Two synthetic routes to bis(1-methyl-imidazole-2-thione)methane and bis(1-benzyl-imidazole-2-thione)methane complexes including sulfur atom insertion into copper–NHC bonds


Dedicated to Professor John A. Gladysz on the occasion of his 65th birthday.

Keywords: NHCs / Thiones / Copper / Sulfur atom insertion / Crystallography

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The synthesis of novel bis-thione ligand, bis(1-benzyl-imidazole-2-thione)methane, SS[Bu] has been reported for the first time. This ligand along with the previously reported bis(1-methyl-imidazole-2-thione)methane, SSMe has been utilised in the synthesis of a series of copper(I) halide complexes. The syntheses have been achieved by two methodologies. The first method involves the direct addition of the ligands to the copper halide salts, CuCl, CuBr and CuI. The second methodology involves an insertion of a sulfur atom into the copper–NHC bond of the preformed organometallic complexes, [CuMe(C2Me5)2] and [Cu(dppe)2] where C2Me5 = 1-(3-methyl-2H-imidazol-1-yl-2-thione)methyl-3-methyl-2H-imidazol-2-ylidene and [Cu(dppe)2] and [Cu(dppe)2].

These sulfur atom insertion reactions provide an indirect route to the first copper–halide complexes containing the SS[Me] and SS[Bu] ligands. All six complexes prepared have been fully characterized by spectroscopic and analytical methods as well as X-ray crystallography. Dinuclear structures were obtained for the complexes containing SSMe, mononuclear complexes were obtained for the copper–chloride and copper–bromide complexes containing SS[Bu] and an extended network containing [Cu4] clusters bridged by the SS[Bu] were formed for the corresponding copper–iodide complex for the latter ligand. The coordination and structural features of the two bis-thione ligands are discussed.

1. Introduction

There has been a significant and long standing interest in the 1-R-imidazole-2-thione heterocycle (Himt), where the R group is an alkyl or aryl group and its incorporation within polydentate ligand motifs (Figure 1). Much of this work has focused on anionic so-called “flexible soft scorpionate ligands” which contain a borohydride bridging unit between the heterocycles, for example [Tm] and [Bm] where R = Me in Figure 1. Neutral bidentate and tridentate ligands bridged by CH2 and CH units have also been extensively studied.[3,4]

![Figure 1 – Bidentate and tridentate ligands containing two or three of the methyl substituted 1-R-imidazole-2-thione units. The anionic ligands, bridged by borohydride are shown on the left and neutral ligands featuring CH2 and CH units are shown on the right.](image)

In a recent publication, we coordinated bis(1-methyl-imidazole-2-thione)methane (SSMe) to a series of zinc salts.[3d] This ditopic ligand has previously been utilised to prepare a wide range of complexes in which it exhibits a range of different coordination modes, some of which are highlighted in Figure 2. Examples of complexes containing SSMe have been reported with d-block metals such as silver,[3f,6o] gold,[3p] rhodium,[3q,p,l] iridium,[3h] nickel,[3b] iron,[3h] cobalt,[3b] zinc,[3a,b] and rhenium[3e] in addition to other metals such as tin,[3o] lead,[3o,k] antimony,[3o,k] and bismuth.[3o,k]

The ligand has a number of interesting features. The number of atoms from one sulfur to the other is seven. This means that for a κ2-SS coordination mode an eight-membered metalla-tricycle is formed with the metal centre. This ring size is larger than normally found in most compounds containing chelating ligands. One of the consequences of this larger chelation size has been a positioning of the central methylene unit in close proximity to the metal centre Figure 3. This is demonstrated in the complexes [Rh(COD)(κ2-SS-SSMe)]X (where X = [PF₆]⁻ and [BF₄]⁻), published in 2006 by Hill.[3g] The ligand in this complex adopts a weak interaction between one of the hydrogen atoms on the central CH₂ unit of the ligand and the rhodium centre at lower temperatures in solution as well as in the solid state. While the C–H–Rh interaction is relatively long for the SSMe ligand, the corresponding B–H–Rh interaction in the related complex [Rh(COD)(κ2-SS-Bm)] was found to be significantly shorter.[5] The activation of the B–H bond in the borohydride based ligands is now well established leading to the formation of metal–borane (η3-acceptor) complexes.[2b] On the other hand, the activation of a C–H bond in the SSMe ligand, is unknown although there are rare examples of related compounds.
where activation has been observed.\textsuperscript{[7]}  

Figure 2 – Highlighting the diverse range of coordination modes of SS\textsuperscript{Me}.  
There are many examples of complexes featuring the κ\textsuperscript{2}-SS (see main text for details).

Other features of the ligands include the ability to bridge two metal centres, either via the two lone pairs on an individual sulfur donor (µ-S), bridging two metal centres via κ\textsuperscript{2},κ\textsuperscript{1} modes (i.e. one metal at each sulfur) or a combination of the two bridging types as shown in the silver and lead complexes in Figure 2.

Figure 3 – The coordination of SS\textsuperscript{Me} to the rhodium centre in [Rh(COD)κ\textsuperscript{2}SS(SS\textsuperscript{Me})][X] (where X = PF\textsubscript{6} and BF\textsubscript{4}), highlighting the eight membered ring formed by the presence of the κ\textsuperscript{2}SS coordination mode versus the two six membered rings formed by the E–H–Rh interactions.

In a related study, we have also investigated the coordination properties of a novel family of ditopic ligands, the first to contain both thione and NHC donor functionalities within the same ligand (e.g. CS\textsuperscript{Me} and CS\textsuperscript{Bu} in Figure 4).\textsuperscript{[8]} It is worthy to note that these ligands differ from SS\textsuperscript{Me} only by the absence of one sulfur atom. Several organometallic complexes were prepared using this mixed donor ligand. Indeed, these ligands were also found to exhibit a range of different coordination motifs. The copper complexes containing the CS\textsuperscript{Me} ligands formed dimeric CuSCuS cores where the ligands were attached with intermediate coordination modes, somewhere between κ\textsuperscript{1}-C,κ\textsuperscript{1}-S and κ\textsuperscript{2}-CS.\textsuperscript{[8a]} The ‘CuSCuS’ bridging interactions in these complexes ranged from weak to strong depending on the halide. On the other hand, the complexes containing the ligands in the silver complexes formed well-defined κ\textsuperscript{2}-CS motifs.\textsuperscript{[8a]} As indicated in Figure 2, some silver complexes containing SS\textsuperscript{Me} have previously been reported by Gardinié et al.\textsuperscript{[9]}  

Even though there is a diverse range of complexes containing the SS\textsuperscript{Me} ligand, until recently there had been no structurally characterised examples of any copper complexes. Bark \textit{et al}. had previously reported that this ligand coordinated to copper metal centres\textsuperscript{[8b]} indicating that 1:1 complexes may have been formed with SS\textsuperscript{Me} and copper(I) salts. However, no further details were provided. In 2015, Brumaghim reported the first structurally characterised copper complexes to contain SS\textsuperscript{Me}. The complex [Cu₂(SS\textsuperscript{Me})\textsubscript{2}][BF\textsubscript{4}]:\textsuperscript{[9]} was prepared along with two others which contained SS\textsuperscript{Me} in addition to other derivative ligands.\textsuperscript{[9]} To the best of our knowledge, there are currently no reported copper–halide complexes containing SS\textsuperscript{Me}. Furthermore, the synthesis of the related ligand, SS\textsuperscript{Bu}, is unknown. Accordingly, we wish to report for the first time copper–halide complexes (chloride, bromide and iodide) of both SS\textsuperscript{Me} and SS\textsuperscript{Bu} ligands. We report the synthesis of the complexes via two different synthetic routes. The preparation of these complexes was achieved by direct coordination of the respective ligand to copper(I) salt. A second route was an indirect method via addition of elemental sulfur to the corresponding organometallic complexes [CuX(CS\textsuperscript{Me})]:\textsuperscript{[2]} (where R = Me; Bn; X = Br, I). This latter reactivity involves the insertion of a sulfur atom into the copper–N-heterocyclic carbene bond.

Figure 4 – Mixed bidentate CS\textsuperscript{Me} ligands containing thione and N-heterocyclic carbene ligands (where R = Me, Bn).

2. Results and Discussion

2.1 Synthesis of bis(1-benzyl-imidazole-2-thione)methane (SS\textsuperscript{Bu})

The syntheses of various substituted bis(1-R-imidazole-2-thione)methanes (SS\textsuperscript{Me}, where R = Me, Bn and Pr) have already been established.\textsuperscript{[1a,b]} On the other hand, the corresponding species bis(1-benzyl-imidazole-2-thione)methane (SS\textsuperscript{Bu}) has not previously been reported. Accordingly, we decided to synthesise it as a new example. The ligand was readily prepared via an analogous route to previous examples from 1,1-dibenzyl-3,3-methylenedimidazolium diiodide\textsuperscript{[10]} (via N-benzylimidazole and diiodomethane). The diiodide imidazolium salt was reacted with elemental sulfur and potassium carbonate in refluxing methanol for 24 h to give the final product SS\textsuperscript{Bu} (Scheme 1). The product obtained was recrystallised from methanol and isolated in excellent yield. The crystalline solids were fully characterized by spectroscopic and analytical methods. The \textsuperscript{1}H NMR spectrum in CDC\textsubscript{1}l confirmed the loss of both imidazolium protons. One singlet was observed for the methylene unit at 6.41 ppm, integrating for two protons, and a signal at 5.22 ppm was observed for the benzyl CH\textsubscript{2} units. The latter signal integrated to four protons again confirming incorporation of two thione units into the product. The \textsuperscript{13}C(\textsuperscript{1}H) NMR spectra showed a characteristic signal at 164.0 ppm confirming the presence of the C=CS groups in the new compound. Mass spectrometry and elemental analysis were also consistent with the formation of the targeted product.

Scheme 1 – Synthesis of bis(1-benzyl-imidazole-2-thione)methane (SS\textsuperscript{Bu}).

2.2 Synthesis of copper(I) complexes via a direct route

As it is a new ligand, the addition of bis(1-benzyl-imidazole-2-thione)methane to transition metal centres has not been studied. We therefore initiated an investigation into its coordination properties to the three copper(I) halide salts (CuCl, CuBr and CuI). We also prepared the analogous SS\textsuperscript{Me} complexes via this same route. The series of complexes, [CuCl(SS\textsuperscript{Me})\textsubscript{2}], (1), [CuBr(SS\textsuperscript{Me})\textsubscript{2}], (2), [Cu(SS\textsuperscript{Bu})\textsubscript{2}], (3), [CuCl(SS\textsuperscript{Bu})\textsubscript{2}] (4), [CuBr(SS\textsuperscript{Bu})\textsubscript{2}] (5) and [Cu(SS\textsuperscript{Bu})\textsubscript{2}] (6) were prepared as outlined in Scheme 2. The specific morphologies obtained for each complex are outlined below. Complexes 1, 2 and 3 were prepared by addition of one equivalent of a dichloromethane solution of the ligand to a methanol solution of the corresponding copper halide. Within a few minutes, solid started to precipitate from the mixture. After 12 h, the products were isolated by filtration, washed with diethyl ether and dried under reduced pressure. Complexes 4, 5 and 6 were readily prepared by addition of one equivalent of the ligand in acetonitrile to a solution of the corresponding copper(I) halide in the same solvent (Scheme 2). Again, within a few minutes, the
solid started to precipitate from the mixture. After 12 h, the products were isolated using a similar work-up procedure as for 1, 2 and 3. The complexes were not particularly soluble in many standard organic solvents. The SSMe complexes were more soluble in MeCN than the corresponding SSMe complexes. All complexes were soluble in DMSO.

2.3 Synthesis of copper(I) complexes via a sulfur atom insertion route

For a good reason, there is a strongly held acceptance that NHC ligands form very strong bonds to transition metals. Despite this, we had previously demonstrated that the copper-carbon bond of complexes containing the CS complexes could be cleaved in the presence of oxygen to provide the corresponding ‘oxidation product’ 1-(3-R-2-thioxo-2H-imidazol-1-yl)methyl)-3-R-2H-imidazol-2-one (i.e. OS)[6]. Others have reported similar observations where imidazole-2-one functional groups have been formed, although such reactivity is very rare.[11] The copper metal centre itself seems to be crucial here since the oxidation products, OS, have not been found to occur when the CSSR ligands are coordinated to any other transition metal centres that we have thus far tested (i.e. Pd, Rh, Ag). In the case of copper, the resulting OS species were found to be poor ligands resulting in demetallation. As it was apparent that formal insertion of oxygen could be achieved, we wondered whether it was possible to insert elemental sulfur into the copper–carbon bond. Insertion of elemental sulfur into metal–carbon bonds has previously been observed[12] as well as the reverse reactivity.[11,12] It was of particular interest to us to test the possibility of providing an indirect route to complexes of the type [CuX(SSMe)n]. Accordingly, the reaction of the [CuX(CS)3] precursors with elemental sulfur was explored. In order to test the feasibility of the reaction, small samples of [CuX(CS)3] where X = Br, I and R = Me, Bn) were placed in NMR tubes in the presence of excess sulfur. DMSO-d6 was added to dissolve the copper complexes. The mixtures were examined by 1H NMR spectroscopy and the conversions to the desired sulfur insertion products were monitored. In all cases, conversion to the new products took place. At room temperature, the transformations were slow; however, upon heating the NMR tubes to 80 °C, they gave complete conversion to the sulfur insertion products. Successful generation of the new complexes led us to attempt to insert oxygen into the copper centre despite several attempts. For this reason, we used acetonitrile as a solvent since the fact that the [CuX(CS)3] complexes were only partially soluble (Scheme 3). A sample of [CuBr(SSMe)3] was placed in acetonitrile and an excess of S8 (20 equivalents of 1/3 S8 per CSSMe ligand) was added. The reactions were monitored by taking small aliquots of the mixture, evaporating the solvent and recording the 1H NMR spectrum in DMSO-d6 at regular intervals. There was approximately 20% conversion of the starting material after 1 h at room temperature. This increased to approximately 50% overnight after which time no further significant conversion was observed. In a separate experiment, a fresh mixture was heated to 50 °C for 3 h to afford full conversion of [CuBr(SSMe)3]; the new more symmetrical product [CuBr(SSMe)3]. The new compound was isolated via a standard workup. Full characterisation (vide infra) revealed it to be the target species, i.e. the product of formal sulfur atom insertion into the copper–NHC bond (Scheme 3). The analogous reaction was attempted with [Cu(CSMe)3], and elemental sulfur. In this case, the reaction proceeded at a slower rate. No conversion was observed at ambient temperatures, only approximately 15% of the target product was observed after 3 h at 50 °C. Full conversion to [Cu(SSMe)3] was only obtained after a further 3 h at 70 °C. For the reaction involving [CuBr(SSMe)3], and elemental sulfur, full conversion was obtained after 5 h at 70 °C and finally for [Cu(CSMe)3]; full conversion was observed after 3 h at 70 °C. It appeared that the length of time required to reach full conversion products was related to the solubility of the starting complexes in acetonitrile. For all four reactions, the products were isolated via a
to the metal centres was further confirmed by positive ESI-mass spectrometry which all showed the peak corresponding to the expected cations, \( [\text{Cu}_2\text{SS}^\text{Me}_2]^{+} \), resulting from loss of one halide ligand from the dinuclear species \( [\text{CuX(SS}^\text{Me})_2] \). Furthermore satisfactory elemental analysis was obtained for the three complexes confirming the 1:1 copper to ligand ratio. Similarly, complexes 4 – 6 were obtained as analytically pure white solids in high yields. The three compounds were characterised by spectroscopic and analytical methods. Again, the \(^1\text{H}\) and \(^{13}\text{C}(^1\text{H})\) NMR data (in DMSO-\(d_6\)) for 4 – 6 were consistent with the coordination of the \( \text{SS}^\text{Bu} \) ligand to the copper centres with a symmetric coordination mode. In this case, this is consistent with the solid state structures (vide infra). The methylene resonances were located as singlet signals at 6.46 ppm (4), 6.66 ppm (5) and 6.65 ppm (6) in the \(^1\text{H}\)-NMR spectra. These are shifted downfield with respect to the free ligand \( \text{SS}^\text{Bu} \) which is located at 6.21 ppm. Coordination of the ligand to the copper centres was further confirmed by ESI-mass spectrometry. Again, the ratio of metal to ligand was confirmed as 1:1 by elemental analysis.

Table 1 – A comparison of the NMR spectroscopic chemical shifts found in the \( \text{SS}^\text{Bu} \) ligands, \( [\text{CuX(CS}^\text{Bu})_2] \), complexes and complexes 1 – 6.

<table>
<thead>
<tr>
<th>Ligand Precursor / Complex</th>
<th>(^1\text{H} ) (ppm)</th>
<th>(^{13}\text{C}(^1\text{H}) ) (ppm)</th>
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<tbody>
<tr>
<td>( \text{SS}^\text{Bu} )</td>
<td>3.44</td>
<td>34.8</td>
</tr>
<tr>
<td>([\text{CuBr} \text{SS}^\text{Bu})_2] )</td>
<td>3.51 / 3.68</td>
<td>6.24</td>
</tr>
<tr>
<td>([\text{CuI} \text{SS}^\text{Bu})_2] )</td>
<td>3.54 / 3.71</td>
<td>6.23</td>
</tr>
<tr>
<td>([\text{CuCl} \text{SS}^\text{Bu})_2] )</td>
<td>3.41</td>
<td>6.49</td>
</tr>
<tr>
<td>([\text{CuBr} \text{SS}^\text{Bu})_2] )</td>
<td>3.48</td>
<td>6.56</td>
</tr>
<tr>
<td>([\text{CuCl} \text{SS}^\text{Bu})_2] )</td>
<td>3.58</td>
<td>6.72</td>
</tr>
<tr>
<td>( \text{SS}^\text{Me} )</td>
<td>5.20</td>
<td>6.21</td>
</tr>
<tr>
<td>([\text{CuBr} \text{SS}^\text{Me})_2] )</td>
<td>5.23 / 5.26</td>
<td>6.26</td>
</tr>
<tr>
<td>([\text{CuCl} \text{SS}^\text{Me})_2] )</td>
<td>5.25 / 5.33</td>
<td>6.26</td>
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<tr>
<td>([\text{CuCl} \text{SS}^\text{Me})_2] )</td>
<td>5.16</td>
<td>6.46</td>
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<tr>
<td>([\text{CuBr} \text{SS}^\text{Me})_2] )</td>
<td>5.22</td>
<td>6.66</td>
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<tr>
<td>([\text{CuCl} \text{SS}^\text{Me})_2] )</td>
<td>5.20</td>
<td>6.65</td>
</tr>
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</table>

[a] NMR experiments carried out in DMSO-\(d_6\), the data for the \( [\text{CuX(CS}^\text{Bu})_2] \) complexes were obtained from reference 8a.

2.5 Structural characterisation of copper complexes

Single crystals were obtained from samples of all six copper complexes (1 – 6) and X-ray diffraction studies were performed. The crystal structures obtained from each of the samples are shown in Figures 5 – 11. During the course of our investigations we also carried out a test reaction in which \( \text{SS}^\text{Me} \) was dissolved in DCM and a methanolic solution containing \( \text{Cu}[\text{BF}_4]_2 \cdot 3\text{H}_2\text{O} \) was added as a layer above. Crystals were obtained after 18 h and the resulting material was characterized by X-ray diffraction. As shown in Figures 12 and 13, the compound was found to contain eight copper(1) centers joined by ten \( \text{SS}^\text{Me} \) ligands, i.e. \( [\text{Cu}_9(\text{SS}^\text{Me})_5][\text{BF}_4]_4 \) (7). Selected bond lengths and distances are highlighted in Tables 2 for comparison of complexes 1, 2 and 3, Table 3 for comparison of complexes 4 and 5 and in the corresponding figure captions for complexes 6 and 7. Crystallographic parameters for all complexes are provided in Tables S1 and S2 in the supplementary information.
**Figure 7** – Molecular structure of [CuI{κ²-SΣ-µ-S·SS}]₂ (3) with atomic labelling scheme depicted. Ellipsoids shown at 50% probability level ($' = 1-x, 1-y, 1-z$).

**Figure 8** – Molecular structure of [CuCl{κ²-SΣ-SS}] (4) with atomic labelling scheme depicted. Ellipsoids shown at 50% probability level.

**Figure 9** – Molecular structure of [CuBr{κ²-SΣ-SS}] (5) with atomic labelling scheme depicted. Ellipsoids shown at 50% probability level.

**Figure 10** – Structure obtained for complex [CuI{µ-S,κ¹-S·SS}] (6). The sulfur atom labelled S1 bridges the CuI and Cu2 centres while S2 is bound only to Cu1. An extended network is formed where the SS ligands bridge the CuI₄ clusters. Ellipsoids shown at 50% probability level (i = 1-x, 1-y, 1-z; ii = -1+x, -1+y, 1-z; iii = 1-x, 1+y, -z). Selected distances (Å): Cu1–Cu2 2.8162(11), Cu1–Cu2i 2.7504(11), Cu2–Cu1i 2.7505(11), Cu2–Cu2i 2.5897(17), Cu1–I1 2.6678(9), Cu1–I2 2.6736(9), Cu2–I1 2.7931(10), Cu2–I1i 2.8127(9), Cu2–I2 2.5934(9), Cu1–S1 2.4136(18), Cu1–S2i 2.3393(17), Cu2–S1 2.3278(17), S1–C1 1.721(6), S2–C5 1.699(7).

**Figure 11** – Core structure obtained for complex 6. A [Cu₄I₄] cluster coordinated to four SS ligands in 6. Ellipsoids shown at 50% probability level ($' = 1+x, 1+y, 1+z$; ii = -1-x, -1+y, -z; iii = 1-x, 1+y, -z)．

**Figure 12** – Crystal structure of 7 obtained from the reaction of Cu[BF₄]₂·3H₂O with SS. The hydrogen atoms, BF₄ counterions and methanol solvent have been omitted for clarity. Ellipsoids depicted at the 50% probability level.
The three copper–halide complexes containing the SS\textsuperscript{Me} ligand (1, 2 and 3) adopt dinuclear structures containing two copper centres and two ligands. One of the sulfur donor atoms on each ligand bridges the copper centres. The ligand therefore adopts a \( \kappa^2\text{-SS} \mu^2\text{-SS} \kappa^2\text{-SS} \) coordination mode. As indicated above, this is in contrast to the solution state structure characterisation of these complexes which suggests a symmetrical environment for the SS\textsuperscript{Me} ligand. It is therefore likely that a mononuclear species exists in solution as indicated in Figure 14. The solid state structures also show short CH–Cu distances (as described below) which do not appear to be present in solution based on the NMR spectroscopic evidence.

![Core structure indicating the connectivity between the copper and sulfur donors in complex 7. Ellipsoids shown at 50% probability level](image1)

**Figure 13** – Core structure indicating the connectivity between the copper and sulfur donors in complex 7. Ellipsoids shown at 50% probability level.

The copper centres in 1, 2 and 3 adopt similar dinuclear motifs in which the metal centres possess highly distorted tetrahedral geometries with angles ranging between 88.82(4)° – 130.74(4)° for 1, 103.064(19)° – 125.42(2)° for 2 and 120.145(15)° – 126.707(17)° for 3. In the case of the bromide and iodide complexes, the widest angle results from the bidentate coordination (S1–Cu–S2) of the SS\textsuperscript{Me} ligand to copper centre indicating a wide bite angle for this ligand. Within the four membered CuSCuS ring, the copper–copper distances are 3.416(1) Å (1), 2.9705(6) Å (2) and 3.0131(4) Å (3) [c.f. \( \Sigma_5\text{-CuCu} = 2.64 \) Å].

This distance is well above the range to be considered as metallophillic interactions or \( \eta^1\text{-d}^{10} \) metal bonding. The short Cu⋯Cu distances seem to originate from bridging thione groups rather than any attractive interactions. The Cu–Cu distance is shorter within the bromide structure where the four membered Cu-S-Cu-S ring exhibits a parallelogram motif [103.064(19)° and 76.938(19)°].

The corresponding angles for the iodide complex are 102.145(15)° and 77.855(15)° resulting in a slightly longer Cu–Cu distance as expected from the larger steric demand of this halide. In contrast, the angles found in the chloride example are 88.82(4)° and 91.17(4)° much closer to a rectangular motif resulting in a significantly larger Cu–Cu distance. The dinuclear structure adopts a ‘zig-zag’ type motif where the two SS\textsuperscript{Me} ligands are located above and below the plane formed by the ‘CuSCuS’ ring (i.e. at opposite sides of the parallelogram motif). As indicated above, the three structures show that one of the hydrogen atoms of the methylene units between the thione rings of the SS\textsuperscript{Me} ligand points towards the copper centre. The Cu–H distances, 2.479 Å for 1, 2.740 Å for 2 and 2.664 Å for 3, are too large to indicate any significant interaction as the sum of the covalent radii of copper (1.32 Å) and hydrogen (0.31 Å) is 1.63 Å.

The Cu–S distances for the thione unit featuring the terminal non-bridging coordination modes were similar in the bromide and iodide complexes, cf. 2.3024(6) Å for 2 and 2.3069(5) Å for 3 [c.f. \( Z_2\text{-CuS} = 2.37 \) Å]. These are similar to distances for the Cu-S terminal thione bonds in the related complex reported by Brumaghim \(^{10} \) which lie in the range of 2.2710(16) Å and 2.3067(15) Å. There is a significant difference for the chloride complex 1 where the Cu–S distance is 2.3541(12) Å. The corresponding Cu–S distances involving the bridging mode for all three complexes ranged from 2.3221(6) Å to 2.4602(5) Å. While the Cu–S distances were significantly shorter for the terminal thione than the bridging ones within complexes 2 and 3, the same is not true for the Cu–S distances in 1 which are 2.4347(13), 2.3462(12) and 2.3541(12) Å. The related copper complex containing the mixed NHC-thione ligand, CS\textsuperscript{Me}, forms a similar dinuclear structure to which involves of the four membered Cu-S-Cu-S rings within a parallelogram motif. Similar sulfur bridged structures to those observed for 1, 2 and 3 have also previously been reported by Raper and Lobana in compounds such as [Cu(\( \mu^2\text{-SS} \) \( \mu^2\text{-SS} \))\( \eta^1\text{-SCN} \)]\( \text{I} \) and [Cu(\( \mu^1\text{-SS} \) \( \mu^2\text{-SS} \))\( \eta^1\text{-SS} \)]\( \text{I} \), where \( \text{S} \text{Me} = \) 1-methyl-imidazole-2-thione. Furthermore, in the complex reported by Brumaghim which contains both SS\textsuperscript{Me} and SS\textsuperscript{Me} ligands, the bidentate ligand coordinates via a \( \kappa^2\text{-SS} \) mode while the SS\textsuperscript{Me} ligands bridge the copper centres.

Crystal structures were obtained for the corresponding SS\textsuperscript{Ba} complexes, 4 and 6 from acetonitrile solutions. The structures of 4 and 5 reveal mononuclear structures (Figures 8 and 9). This, of course, is in contrast to the three other SS\textsuperscript{Me} complexes. Interestingly, the corresponding [CuX(CS\textsuperscript{Me})]\( \eta^1\text{-SS} \) compounds form dinuclear structures and it appears that the additional sulfur atom within the new complex changes the morphology. Complex 6, the iodide complex bearing the SS\textsuperscript{Ba} ligand, gave a different structural motif (Figures 10 and 11). The solid state structures of 4 and 5 reveal a bidentate coordination mode, \( \kappa^2\text{-SS} \), of the SS\textsuperscript{Me} ligand to the copper metal centres forming eight-membered chelating rings. These isostructural complexes adopt trigonal geometries with angles ranging between 110.66(2)° – 134.28(2)° for 4 and 110.96(3)° – 136.25(3)° for 5. The sum of the angles around the copper centres equate to 359.95° and 359.96°, respectively, indicating that the coordination about the copper centres is essentially planar. The largest angle about the copper metal is found to be the S–Cu–S angles involving the bite angle of the ligand which in these cases are 134.28(2)° and 136.25(3)° respectively. These angles are significantly larger than those found in the corresponding complexes containing SS\textsuperscript{Me} ligand. The larger bite angle presumably precludes the dimer formation which is observed with the former complexes. As a consequence, the binding of the ligand to the copper centre appears to be stronger than found in complexes 1, 2 and 3; the copper–sulfur distances are 2.2071(2) Å and 2.2129(3) Å for 4 and 2.2071(2) Å and 2.2129(3) Å for 5. The positioning of the methylene group is of interest. As with complexes 1, 2 and 3, the methylene groups in 4 and 5 appear to point towards the CuX unit. The eight-membered ring adopts a conformation where the five atoms, C=S–Cu–S=C lie on a plane. The N=C–N atoms are positioned above this plane where the CH\(_2\) unit is closer to the copper centre.

The structure obtained for complex 6 was different from the two morphologies described above. In this case, the SS\textsuperscript{Ba} ligand coordinates via a \( \kappa^2\text{-SS} \) coordination mode for one of the sulfur donors and a \( \mu^2\text{-} \) bridging mode to two copper centres for the
other sulfur donor. The copper and iodine centres form CuI₄ cluster motifs[17] which are linked together by the SS₄n ligands. In the structure, for each SS₄n ligand there is one copper and one iodide and the stoichiometry of the overall structure is \([\text{Cu(SS}_n^4\text{)}_n]\). Here, the copper–sulfur distances are 2.3393(17) Å for the bond involving the \(\kappa^3\)-S coordination mode to one copper centre and 2.4136(18) Å and 2.3278(17) Å for the \(\mu^2\)-bridging mode to two copper centres.

Finally, the structure obtained from the reaction of the copper(I) salt, Cu[BF₄]₂·3H₂O with SS₄Me showed that a reduction in the oxidation state of the metal centre had occurred.

The mechanism by which this reduction occurs is currently unknown. The structure exhibits a complicated arrangement of the copper and ligands. It shows four copper centres bridged by four sulfur donors from the ligands to form an eight membered ring structure. Two further copper centres are additionally tethered on either side of the central ring motif via bridging of the thione donors in the SS₄Me ligands. In total there are eight copper centres and ten SS₄Me ligands within the structure. The S–Cu–S angles across the structure range from 97.49(3)° to 131.34(3)°. The Cu–S distances range from 2.2135(9) Å to 2.4172(8) Å.

### Table 2 – A comparison of selected distances (Å) and angles (°) for the SS₄Me complexes, 1, 2 and 3.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-S</td>
<td>2.4347(13) / 2.3462(12)</td>
<td>2.4502(6) / 2.3232(6)</td>
<td>2.4602(5) / 2.3325(5)</td>
</tr>
<tr>
<td>Cu-S</td>
<td>2.3541(12)</td>
<td>2.3024(6)</td>
<td>2.3009(5)</td>
</tr>
<tr>
<td>C-Cu</td>
<td>3.416(1)</td>
<td>2.9705(6)</td>
<td>3.013(10)</td>
</tr>
<tr>
<td>Cu-X</td>
<td>X = Cl; 2.2863(12)</td>
<td>X = Br; 2.4810(4)</td>
<td>X = I; 2.6471(2)</td>
</tr>
<tr>
<td>Cl(1-S) / Cl(5)-S(6)</td>
<td>1.711(4) / 1.700(4)</td>
<td>1.714(2) / 1.707(2)</td>
<td>1.7121(17) / 1.7057(18)</td>
</tr>
<tr>
<td>Cu-H involving methylene unit</td>
<td>2.489</td>
<td>2.740</td>
<td>2.646</td>
</tr>
<tr>
<td>internal S-Cu-S within CuSCuS unit</td>
<td>88.82(4)</td>
<td>103.06(4)(9)</td>
<td>102.145(15)</td>
</tr>
<tr>
<td>Cu-S-Cu</td>
<td>91.17(4)</td>
<td>76.938(19)</td>
<td>77.855(15)</td>
</tr>
<tr>
<td>S-Cu-S within SS₄n ligand</td>
<td>111.59(4)</td>
<td>125.42(2)</td>
<td>126.70(17)</td>
</tr>
<tr>
<td>S-Cu-S between two SS₄n ligands</td>
<td>99.56(4)</td>
<td>107.05(2)</td>
<td>108.59(17)</td>
</tr>
<tr>
<td>N-Cu-S angles CuSCuS unit</td>
<td>130.74(4) / 112.74(5)</td>
<td>104.182(17) / 107.701(18)</td>
<td>103.899(13) / 105.234(12)</td>
</tr>
<tr>
<td>X-Cu-S angle terminal thione</td>
<td>111.07(3)</td>
<td>107.525(9)</td>
<td>108.434(13)</td>
</tr>
<tr>
<td>Cu-C-S angles CuSCuS unit</td>
<td>109.24(15) / 115.37(15)</td>
<td>96.83(7) / 120.15(8)</td>
<td>96.19(6) / 119.09(6)</td>
</tr>
<tr>
<td>Cu-S-C terminal thione</td>
<td>113.61(15)</td>
<td>104.10(8)</td>
<td>103.80(6)</td>
</tr>
<tr>
<td>N-C-N (methylene unit)</td>
<td>111.8(3)</td>
<td>111.65(17)</td>
<td>111.43(14)</td>
</tr>
</tbody>
</table>

### Table 3 – A comparison of selected distances (Å) and angles (°) for the SS₄Mo complexes, 4 and 5.

<table>
<thead>
<tr>
<th></th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-S</td>
<td>2.2032(5) / 2.2178(5)</td>
<td>2.2071(9) / 2.2129(5)</td>
</tr>
<tr>
<td>Cu-X</td>
<td>X = Cl; 2.2430(5)</td>
<td>X = Br; 2.3731(5)</td>
</tr>
<tr>
<td>Cl(1-S) / Cl(5)-S(6)</td>
<td>1.7035(18) / 1.7012(18)</td>
<td>1.701(3) / 1.705(3)</td>
</tr>
<tr>
<td>Cu-H involving methylene unit</td>
<td>2.617</td>
<td>2.595</td>
</tr>
<tr>
<td>S-Cu</td>
<td>134.28(2)</td>
<td>136.25(3)</td>
</tr>
<tr>
<td>X-Cu-S</td>
<td>115.01(2) / 110.66(2)</td>
<td>112.76(3) / 110.96(3)</td>
</tr>
<tr>
<td>Cu-S-C</td>
<td>108.31(6) / 110.69(6)</td>
<td>108.45(11) / 114.70(11)</td>
</tr>
<tr>
<td>N-C-N (methylene unit)</td>
<td>111.40(14)</td>
<td>111.6(2)</td>
</tr>
</tbody>
</table>

### 3. Conclusions

In summary, a novel ditopic bis-thione ligand, H₂C(1-benzyl-imidazole-2-thione)₂ (SS₄n) was synthesized and fully characterised. The first studies into its coordination chemistry has been carried out on a series of copper–halide complexes. The first copper-halide complexes of the previously studied ligand, H₂C(1-methyl-imidazole-2-thione)₂, SS₄Me have also been prepared. In addition to the direct synthesis of these complexes, via the addition of the corresponding ligand to the copper(I) halides, the complexes [CuBr(SS₄Mo)₂], [Cu(SS₄Mo)₂], and [CuBr(SS₄Mo)] were synthesised via an interesting sulfur atom insertion methodology to the corresponding copper complexes containing the mixed ditopic NHCl/thione ligands, CS₄. Single crystals were obtained from all complexes and were characterised by X-ray crystallography. Interestingly, the structures revealed different coordination modes for the SS₄Me and SS₄Mo ligands. All three copper(I) halide complexes (chloride, bromide and iodide) containing the former ligand exhibited a dinuclear structure bridged by one of the sulfur donors of the SS₄Mo ligand. This is a new bridging coordination mode to that previously observed for this ligand. Two of the three copper(I) halides gave straightforward mononuclear complexes featuring a \(\kappa^2\)-SS coordination mode in the corresponding chloride and bromide complexes containing SS₄Mo. A different coordination mode was observed for [Cu(SS₄Mo)₂]₄ where the two sulfur donors were connected to different copper centres, one sulfur donor coordinated with a \(\kappa^3\)-S mode while the other sulfur donor bridged two copper centres. The ligand within the structure was bridged by a CuI₄ cluster. Thus, we have expanded the range of coordination modes of the SS₄ ligands. It is apparent that there is great flexibility in the strength of binding and the degree of coordination modes possible in the coordination of these SS₄Me and SS₄Mo ligands.

### 4. Experimental Section

#### 4.1 General Remarks

The synthetic steps to prepare the ligand, SS₄Mo and the direct route to prepare the complexes were carried out under aerobic conditions. The synthesis involving the insertion of sulfur into the copper mixed NHCl/thione complexes required the reactions to be carried out under a nitrogen atmosphere using standard Schlenk techniques since the precursors are air sensitive. All chemicals and solvents were used as received. For those solvents required for the copper mixed NHCl/thione reactions, anhydrous solvents were used. These were kept in Young’s flasks under N₂ over molecular sieves (4 Å). The ligand, SS₄Mo and the complexes [CuX(CS₄)]₂ (where X = Br, I; R = Me, Bn) were prepared according to the procedures outlined in reference 8a. 'H
NMR spectra were recorded at room temperature on a JEOL Lambda 300 spectrometer operating at 300 MHz, a JEOL ECP 400 spectrometer operating at 400 MHz or a Bruker Avance III 400 MHz NMR spectrometer. ¹³C(¹H) NMR spectra were recorded at room temperature on a JEOL ECP 400 spectrometer or a Bruker Avance III 400 MHz NMR spectrometer. Electrospray Mass Spectra (ESI) were recorded on a Bruker Daltonics Apex 4e 7.0T FT-MS mass spectrometer. Infrared spectra were recorded in the region 4000-650 cm⁻¹ on a Perkin-Elmer Spectrum 100 FT-IR spectrometer (solid state, powder film). Elemental analyses were performed by the microanalytical laboratory, School of Chemistry, University of Bristol.

4.2 Bis(1-benzyl-imidazole-2-thione)methane, SS₉₉

A round bottomed flask equipped with a stirring bar was charged with N,N'-methylenebis(3-methylimidazoliodiide) (4.00 g, 6.85 mmol) and methanol (35 mL) to give a clear solution. Sulfur (0.449 g, 13.70 mmol, 2.0 equiv.) and potassium carbonate (0.959 g, 6.85 mmol, 1.0 equiv.) were added under stirring to the solution to give a suspension. The mixture was heated to reflux for 24 h. It was allowed to cool to room temperature and all volatiles removed. The residue was extracted with chloroform (100 mL), filtered, and the filtrate evaporated to dryness. The residue was redissolved in a minimum of dichloromethane. Addition of methanol precipitated the product as a white solid (2.5 g, 6.39 mmol, 93%). ¹H-NMR (300 MHz, CDCl₃): δ = 5.22 (s, 4H, CH₂Ph), 6.41 (s, 2H, NCH₂N), 6.51 (d, JHH = 2.5 Hz, 2H, CH=CH), 7.35 (m, 10H, o/m-phenylene), 7.64 (d, JHH = 2.5 Hz, 2H, CH=CH). ¹³C(¹H)-NMR (75 MHz, CDCl₃): δ = 51.4 (CH₂Ph), 116.5 (CH=CH), 119.0 (CH=CH), 128.4 (o/p-CH₃), 129.1 (m-CH₃), 135.2 (ν-CH₃), 164.0 (C=S). IR (cm⁻¹): 3135.6, 3089.5, 2942.0, 1576.4, 1445.3, 1412.3, 1374.5, 1302.8, 1187.4, 1078.1, 909.8, 742.9, 692.6. MS (ESI²), m/z 415.1 [SS₉₉⁺] + Na⁺, 391.16 [SS₉₉⁻] - H⁺. Elemental Analysis: Calc. for C₂₅H₂₅N₂S₂: C 64.26; H 5.14; N 14.27; Found: C 64.39; H 5.29; N 14.13.

[CuCl(SS₉₉)]⁺ (1)

CuCl (50 mg, 0.50 mmol) was dissolved in acetonitrile (80 mL). A solution of SS₉₉ (120 mg, 0.50 mmol) in acetonitrile (30 mL) was added in one portion. The solutions were mixed and stirred overnight, resulting in an off-white precipitate. The solid was isolated by filtration and rinsed with acetonitrile. The resulting solid was dried to give 32 mg (0.10 mmol) per sulfur. The mixture was stirred at 70 °C for 3 h after which time the mixture was diluted with 10 mL of acetonitrile and filtered. The volume of the filtrate was reduced to 2 mL and diethyl ether was added to precipitate an off-white solid. The solid was isolated by filtration, washed with a portion of diethyl ether and dried under reduced pressure. Yield = 38 mg (0.044 mmol, 44%). ¹H NMR (400 MHz, DCl₃): δ = 3.58 (6 H, s, NCH₂N), 2.82 (s, 4H, CH₂Ph), 7.44 (2H, d, JHH = 2.5 Hz, 2H, CH=CH). ¹³C(¹H) NMR (100 MHz, DCl₃): δ = 117.9 (NCH₂N), 121.9 (NCH₂N), 118.8 (NCH₂N), 121.0 (NCH₂N), 158.2 (C=S). MS (ESI²), m/z 455 [CuCl(SS₉₉)]⁺, 431 [CuCl(SS₉₉)]⁻ + Na⁺, 391.16 [SS₉₉⁻] - H⁺. Elemental Analysis: Calc. for C₂₅H₂₅N₂S₂: C 64.26; H 5.14; N 14.27; Found: C 64.39; H 5.29; N 14.13.

[CuCl(SS₉₉)]⁻ (2)

Direct route CuBr (72 mg, 0.50 mmol) was dissolved in acetonitrile (30 mL). A solution of SS₉₉ (120 mg, 0.50 mmol) in acetonitrile (30 mL) was added in one portion. The solutions were mixed and stirred overnight, resulting in an off-white precipitate. The solid was isolated by filtration and rinsed with acetonitrile. The resulting solid was dissolved to give 2 as an off-white solid. Yield = 137 mg (0.178 mmol, 71%). Sulfur insertion route [CuBr(SS₉₉)]⁺ (70.4 mg, 0.10 mmol) was partially dissolved in acetonitrile (20 mL) in a Schlenk flask. To this was added excess of sulfur (64 mg, 2.00 mmol per sulfur). The mixture was stirred at 50 °C for 3 h after which time the mixture was filtered. The volume of the filtrate was reduced to 2 mL and diethyl ether was added to precipitate an off-white solid. The solid was isolated by filtration, washed with a portion of diethyl ether and dried under reduced pressure. Yield = 42 mg (0.055 mmol, 55%). ¹H NMR (400 MHz, DCl₃): δ = 3.54 (6 H, s, NCH₂N), 6.43 (2H, s, NCH₂N), 6.95 (2H, d, JHH = 2.5 Hz, NCH₂N), 7.27 (2H, d, JHH = 2.5 Hz, NCH₂N). IR (cm⁻¹): 3390.3, 3093.4, 1672.7, 1570.9, 1496.2, 1451.8, 1408.5, 1354.5, 1230.6, 1190.5, 1166.0, 1079.6, 1028.5, 847.1, 693.6. Elemental analysis: Calc. for C₁₂H₁₄ClCuN₂S₂: C 51.31; H 4.10; N 11.40; Found: C 51.16; H 4.03; N 11.44.

[CuBr(SS₉₉)]⁺ (5)

Direct route A round-bottomed flask equipped with a stirring bar was charged with the ligand, SS₉₉ (0.1503 g; 0.383 mmol) and acetonitrile (10 mL) to give a white milky suspension. Anhydrous CuBr (0.055 g, 0.38 mmol) was added in one portion under vigorous stirring to give a pale green mixture which became briefly transparent after a few minutes. The mixture was stirred overnight to give a white precipitate; it was sonicated for a few seconds and further stirred for 30 min. Diethyl ether (10 mL) was added and stirring was continued for 5 min to give the product as a white powder which was washed, washed with diethyl ether (5 mL) and dried in air. Yield = 0.1394 g, 0.284 mmol, 75%. ¹H-NMR (300 MHz, d₆-DMSO): δ = 5.16 (s, 4H, PhCH₂), 6.46 (s, 2H, NCH₂N), 7.29 (s, 10H, 2x o/m-phenylene), 7.40 (s, 2H, CH=CH), 7.57 (overlapping signals, 2H, CH=CH). ¹³C(¹H) NMR (100 MHz, d₆-DMSO) δ = 36.2 (NCH₂N), 56.6 (NCH₂N), 119.7 (NCH₂N), 121.9 (NCH₂N), 158.2 (C=S). MS (ESI²), m/z 455 [CuBr(SS₉₉)]⁺, 431 [CuBr(SS₉₉)]⁻ + Na⁺, 391.16 [SS₉₉⁻] - H⁺. Elemental Analysis: Calc. for C₁₉H₁₇ClCuN₂S₂: C 51.31; H 4.10; N 11.40; Found: C 51.16; H 4.03; N 11.44.
was sonicated for a few seconds and further stirred for 30 min. Diethyl ether (10 mL) was added and stirring was continued for 5 min to give the product as a white powder which was filtered, washed with diethyl ether (5 mL) and dried in air (0.1802 g, 0.334 mmol, 88%). 

**Sulfur insertion route** \([\text{CuBr} \left( \text{CS} \right)_{2}]\): (103 mg, 0.102 mmol) was partially dissolved in acetonitrile (20 mL) in a Schlenk flask. To this was added an excess of sulfur (64 mg, 2.00 mmol) and diethyl ether was added to precipitate and off-white solid. The solid was extracted with acetonitrile (2 × 10 mL). The solvent of the combined organic phases was removed by oil pump vacuum and the off-white solid dried under reduced pressure. Yield = 66 mg (0.11 mmol, 66%). 

The volume of the filtrate was reduced to 2 mL and diethyl ether was added to precipitate the product as an off-white powder which was filtered, washed for a few seconds and further stirred for 30 min. Diethyl ether (10 mL) was added and stirring was continued for 5 min to give the product as a white powder which was filtered, washed with diethyl ether (5 mL) and dried in air (0.1440 g, 0.247 mmol, 64%). 

**Direct route** A round-bottomed flask equipped with a stirring bar was charged with the ligand, \(\text{SS}^{\text{Bu}}\) (0.1504 g; 0.383 mmol) and acetonitrile (10 mL) to give a white milky suspension. Anhydrous Cul (0.073 g, 0.383 mmol) was added in one portion under vigorous stirring to give a pale green mixture which became transparent after a few minutes. The mixture was stirred overnight to give a white precipitate; it was sonicated for a few minutes and further stirred for 30 min. Diethyl ether (10 mL) was added and stirring was continued for 5 min to give the product as an off-white powder which was filtered, washed with diethyl ether (5 mL) and dried in air (0.2947 g, 0.427 mmol, 64%). 

Using \([\text{CuBr} \left( \text{CS} \right)_{2}]\) (5 mg, 0.005 mmol) and elemental sulfur (3.2 mg, 0.11 mmol per sulfur). The reaction was allowed to stir at 80 °C for 2 h after which time complete conversion to complex 5 was confirmed. Using \([\text{CuI} \left( \text{CS} \right)_{2}]\) (0.10 mmol) and elemental sulfur (10.6 mg, 0.33 mmol per sulfur). This required 30 min for complete conversion to complex 6.

**Crystallography** X-ray diffraction studies were carried out on the complexes 1, 2, 3, 4, 5, and 6 at 100(2) K on a Bruker APEX II diffractometer using graphite monochromated Mo-K\(\alpha\) radiation (\(\lambda = 0.71073 \AA\)). Data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre. Using Olex2,[8] the structures were solved by direct methods in ShelXS-1997[9] and refined by least squares minimisation against \(F^2\) in ShelXL-2015[20]. Crystal structures and refinement data are given in Tables S1 and S2 in the supplementary information. Single crystals of complexes 1 - 6 were obtained by slow diffusion of acetonitrile solutions of the corresponding copper(I) salts into acetonitrile solutions of the \(\text{SS}^{\text{Bu}}\) or \(\text{SS}^{\text{Bu}}\) ligands. Single crystals of complex 7 were obtained by slow diffusion of a methanolic solution of copper(II) tetrafluoroborate hydrate to a dichloromethane solution of \(\text{SS}^{\text{Bu}}\). The crystals of 7 contained two molecules of methanol per complex. A suitable crystal from each sample was selected and placed on the diffractometer. Anisotropic parameters, bond lengths and (torsion) angles for these structures are available from the cif file which can be found in the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The corresponding CCDC codes for complexes 1 – 7 are 1539313 - 1539319.

**Acknowledgments**

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Highlights:

Insertion of elemental sulfur into the copper–NHC bonds

Synthesis of bis(1-benzyl-imidazole-2-thione)methane via direct and indirect methods

Structural diversity of copper(I) halides complexes containing bis-thione ligands