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Synthesis and X-ray Characterization of Mono- and Polynuclear Thiolatocopper(I) Complexes: The Effect of Steric Bulk on Coordination Number and Nuclearity

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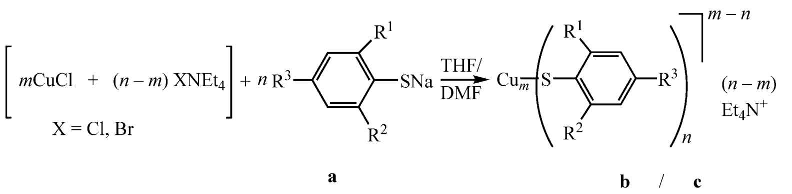
We have synthesized a number of Cu^I complexes of thiophenolato ligands with different alkyl substituents in the *ortho* positions in a single-step procedure starting from a readily available copper(I) precursor to evaluate the coordination preferences of the metal atom. In most cases similar reaction conditions led to the formation of two complexes: a mononuclear complex and a polynuclear cluster, as evident from X-ray crystallography. One dinuclear complex formed has the unique geometry of an $L_2Cu_2(\mu\text{-}L)_2$ core that has not previously been observed for related systems. The steric bulk around the metal atom has a clear effect on the coordination sphere of the complex obtained. Ligands with no *ortho* substituents and those with one substituent with a size varying from methyl to *tert*-butyl all lead to the formation of three-coordinate complexes for the mononuclear species, and clusters of different sizes where larger substituents lead to larger cages and all copper centers are three-coordinate as well. The introduction of two methyl substituents (one in each *ortho* position) leads to either a mononuclear two-coordinate copper complex or a polynuclear cluster where two copper centers are three-coordinate and three are two-coordinate.

Introduction

The recent discovery of a number of proteins from the family of copper metallochaperones, and their structural identification by X-ray crystallography, has refocused attention on copper(I) chemistry.[1–14] These proteins have a conserved motif of MTCXXC (single-letter abbreviation of amino acids, where X represents any amino acid), and binding to the copper(I) center is achieved through the two cysteine residues, with a potential third ligand in some cases. This coordination sphere, namely a low coordination number and soft thiolato ligands, favors the valence state of copper(I) over copper(II) and thus lowers the oxidation potential, which means that the possibly harmful redox behavior of copper is avoided as is any interference with other beneficial redox processes.

Numerous studies have been reported on copper(II) chemistry, including those directed towards modeling various copper protein active sites.[15–18] Herein we focus on understanding the structure and coordination preferences of thiolatocopper(I) complexes of monodentate ligands and evaluating the conditions required to obtain two-coordinate copper centers.[19–32] Hence, thiophenolato ligands with varying steric demands were employed, leading to complexes with different coordination spheres around the copper center (Scheme 1).



1: $R^1 = R^2 = H$; $R^3 = t\text{Bu}$; $n = 3$ $m = 1$
2: $R^1 = i\text{Pr}$; $R^2 = R^3 = H$; $n = 3$ $m = 1$ / $n = 4$ $m = 2$
3: $R^1 = t\text{Bu}$; $R^2 = R^3 = H$; $n = 3$ $m = 1$ / $n = 6$ $m = 4$
4: $R^1 = R^2 = \text{Me}$; $R^3 = H$; $n = 2$ $m = 1$ / $n = 6$ $m = 5$

Scheme 1.

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Results and Discussion

Our reaction conditions were aimed at obtaining two-coordinate copper(I) complexes as structural models for the active site of copper metallochaperones.[4,33] Thus, our straightforward and single-step synthetic procedure generally involved mixing of the commercially available copper(I) precursor CuCl with approximately 1 equiv. of Et_4NX (X = Cl, Br) in thf or dmf and stirring overnight at room temp., followed by addition of 1.5–2 equiv. of the thiolato ligand which had previously been stirred with an excess of NaH overnight, and stirring the resulting mixture for 24 h. Crystallization from a suitable solvent gave single crystals suitable for X-ray crystallography. In most cases the mononuclear complex obtained was accompanied by a polynuclear cluster, which was crystallized under similar reaction conditions, occasionally in the same flask. The complexes formed do not necessarily feature the stoichiometry employed between the copper(I) salt, ligand (**1a**–**4a**), and counterion, and the net reaction stoichiometry of the different complexes formed is presented in Scheme 1. We will begin our discussion with the series of mononuclear complexes obtained (**1b**–**4b**), followed by a description of the clusters (**2c**–**4c**).

Mononuclear Complexes

Treatment of the sodium salt of **1a** with the copper(I) precursor in thf (Scheme 1) gave a colorless solution. Crystallization from thf at –30 °C gave colorless crystals that were analyzed by crystallography despite their significant disorder. The structure of one anion of the product $[Et_4N]_2[Cu\{S(p\text{-}t\mathrm{BuC_6H_4})\}_3]$ (**1b**), out of several found in the asymmetric unit, is presented in Figure 1, and selected bond lengths and angles for this molecule are summarized in Table 1. All molecules in the asymmetric unit are very similar to one another in terms of general structure and bond characteristics.

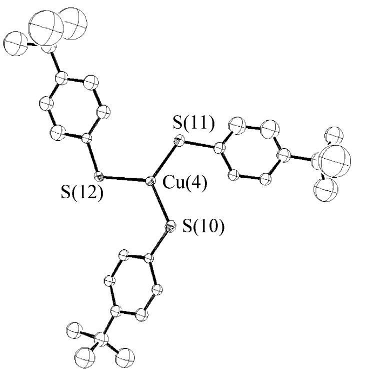


Figure 1. ORTEP drawing of one dianion in $[Et_4N]_2[Cu\{S(p\text{-}t\mathrm{BuC_6H_4})\}_3]$ (**1b**) showing 50% probability ellipsoids. H atoms, solvent molecules, counterions, and disorder have been omitted for clarity.

The structure features a three-coordinate copper(I) center with a highly planar-trigonal geometry, as shown by the sum of the angles around the metal atom (360.0°). Three thiolato ligands bind to the metal atom with two Et_4N^+ counterions stabilizing the copper(I) state. All Cu–S bond lengths (2.24–2.26 Å) are similar, thereby indicating one average bond type of mostly covalent nature. A somewhat broader range is observed for the S–Cu–S angles (117–124°), with a mean value of 120° in agreement with the trigonal geometry. These values are also in agreement with those obtained for other related three-coordinate Cu^I complexes of thiophenolato ligands without *ortho* substituents.[21–23] These latter complexes were obtained under different reaction conditions, the main difference being the significantly lower ligand to metal stoichiometry employed in our case. This suggests that the coordination number of three is favored for the copper(I) center in this system.

Table 1. Selected bond lengths [Å] and angles [°] for a representative dianion of **1b**–**3b**.

$[Cu\{S(p\text{-}t\mathrm{BuC_6H_4})\}_3]^{2-}$ in **1b**			
Cu(4)–S(10)	2.257(3)	S(10)–Cu(4)–S(11)	124.17(11)
Cu(4)–S(11)	2.234(3)	S(11)–Cu(4)–S(12)	117.49(12)
Cu(4)–S(12)	2.244(3)	S(12)–Cu(4)–S(10)	118.33(12)
$[Cu\{S(o\text{-}i\mathrm{PrC_6H_4})\}_3]^{2-}$ in **2b**			
Cu(1)–S(1)	2.251(1)	S(1)–Cu(1)–S(2)	118.78(4)
Cu(1)–S(2)	2.271(1)	S(2)–Cu(1)–S(3)	115.37(4)
Cu(1)–S(3)	2.239(1)	S(3)–Cu(1)–S(1)	125.68(4)
$[Cu\{S(o\text{-}t\mathrm{BuC_6H_4})\}_3]^{2-}$ in **3b**			
Cu(1)–S(1)	2.232(2)	S(1)–Cu(1)–S(2)	122.89(6)
Cu(1)–S(2)	2.244(2)	S(2)–Cu(1)–S(3)	115.06(7)
Cu(1)–S(3)	2.291(2)	S(3)–Cu(1)–S(1)	121.67(7)

We were now interested in exploring the influence of steric effects on the coordination number of the complex formed, and found that increasing the bulk by adding an *ortho*-isopropyl group, or even a larger -*tert*-butyl group, does not have a significant influence on the outcome as regards the coordination parameters of the copper(I) complex obtained. Thus, treating the sodium salt of **2a** or **3a** with the copper(I) precursor in dmf under similar reaction conditions (Scheme 1) gave colorless solutions from which $[Et_4N]_2[Cu\{S(o\text{-}i\mathrm{PrC_6H_4})\}_3]$ (**2b**) and $[Et_4N]_2[Cu\{S(o\text{-}t\mathrm{BuC_6H_4})\}_3]$ (**3b**) were crystallized, respectively, by slow diffusion of thf/hexane at room temperature. The X-ray structures of **2b** and **3b** are presented in Figures 2 and 3, respectively, and selected bond lengths and angles are summarized in Table 1.

Both **2b** and **3b** feature a similar anionic three-coordinate copper(I) complex with a D_{3h}-symmetric core, which is reduced to the C_3 symmetry of the entire anion by the ligand structure. Two anions surrounded by two Et_4N^+ cations each are present in the asymmetric unit of each structure. The bond lengths and angles are in a similar range to those of **1b** (Table 1) and most of the previously reported three-coordinate (thiophenolato)copper(I) structures.[21–23,34] The high planarity of the core is only very slightly reduced by the substituents' bulk, with the sum of the S–Cu–S angles being 359.8° for **2b** and 359.6° for **3b**, which indicates little influence of the steric groups.

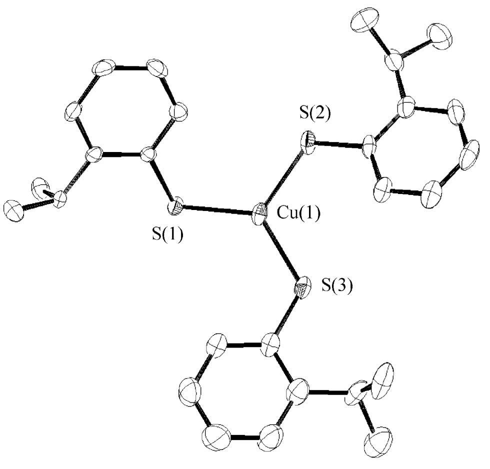


Figure 2. ORTEP drawing of one dianion of $[Et_4N]_2[Cu\{S(o\text{-}iPrC_6H_4)\}_3]$ (**2b**) showing 50% probability ellipsoids. H atoms, solvent molecules, and counterions have been omitted for clarity.

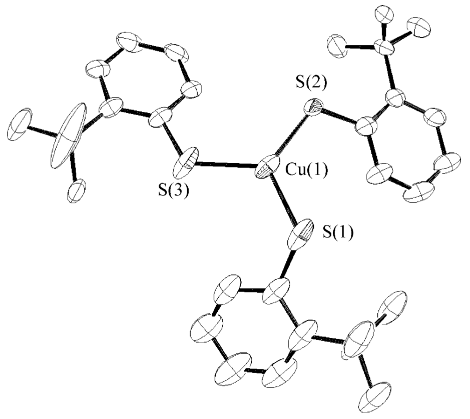
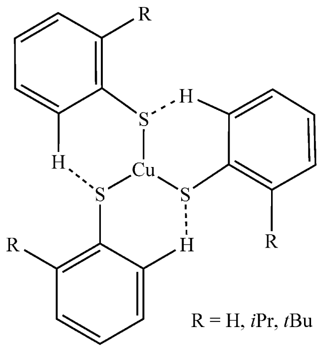


Figure 3. ORTEP drawing of one dianion of $[Et_4N]_2[Cu\{S(o\text{-}tBuC_6H_4)\}_3]$ (**3b**) showing 50% probability ellipsoids. H atoms, solvent molecules, and counterions have been omitted for clarity.

The H···S distance between the hydrogen atom in the second *ortho* position and the nearest sulfur atom in the structures of **2b** and **3b** (Scheme 2) is between 2.7 and 3.0 Å, which suggests that an additional bulky substituent at this position should interfere with the trigonal structure and may lead to a different coordination sphere.[19] Indeed, treatment of the copper(I) precursor with the sodium salt of ligand **4a** (Scheme 1) according to the same procedure as for **1a**–**3a** gave a colorless solution from which single crystals formed upon diffusion of a thf/hexane solution at room temperature. The X-ray structure of the anion of product $[Et_4N][Cu\{S(o,o'\text{-}Me_2C_6H_3)\}_2]$ (**4b**) is presented in Figure 4, and selected bond lengths and angles are summarized in Table 2.



Scheme 2.

Table 2. Selected bond lengths [Å] and angles [°] for the anion of **4b**.

$[Cu\{S(o,o\text{-}Me_2C_6H_3)\}_2]^-$			
Cu(1)–S(1)	2.127(1)	S(1)–Cu(1)–S(2)	165.22(7)
Cu(1)–S(2)	2.111(3)	C(1)–S(1)–Cu(1)–S(2)	166.1
		C(1)–S(1)–S(2)–C(9)	42.1

The structure features a two-coordinate copper(I) anionic center with one Et_4N^+ counterion. The position of S(2) at 70% probability gives an S–Cu–S angle of 165.2°, which deviates quite substantially from linearity. The short Cu–S bond lengths of 2.11–2.13 Å[19,20] are in accordance with strong covalent-type bonds. Interestingly, a comparison of the X-ray structure of **4b** with the two previously reported two-coordinate thiolatocopper(I) complexes[19,20] showed two distinctive features for **4b**, namely the abovementioned substantial deviation of the S–Cu–S angle from

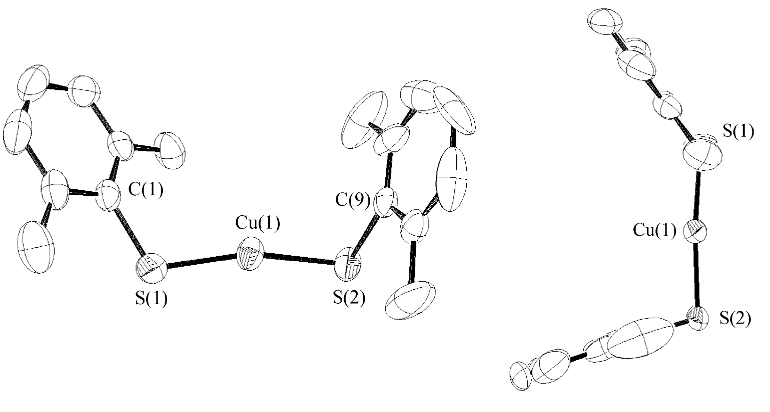


Figure 4. ORTEP drawing of the $[Cu\{S(o,o'\text{-}Me_2C_6H_3)\}_2]^-$ anion in **4b** showing 50% probability ellipsoids. H atoms, the counterion, and disorder have been omitted for clarity.

linearity and the fact that the aromatic rings of the ligands both face in the same direction as the Cu–S bonds in this solid-state structure.

Complex **4b** may thus be considered as a basic structural model of copper metallochaperone proteins, which feature a two-coordinate copper(I) center bound to two thiolato ligands.[4,33] It has been suggested that additional coordination of a third ligand to the copper atom may take place in the natural systems,[4,9,10,35,36] and further support for this notion comes from the S–Hg–S angle observed in the X-ray structure of Atx1 (167°).[4] This actually means that **3b** bears a high coordination resemblance to the active site of Atx1, resulting from its simple steric demands and crystal packing, without the protein folding surroundings.

Polynuclear Clusters

Complex **1b** was the only product that we were able to identify in several reactions with ligand **1a**, both according to X-ray crystallography and NMR spectroscopy (see above). In contrast, all other bulkier ligands (**2a**–**4a**; Scheme 1) allowed the identification of trace amounts of a polynuclear complex under conditions similar to those applied for formation of the mononuclear complexes **2b**–**4b**, although with a small difference in the applied stoichiometric ratio of ligand/metal in some cases. Thus, another type of colorless single crystals was obtained from the same reaction flask where **2b** had been crystallized following the reaction of the sodium salt of **2a** with the copper(I) precursor in a ligand/metal ratio of about 1.5:1. The X-ray structure of these crystals indicated the formation of the dinuclear complex $[Et_4N]_2[Cu_2\{\mu\text{-}S(o\text{-}i\text{Pr}C_6H_4)\}_2\{S(o\text{-}i\text{Pr}C_6H_4)\}_2]$ (**2c**; Figure 5); selected bond lengths and angles are summarized in Table 3.

Table 3. Selected bond lengths [Å] and angles [°] for the dianion of **2c**.

$[Cu_2\{\mu\text{-}S(o\text{-}i\text{Pr}C_6H_4)\}_2\{S(o\text{-}i\text{Pr}C_6H_4)\}_2]^{2-}$			
Cu(1)–S(1)	2.340(1)	S(1)–Cu(1)–S(2)	91.00(4)
Cu(1)–S(2)	2.300(1)	S(2)–Cu(1)–S(3)	145.05(4)
Cu(1)–S(3)	2.180(1)	S(3)–Cu(1)–S(1)	123.94(4)
Cu(2)–S(1)	2.338(1)	S(1)–Cu(2)–S(2)	90.44(4)
Cu(2)–S(2)	2.325(1)	S(2)–Cu(2)–S(4)	127.56(4)
Cu(2)–S(4)	2.188(1)	S(4)–Cu(2)–S(1)	142.00(4)
Cu(1)···Cu(2)	2.584	Cu(1)–S(1)–Cu(2)–S(2)	46.9

Complex **2c** features a C_2-symmetric $Cu_2SC^{Ar}_4$ core where the two copper(I) centers are each three-coordinate with very high planarity, as shown by the value of 360.0° for the sum of the S–Cu–S angles around each metal center. Two thiolato ligands are terminal and two bridge the two metal atoms, thereby preserving the 2:1 ligand/metal ratio, with a total of two Et_4N^+ counterions. Two of the aromatic rings of the thiolato ligands face in the same direction, giving rise to a nonpropeller-type geometry. The Cu–S bond lengths of the bridging ligand (2.30–2.34 Å) are longer than those of the terminal ones (2.18–2.19 Å), as expected, and similar values are observed between each bridging ligand and the copper centers, thus indicating a similar average bond for the symmetrical core. Naturally, one S–Cu–S angle for each metal atom (90.4–91.0°) is more acute than the other two (123.9–145.0°) to accommodate the four-membered ring of the Cu–S–Cu–S core. Additionally, the steric demands of the ring also contribute to rather acute Cu–S–Cu angles (mean value of 67.5°). The Cu···Cu distance is 2.584 Å, with no evidence of a metal–metal interaction. To the best of our knowledge, this is the first example of a dinuclear thiolatocopper(I) complex where both copper atoms are three-coordinate.

Under similar conditions to those that led to **3b** as discussed above (Scheme 1), both in terms of reaction procedure and crystallization conditions, formation of another type of light yellow crystals was observed. X-ray analysis revealed their structure to be $[Et_4N]_2[Cu_4\{\mu\text{-}S(o\text{-}t\text{Bu}C_6H_4)\}_6]$ (**3c**), as shown in Figure 6; selected bond lengths and angles are summarized in Table 4.

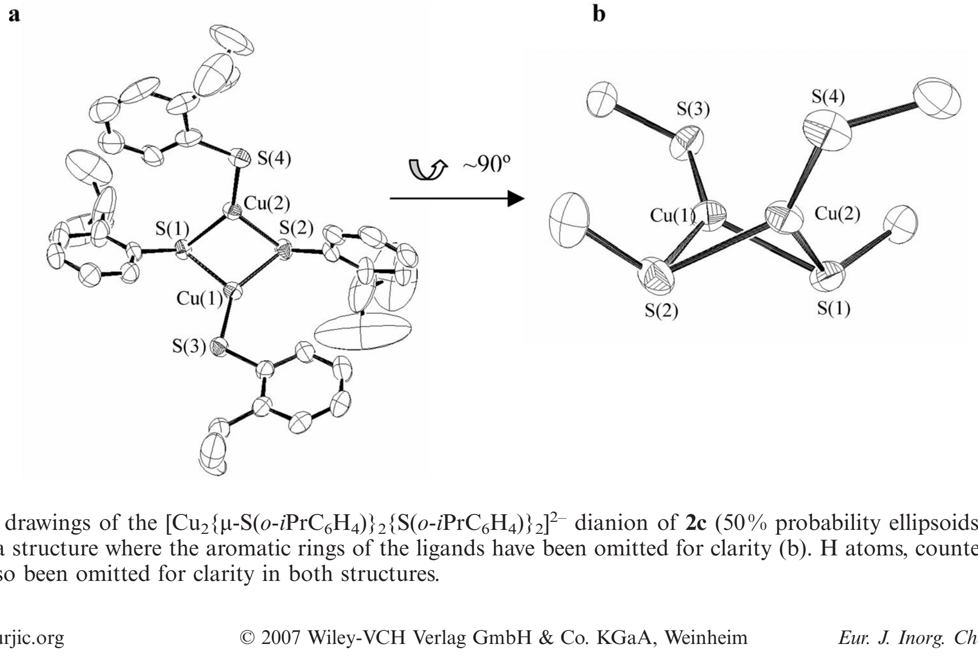


Figure 5. ORTEP drawings of the $[Cu_2\{\mu\text{-}S(o\text{-}i\text{Pr}C_6H_4)\}_2\{S(o\text{-}i\text{Pr}C_6H_4)\}_2]^{2-}$ dianion of **2c** (50% probability ellipsoids) showing the full structure (a) and a structure where the aromatic rings of the ligands have been omitted for clarity (b). H atoms, counterions, and solvent molecules have also been omitted for clarity in both structures.

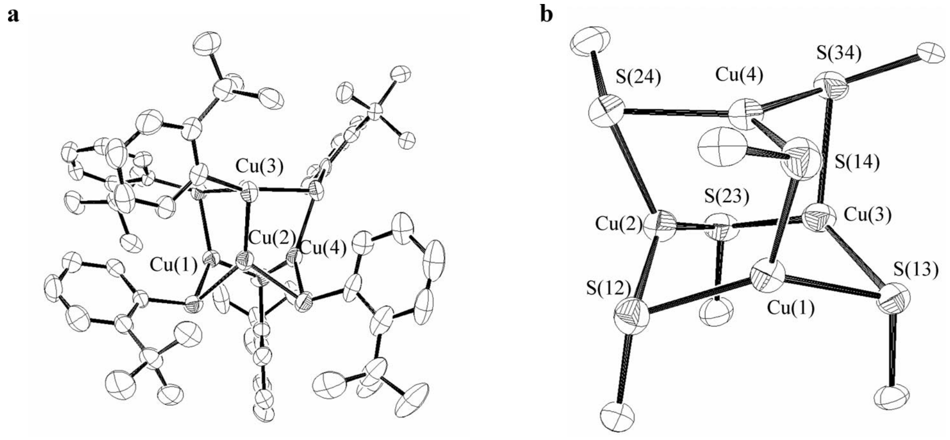


Figure 6. ORTEP drawing of the $[Cu_4\{\mu\text{-}S(o\text{-}tBuC_6H_4)\}_6]^{2-}$ dianion in **3c** showing 50% probability ellipsoids: (a) full structure; (b) the aromatic rings of the ligands have been omitted for clarity. H atoms and counterions have also been omitted for clarity in both cases.

Table 4. Selected bond lengths [Å] and angles [°] for the dianion of **3c**.

$[Cu_4\{\mu\text{-}S(o\text{-}tBuC_6H_4)\}_6]^{2-}$			
Cu(1)–S(12)	2.241(2)	S(12)–Cu(1)–S(13)	138.50(9)
Cu(1)–S(13)	2.307(2)	S(13)–Cu(1)–S(14)	102.80(9)
Cu(1)–S(14)	2.332(3)	S(14)–Cu(1)–S(12)	118.26(9)
Cu(2)–S(12)	2.321(2)	S(12)–Cu(2)–S(23)	137.95(9)
Cu(2)–S(23)	2.236(3)	S(23)–Cu(2)–S(24)	122.7(1)
Cu(2)–S(24)	2.296(2)	S(24)–Cu(2)–S(12)	99.00(9)
Cu(3)–S(13)	2.256(2)	S(13)–Cu(3)–S(23)	138.13(9)
Cu(3)–S(23)	2.317(3)	S(23)–Cu(3)–S(34)	100.69(8)
Cu(3)–S(34)	2.315(2)	S(34)–Cu(3)–S(13)	120.69(9)
Cu(4)–S(14)	2.279(3)	S(14)–Cu(4)–S(24)	121.6(1)
Cu(4)–S(24)	2.295(3)	S(24)–Cu(4)–S(34)	118.5(1)
Cu(4)–S(34)	2.270(3)	S(34)–Cu(4)–S(14)	119.79(9)
Cu(1)···Cu(2)	2.766		
Cu(1)···Cu(3)	2.715		
Cu(2)···Cu(3)	2.716		

The structure features an adamantane-like tetrahedron of metal atoms enveloped by a disordered octahedron of six μ_2-thiolato ligands.[22–24,27–30,37–39] Each of the six ligand units in the tetranuclear copper(I) cluster bridges the edges of the tetrahedral array of copper atoms, and each copper center is three-coordinate with high planarity of the trigonal geometry (sum of the angles around the copper center of 359.6–359.9°), with a total of two Et_4N^+ counterions. The high T_d symmetry of the core is reduced by the substituted aromatic ligands and their position, where the aromatic rings on two of the bound thiolato ligands for three of the four copper atoms [Cu(1), Cu(2), and Cu(3); Figure 6] face in opposite directions rather than giving the propeller-type geometry observed for Cu(4).[24] The ranges of Cu–S bond lengths (2.24–2.33 Å) and S–Cu–S angles (99–138°, with a mean value of 119.0°)[24] are somewhat broader than the equivalent values obtained for **1b**–**3b**, and the Cu···Cu distances (2.71–2.78 Å) provide no significant structural evidence for a copper–copper interaction. The Cu–S–Cu angles lie in a somewhat narrower range (72.0–74.6°). The Cu–S bond lengths, Cu···Cu distances, S–Cu–S angles, and Cu–S–Cu angles are also all similar to those obtained for other Cu_4S_6 clusters of ligands having no significant steric bulk, including both aliphatic thiolato ligands[22,27,30] and thiophenolato ligands having no *ortho* substituents,[23,24,29] which are commonly obtained from Cu^{II} precursors with higher ligand/metal stoichiometric ratios. In addition, these values deviate only slightly from the ideal values of 2.64 Å for a Cu···Cu distance and 2.29 Å for a Cu–S distance in such cores,[22,23] which suggests that the *ortho* substituents do not have much effect on the metal–sulfur core.

The disubstituted ligand **4a** (Scheme 1) also leads to a polynuclear structure upon treatment of its sodium salt with the copper(I) precursor under the reaction conditions used for the synthesis of **4b**. The pentanuclear complex $[Et_4N][Cu_5\{\mu\text{-}S(o,o'\text{-}Me_2C_6H_3)\}_6]$ (**4c**) crystallized from dichloromethane at –30 °C as pale-yellow single crystals suitable for X-ray crystallography. The structure of this complex is presented in Figure 7 and selected bond lengths and angles are summarized in Table 5.

The structure features a trigonal bipyramid of copper atoms within a trigonal antiprism of μ_2-thiolato ligands, with a D_3-symmetrical core.[25,31,32] A single Et_4N^+ cation counters the cluster charge. Three of the five copper atoms in the cluster of **4c** are two-coordinate and two are three-coordinate. The three-coordinate centers have a trigonal geometry with a somewhat reduced planarity (sum of the angles around the metal atom 358.7°). All six thiolato ligands are bridging, with Cu–S distances of 2.24–2.29 Å that are rather similar to the ones obtained for previous three-coordinate structures. The shorter distances to the two-coordinate metal atoms (2.17–2.19 Å) are only slightly shorter than those obtained for **4b**. The S–Cu–S angles range from 112 to 130° for the three-coordinate copper atoms, which is only a slightly broader range than that obtained for **1b**–**3b**. The S–Cu–S angles for the two-coordinate copper atoms are 164–166°, similar to the value obtained for **4b**, and again deviate significantly from linearity. The mean value of the Cu–S–Cu angles (75.5°) is somewhat higher than that

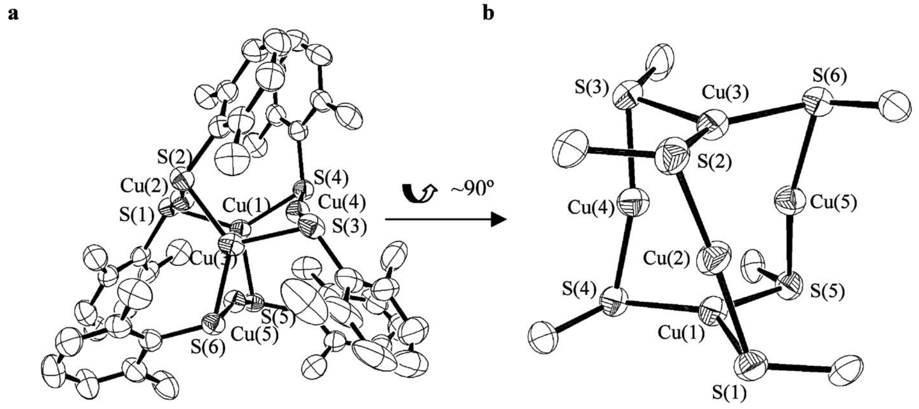


Figure 7. ORTEP drawing of the $[Cu_5\{\mu\text{-}S(o\text{-}tBuC_6H_4)\}_6]^-$ anion of **4c** showing 50% probability ellipsoids: (a) full structure; (b) aromatic rings of the ligands have been omitted for clarity. H atoms, counterions, and solvent molecules have also been omitted for clarity in both cases.

Table 5. Selected bond lengths [Å] and angles [°] for the anion of **4c**.

$[Cu_5\{\mu\text{-}S(o,o\text{-}Me_2C_6H_3)\}_6]^-$			
Cu(1)–S(1)	2.2583(9)	S(1)–Cu(1)–S(4)	130.76(4)
Cu(1)–S(4)	2.242(1)	S(4)–Cu(1)–S(5)	111.71(4)
Cu(1)–S(5)	2.2866(9)	S(5)–Cu(1)–S(1)	116.23(4)
Cu(3)–S(2)	2.256(1)	S(2)–Cu(3)–S(3)	112.88(4)
Cu(3)–S(3)	2.284(1)	S(3)–Cu(3)–S(6)	115.47(4)
Cu(3)–S(6)	2.247(1)	S(6)–Cu(3)–S(2)	130.29(4)
Cu(2)–S(1)	2.1775(9)	S(1)–Cu(2)–S(2)	166.54(4)
Cu(2)–S(2)	2.170(1)	S(3)–Cu(4)–S(4)	163.91(4)
Cu(4)–S(3)	2.174(1)	S(5)–Cu(5)–S(6)	162.74(4)
Cu(4)–S(4)	2.173(1)		
Cu(5)–S(5)	2.1805(9)		
Cu(5)–S(6)	2.191(1)		
Cu(1)···Cu(2)	2.674		
Cu(1)···Cu(3)	3.885		
Cu(2)···Cu(4)	3.351		

observed for the smaller cluster in **3c**. The Cu···Cu distances range between 2.67 and 3.88 Å, with no significant structural evidence for a metal–metal interaction. The Cu_5S_6-type cluster observed for **4c** is less common but is nonetheless similar in its general geometry to other previously reported Cu_5S_6 core structures that have been obtained mainly from Cu^{II} precursors with aliphatic thiolato ligands exhibiting no significant steric bulk, with higher ligand/metal stoichiometric ratios.[20,25,31,32]

Conclusions

We have obtained a series of mononuclear thiolatocopper(I) complexes accompanied by a series of polynuclear clusters obtained from the same ligands under similar reaction conditions. Clearly, increasing the steric bulk around the metal atom by adding a second substituent in the position *ortho* to the thiol group reduces the coordination number. Generally, the preferred coordination number of the metal atom obtained with ligands inducing small steric effects is three, regardless of the stoichiometric ratio employed. This coordination number was obtained with a ligand having no *ortho* substituents as well as with a range of ligands singly *ortho*-substituted, namely, with H to *t*Bu *ortho* groups, both in the mononuclear complexes and in all of the copper atoms in the polynuclear structures obtained from these ligands. Two-coordinate copper(I) centers have only been observed with the dimethylthiophenolato ligand, which has two *ortho* substituents, both in the mononuclear complex and for three of the copper centers in the pentanuclear cluster. Additionally, if we consider the steric effects produced by the ligands to follow the order 2 *ortho*-Me groups > 1 *ortho*-*t*Bu group > 1 *ortho*-*i*Pr group > 0 *ortho* substituents (H atoms), when exploring the clusters obtained taking this order into consideration we find that the larger the steric bulk the larger the cage that is formed under the conditions employed, with the smallest dinuclear structure exhibiting a unique geometry that has not been observed previously with related ligands. Tuning steric effects can therefore have a major influence on the coordination sphere of the copper(I) complexes obtained.

Experimental Section

4-*tert*-Butylthiophenol (**1a**; 97%), 2-isopropylthiophenol (**2a**; tech. 90%), 2,6-dimethylthiophenol (**4a**; 95%), and tetraethylammonium bromide (98%) were purchased from Aldrich Chemical Company Inc. and used without further purification. 2-*tert*-Buthylthiophenol (**3a**; tech. 80%) was purchased from Alfa Aesar Inc. and used without further purification. Tetraethylammonium chloride (98%) was purchased from Sigma Inc. and used without further purification. Copper chloride (CuCl) was purchased from Fluka Inc. and used without further purification. All syntheses that required a conditions were performed in an M. Braun dry box or under nitrogen using Schlenk line techniques. Anhydrous dmf was purchased from Aldrich Chemical Company Inc. and used without further purification. All other solvents were distilled from K or K/benzophenone under nitrogen and stored in the dry box. X-ray diffraction data were obtained with a Bruker Smart Apex diffractometer. CCDC-647993 to -647999 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. NMR spectroscopic data were recorded with an AMX-300 or AMX-400 Bruker spectrometer. Elemental analysis was performed in the microanalytical laboratory of our institute. Reliable elemental analysis for complexes of coordination number higher than two could not be performed due to their enhanced susceptibility to oxidation.

[Et$_4$N]$_2$[Cu{S(*p*-*t*BuC$_6$H$_4$)}$_3$] (1b): A suspension of sodium hydride (0.58 mmol) in 2 mL of thf was added to a solution of **1a** (0.25 mmol) in thf (2 mL) at room temp. under nitrogen. Copper(I) chloride (0.13 mmol) in thf (2 mL) was added to a solution of tetraethylammonium bromide (0.13 mmol) in thf (2 mL) at room temp. under nitrogen and the two solutions were stirred separately in sealed flasks for 24 h. The solution containing the ligand was then added to the solution containing the copper salt and the reaction mixture was stirred overnight. The thf was removed under reduced pressure, and colorless crystals of **1b** (33 mg, 49%) were obtained from thf at –30 °C. ^{1}H NMR (300 MHz, CDCl$_3$, Me$_4$Si, 25 °C): δ = 7.2 (d, J = 8.3 Hz, 6 H, Ar), 6.9 (d, J = 8.3 Hz, 6 H, Ar), 3.2 (q, J = 7.2 Hz, 16 H, NCH_2CH$_3$), 1.2 (s, 27 H, *t*Bu), 1.2 (tt, J = 7.2, 1.8 Hz, 24 H, NCH$_2$CH_3) ppm. **Crystal Data:** Complex **1b** was crystallized from thf at –30 °C. The asymmetric unit contains five anions and ten cations and is disordered. $C_{46}H_{79}CuN_2S_3$, M = 819.83, triclinic, a = 20.317(3), b = 25.894(3), c = 27.231(3) Å, α = 109.280(2), β = 101.349(2), γ = 96.776(2)°, V = 12997(3) Å^3, T = 173(2) K, space group $P\bar{1}$, Z = 10, μ(Mo-K_α) = 0.569 mm^{-1}, 146212 reflections measured, 56251 unique (R_int = 0.1079). $R(F_o^2)$ for [$I > 2\sigma(I)$] = 0.2100, Rw for [$I > 2\sigma(I)$] = 0.4616.

[Et$_4$N]$_2$[Cu{S(*o*-*i*PrC$_6$H$_4$)}$_3$] (2b): Complex **2b** was synthesized in analogy to **1b** by treating a solution of **2a** (0.28 mmol) previously stirred with sodium hydride (0.46 mmol) in dmf with a solution of copper chloride (0.19 mmol) previously stirred with tetraethylammonium chloride (0.21 mmol) in dmf. Colorless crystals of **2b** (17 mg, 23%) were obtained from hexane and thf by slow diffusion at room temp. ^{1}H NMR (300 MHz, CDCl$_3$, Me$_4$Si, 25 °C): δ = 7.7 (dd, J = 7.5, 1.5 Hz, 3 H, Ar), 7.0 (dd, J = 7.4, 1.8 Hz, 3 H, Ar), 6.8 (dt, J = 7.3, 1.7 Hz, 3 H, Ar), 6.7 (dt, J = 7.2, 1.8 Hz, 3 H, Ar), 4.0 [sept, J = 6.9 Hz, 3 H, CH(CH$_3$)$_2$], 3.1 (q, J = 7.3 Hz, 16 H, NCH_2CH$_3$), 1.2 [d, J = 6.9 Hz, 18 H, CH(CH_3)$_2$], 1.2 (tt, J = 7.28, 1.5 Hz, 24 H, NCH$_2$CH_3) ppm. **Crystal Data:** Complex **2b** was crystallized from hexane and thf by slow diffusion at room temp. The asymmetric unit contains two anions and four cations. $C_{43}H_{73}CuN_2S_3$, M = 777.75, orthorhombic, a = 24.386(2), b = 24.543(2), c = 15.3518(14) Å, V = 9188.4(14) Å^3, T = 100(2) K, space group $P2(1)2(1)2$, Z = 8, μ(Mo-K_α) = 0.640 mm^{-1}, 98306 reflections measured, 18045 unique (R_int = 0.0521). $R(F_o^2)$ for [$I > 2\sigma(I)$] = 0.0488, Rw for [$I > 2\sigma(I)$] = 0.1290.

[Et$_4$N]$_2$[Cu{S(*o*-*t*BuC$_6$H$_4$)}$_3$] (3b): 3b was synthesized in analogy to **1b** by treating a solution of **3a** (0.49 mmol) previously stirred with sodium hydride (0.62 mmol) in dmf with a solution of copper chloride (0.23 mmol) previously stirred with tetraethylammonium chloride (0.26 mmol) in dmf. Colorless crystals of **3b** (70 mg, 52%) were obtained from hexane and thf by slow diffusion at room temp. ^{1}H NMR (300 MHz, CDCl$_3$, Me$_4$Si, 25 °C): δ = 7.6 (br. s, 3 H, Ar), 7.1 (br. s, 3 H, Ar), 6.7 (s, 6 H, Ar), 3.2 (q, J = 7.2 Hz, 16 H, NCH_2CH$_3$), 1.5 (s, 27 H, *t*Bu), 1.16 (tt, J = 7.2, 1.8 Hz, 24 H, NCH$_2$CH_3) ppm. **Crystal Data:** Complex **3b** was crystallized from hexane and thf by slow diffusion at room temp. The asymmetric unit contains two anions, four cations, and solvent. $C_{46}H_{79}CuN_2S_3\cdot0.5\text{thf}$, M = 855.88, monoclinic, a = 16.607(4), b = 25.473(6), c = 23.608(5) Å, β = 102.922(4)°, V = 9734(4) Å^3, T = 100(1) K, space group Ia, Z = 8, μ(Mo-K_α) = 0.611 mm^{-1}, 53563 reflections measured, 21026 unique (R_int = 0.0406). $R(F_o^2)$ for [$I > 2\sigma(I)$] = 0.0749, Rw for [$I > 2\sigma(I)$] = 0.1903.

[Et$_4$N][Cu{S(*o*,*o*′-Me$_2$C$_6$H$_3$)}$_2$] (4b): Complex **4b** was synthesized in analogy to **1b** by treating a solution of **4a** (0.51 mmol) previously stirred with sodium hydride (0.70 mmol) in thf with a solution of copper chloride (0.30 mmol) previously stirred with tetraethylammonium chloride (0.32 mmol) in thf. Colorless crystals of **4b** (57 mg, 48%) were obtained from hexane and thf by slow diffusion at room temp. $C_{24}H_{38}CuNS_2$ (468.25): calcd. C 61.56, H 8.18, N 2.99; found C 62.01, H 8.44, N 3.10. ^{1}H NMR (400 MHz, CDCl$_3$, Me$_4$Si, 25 °C): δ = 6.9 (d, J = 7.4 Hz, 4 H, Ar), 6.7 (t, J = 7.4 Hz, 2 H, Ar), 2.7 (q, J = 7.3 Hz, 8 H, NCH_2CH$_3$), 2.5 (s, 12 H, CH_3), 1.0 (tt, J = 7.3, 1.7 Hz, 12 H, NCH$_2$CH_3) ppm. **Crystal Data:** Complex **4b** was crystallized from hexane and thf by slow diffusion at room temp. The asymmetric unit contains one anion, one cation and one disordered S atom. $C_{24}H_{38}CuNS_2$, M = 468.21, monoclinic, a = 11.0173(8), b = 14.5458(11), c = 15.5467(12) Å, β = 101.0680(10)°, V = 2445.1(3) Å^3, T = 173(2) K, space group $P2_1/c$, Z = 4, μ(Mo-K_α) = 1.074 mm^{-1}, 27240 reflections measured, 5808 unique (R_int = 0.0554). $R(F_o^2)$ for [$I > 2\sigma(I)$] = 0.0564, Rw for [$I > 2\sigma(I)$] = 0.1269.

[Et$_4$N]$_2$[Cu$_2${μ-S(*o*-*i*PrC$_6$H$_4$)}$_2${S(*o*-*i*PrC$_6$H$_4$)}$_2$] (2c): Complex **2c** was synthesized similarly to **2b** by treating a solution of **2a** (0.28 mmol) previously stirred with sodium hydride (0.46 mmol) in dmf with a solution of copper chloride (0.19 mmol) previously stirred with tetraethylammonium chloride (0.21 mmol) in dmf. Colorless crystals of **2c** (approx. 10 mg, 10%) were obtained from hexane and thf by slow diffusion at room temp. **Crystal Data:** Complex **2c** was crystallized from hexane and thf by slow diffusion at room temp. The asymmetric unit contains one anion and two cations. $C_{52}H_{84}Cu_2N_2S_4$, M = 992.53, monoclinic, a = 15.1590(9), b = 17.7437(10), c = 20.2433(12) Å, β = 90.9740(10)°, V = 5442.0(6) Å^3, T = 173(2) K, space group $P2_1/c$, Z = 4, μ(Mo-K_α) = 0.969 mm^{-1}, 59897 reflections measured, 11892 unique (R_int = 0.0291). $R(F_o^2)$ for [$I > 2\sigma(I)$] = 0.0702, Rw for [$I > 2\sigma(I)$] = 0.1970.

[Et$_4$N]$_2$[Cu$_4${μ-S(*o*-*t*BuC$_6$H$_4$)}$_6$] (3c): Complex **3c** was synthesized similarly to **3b** by treating **3a** (0.34 mmol) previously stirred with sodium hydride (0.66 mmol) in dmf with copper chloride (0.39 mmol) previously stirred with ammonium chloride (0.39 mmol) in dmf solution. Pale-yellow crystals of **3c** (approx. 8 mg, 10%) were obtained from hexane and thf by slow diffusion at room temp. **Crystal Data:** Complex **3c** was crystallized from hexane and thf by slow diffusion at room temp. The asymmetric unit contains one anion and two cations. $C_{76}H_{118}Cu_4N_2S_6$, M = 1506.24, monoclinic, a = 18.4258(14), b = 29.451(2), c = 21.0690(16) Å, β = 101.9630(10)°, V = 11185.0(15) Å^3, T = 100(2) K, space group Ia, Z = 4, μ(Mo-K_α) = 0.890 mm^{-1}, 59102 reflections measured, 24286 unique (R_int = 0.0730). $R(F_o^2)$ for [$I > 2\sigma(I)$] = 0.0879, Rw for [$I > 2\sigma(I)$] = 0.2423.

[Et$_4$N][Cu$_5${μ-S(*o*,*o*-Me$_2$C$_6$H$_3$)}$_6$] (4c): Complex **4c** was synthesized similarly to **4b** by treating a solution of **4a** (0.38 mmol) previously stirred with sodium hydride (0.70 mmol) in thf with a solution of copper chloride (0.27 mmol) previously stirred with tetraethylammonium bromide (0.28 mmol) in thf. Pale-yellow crystals of **4c** (approx. 8 mg, 10%) were obtained from CH$_2$Cl$_2$ at –30 °C. **Crystal Data:** Complex **4c** was crystallized from CH$_2$Cl$_2$ and traces of toluene at –30 °C. The asymmetric unit contains one anion, one cation and solvents. $C_{56}H_{74}Cu_5NS_6\cdot C_7H_8\cdot CH_2Cl_2$, M = 1448.28, orthorhombic, a = 20.7894(12), b = 21.0811(12), c = 15.0306(9) Å, V = 6587.4(7) Å^3, T = 173(2) K, space group $Pna2_1$, Z = 4, μ(Mo-K_α)

= 1.898 mm^{-1}, 72115 reflections measured, 14359 unique (R_{int} = 0.0402). $R(F_o^2)$ for $[I > 2\sigma(I)] = 0.0367$, Rw for $[I > 2\sigma(I)] = 0.0844$.

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