1**. Selected bond lengths (Å) and angles (°): C1–S1 1.8134(6), C1–S2 1.8139(7), C3–S1 1.819(7), C5–S2 1.8111(7), C1–C2 1.5275(9), C2–C2# 1.5301(13); S2–C1–S1 112.72(3), C3–S1–C1 98.75(3), C5–S2–C1 99.00(3), S1–C1–C2 108.15(4), S2–C1–C2 110.05(4), C1–C2–C2# 113.12(7), C3–C4–C5 112.86(6).

#### Reaction of L1 with Cul

The reaction of CuI with 1 equivalent of L1 in a CH<sub>2</sub>Cl<sub>2</sub>/MeCN mixture affords CP1 in 89% yield (Scheme 1). X-ray suitable single crystals crystallizing in the monoclinic space group P2<sub>1</sub>/n were obtained from dissolution of solid samples in hot MeCN. In CP1, two sulphur atoms of L1 remain non-coordinated (Figures 2 and S1). Noteworthy, CP1 also contains three different types of rhomboids featuring different metric parameters. Within the Cu2-Cu2 SBU, the Cu–Cu distance is the shortest (dCu2···Cu2 2.8399(5) Å) and reaches 2.8820(4) Å within the Cu1-Cu4 SBU and 2.9436(5) Å in the Cu3-Cu3 SBU. Examples of CPs incorporating different types of Cu( $\mu_2$ -X)<sub>2</sub>Cu rhomboids within the same array are quite rare. We have already encountered such observations in two cases: a 1D CP[{Cu( $\mu_2$ -Br)<sub>2</sub>Cu}( $\mu$ -*p*-MeC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>C≡CCH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Me-*p*)<sub>2</sub>]<sub>n</sub>, showing two different type of Cu( $\mu_2$ -Br)<sub>2</sub>Cu SBUs with  $\Delta$ (Cu–Cu 0.0356 Å) and in a 1D ribbon [{Cu( $\mu_2$ -I)<sub>2</sub>Cu SBUs with  $\Delta$ (Cu–Cu 0.0489 Å).<sup>22, 27</sup> The difference in the Cu–Cu distance in CP1 is clearly much more significant with  $\Delta$ (Cu–Cu 0.1037 Å). To our knowledge, the occurrence of three different rhomboids in a network is unprecedented.

When the reaction was performed in a 1:2 ratio, the resulting colourless product was crystallographically characterized as a 2D CP of composition  $[{Cu(\mu_2-I)_2Cu}(\mu_4-L1)]_n$  (CP2) (Scheme 1). Likewise, as in CP1, the CP2 network is also built upon Cu( $\mu_2$ -I)\_2Cu rhomboids but unlike in CP1, all sulphur atoms are now coordinated in a  $\mu$ -1 $\kappa$ S:2 $\kappa$ S:3 $\kappa$ S:4 $\kappa$ S coordination mode (Figures 3 and S2). Both copper(I) ions of the central dimeric Cu<sub>2</sub>I<sub>2</sub> motif possess the same fourfold coordination to two iodine and two sulphur atoms, respectively, resulting in a distorted tetrahedral geometry. A more striking observation is the short Cu–Cu distance of 2.6131(9) Å. This distance is much shorter than what was already observed for other 2D CPs containing the S<sub>2</sub>Cu<sub>2</sub>I<sub>2</sub>S<sub>2</sub> motif obtained by the reaction of CuI with the parent 2-methyldithiane L2 (*d*Cu···Cu 2.7664 Å),<sup>21</sup> the bis(benzylthio)butane (*d*Cu···Cu 2.796 Å)<sup>28</sup> and 1,4-bis(phenylthio)but-2-ene ligands (*d*Cu···Cu 2.6485 Å).<sup>29</sup> This distance is even shorter than that found in [Cu<sub>2</sub>I<sub>2</sub>(THT)<sub>4</sub>] (THT = tetrahydrothiophene) (*d*Cu···Cu 2.675(2) Å).<sup>16</sup>.

Increasing further the CuI amount to 4 equivalents led to the formation of the 2D **CP3** containing  $Cu1(\mu_2-I_2)(\mu_4-I_1)Cu2$  SBUs (Figures 4 and S3). Each Cu1-Cu2 segment is

bridged by a  $\mu_2$ -type I2 atom with Cu1–I2 and Cu2–I2 distances of 2.5953(10) Å and 2.5791(10) Å, respectively. Three Cu1-Cu2 segments are capped by a  $\mu_4$  type I1 ligand with two coordination to the same Cu1-Cu2 segments and two to Cu1 and Cu2 atoms coming from two different segments. Quite similar motifs were encountered in the 1D ribbon obtained by reaction of 2-trimethylsilyl-1,3-dithiane with CuI.<sup>22</sup> However, the connectivity between copper atoms differs in **CP3** with much shorter Cu1-Cu2 distance: 2.8584(13) Å *vs* 3.3975 Å but much longer Cu2-Cu2 and Cu1-Cu1 separations 3.361 Å *vs* 2.8203 Å for Cu1-Cu1 and 3.578 Å *vs* 3.362 Å for Cu2-Cu2. The experimental and simulated PXRD spectra of **CP1, CP2** and **CP3** are depicted in the Supporting Information as Fig. S11, S12 and S13, respectively..



2D **CP3** [{Cu( $\mu_4$ -I)( $\mu_2$ -I)Cu}<sub>2</sub>( $\mu_4$ -L1)]<sub>n</sub>

Scheme 1. Synthesis of CP1, CP2 and CP3 employing various CuI-to-L1 ratios.



**Figure 2.** View down the *a* axis on a segment of the 2D layer of  $[\{Cu(\mu_2-I)_2Cu\}(\mu_2-L1)_2]_n$  (CP1). Selected bond lengths (Å) at 100 K: Cu1–I1 2.6701(3), Cu1–I4<sup>4</sup> 2.6761(3), Cu2–I2 2.6518(3), Cu2<sup>2</sup>–I2 2.6832(3), Cu3–I3 2.6440(3), Cu3<sup>3</sup>–I3 2.6936(3), Cu4–I4 2.6518(3), Cu4<sup>1</sup>–I1 2.6761(3), Cu1–Cu4<sup>1</sup> 2.8820(4), Cu2–Cu2<sup>2</sup> 2.8399(5), Cu3–Cu3<sup>3</sup> 2.9436(5), Cu1–S2 2.2880(5), Cu1–S3 2.2924(5), Cu2–S6 2.2829(5), Cu2–S7 2.2788(5), Cu3–S10 2.3139(5), Cu3–S11 2.3183(5), Cu4–S14 2.3157(5), Cu4–S15 2.3123(5), Symmetry transformations used to generate equivalent atoms: <sup>1</sup>+ *x*, + *y*, 1+*z*; <sup>2</sup>1-*x*, 2-*y*, 1-*z*; <sup>3</sup>1-*x*, 1-*y*, 1-*z*; <sup>4</sup>+*x*, +*y*, -1+*z*.



**Figure 3.** View down the *b* axis on a segment of the 2D layer of  $[{Cu(\mu_2-I)_2Cu}(\mu_4-L1)]_n$  (**CP2**). Selected bond lengths (Å) at 100 K: Cu–S1 2.3025(9), Cu–S2 2.3045(9), Cu–Cu# 2.6131(9), Cu–I 2.6414(5), Cu–I# 2.6690(5). Symmetry transformations used to generate equivalent atoms: <sup>1</sup>-*x*, 2-*y*, 1-*y*; <sup>2</sup>-1+*x*, +*y*, +*z*; <sup>3</sup>1-*x*, 2-*y*, 2-*z*.



**Figure 4.** *Top* View down the *c* direction on a segment of the 2D layer of  $[\{Cu(\mu_4-I)(\mu_2-I)Cu\}_2(\mu_4-L1)]_n$ (**CP3**). Selected bond lengths (Å) at 100 K: I1–Cu1<sup>1</sup> 2.7914(10), I1–Cu1 2.6056(9), I1–Cu2 2.6043(11), I1–Cu2<sup>2</sup> 2.8749(12), I2–Cu1<sup>3</sup> 2.5953(10), I2–Cu2 2.5791(10), Cu1–Cu2<sup>4</sup> 2.8584(13), Cu1–S1 2.2713(17), Cu2–S2 2.2624(17) Symmetry transformations used to generate equivalent atoms: <sup>1</sup>-*x*,1-*y*,1-*z*; <sup>2</sup>1-*x*,1-*y*,1-*z*; <sup>3</sup>1+*x*,+*y*,+*z*; <sup>4</sup>-1+*x*,+*y*,+*z*; <sup>5</sup>1-*x*,-*y*,1-*z*. *Bottom* view of the Cu1–Cu2 segments spanned by  $\mu_2$ -I and  $\mu_4$ -I atoms.

#### Reaction of L1 with CuBr

We recently reported the coordination of the 2-methyl-1,3-dithiane **L2** ligand toward CuBr in a 1:1 ratio. The crystal structure evidences the formation of the 1D CP [{Cu( $\mu_2$ -Br)\_2Cu}{( $\mu_2$ -L2)\_2]\_n in which the SBUs are constituted of dinuclear Cu( $\mu_2$ -Br)\_2Cu rhomboids spanned by both sulphur atoms of L2 with nonbonding Cu···Cu# contacts of 3.176 Å.<sup>21, 22</sup>

To compare the coordination properties of L1 vs. L2, we reacted CuBr with L1 employing a 2:1 metal-to-ligand ratio (Scheme 2). After addition of the ligand to a MeCN solution of CuBr, instantaneous precipitation of a large amount of a colourless product was noticed. However, since we failed to obtain X-ray-suitable single-crystals from hot MeCN, a part of the sample was dissolved in refluxing propionitrile in which crystals suitable for X-Ray analyses could be obtained. The resulting 2D material of composition  $[{Cu(\mu_2-Br)}_2(\mu_4-$ L1)]<sub>n</sub> CP4 crystallized in the monoclinic space group  $P2_1/c$  (Figures 5 and S4). The homogeneity of the sample was ascertained by recording the PXRD pattern (Fig. S12). Surprisingly, despite the similar reaction conditions for the preparation of [{ $Cu(\mu_2-$ I)<sub>2</sub>Cu $(\mu_4$ -L1)]<sub>n</sub> (CP2), the 2D architecture of CP4 shown in Figure 5 is strikingly different. The Cu atoms are not associated in the form of rhomboidal  $Cu(\mu-Br)_2Cu$  dimers but as isolated Cu atoms interconnected via a single  $\mu$ -2 halide ligand with a Cu1-Cu2 distance of 3.681 Å, far above the sum of the van der Waals radii of two Cu atoms. The same structural arrangement was obtained in our group upon reaction of 1,3-dithiolane with CuBr in a 1:1 ratio leading to a 1D CP crystallizing, as CP4, in the  $P2_1/c$  space group.<sup>20</sup> In **CP4**, the 2D-dimensionality is ensured through the use of the tetrathioether **L1** ligand. To our knowledge, these two CPs constitute the only examples encountered in thioetherassembled Cu(I) CPs.

Since both **L1** and the products of the reaction between **L1** and CuBr are poorly soluble in acetonitrile, we tried to grow crystals by slow diffusion of an acetonitrile solution of CuBr into a dichloromethane solution of **L1** in a 1:1 ratio. Well-shaped colourless crystals were obtained under these conditions. Surprisingly, a single-crystal diffraction analysis revealed the formation of a 1D material **CP5** having a composition (CuBr)<sub>3</sub>(**L1**)(MeCN)], *i.e.* a 3:1 metal-to-ligand ratio (Fig 6). We therefore repeated the reaction of **L1** with CuBr in acetonitrile using a 1:3 ratio (Scheme 2). Figure 7 shows the excellent concordance

between the experimental PXRD pattern recorded at room temperature for the obtained white precipitate and the calculated one issued from single crystal X-ray data recorded at 100 K. This confirms (*i*) the formation of the same product (**CP5**) and (*ii*) the absence of any phase transition in this 193 K range. Furthermore, elemental analyses also confirmed this 3:1 CuBr-to-**L1** composition. The IR spectrum of **CP5** also presents two weak peaks at 2309 and 2265 cm<sup>-1</sup> characteristic of the v(C=N) vibration of coordinated acetonitrile (Figure S20).<sup>30</sup> As for **CP4**, the Cu atoms are interconnected through  $\mu_2$ -bromide ligands, but **CP5** contains (*i*) six crystallographically independent CuBr units, (*ii*) two differently ligating **L1** and (*iii*) two metal-bound acetonitrile molecules. Five of the copper(I) centers present CuBr2S2 (Cu3, Cu5 and Cu6) or CuBr2NS (Cu1 and Cu4) classical tetrahedral coordination geometry. Surprisingly, Cu2 adopts a triangular CuBr2S geometry with a sum of bond angles around Cu2(I) center (∠Br3-Cu2-S3, ∠S3-Cu2-Br2 and ∠Br3-Cu2-Br2) equal to 359.97° and Cu2-S3, Cu2-Br3 and Cu2-Br2 bond lengths equal to 2.2173(11), 2.3649(7) and 2.3694(7) Å, respectively. The very loose Cu2···S6 contact of 3.045 Å cannot be considered as bonding.

Whereas a triangular geometry around a Cu(I) center has been encountered with thiolate and thion ligands,<sup>31, 32</sup> to our knowledge, just only one other thioether example has been reported in the literature. In 2001, Schröder *et al* reacted CuCl with the tetradendate ligand 1,4,7,10-tetrathiacyclododecane ([12]aneS4) yielding the mononuclear complex [CuCl([12]aneS4)], for which the copper(I) centre is disordered over two positions in an approximate 7 : 1 ratio.<sup>9</sup> In the minor component, the Cu atom adopts a distorted trigonal planar coordination geometry ( $\Sigma$ (angles) =359.5°) with two coordination to sulphur atoms [Cu–S 2.279(8), 2.320(8) Å] and one to a chloride ligand [Cu–Cl 2.266(7) Å]. Noteworthy in the unprecedented architecture of **CP5** is also the dissymmetric µ4-bonding mode of S1 atom with bridges as 4-electron donor both the Cu1 and Cu6 atoms [Cu1-S1 2.2730(11), Cu6-S1 2.7692(11) Å]. **CP5** extends to a 2D supramolecular layered framework through intermolecular C-H…Br interactions. (Fig. S5 and Table S8).



1D **CP5** [{ $Cu(\mu_2-Br)$ }<sub>3</sub>(CH<sub>3</sub>CN)( $\mu_4-L1$ )<sub>0.5</sub>( $\mu_5-L1$ )<sub>0.5</sub>]<sub>n</sub>

Scheme 2. Synthesis of CP4 and CP5.



**Figure 5.** View down the *c* axis on a layer of the 2D network of  $[{Cu(\mu_2-Br)}_2(\mu_4-L1)]_n$  (**CP4**). The H atoms are omitted for clarity. Selected bond lengths [Å] at 100 K: Cu1–S1 2.2857(7), Cu1–S3<sup>2</sup> 2.3220(7), Cu2–S2 2.2743(7), Cu2–S4<sup>3</sup> 2.3046(7), Cu1–Br1 2.4525(5), Cu1–Br2 2.4887(5), Cu2<sup>1</sup>–Br1 2.5229(5), Cu2–Br2 2.5022(5); Symmetry transformations used to generate equivalent atoms: <sup>1</sup>1+*x*, <sup>1</sup>/<sub>2</sub>-*y*, <sup>1</sup>/<sub>2</sub>+*z*; <sup>2</sup>1-*x*, 1-*y*, 1-*z*; <sup>3</sup>1-*x*, -1/2+*y*, 1/2-*z*; <sup>4</sup>1-*x*, -1/2+*y*, 1/2-*z*.



d(Cu2.....S6) 3.045 Å

**Figure. 6.** View of a segment of the 1D ribbon of  $[{Cu(\mu_2-Br)}_3(MeCN)(\mu_4-L1)_{0.5})(\mu_5-L1)_{0.5}]_n$  (CP5) running along the *b* axis. The H atoms are omitted for clarity. Selected bond lengths [Å] at 100 K: Cu1–Br1 2.5911(7), Br1–Cu6 2.3911(7), Br2–Cu2 2.3694(7), Br2–Cu4<sup>1</sup> 2.5665(7), Br3–Cu2 2.3649(7), Br3–Cu3 2.5187(7), Br4–Cu3 2.4179(7), Br4–Cu4 2.4928(7), Br5–Cu1<sup>2</sup> 2.4852(7), Br5–Cu5 2.4270(6), Br6–Cu5 2.5198(6), Br6–Cu6 2.3610(7), Cu1–S1 2.2730(11), Cu1–N1 1.969(4), Cu2–S3 2.2173(11), Cu3–S4

2.2771(11), Cu3–S5 2.3222(11), Cu4–S6 2.2772(12), Cu4–N2 1.984(4), Cu5–S2<sup>2</sup> 2.3362(11), Cu5–S7 2.2716(11), Cu6–S1 2.7692(11), Cu6–S8 2.2299(12), Cu2–S3 2.2173(11), Cu3–S4 2.2771(11), Cu3–S5 2.3222(11), Cu4–S6 2.2772(12), Cu4–N2 1.984(4), Cu5–S2<sup>2</sup> 2.3362(11), Cu5–S7 2.2716(11), Cu6–S1 2.7692(11), Cu6–S8 2.2299(12); Symmetry transformations used to generate equivalent atoms:  ${}^{1}+x,-1+y,+z$ ;  ${}^{2}+x,1+y,+z$ .



Figure 7. Comparison of the experimental PXRD pattern of CP5 with the simulated one.

#### Reaction of L1 with CuCl

The coordination aptitude of **L1** towards CuCl was also compared to that of **L2**. For memory, we have shown that, when reacting **L2** with CuCl in a 1:1 ratio, the 1D CP  $[{Cu(\mu_2-Cl)_2Cu}(\mu_2-L2)_2]_n$  was obtained, in which the SBUs are constituted of dinuclear  $Cu(\mu_2-Cl)_2Cu$  rhomboids.<sup>22</sup>

Fast and almost quantitative precipitation of a colourless product occurred also upon mixing a MeCN solution of **L1** with two equivalents of CuCl (Scheme 3). Since attempts to grow X-ray suitable crystals from hot MeCN failed due to its poor solubility, a sample was dissolved in hot benzyl cyanide.



Scheme 3. Synthesis of CP6.

Now, small needle-shaped single crystals could be grown, crystallizing in the monoclinic space group C2/m. In line with the elemental analysis, an X-ray diffraction analysis confirmed a composition of two CuCl units per L1 molecule. The crystal structure of  $[{Cu(\mu_2-Cl)_2Cu}(\mu_4-L1)]_n$  (CP6) shown in Figures 8 and S6 reveals formation of a twodimensional network, in which centrosymmetric  $\{Cu(\mu_2-Cl)_2Cu\}$  SBUs are interconnected through bridging L1 molecules, in which all 4 S-donors are involved in the bonding, reminiscent to the architecture of  $\{Cu(\mu_2-I)_2Cu\}(\mu_4-L1)\}_n$  (CP2). Like in the latter, all 4 atoms of the { $Cu(\mu_2-X)_2Cu$ } units lie in the same plane. However, whereas in **CP2** the Cu....Cu contacts are unusually short, those of CP6 are now extremely elongated and lie now at the far side (2.6131(9) vs. 3.147 Å). Among the rare examples of 2D networks incorporating  $\{S_2Cu(\mu_2-Cl)_2CuS_2\}$  rhomboids are  $[\{Cu(\mu_2-Cl)_2Cu\}\{\mu-BzS(CH_2)_6SBz\}_2]_n$  $(dCu\cdots Cu \ 2.9570(14) \ \text{Å})$  and  $[\{Cu(\mu_2-Cl_2Cu)\}\{\mu-BzS(CH_2),SBz\}_2]_n \ (dCu\cdots Cu$ 2.6939(4) Å).<sup>28</sup> The comparison of these three CuCl-based 2D compounds demonstrates that also in  $\{Cu(\mu_2-Cl)_2Cu\}$  rhomboids an extreme flexibility of the Cu····Cu contacts may occur ranging from bonding to clearly non-bonding. Note that as mentioned above, in the reaction of CuCl with 2-methyldithiane L2, a 1D ribbon  $[{Cu(\mu_2-Cl)_2Cu}(\mu_2-L2)_2]_n$  was generated, featuring somewhat shorter Cu....Cu contacts with respect to those of CP6 (3.0517(8) vs. 3.147 Å). The Cu–S bond length of **CP6** matches with that of [{Cu( $\mu_2$ -Cl)<sub>2</sub>Cu $(\mu_2$ -L2)<sub>2</sub>]<sub>n</sub> (2.2924(8) vs. 2.3060(4) Å). <sup>22</sup> The experimental and simulated PXRD patterns of **CP6** are depicted in the Supporting Information as Fig. S15.



**Figure 8.** View down the *a* axis on a segment of the 2D layer of  $[{Cu(\mu_2-Cl)_2Cu}(\mu_4-L1)]_n$  (CP6). The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) at 100 K: Cu–S 2.2924(8), Cu···Cu# 3.147, Cu–Cl 2.2961(11), Cu–Cl# 2.4549(12); S–Cu–S# 109.01(4), S–Cu–Cl 118.74(2), S–Cu–Cl# 105.28(3), Cl–Cu–Cl# 97.110(14), Cu–Cl–Cu# 82.89(4). Symmetry transformations used to generate equivalent atoms: <sup>1</sup>1-*x*, 2-*y*, 2-*z*; <sup>2</sup>+*x*, 2-*y*, +*z*; <sup>3</sup>1-*x*, 1-*y*, 1-*z*.

#### Reaction of L1 and L2 with $HgI_2$

Another soft metal ion having a high affinity to organosulfur ligands is the closed-shell d<sup>10</sup> Hg(II) ion. Selected examples of molecular complexes and CPs ligated with dialkylsulfides and acyclic dithioether are CH<sub>3</sub>SCH<sub>2</sub>CH<sub>3</sub>•HgCl<sub>2</sub>,<sup>33</sup> [HgCl<sub>2</sub>(CH<sub>3</sub>SPh)]<sub>n</sub>,<sup>34</sup> [(EtS(CH<sub>2</sub>)<sub>2</sub>SEt)HgBr( $\mu$ -Br)Hg(Br)( $\mu$ -Br)<sub>2</sub>Hg(Br)( $\mu$ -Br)( $\mu$ -Br)<sub>2</sub>Hg(Br)( $\mu$ -Br)( $\mu$ -Br

We were intrigued whether L1 could be used as assembling ligand to construct original coordination network as observed with CuX salts. This is *a priori* not a evident task, since

several papers report on the use of Hg(II) salts as Lewis acids to cleave cyclic thioacetals such as dithiolanes and dithianes, converting them to aldehydes or ketones.<sup>43-45</sup> For example, a protocol allowing an efficient and fast deprotection of cyclic thioacetals by Hg(NO<sub>3</sub>)<sub>2</sub> even in the solid state has been described.<sup>46</sup>

On the other hand, an IR spectroscopic investigation dating from the sixties indicated formations of tetrahedral adducts  $HgX_2S_2$  through equatorial donation of a sulphur lonepair of 1,3-dithiane. According to this study, the mercury-sulphur bond varies in strength in the order Cl > Br > I.<sup>47</sup> An adduct formation between  $Hg(OAc)_2$  and 1,3-dithiane in solution was also evidenced by <sup>199</sup>Hg NMR spectroscopy.<sup>48</sup> An ESI-mass spectroscopy investigation indicated formation of a stable associate between  $HgCl_2$  and 1,1'-bis(1,3dithiane-2-yl)ferrocene.<sup>49</sup> Even the possibility to use 1,3-dithiane as assembling ligand for the construction of a CP has been demonstrated in the seventies by the crystallographic characterization of 1D-polymeric 1,3-dithiane-dimercury(I) dinitrate.<sup>50, 51</sup>

We first treated **L1** with two equivalents of HgI<sub>2</sub> in refluxing toluene. However, even after a reaction time of several hours, unreacted red  $\alpha$ -HgI<sub>2</sub> co-crystalized along with the paleyellow product [(HgI<sub>2</sub>)( $\mu$ <sub>2</sub>-L1)]<sub>n</sub> (CP7). To circumvent this co-crystallization, addition of a further equivalent of L1 was required to complete the reaction, allowing to isolate now pure CP7 in over 85% yield (Scheme 4).



Scheme 4. Synthesis of CP7 and D1.

A crystal structure determination (Fig. 9) of this air-stable material confirmed the 1:1 metal-to-ligand composition. This material forms a meander-like 1D ribbon, in which HgI<sub>2</sub> units are exclusively ligated through the S1 and S3 atoms of the centrosymmetric L1 molecules. The S2 and S4 atoms are not involved in any Hg-S bonding. The mean Hg-S bond length of 2.6574(8) Å matches well with those reported for 1D CP [HgI<sub>2</sub>{ $\mu_2$ -1,4bis(methylsulfanyl)methyl)benzene}]<sub>n</sub> (2.6431(13) and 2.6619(13) Å).<sup>40</sup> Far longer Hg–S found for the dinuclear complex bond lengths are  $[(HgI_2)_2(\mu_2-(1,2,4,5$ tetrakis(cyclohexylsulfanyl)methyl)benzene] (2.749(3) and 2.787(3) Å) and 1D-polymeric  $[HgI_2(\mu-1,4,8,11-tetrathiacyclotetradecane)]_n$  (2.752 (3) Å).<sup>52, 53</sup> The two Hg–I bond lengths are slighly different, their mean distance of 2.7077(2) Å is similar to that of  $[HgI_2(\mu_2-1,4-bis((methylsulfanyl)methyl)benzene)]_n$  (2.7241(4) Å). For the latter two compounds, the mean Hg–I bond lengths are shorter and lie between 2.661(2) and 2.658(1) Å. The coordination sphere around the mercury atom is somewhat distorted from regular tetrahedral; the bond angles range 102.866-121.843°. The I1–Hg–I2 angle of 121.843° is more acute than for the other three compounds, which are 124.98(2), 145.87(3), and 136.31(6)°, respectively. The experimental and simulated PXRD patterns of CP7 are depicted in the Supporting Information as Fig. S16.



**Figure 9.** View of a segment of the 1D chain of  $[(HgI_2)(\mu_2-L1)]_n$  (**CP7**). The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) at 100 K: Hg–S1 2.6712(8), Hg–S3 2.6436(7), Hg–I1 2.6950(2), Hg–I2 2.7203(2); S1–Hg–S3 110.53(2), S1–Hg–I1 105.027(17), S1–Hg–I2 102.866(17), S3–Hg–I1 110.603(17), S3–Hg–I2 105.53(2), I1–Hg–I2 121.843(8), Symmetry transformations used to generate equivalent atoms: <sup>1</sup>2-*x*, -*y*, 2-*z*; <sup>2</sup>2-*x*, 1-*y*, 1-*z*.

A survey of the CSD database (version 5.41 – March 2020 update) reveals that despite an indexation of over 135 entries for  $HgX_2 \bullet$  thioether compounds, most of these examples are dominated by HgCl2 and HgBr2 adducts. The few examples of HgI2 adducts are essentially thiamacrocyclic complexes such 1D as [HgI<sub>2</sub>(µ-1,4,8,11tetrathiacyclotetradecane)]<sub>n</sub> or the molecular complex  $[HgI_2(2,5-dioxa-8,11-dithia-$ 1,6(1,2)-dibenzenacyclododecaphane-S,S'].<sup>52, 53</sup> Among the few acyclic HgI<sub>2</sub> adducts are the above mentioned CP  $[HgI_2{\mu_2-1,4-bis(methylsulfanyl)methyl)benzene)}]_n$  and dinuclear  $[(HgI_2)_2(\mu_2-(1,2,4,5-tetrakis(cyclohexylsulfanyl)methyl)benzene]$ .<sup>40, 53</sup> This paucity of structurally characterized  $HgI_2$  adducts and the fact that  $HgI_2$  does not form a 2:1 material with L1, intrigued us to conduct the analogous reaction with 2-methyl-1,3dithiane L2. Although sterically less crowed than L1, we failed to convert entirely HgI<sub>2</sub> to a thioether complex even in hot toluene, using a 1:1 L2-to-Hg ratio. The co-crystallization of HgI<sub>2</sub> could only be suppressed by adding a slight excess of L2 to a toluene suspension of  $HgI_2$  (Scheme 4). After this modification, the thioether adduct **D1** was straightforwardly obtained upon heating in toluene during 2h. After allowing to reach ambient temperature, a product of composition [(HgI<sub>2</sub>)(L2)] crystallized in form of large yellow blocks. Surprisingly, instead of an anticipated polymeric network, an X-ray diffraction study revealed formation of a discreet dinuclear complex [{ $IHg(\mu_2-I)_2HgI$ }( $\kappa^1-L2$ )<sub>2</sub>] **D1** (Fig. 10). In this molecular compound, which, from a topological point of view, is considered formally a 0D, each Hg(II) atom bears one terminal I2 ligand, the second I1 ligand is  $\mu_2$ bridging assuring the connectivity with the neighboured Hg atoms. The intermetallic separation of 4.099 Å is far too loose to be considered as bonding. The distorted tetrahedral coordination around each mercury atom is completed by a dative bond with the S1 atom of the L2 ligand, where the S2 atom does not participate in bonding. To the best of our knowledge, there is just one other crystallographically molecular complex featuring a  $S(I)Hg(\mu_2-I)_2Hg(I)S$  scaffold, namely  $[(NO_2S_2)S(I)Hg(\mu_2-I)_2Hg(I)(NO_2S_2)]$  ligated by the 18-membered thiaoxamacrocycle bis(16-(4-(4-nitrophenylazo)phenyl)-2,5-dioxa-13,19dithia-16-azatricyclo(19.4.0.06,11)pentacosa-1(21),6,8,10,22,24-hexaene) (CSD refcode PEGXU).<sup>54, 55</sup> The metric parameters of the latter complex are quite similar with those of **D1**. In both compounds, the three Hg-I bond distances are quite different, the shortest being the terminal one (2.6920(6) *vs.* 2.6610(3) Å), the bond lengths of the dissymmetrically bridging  $\mu_2$ -iodo ligand are 2.7080(6) *vs.* 2.7252(3) and 3.1541(7) *vs.* 3.2078(3) Å, respectively. Also, the Hg–S bond lengths of the two compounds match well (2.5983(18) *vs.* 2.5962(9) Å).



**Figure 10.** View of dinuclear complex [ $\{IHg(\mu_2-I)_2HgI\}(\kappa^1-L2)_2$ ] (**D1**). The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) at 100 K: Hg–S1 2.5962(9), Hg–I1 2.7252(3), Hg–I2 2.6610(3), Hg–I1# 3.2078(3); S1–Hg–I1 114.35(2), S1–Hg–I2 116.58(2), S1–Hg–I1# 91.07(2), I1–Hg–I2 127.203(11), I1–Hg–I1# 92.996(10). Symmetry transformation used to generate equivalent atoms: <sup>1</sup>1-*x*, 1-*y*, 1-*z*.

#### Reactions of L1 and L2 with HgBr<sub>2</sub>

To investigate the effect of the nature of the halide on the architecture, L1 was also mixed with one equivalent of HgBr<sub>2</sub> and heated in hot toluene for 3h. After allowing to reach ambient temperature, colourless needle-shaped crystals were formed and isolated in 68% yield (Scheme 5). Elemental analysis confirmed a 1:1 composition [(HgBr<sub>2</sub>)(L1)] as for CP7.



Scheme 5. Synthesis of CP8, CP9, M1 and CP10.

However, crystallographic analysis indicated that instead of the triclinic space group P-1 encountered for **CP7** this material had crystalized in the orthorhombic space group  $Pna2_1$  (Table S5). Indeed, an X-ray diffraction study revealed that in the 1D polymeric ribbon of  $[(HgBr_2)(\mu_2-L1)]_n$  (**CP8**) shown in Figure 11, the meander-like conformation of **CP7** is no longer present and a description as linear is more appropriate. Each tetrahedrally coordinated Hg center is ligated by two terminal bromide ligands and the S1 and S4 donor sites of **L1**. The mean Hg–S bond length of **CP8** is slightly shorter than that of its iodo-analogue **CP7** (2.6362(16) *vs.* of 2.6574(16) Å). A somewhat reminiscent single-chain structure has been reported for [{BzS(CH<sub>2</sub>)<sub>4</sub>SBz}HgBr<sub>2</sub>]<sub>n</sub>, in which adjacent HgBr<sub>2</sub> units (Hg–Br 2.5823(8) and 2.5165(8) Å) are linked by the bridging dithioether ligand.<sup>38</sup> The packing of the parallel running ribbons of **CP8** is shown in the ESI as Figure S7 and the experimental and simulated PXRD patterns of **CP8** are depicted in the Supporting Information as Fig. S17.



**Figure 11.** View of a segment of the 1D chain of  $[(HgBr_2)(\mu_2-L1)]_n$  (**CP8**). The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) at 100 K: Hg–S1 2.6098(16), Hg–S4 2.6625(16), Hg–Br1 2.5841(11), Hg–Br2 2.5810(11); S1–Hg–S4 116.69(4), S1–Hg–Br1 103.77(4), S1–Hg–Br2 108.63(4), S4–Hg–Br1 108.42(4), S4–Hg–Br2 103.80(4), Br1–Hg–Br2 115.716(18), Symmetry transformations used to generate equivalent atoms:  ${}^{1}-1/2+x$ , 1/2-y, +z;  ${}^{2}1/2+x$ , 1/2-y, +z.

The same simple tetrahedral  $HgBr_2S_2$  motif was obtained when reacting  $HgBr_2$  with an excess of L2 in hot toluene. Upon cooling, fine colourless needles of the mononuclear complex [HgBr<sub>2</sub>( $\kappa^1$ -L2)<sub>2</sub>] (M1) crystallizing in the orthorhombic space groups  $P2_12_12_2$ (Table S7) were formed in 86% yield (Scheme 5). The molecular structure of M1 is shown in Figure 12 and consists of a bent HgBr<sub>2</sub> unit coordinated by two  $\kappa^1$ -bound 2methyldithiane ligands. The Hg–S bond length is slightly shorter than the mean distance found in **CP8** (2.6188(17) vs. 2.6362(16) Å). In contrast to [HgBr<sub>2</sub>{(PhSCH<sub>2</sub>)<sub>2</sub>SiPh<sub>2</sub>}],<sup>41</sup> in which the HgBr<sub>2</sub> angle is close to linearity, the angle Br-Hg-Br of M1 is strongly bent (160.39(4) vs. 115.96(3°). The only other crystallographically characterized molecular HgBr<sub>2</sub> complex ligated by a non-macrocyclic thioether ligand is [HgBr<sub>2</sub>(N-Benzoyl-1,3thiazolidine)<sub>2</sub>] (CSD refcode DICMEI) which features a more distorted tetrahedral geometry than M1 with Br-Hg-Br and S-Hg-S angles of 124.4(9) and 83.9(2)°, respectively.<sup>56</sup> With the objective to prepare a dinuclear compound [{BrIHg( $\mu_2$ -Br)<sub>2</sub>HgBr $(\kappa^1$ -L2)<sub>2</sub>] comparable to D1, M1 was reacted with an second equivalent of HgBr<sub>2</sub> in hot toluene according to Scheme 5. To our surprise, a single-crystal diffraction study revealed formation of a colourless 1D polymeric material  $[HgBr_2(\mu_2-L2)]_n$  (CP10). The crystal structure of **CP10** is shown in Figures 13 and S9 and presents a highly symmetric 1D chain with crystallography identical S atoms. The most relevant bond distances and angles are given in the caption of Figure 13 and deserve no special comment. Noteworthy is the occurrence of some weak intermolecular  $H\cdots Br$  bonding between the parallel running 1D chains of **CP10** generating a 3D supramolecular network (Fig. S9 and Table S9).



**Figure 12.** View of the molecular structure of  $[(HgBr_2)(\kappa^1-L2)]$  (**M1**). The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) at 100 K: Hg–S1 2.6188(7), Hg–Br 2.5913(7); S1–Hg–S1<sup>1</sup> 118.90(7), S1–Hg–Br 109.06(4), Br–Hg–Br<sup>1</sup> 115.96(3), Symmetry transformation used to generate equivalent atoms: <sup>1</sup>1-*x*, 1-*y*, +*z*.



**Figure 13.** View of a segment of the 1D chain of  $[(HgBr_2)(\mu_2-L2)]_n$  (**CP10**) running along the *a* axis. The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) at 100 K: Hg–S 2.6486(10), Hg–Br 2.5553(5); S1–Hg–S1<sup>1</sup> 113.21 (5), S–Hg–Br 102.46(4), S–Hg–Br<sup>1</sup> 109.81(2), Br–Hg–Br<sup>1</sup> 115.576(3), Symmetry transformation used to generate equivalent atoms: <sup>1</sup>1-*x*, 1-*y*, +*z*; <sup>2</sup>1/2-*x*, +*y*, +*z*.

We next treated **L1** with two equivalents of HgBr<sub>2</sub> in refluxing toluene. In this case, isolation of the pure reaction product was not hampered by co-crystallization of unreacted HgBr<sub>2</sub>. Elemental analysis of the needle-shaped colourless material, which has been isolated in 76% yield, supported a 2:1 HgBr<sub>2</sub>-to-**L1** ratio HgBr<sub>2</sub> (Scheme 5). An X-ray diffraction study of the product [{BrHg( $\mu_2$ -Br)<sub>2</sub>HgBr}( $\mu_2$ -L1)] (CP9), crystallizing in the monoclinic space group *C2/c* corroborates this composition. The crystal structure shown

in Fig. 14 reveals the formation of 1D ribbons, in which dinuclear BrHg( $\mu_2$ -Br)<sub>2</sub>HgBr units are interconnected through bridging centrosymmetric **L1** molecules. In contrast to the meander-type architecture of **CP7**, that of **CP9** can be described as stretched linear. The alignment of the parallel running ribbons in the packing is shown in Fig. S8. Within the dinuclear Hg<sub>2</sub>Br<sub>4</sub> SBUs, the two crystallographically identical Hg atoms are solely connected through two bridging bromo ligands, the loose separation of 4.091 Å excludes any intermetallic interaction. Overall, the motif is quite reminiscent to that of **D1**. Among the 30 entries for HgBr<sub>2</sub>• thioether adducts, there are two examples featuring a similar unit, namely 1D CP [Hg<sub>2</sub>Br<sub>4</sub>{BzS(CH<sub>2</sub>)<sub>4</sub>SBz}]<sub>n</sub> (*d*Hg···Hg 3.884 Å) and the molecular complex [Hg<sub>2</sub>Br<sub>4</sub>(phenothiazine-*S*)] (*d*Hg···Hg 4.001 Å).<sup>37, 57</sup>

Each Hg atom is tetrahedrally coordinated by one terminal Br2 atom, two  $\mu_2$ -type Br1 atoms and a datively bound S1 atom. The mean Hg–S bond length is somewhat shorter than that of **CP8** (2.5456(8) *vs*. 2.5825(11) Å). There is furthermore a very loose contact of 3.149 Å between the S2 atom and the Hg center, represented by the dashed lines in Fig. 14. Taking in account this incipient pentacoordination, the geometry may be alternatively considered as square pyramidal with Br2 occupying the apical position.



**Figure 14.** View of a segment of the 1D chain of  $[\{BrHg(\mu_2-Br)_2HgBr\}(\mu_2-L1)]_n$  (**CP9**). The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) at 100 K: Hg–S1 2.5456(8), Hg–Br1 2.5519(3), Hg–Br1# 3.0634(4), Hg–Br2 2.5383(4); S1–Hg–Br1 136.08(2), S1–Hg–Br1# 78.929(19), S1–Hg–Br2 111.05(2), Br1–Hg–Br2 112.750(12), Br1#–Hg–Br2 114.645(11), Br1–Hg–Br1# 85.973(102). Symmetry transformations used to generate equivalent atoms: <sup>1</sup>1-*x*, +*y*, 1/2-*z*; <sup>2</sup>-*x*, 1-*y*, 1-*z*.

#### Reaction of L1 with HgCl2

A 1D polymer featuring an architecture very similar to that of **CP8** was formed upon coordination of **L1** on  $HgCl_2$  in hot toluene (Scheme 6). Unfortunately, the poor

crystallographic quality of the colourless needles of the crystal structure shown in Fig. 15 does not allow a detailed discussion of the metric parameters. However, and in line with the elemental analysis, the data sets confirm without ambiguity the formation of a ribbon with composition  $[(HgCl_2)(\mu_2-L1)]_n$ , (CP11) in which tetrahedral HgCl<sub>2</sub> units are linked through bridging L1 ligands. The PXRD pattern also confirms the purity of the sample (Fig. S18).



Scheme 6. Synthesis of CP11.



**Figure 15.** View of a segment of the 1D chain of  $[(HgCl_2)(\mu_2-L1)]_n$  (CP11). The H atoms are omitted for clarity.

#### Reaction of CP1 with HgI2

The fact that the network of  $[{Cu(\mu_2-I)_2Cu}(\mu_2-L1)_2]_n$  (CP1) incorporates two noncoordinated sulphur atoms per L1 ligand, potentially available as donor sites for complexation of further metal centres, intrigued us to probe the construction of heterometallic networks. With this objective in mind, we prepared first CP1 *in situ* using hot acetonitrile as solvent (Scheme 7). After allowing to reach ambient temperature, one equivalent of HgI<sub>2</sub> was added to precipitated CP1. After stirring for 4h, an important part of the suspended **CP1** had been dissolved as well as red HgI2. The mixture was then heated to 80°C for one hour giving a yellowish clear solution. After allowing to reach ambient temperature, the growth of yellow crystals commenced. After partial evaporation of the solvent, the crystals were collected and analysed by X-ray diffraction.



Scheme 7. Synthesis of the heterometallic 1D polymer CP12.

Figure 16 shows that the initial 2D network of **CP1** has been broken and instead a heterometallic 1D ribbon has been formed. The chain is constructed of tetranuclear  $[IHg(\mu_2-I)_2HgI(\mu_2-I)Cu]$  blocks consisting of dimerized HgI<sub>2</sub> units interconnected by two  $\mu_2$ -I atoms. The tetrahedral coordination sphere around each Hg atom is completed by one terminal iodo ligand. These centrosymmetric  $IHg(\mu_2-I)_2HgI$  block share furthermore a second bridging  $\mu_2$ -I ligand with a Cu(I) atom, which bears two metal-bound MeCN ligands. The Hg...Hg and Hg...Cu separations of 3.394 and 3.991 Å exclude any intermetallic interactions.<sup>58</sup> These tetranuclear SBUs are linked through the S1 atoms of L1, generating thus a linear 1D ribbon. The Cu–S1 distance of 2.3005(7) Å is similar to the mean Cu–S bond lengths of 2.3003 Å encountered in **CP1**, all other metric parameters are presented in the caption of Figure 16. The parallel running arrangement of the ribbons of **CP12** in the packing is shown in Figure S10 and the PXRD pattern in Figure S19.



**Figure 16.** View of a segment of the heteronuclear 1D chain of  $[{IHg(\mu_2-I)_2HgI(\mu_2-I)_2}{Cu(MeCN)_2}_2(\mu_2-L1)]_n$  (CP12) running along the *c* axis. The H atoms are omitted for clarity. Selected bond lengths (Å) and

angles (°) at 100 K: Hg–I1 2.7283(3), Hg-I2 2.6848(3), Hg–I3 3.0222(3), Hg–I3<sup>1</sup> 2.8429(3), I1–Cu 2.6731(4), Cu–S1 2.3005(7), Cu–N1 1.984(2), Cu–N2 1.964(2); I1–Hg–I3<sup>1</sup> 110.012(8), I1–Hg–I3 97.895(7), I2–Hg–I1 124.575(8), I2–H1–I3<sup>1</sup> 114.804(8), I3<sup>1</sup>–Hg–I3 95.813(8), Cu1–I1–Hg 95.251(9), Hg<sup>1</sup>–I3–Hg 84.187(8), S1–Cu–I1 99.411(18), N1–Cu–I1 107.18(7), N1–Cu–S1 109.68(7), N2–Cu–I1 108.34(7), N2–Cu–S1 117.13(7), N2–Cu–N1 113.70(9), Symmetry transformations used to generate equivalent atoms: <sup>1</sup>-*x*,1-*y*,2-*z*; <sup>2</sup>1-*x*,2-*y*,1-*z* 

The presence of two Cu-bound acetonitrile ligands indicated by elemental analysis is also confirmed by the IR spectrum of **CP12**, which exhibits two v(CN) vibrations at 2296 and 2267 cm<sup>-1</sup> (Figure S21). Metal-bound MeCN ligands are often coordinated in a quite labile manner on a given metal center.<sup>59, 60</sup> However, in the case of **CP12**, no degradation of the yellow crystals by dissociation of volatile MeCN was observed, even upon exposure to air for prolonged periods.

Although several other examples of mixed paramagnetic Cu(II)/Hg compounds featuring an [Cu( $\mu_2$ -X)Hg( $\mu_2$ -X<sub>2</sub>HgX( $\mu_2$ -X)Cu] array like tetranuclear [Cu(bipy)<sub>2</sub>Hg<sub>2</sub>Cl<sub>6</sub>]<sub>2</sub> and 1D polymeric [Cu<sub>2</sub>(bipy)<sub>4</sub>Hg<sub>2</sub>Br<sub>6</sub>][Hg<sub>4</sub>Br<sub>10</sub>] are literature-known, an architecture as encountered for **CP12** is unprecedented.<sup>61, 62</sup> The most reminescent is that of [( $\mu$ -7,10,21,24-tetraoxa-4,13,18,27-tetrathiatricyclo[14.12.1.12,15]triaconta-1(29),2(30),15triene)-hexakis( $\mu$ -I)-bis(MeCN)-diiodo-tetra-copper(I)-di-mercury(II), in which a macrocyclic tetrathioether ligand is coodinated through two *S*-donor sites to a CuI(MeCN) fragment, which in turn is linked to mononuclear Hg(II) centres via shared  $\mu$ -I bridges (refcode JIBLEO).<sup>63</sup>

#### **Thermal properties**

All compounds were found to be stable for several months under ambient atmosphere. Since the thermal stability is of crucial role for application in material sciences, that of the copper-based **CP1-CP6** has been measured under air flow in the temperature range 20-850°C. TGA traces are depicted in Figure 17 and the first derivative plots of the TGA traces are given in the Supporting Information (Figures S22–S27). Decomposition temperatures (corresponding to a 5% loss of the total mass) are compared to those obtained with **L2**-based CPs reported previously and are summarized in Table 1.<sup>22</sup>

All CPs obtained with L1, except CP5, present high thermal stability with  $T_{dec}$  ranging from 232°C to 272°C. The thermal stability of **CP5** is the lowest ( $T_{dec} = 150$ °C) due to the loss of coordinated acetonitrile. After that initial degradation step, the decomposition profile of **CP5** looks alike those obtained with others copper iodide-based CPs. The presence of  $Cu(\mu_2-I_2)(\mu_2-I_4)Cu$  SBUs in **CP3** led to the highest thermal stability. As previously observed,<sup>22, 29</sup> the decomposition profiles of **CP1**, **CP2** and **CP3** containing iodide present two well-defined decomposition steps while those of CP4 and CP5 containing bromide presents three main losses. The decomposition of CP6 is even more complicated with at least four decomposition steps. This complicated decomposition profile led to an important difference between the theoretical and experimental values based on the ligand degradation (57% and 40%, respectively). However, for the other CPs, there is a good matching between the values. Finally, expect for **CP6**, the final residues might be attributed to the formation of CuO as evidenced by comparison between theoretical and experimental values. Comparison of the thermal stabilities between the different CPs obtained from L1 and L2 shows that L1-based CPs present higher thermal stabilities. The higher stability found in the present paper for CPs obtained with L1 might be attributed either to the fact that L2 has a boiling point of 78°C while L1 is a solid with melting point of  $132-135^{\circ}$ C or to the higher dimensionality obtained with L1 (2D vs 1D) while having same SBUs (see for example comparison between the 2D CP2 and the 1D CP [{Cu( $\mu_2$ -I)\_2Cu}( $\mu_2$ -L2)\_2]<sub>n</sub>).



**Figure 17.** TGA traces of **CP1-CP6** under air flow (rate 10°C.min<sup>-1</sup>)

Table I. TGA data for CPI-CP6.	Table 1.	TGA	data for	<b>CP1-CP6</b> .
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			Mass	Mass loss		Residual mass	
CP	$T_{\text{Dec}}$	Т	(%w	(%wt)		(%wt)	
CI	(°C)	(°C)	Theo	Exp	Theo.	Exp	
<b>2D CP1</b> [{Cu( $\mu_2$ -l) <sub>2</sub> Cu}( $\mu_2$ -L1) <sub>2</sub> ] <sub>n</sub>	236	100-340	58 <sup><i>a</i></sup>	52	17 <sup>c</sup>	19	
<b>2D CP2</b> [{Cu( $\mu_2$ -I) <sub>2</sub> Cu}( $\mu_4$ -L1)] <sub>n</sub>	235	100-345	41 <sup><i>a</i></sup>	39	25 <sup>c</sup>	28	
<b>2D CP3</b> [{Cu( $\mu_4$ -I)( $\mu_2$ -I)Cu} <sub>2</sub> ( $\mu_4$ -	272	100-340	26	28	31	28	
<b>L1</b> )] <sub>n</sub>		100-540	20	20	51	20	
$\mathbf{1D} \left[ \{ Cu(\mu_2 \textbf{-} \mathbf{I})_2 Cu \} (\mu_2 \textbf{-} \mathbf{L2})_2 \right]_n^d$	160 <sup>d</sup>						
<b>2D CP4</b> [{Cu( $\mu_2$ -Br)} <sub>2</sub> ( $\mu_4$ -L1)] <sub>n</sub>	241	100-350	46 <sup><i>a</i></sup>	48	29 <sup>c</sup>	34	
<b>1D</b> [{Cu( $\mu_2$ -Br) <sub>2</sub> Cu}( $\mu_2$ -L2) <sub>2</sub> ] <sub>n</sub> <sup>d</sup>	$187^{d}$						
<b>1D CP5</b> [{ $Cu(\mu_2-Br)$ } <sub>3</sub> (MeCN)( $\mu_4-$	150	60-160	5.6 <sup>b</sup>	5.6	32 <sup><i>c</i></sup>	31	
$L1)_{0.5})(\mu_5-L1)_{0.5}]_n$		150-300	36 <sup><i>a</i></sup>	40			
<b>2D CP6</b> [{Cu( $\mu_2$ -Cl) <sub>2</sub> Cu}( $\mu_4$ -L1)] <sub>n</sub>	232	100-350	57 <sup><i>a</i></sup>	40	34 <sup><i>c</i></sup>	44	
$\mathbf{1D} \left[ \{ \mathrm{Cu}(\mu_2 \operatorname{-} \mathbf{Br})_2 \mathrm{Cu} \} (\mu_2 \operatorname{-} \mathbf{L2})_2 \right]_n^d$	173 <sup>d</sup>						

<sup>*a*</sup> values determined based on ligand loss <sup>*b*</sup> value determined based on CH<sub>3</sub>CN loss <sup>*c*</sup> values determined based on the formation of CuO

<sup>*d*</sup> data from ref [21]

#### **Concluding Remarks and Perspectives**

This investigation has shown that commercially available and inexpensive 2,2'ethylenebis(1,3-dithiane) has, apart from its application as substrate in organic chemistry, also a promising potential as ligand in coordination chemistry. It may act, in function of the reaction conditions, both as tetradentate  $\mu_4$ - or bidendate  $\mu_2$ -type ligand, in which Sdonor atoms behave as a 2-electron donor. However, the observation of a bridging S atom in CP5 acting as a 4-electron donor demonstrates that, in contrast to tetradentate organophosphorous ligands, L1 is even able to extend its coordination to a  $\mu_5$ -bonding mode. In the case of the complexation with Cu(I) salts, in all cases formation of stable coordination polymers is observed, but a rational control of the network architecture is a difficult task.<sup>7, 64</sup> As already noticed in previous papers and by other research groups working on Cu(I) • thioether compounds, the outcome depends on too many factors like nature of the halide, metal-to-ligand ratio, reaction temperature, choice of the solvent, order of the addition of the reactants *etc.* But this unpredictability also opens the possibility to isolate and characterize hitherto unknown network architectures, as it is the case in the present study. Both CP1 and CP2 incorporate the very common rhomboid-shaped Cu( $\mu_2$ -I)<sub>2</sub>Cu motif as connecting nodes, but with very diverging  $Cu \cdots Cu$  separations ranging from 2.6131(9) to 2.9436(5) Å underlying the structural flexibility of this SBU. **CP1** represents furthermore an unique case incorporating three crystallographically non-equivalent  $Cu(\mu_2$ -I)<sub>2</sub>Cu SBUs. The 2D CP3 obtained by increasing the CuI ratio features both  $\mu_4$ -type and  $\mu_2$ -type halide ligands.

The situation becomes even more curious in the case of CuBr. In both **CP4** and **CP5**, no  $Cu(\mu_2-Br)_2Cu$  SBUs are present, instead (-Cu-Br-Cu-Br-)<sub>n</sub> chains are interconnected by  $\mu_4$ - or  $\mu_5$ -bridging **L1** ligands. The bonding situation within the 1D ribbon of [{Cu( $\mu_2$ -Br)}\_3(MeCN)( $\mu_4$ -L1)<sub>0.5</sub>)( $\mu_5$ -L1)<sub>0.5</sub>]<sub>n</sub> (CP5) gets even more exotic since this compound features also metal-coordinated MeCN molecules and, as highlight, presents an extremly scarce case of a low-coordinate trigonal Cu center. So the nuclearity differs much of the simple 1D architecture of [{Cu( $\mu_2$ -Br)\_2Cu}( $\mu_2$ -L2)<sub>2</sub>]<sub>n</sub> encountered with the structurally related 2-methyl-1,3-dithane L2 ligand. With CuCl, a 2D network [{Cu( $\mu_2$ -Cl)\_2Cu}( $\mu_4$ -L1)]<sub>n</sub> (CP6), at first glance, reminiscent to that of CP2 is formed, however the very loose

Cu···Cu contact of 3.147 Å underpins the high structural flexibility of the Cu( $\mu_2$ -X)<sub>2</sub>Cu motifs. As expected from the use of this tetrathioether ligand **L1**, the dimensionality of the resulting CPs was increased from 1D to 2D compared to those obtained with L2. Unfortunately, probably due to the steric hindrance in **L1**, we failed to isolate MOF-like 3D networks incorporating strongly luminescent polynuclear (CuI)<sub>n</sub> (n = 4, 6, 8) cluster as obtained with **L2** and other dithioether ligands.<sup>13, 21, 28, 65, 66</sup>

Although we did not investigate in depth the coordination chemistry of L1 and L2 towards  $HgX_2$  salts, we have evidenced that the composition of the resulting compounds can be influenced by the  $HgX_2$ -to-L ratio and that the dimensionality remains invariably 1D for L1. In contrast, reaction of L2 with  $HgI_2$  and  $HgBr_2$  may lead to formation of a discreet mono- or dinuclear complexes but may also give rise to a polymeric 1D chain. The fact that in sulphur-rich CP1 every second S atom is not engaged in dative M-S bonding has been successfully exploited to construct the heterometallic material [ $\{IHg(\mu_2-I)_2HgI(\mu_2-I)_2\{Cu(MeCN)_2\}_2(\mu_2-L1)\}_n$  (CP12) by addition of  $HgI_2$ . Several other compounds such as CP7, CP8, D1 and M1 also bear such potential *S*-donor sites. This feature opens the possibility for forthcoming work to construct systematically heterometallic assemblies by coordination of other ML<sub>n</sub> fragments or MX<sub>n</sub> salt, which may in turn serve as promising precursors for heterometallic sulphide phases and related materials.

#### **EXPERIMENTAL SECTION**

#### **Materials and Apparatus**

The CuX and HgX<sub>2</sub> salts, **L1** and **L2** were commercial obtained from Acros, Alfa Aesar and Aldrich. Infrared spectra were recorded with a 2 cm<sup>-1</sup> resolution on a Bruker vertex70 FTIR spectrometer using of a Platinum ATR accessory equipped with a diamond crystal. Thermogravimetric analysis (TGA) was carried out on a TA Instruments Q600 in an alumina crucible under an air flow with a heating rate of 10 °C min<sup>-1</sup> up to 850 °C.

#### **Syntheses**

**CP1.** To a solution a solution of CuI (191 mg, 1.0 mmol) in acetonitrile (20 mL) was added **L1** (271.5 mg, 1.02 mmol) in two portions.). Precipitation of a white product occurred immediately. The mixture was stirred for 2h at room temperature, and then heated to reflux

for 5 min to assure completion of the reaction. After reaching ambient temperature, the resulting microcrystalline precipitate was filtered off and air-dried. Yield (89%). To obtained X-ray suitable single-crystals, a 100 mg amount was redissolved in boiling MeCN and then allowed to reach slowly ambient temperature. mp =  $272^{\circ}$ C IR (ATR): 2931, 2900, 2826, 1427, 1410, 1307, 1272, 1252, 1237, 1177, 1134, 1108, 1028, 995, 906, 871, 829, 787, 756, 734, 678, 657, 616, 489, 421 cm<sup>-1</sup>. Anal. Calc. for C<sub>10</sub>H<sub>18</sub>CuIS<sub>4</sub> (456.96): C, 26.28; H, 3.97; S, 28.07. Found: C, 26.46; H, 3.95; S, 27.93 %.

**CP2.** L1 (271.5 mg, 1.02 mmol) was dissolved in a mixture of acetonitrile (30 mL) and dichloromethane (5 mL). To this solution was added a solution of CuI (388 mg, 2.03 mmol) in acetonitrile (20 mL). Precipitation of a white product occurred immediately. The mixture was stirred 2h at room temperature. The resulting precipitate was filtered and washed with 20 mL of acetonitrile and then 20 mL of dichloromethane. Yield: 80%. A small amount of the white powder was dissolved in hot acetonitrile. After two weeks, colourless crystals suitable for single X-ray diffraction were obtained.mp = 232°C. IR (ATR): 2969, 2919, 1409, 1277, 1245, 1186, 1148, 1106, 1089, 983, 953, 850, 726, 691, 670, 468 cm<sup>-1</sup>. Anal. Calc. for C<sub>10</sub>H<sub>18</sub>Cu<sub>2</sub>I<sub>2</sub>S<sub>4</sub> (647.36): C, 18.55; H, 2.80; S, 19.81. Found: C, 18.91; H, 2.80; S, 19.58%.

**CP3.** L1 (279.5 mg, 1.05 mmol) was dissolved in a mixture of acetonitrile (10 mL) and dichloromethane (5 mL). To this solution was added a solution of CuI (900 mg, 4.72 mmol) in acetonitrile (40 mL). Precipitation of a white product occurred immediately. The mixture was stirred 2h at room temperature. The resulting precipitate was filtered and washed with 20 mL of acetonitrile and then 20 mL of dichloromethane. Yield: 88%. Crystals suitable for X-Ray diffraction were obtained by slow diffusion of a dichloromethane solution of L1 into an acetonitrile solution of CuI (ratio ligand/metal 1:4) at room temperature. mp =  $281^{\circ}$ C. IR (ATR): 2941, 2926, 2893, 2831, 1421, 1339, 1315, 1284, 1240, 1188, 1136, 1032, 1002, 906, 872, 832, 790, 676, 655, 624, 429 cm<sup>-1</sup>. Anal. Calc. for C<sub>10</sub>H<sub>18</sub>Cu<sub>4</sub>I<sub>4</sub>S<sub>4</sub> (1028.31): C, 11.68; H, 1.76; S, 12.47. Found: C, 11.96; H, 1.76; S, 12.13%.

**CP4.** To a solution of CuBr (287 mg, 2.0 mmol) in acetonitrile (16 mL) was added **L1** (266.5 mg, 1.0 mmol) in two portions.). Precipitation of a white product occurred

immediately. The mixture was stirred for 2h at room temperature, and then heated to reflux for 5 min to assure completion of the reaction. After reaching ambient temperature, the resulting microcrystalline precipitate was filtered off and air-dried. Yield (92%). To obtained X-ray suitable single-crystals, a 100 mg amount was redissolved in boiling EtCN and then allowed to reach slowly ambient temperature. mp =  $244^{\circ}$ C IR (ATR): 2988, 2892, 1421, 1342, 1276, 1242, 1214, 1189, 1157, 1125, 1051, 1011, 991, 925, 902, 863, 833, 773, 743, 676, 649, 601, 506, 486, 463; 429 cm<sup>-1</sup>. Anal. Calc. for C<sub>10</sub>H<sub>18</sub>Cu<sub>2</sub>Br<sub>2</sub>S<sub>4</sub>(553.41): C, 21.70; H, 3.28; S, 23.18. Found: C, 21.75; H, 3.25; S, 22.62%.

**CP5. L1** (125 mg, 0.5 mmol) was dissolved dichloromethane (5 mL). To this solution was added a solution of CuBr (208 mg, 1.45 mmol) in acetonitrile (25 mL). Precipitation of a white product occurred immediately. The mixture was stirred 2h at room temperature. The resulting precipitate was filtered and washed with 20 mL of acetonitrile and then 20 mL of dichloromethane. A small amount of the white powder was dissolved in hot acetonitrile. After two weeks, colourless crystals suitable for single X-ray diffraction were obtained. Yield: 75 %. mp = 236°C IR (ATR): 2972, 2933, 2910, 2837, 2309, 2265, 1433, 1408, 1376, 1344, 1274, 1259, 1244, 1209, 1187, 1174, 1162, 1033, 1010, 923, 897, 869, 856, 832, 775, 668, 646, 602, 482, 464, 421 cm<sup>-1</sup>.Anal. Calc. for  $C_{24}H_{42}Br_6Cu_6N_2S_8$  (1475.77): C, 19.53; H, 2.87; N, 1.90, S, 17.38. Found: C, 19.74; H, 2.90; N, 1.94; S, 16.97%

**CP6.** To a solution of CuCl (200 mg, 2.0 mmol) in acetonitrile (15 mL) was added solid **L1** (271.5 mg, 1.02 mmol) in three portions. Precipitation of a white product occurred immediately. The mixture was stirred 2h at room temperature. The resulting precipitate was filtered off, washed with 5 mL of acetonitrile and dried. Yield: 93%. A 100 mg amount of this material was dissolved in hot benzylcyanide. Upon cooling, colourless crystals suitable for X-ray diffraction were obtained. mp = 215°C. IR (ATR): 2941, 2906, 1447, 1421, 1311, 1267, 1229, 1181, 1160, 1106, 1027, 896, 874, 827, 798, 742, 687, 654, 438 cm<sup>-1</sup>. Anal. Calc. for C<sub>5</sub>H<sub>9</sub>ClCuS<sub>2</sub> (232.23): C, 25.86; H, 3.91; S, 27.61. Found: C, 26.28; H, 4.20; S, 26.69.

**CP7.** To a suspension of  $HgI_2$  (227 mg, 0.50 mmol) in toluene (10 mL) was added solid **L1** (271.5 mg, 1.02 mmol) in two portions. After stirring for 30 min, the mixture was heated to 110° C to give a clear solution. After 2h, the heating was stopped, and pale-yellowish

crystals started to grow upon cooling. After 2d, the supernatant toluene solution was decanted, and the stable crystals air-dried. Partial evaporation of the toluene solution afforded a further crop of **CP7**. Yield: 85%. mp = 148°C. IR (ATR): 2979, 2900, 1408, 1304, 1242, 1169, 1124, 1061, 897, 865, 784, 730, 653, 482 cm<sup>-1</sup>. Anal. Calc. for  $C_{10}H_{18}HgI_2S_4$  (720.87): C, 16.66; H, 2.51; S, 17.79. Found: C, 16.75; H, 2.49; S, 17.67 %.

**D1.** To a suspension of HgI<sub>2</sub> (227 mg, 0.50 mmol) in toluene (10 mL) was added **L2** (74 mg, 0.55 mmol) via syringe (66  $\mu$ L). After stirring for 30 min, the mixture was heated to 110° C to give a clear solution. After 2h, the heating was stopped, and large yellow crystals were grown upon cooling. After 2d, the supernatant toluene solution was decanted, and the stable product air-dried. Partial evaporation of the toluene solution afforded a further crop of crystalline **D1**. Yield: 92%. mp = 113 °C. IR (ATR): 2925, 2895, 2824, 1438, 1416, 1374, 1341, 1274, 1236, 1190, 1119, 1076, 1053, 993, 973, 896, 859, 818, 713, 669, 645, 622, 479, 436 cm<sup>-1</sup>. Anal. Calc. for C<sub>10</sub>H<sub>20</sub>Hg<sub>2</sub>I<sub>4</sub>S<sub>4</sub>(1177.28): C, 10.20; H, 1.71; S, 10.89. Found: C, 10.39; H, 1.72; S, 10.97 %.

**CP8.** To a suspension of HgBr<sub>2</sub> (360 mg, 1.0 mmol) in toluene (10 mL) was added solid **L1** (271.5 mg, 1.02 mmol). After stirring for 30 min, the mixture was heated to 110° C to give a clear solution. After 2h, the heating was stopped, and colourless crystals commenced to grown upon cooling. After 2 days, the supernatant toluene solution was decanted, and the stable crystals air-dried. Partial evaporation of the toluene solution afforded a further small crop of **CP8**. Yield: 68%. mp = 170° C. IR (ATR): 2954, 2926, 2901, 2819, 1430, 1419, 1403, 1308, 1271, 1237, 1165, 1130, 1109, 1023, 904, 870, 828, 795, 753, 727, 678, 654, 634, 489, 417 cm<sup>-1</sup>. Anal. Calc. for  $C_{10}H_{18}Br_2HgS_4$  (626.89): C, 19.16; H, 2.89; S, 20.46. Found: C, 20.50; H, 3.08; S, 21.66 %.

**CP9.** This colourless compound was prepared in a similar manner by heating a mixture of HgBr<sub>2</sub> (360 mg, 1.0 mmol) in toluene (12 mL) with **L1** (133.0 mg, 0.5 mmol). Yield:76%. mp =  $177^{\circ}$  C. IR (ATR): 2965, 2898, 2824, 1451, 1414, 1323, 1260, 1240, 1177, 1109, 1071, 1050, 1041, 861, 830, 798, 722, 639, 436 cm<sup>-1</sup>Anal. Calc. for C<sub>5</sub>H<sub>9</sub>Br<sub>2</sub>HgS<sub>2</sub> (493.65): C, 12.16; H, 1.84; S, 12.99. Found: C, 12.38; H, 1.84; S, 12.91 %.

**M1.** To a suspension of HgBr<sub>2</sub> (360 mg, 1.0 mmol) in toluene (12 mL) was added **L2** (295 mg, 2.2 mmol) via syringe. After stirring for 30 min, the mixture was heated to  $110^{\circ}$  C to

give a clear solution. After 2h, the heating was stopped, and fine colourless crystal needles were grown upon cooling. After 1d, the supernatant toluene solution was decanted, and the stable product air-dried. Partial evaporation of the toluene solution afforded a further crop of crystalline **M1**. Yield: 86%. mp = 105 °C. IR (ATR): 2965, 2950, 2909, 1442, 1433, 1422, 1399, 1379, 1345, 1270, 1257, 1231, 1171, 1115, 1075, 1051, 996, 973, 900, 863, 813 cm<sup>-1</sup>.

**CP10.** To a suspension of **M1** (126 mg, 0.2 mmol) in toluene (8 mL) was added HgBr<sub>2</sub> (72 mg, 0.2 mmol). After stirring for 30 min, the mixture was heated to  $110^{\circ}$  C to give a clear solution. After 1h, the heating was stopped, and large transparent crystals were grown upon cooling. After 1d, the supernatant toluene solution was decanted, and the stable product airdried. Yield: 86%. mp = 112 °C. IR (ATR): 2967, 2934, 2910, 1449, 1424, 1398, 1337, 1249, 1231, 1165, 1116, 1077, 1057, 999, 968, 901, 864, 812 cm<sup>-1</sup>. Anal. Calc. for C<sub>5</sub>H<sub>10</sub>HgBr<sub>2</sub>S<sub>2</sub> (494.66): C, 12.14; H, 2.04; S, 12.96. Found: C, 12.47; H, 2.07; S, 13.46 %.

**CP11.** This compound was prepared in a similar manner as described for **CP8** by heating a 1:1 mixture of **L1** and HgCl<sub>2</sub> in toluene. Yield: 73%. mp = 160°C. IR (ATR): 2964, 2902, 2859, 1453, 1415, 1325, 1264, 1242, 1178, 1115, 1033, 1003, 899, 862, 833, 803, 728, 674, 642, 564, 504 cm<sup>-1</sup>. Anal. Calc. for  $C_{10}H_{18}Cl_2HgS_4$  (538.01): C, 22.32; H, 3.37; S, 23.84. Found: C, 21.62; H, 3.24; S, 22.77 %.

**CP12**. To a solution a solution of CuI (191 mg, 1.0 mmol) in acetonitrile (20 mL) was added **L1** (271.5 mg, 1.0 mmol) in two portions. After precipitation of a *in situ* generated **CP1**, the slurry was stirred for 1h at room temperature, and then heated to 80 C° for 15 min to assure completion of the reaction. After cooling ambient temperature, red HgI<sub>2</sub> (454 mg, 1.0 mmol) was added in two portions. Dissolution of HgI<sub>2</sub> occurred rapidly and an important part of **CP1** went in solution. After stirring for 4h, the mixture was heated for 10 min to give a clear yellowish solution. Upon cooling, yellow crystals formed progressively. The solvent volume was reduced to 15 ml by partial evaporation from the opened Schlenk flask. Yield: 67%. A further crop of **CP12**, contaminated by small amounts of **CP7**, was obtained by storing the solution in a refrigerator. mp = 110°C. IR (ATR): 2979, 2955, 2940, 2907, 2852, 2821, 2295, 2267, 1446, 1413, 1357, 1313, 1274, 1256, 1239, 1177, 1139, 1023, 903, 863,

831, 795, 744, 678, 658, 494, 421 cm<sup>-1</sup>. Anal. Calc. for C<sub>9</sub>H<sub>15</sub>CuHgI<sub>3</sub>N<sub>2</sub>S<sub>4</sub> (860.21): C, 12.56; H, 1.75; N, 3.25; S, 7.45. Found: C, 12.84; H, 1.77; N, 3.19; S, 7.74 %.

#### X-ray Crystallography

X ray powder patterns were obtained at 295 K on a D8 Advance Bruker diffractometer using Ni-filtered K-a radiation. The crystal structures of the compounds L1, CP1, CP2, CP3, CP4, CP5, CP6, D1, CP7, CP8, M1, CP9, CP11 and CP12 were determined using the Bruker D8 Venture four-circle diffractometer equipped with a PHOTON II CPAD detector by Bruker AXS GmbH. The X-ray radiation was generated by the  $I\mu S$  microfocus source Mo ( $\lambda = 0.71073$ Å) from *Incoatec GmbH* equipped with HELIOS mirror optics and a single-hole collimator by Bruker AXS GmbH. The crystals were covered with an inert oil (perfluoropolyalkyl ether) and mounted on the MicroMount, MicroGripper or MicroLoop from MiTeGen. The APEX 3 Suite (v.2019.1-0) software integrated with SAINT (integration) and SADABS (adsorption correction) programs by Bruker AXS GmbH were used for data collection. The processing and finalization of the crystal structure were performed using the Olex2 program.<sup>67</sup> The crystal structures were solved by the ShelXT structure solution program using the Intrinsic Phasing option, which were further refined by the ShelXL refinement package using Least Squares minimization.<sup>68, 69</sup> The non-hydrogen atoms were anisotropically refined. The C-bound H atoms were placed in geometrically calculated positions, and a fixed isotropic displacement parameter was assigned to each atom according to the riding-model: C-H = 0.98-1.00 Å with  $U_{iso}(H) = 1.5U_{eq}(CH_3)$  and  $1.2U_{eq}(CH)$  for other hydrogen atoms. The crystallographic data and structural refinement are listed in ESI in Tables S1-S7. The crystallographic data for the structures L1, CP1, CP2, CP3, CP4, CP5, CP6, D1, CP7, CP8, M1 CP9, CP10 and CP12 have been published as supplementary publication number 2060086(L1), 2060098 (CP1), 2060088 (CP2), 2105375 (CP3), 2060084 (CP4), 2060105 (CP5), 2060085 (CP6), 2060101 (CP7), 2060104 (D1), 2060108 (CP8), 2060103 (CP9), 2060110 (M1), 2060111 (CP10), 2105376 (CP12) the Cambridge Crystallographic Data Centre. A copy of these data can be obtained for free by with applying to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK, fax: 144-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

#### **Conflicts of interest**

There are no conflicts to declare.

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#### Footnote

Electronic supplementary information (ESI) available: summary of X-ray data collection and refinement for all structures studied, structure views of **CP1-CP6**, **CP8-CP10**, powder X-Ray Patterns of **CP1-CP4**, **CP6-CP8**, **CP11-12**, ATR-IR spectra of **CP5**, **CP12**, TGA traces of **CP1-CP6**.

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