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# Variations in the Cu(I)–Cu(I) Distances in Multinuclear Clusters with Identical Coordination Geometries. Short Metal–Metal Contacts Induced by Oligomerization

**Santosh P. Abraham,[†] Ashoka G. Samuelson,[*,†] and Jayaraman Chandrasekhar[*,‡]**

Department of Inorganic and Physical Chemistry and Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India

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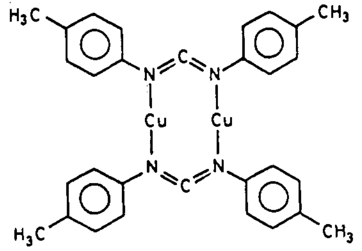
Factors contributing to the variations in the Cu(I)–Cu(I) distances in two clusters with identical ligand and coordination geometries have been analyzed. While the hexamer, **4**, exhibits metal–metal distances in the range 2.81–3.25 Å, shorter contacts are found in the corresponding tetramer, **3** (2.60–2.77 Å). EHT calculations reveal relatively little attractive interactions in the corresponding $Cu_4^{4+}$ and $Cu_6^{6+}$ cores. Introduction of the ligands lowers the reduced overlap populations between the metals further. MNDO calculations with model electrophiles have been carried out to determine the bite angle requirements of the ligands. These are satisfactorily met in the structures of both **3** and **4**. The key geometric feature distinguishing **3** and **4** is the Cu–S–Cu angle involving the bridging $S^-$ unit. In **4**, the corresponding angles are about 90°, while the values in **3** are smaller (70–73°). Wider angles are computed to be energetically favored and are characterized by an open three-center bond and a long Cu–Cu distance. The bridging angles are suggested to be primarily constrained by the mode of oligomerization. Implications of these results for the stability and reactivity of these clusters and for short metal–metal distances in $d^{10}$ systems in general are discussed.

## Introduction

A multitude of copper(I) clusters with fairly short metal–metal distances are known.[1–3] Except in the case of Au(I), where relativistic interactions play a major role,[4] the experimental results involving $d^{10}$–$d^{10}$ interactions have been interpreted in terms of soft bonding forces through the participation of metal s and p shells.[5,6] However, this proposal has been disputed.[7] In several complexes with short Cu–Cu distances, it has been proposed that the ligands bring the metals closer in order to maximize M–L interactions. For example, in the case of the $Cu_2(form)_2$ complex, **1**, characterized by Cotton et al.,[7a] substantial loss in the M–L interactions would occur if the M–M distance was increased. Similarly, the bite angle requirements of the ligands have been suggested to control the M–M distance in **2**.[7b] Another explanation for short M–M distances in bridged clusters is based on the nature of M–L–M three-center bonding.[8] A short distance is predicted if a closed electron-deficient three-center bond is involved. This is favored in systems with an acute M–L–M angle. If the bridging angle is wider, the ligand p(π) orbital forces an open three-center bond and hence a long M–M distance results.



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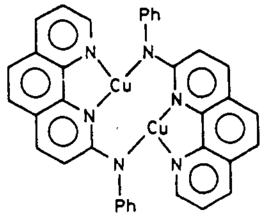

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In order to unravel the relative importance of the different factors which may contribute to short M–M distances in $d^{10}$ systems, it is highly desirable to examine structures with varying metal contacts but with similar ligands and coordination geometries. In this study, we analyze in detail the geometric and electronic effects in two Cu(I) clusters which satisfy the above requirements. The extent of direct metal–metal bonding as well as ligand-induced attraction between the metal centers is evaluated using EHT calculations. The geometric constraints enforced by the preferred bite angles of the ligands are assessed using MNDO calculations on model systems. The importance of the three-center bonding model in determining the M–M distances is also analyzed. The conclusions derived from the present study are

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[†] Department of Inorganic and Physical Chemistry.

[‡] Department of Organic Chemistry.

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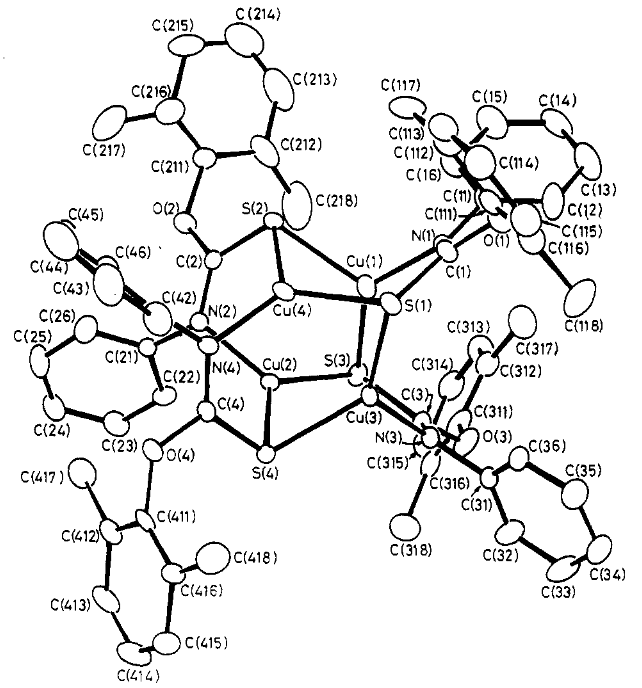


**Figure 1.** ORTEP view of [Cu($\mu$-SC(=NC$_6$H$_5$)(OC$_6$H$_3$(Me)$_2$-2,6))]$_4$ (**3**).

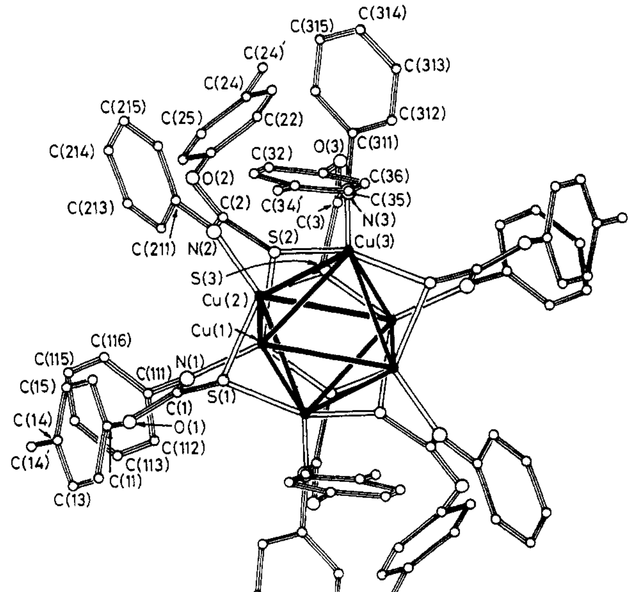


**Figure 2.** ORTEP view of [Cu($\mu$-SC(=NC$_6$H$_5$)(OC$_6$H$_4$(Me)-4))]$_6$ (**4**).

shown to have significant implications for the chemical behavior of these complexes as well as for the interpretation of short M–M distances in d$^{10}$ clusters in general.

## Key Structural Features of 3 and 4

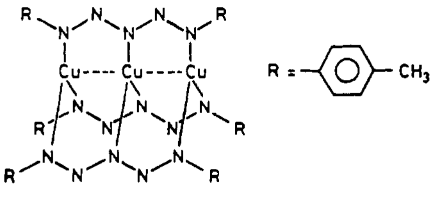
The two copper(I) clusters which we compare are the tetramer tetrakis[($\mu$-(phenylimino)(2,6-dimethylphenoxy)methanethiolato)copper(I)][9] (**3**) (Figure 1) and the hexamer hexakis[($\mu$-(phenylimino)(4-methylphenoxy)methanethiolato)copper(I)][10] (**4**) (Figure 2). The ligands in both complexes are virtually the same (N(Ph)=C(OAr)S$^-$), the marginal difference being in the substituents on the OAr units. The coordination spheres around the metals are identical in these complexes. A nitrogen atom from one ligand and two sulfur atoms from two other ligands are bonded to each copper, resulting in a trigonal coordination sphere. The copper atoms are in the plane formed by the ligating atoms. Further, each ligand is bonded to three different copper atoms, to one copper through the nitrogen, and to two other copper atoms through the bridging sulfur.

A comparison of important bond distances and the contacts between the copper atoms in **3** and **4** is made in Table I. The Cu–Cu distances between neighboring metal atoms in the tetramer fall into two distinct categories. Those bridged by sulfur and NCS are generally shorter (2.608(1)–2.697(1) Å) than those bridged by two NCS fragments (2.755(1)–2.768(1) Å). Interestingly, both sets of distances are distinctly shorter than those found in the hexamer. In **4**, copper atoms bridged by two NCS bridges have contacts ranging from 2.811(1) to 2.874(1) Å. Those bridged by S alone are relatively far apart, 3.062(1)–3.253(1) Å. Thus, in spite of the similarities of the ligand manifold and coordination geometries, the Cu–Cu distances in the two compounds are significantly different.

## Discussion

The metal–metal separation in these complexes may be determined by direct Cu–Cu bonding, by the bite angle requirements of the ligand (N(Ph)=C(OAr)S$^-$) or by geometric and electronic effects of the bridging sulfide unit. We shall examine each of these factors in turn.

**Direct Metal–Metal Bonding.** The magnitudes of direct copper–copper bonding interactions have been gauged using reduced overlap populations (ROP) obtained from EHT calculations.[11] These values are listed for the Cu$_4^{4+}$ and Cu$_6^{6+}$ cores and for models of the tetrameric and hexameric complexes (Table II). The values are generally quite small for both the tetramer and hexamer cores. The largest value for the tetramer is 0.07, while that for the hexamer is just 0.03. The ROP values are substantially smaller than those computed by Hoffmann et al. for **5** (0.13), for which attractive metal–metal interactions via involvement of the s and p shell orbitals were invoked.[12] In fact, the ROP for the tetramer (**3**) is smaller than the value we have computed for the metal core of **1** and **2**, for which Cotton et al. and Trogler suggest purely repulsive interactions from X$\alpha$ calculations.[7] Another noteworthy feature in Table II is that the ROP values for **3** and **4** are markedly reduced by the introduction of the ligands. This behavior is entirely different from that noted for **1** and **2** (Table II) and **5**.[12] It may therefore be concluded that direct metal–metal bonding is insignificant in both **3** and **4** and the ligands are not capable of inducing attractive interactions between the metal atoms.



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**Ligand Bite Angle Requirements.** The directionality of the donor orbitals on the ligands would determine the preferred positions of the metal atoms. In bridging ligands, this can bring about short metal–metal contacts. We used the MNDO method to determine the preferred direction of approach of a test electrophile (H$^+$) toward the N and the S atoms of the ligand

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**Table I.** Selected Bond Distances (Å) with Their Estimated Standard Deviations in Parentheses for **3** and **4**

| complex | atoms | dist | atoms | dist |
|---|---|---|---|---|
| **3** | Cu1–Cu2 | 2.6973(5) | Cu2–S3 | 2.281(1) |
| | Cu1–Cu3 | 2.7679(5) | Cu2–S4 | 2.252(1) |
| | Cu1–Cu4 | 2.6622(5) | Cu2–N2 | 2.009(4) |
| | Cu2–Cu3 | 2.6078(3) | Cu3–N3 | 2.010(4) |
| | Cu2–Cu4 | 2.7550(2) | Cu3–S1 | 2.272(2) |
| | Cu3–Cu4 | 2.6468(2) | Cu3–S4 | 2.289(1) |
| | Cu1–S2 | 2.310(2) | Cu4–S1 | 2.319(2) |
| | Cu1–S3 | 2.253(2) | Cu4–N4 | 1.991(3) |
| **4** | Cu1–Cu2 | 2.822(1) | Cu2–Cu6 | 3.063(1) |
| | Cu1–Cu3 | 3.237(1) | Cu3–Cu4 | 2.872(1) |
| | Cu1–Cu4 | 4.472(1) | Cu3–Cu5 | 3.063(1) |
| | Cu1–Cu5 | 3.256(1) | Cu3–Cu6 | 4.176(1) |
| | Cu1–Cu6 | 2.872(1) | Cu4–Cu5 | 2.822(1) |
| | Cu2–Cu3 | 2.811(1) | Cu5–Cu6 | 2.811(1) |
| | Cu2–Cu4 | 3.256(1) | Cu1–N1 | 2.005(6) |
| | Cu2–Cu5 | 4.138(1) | Cu3–N3 | 2.021(6) |
| | Cu2–N2 | 2.036(6) | Cu5–N5 | 2.036(6) |
| | Cu4–N4 | 2.005(6) | Cu1–S2 | 2.232(2) |
| | Cu6–N6 | 2.021(6) | Cu2–S1 | 2.422(2) |
| | Cu1–S6 | 2.232(2) | Cu4–S3 | 2.232(2) |
| | Cu2–S3 | 2.275(2) | Cu5–S4 | 2.242(2) |
| | Cu3–S4 | 2.244(2) | Cu6–S1 | 2.244(2) |
| | Cu4–S5 | 2.232(2) | Cu4–Cu6 | 3.237(1) |
| | Cu5–S6 | 2.275(2) | Cu3–S2 | 2.246(2) |
| | Cu6–S5 | 2.246(2) | | |

**Table II.** Reduced Overlap Population for the Complexes and the Metal Core

| | | reduced overlap pop. | | |
|---|---|---|---|---|
| complex | atoms | core | complex | bridges |
| **1** | Cu1–Cu2 | 0.0901 | 0.0987 | NCN |
| **2** | Cu1–Cu2 | 0.0588 | 0.0623 | NCN |
| **3** | Cu1–Cu2 | 0.0520 | 0.0110 | S, NCS |
| | Cu1–Cu3 | 0.0405 | 0.0145 | N, NCS |
| | Cu1–Cu4 | 0.0582 | 0.0169 | S, NCS |
| | Cu2–Cu3 | 0.0703 | 0.0235 | S, NCS |
| | Cu2–Cu4 | 0.0424 | 0.0154 | NCS, NCS |
| | Cu3–Cu4 | 0.0623 | 0.0196 | S, NCS |
| **4** | Cu1–Cu2 | 0.0329 | 0.0163 | NCS, NCS |
| | Cu1–Cu3 | 0.0056 | –0.0045 | S |
| | Cu1–Cu4 | 0.0000 | –0.0002 | none |
| | Cu1–Cu5 | 0.0051 | –0.0034 | S |
| | Cu1–Cu6 | 0.0273 | 0.0117 | NCS, NCS |
| | Cu2–Cu3 | 0.0343 | 0.0179 | NCS, NCS |
| | Cu2–Cu4 | 0.0051 | –0.0034 | S |
| | Cu2–Cu5 | 0.0000 | –0.0004 | none |
| | Cu2–Cu6 | 0.0124 | –0.0029 | S |
| | Cu3–Cu4 | 0.0273 | 0.0117 | NCS, NCS |
| | Cu3–Cu5 | 0.0124 | –0.0029 | S |
| | Cu3–Cu6 | 0.0000 | –0.0004 | none |
| | Cu4–Cu5 | 0.0329 | 0.0163 | NCS, NCS |
| | Cu4–Cu6 | 0.0056 | –0.0045 | S |
| | Cu4–Cu5 | 0.0343 | 0.0170 | NCS, NCS |

(N(Ph)═C(OAr)S$^-$). The ideal bite angle at N is calculated to be 121°, while that at S is much smaller, 96°. The variation in the energy as a function of the bridge angles and the minima are consistent with the computed and experimental geometries of acid–base complexes involving N and S donor molecules.[13-15] The hexamer and tetramer have similar C═N—Cu and C—S—Cu angles, which are well in the range expected from the model calculations (Table III). Therefore, bite angle requirements cannot be held responsible for the different sets of Cu–Cu distances involving NCS-bridged metal atoms in **3** and **4** (average 2.76 and 2.83 Å, respectively). The shorter metal–metal contacts in the tetramer may be a secondary consequence of a more fundamental effect.

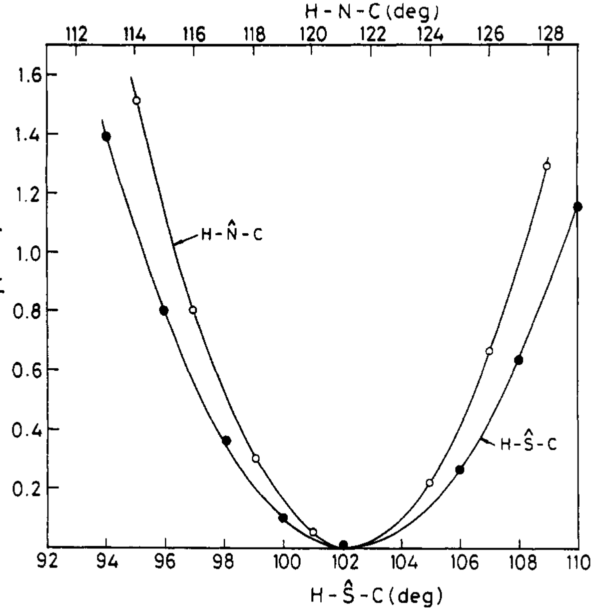

**Figure 3.** Variations in $\Delta H_f$ (MNDO) with H–N–C and H–S–C angles.

**Table III.** Ranges of Selected Bond Angles (deg) with their Estimated Standard Deviations in Parentheses for **3** and **4**

| complex | Cu–S–C | Cu–N–C | Cu–S–Cu |
|---|---|---|---|
| **3** | 99.6(2)–109.1(2) | 116.9(3)–118.0(3) | 70.1(1)–73.0(1) |
| **4** | 100.5(2)–107.2(3) | 114.9(5)–118.2(6) | 86.2(1)–92.6(1) |

**Geometric and Electronic Factors Involving the Bridging Sulfide.** Among the different Cu–Cu distances in the tetramer and the hexamer the largest variation involves those bridged by a common sulfide unit (2.65 and 3.12 Å, respectively). Therefore the bridging sulfide has a crucial role to play in producing differential metal–metal contacts.

A measure of the preferred angle between the sulfur lone pairs in the ligand (N(Ph)═C(OAr)S$^-$) was obtained by optimizing at the MNDO level the location of two protons interacting with the ligand. The computed H–S–H angle of 96° may be considered to be the ideal Cu–S–Cu angle in the absence of additional electronic effects. The corresponding angles in the hexamer (86–92°) are fairly close to this value. In contrast, the Cu–S–Cu angles in the tetramer are acute, 70–73°. These results suggest that the metal–ligand interactions are quite optimal in the hexameric structure, but not in the tetramer. Consistently, the Cu–S distances of the hexamer are shorter.

To determine the effect of the Cu–S–Cu angle on metal–metal interactions, EHT calculations were performed on a simple model with a (N(Ph)═C(OAr)S$^-$) ligand bridging a $\mathrm{Cu_2^{2+}}$ unit. With a fixed Cu–Cu distance, for the Cu–Cu ROP values are higher at more acute Cu–S–Cu angles. For example, the metal–metal ROP is as large as 0.06 at an angle of 65°. However, the ROP becomes negative indicating antibonding interactions for angles beyond 80°. Thus, acute bridging angles, as found in the tetramer, promote ligand-mediated metal–metal bonding.

The above results are quite consistent with previous studies[8] on the nature of three-center Cu–X–Cu bonds. Analysis of sulfide-bridged Cu(I) structures from the Cambridge Crystal Structure Database by van Koten and co-workers[8a] revealed three sets of preferred Cu–S–Cu angles, and the Cu–Cu distances were strikingly shorter in structures with acute bridging angles. Alemany et al.[16] arrived at a similar conclusion on the basis of a theoretical study of $\mathrm{Cu_2X_2}$ structures (X = S, P). These trends have been interpreted in terms of two extreme models of Cu–

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(13) For a representative analysis of crystal structures involving sulfur bases see: (a) Rosenfield, R. E., Jr.; Parthasarathy, R.; Dunitz, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 4860. (b) Guru Row, T. N.; Parthasarathy, R. *J. Am. Chem. Soc.* **1981**, *103*, 477.

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**Figure 4.** Closed and open three-center bondings in Cu–S–Cu bridges.

S–Cu bonding, in analogy to the bonding patterns in boranes. If the angle at the bridging ligand is acute, a closed three-center two-electron bond is indicated with attractive Cu–Cu interactions (Figure 4a). On the other hand, an open three-center bond (Figure 4b) has been invoked for bridges with wider Cu–X–Cu angles leading to antibonding interactions between the metal atoms.

Our calculated results on the metal cores and model complexes suggest a small modification of the above bonding descriptions. Instead of using the extreme model of an electron-deficient closed three-center two-electron bond for acute Cu–S–Cu bridges, we feel that both the closed and open bonding interactions are generally possible. Thus, the Cu–S–Cu units are characterized by three-center four-electron bonding in both the tetramer and the hexamer, although the closed bond with indirect attractive interaction between the metal atoms is more important in the tetramer. This interpretation would account for the shorter metal–metal contacts in the tetramer as well as the general reduction in Cu–Cu ROPs on inclusion of the ligands.

**Oligomerization Control of Cu–S–Cu Angles.** While the direct relation between the angle at the bridging sulfide and Cu–Cu distances is understandable, the question remains as to why the tetramer adopts an acute angle. It is possible that there are two minima on the potential energy surface corresponding to angles near 70 and 100°.[16] However our EHT results with fixed Cu–S distances do not show a minimum at acute angles. We therefore considered the geometric constraints associated with the formation of oligomeric complexes.

The hexamer and the tetramer can be viewed as an agglomeration of three and two tub-shaped $(CuNCS)_2$ units, respectively. The hexamer can be readily constructed from three parallel tubs (Figure 5 (top)). The trigonal coordination at the metal as well as optimum Cu–S–Cu bridging angles for maximum metal–ligand bonding can be achieved. The only impediment to the formation of the hexamer is potential steric repulsions between the aryloxy groups on adjacent tubs.

In contrast to the hexamer, greater geometric constraints are involved in the formation of the tetramer. If the tubs are brought together in a parallel mode, the coordination around the metal atoms would correspond to a highly distorted T shape. In order to achieve the favored trigonal coordination about the metal atoms, the tubs have to be brought together in a mutually orthogonal orientation (Figure 5 (bottom)). In this alignment, the two tubs forming the tetramer cannot avoid having acute Cu–S–Cu angles, irrespective of the distance between the dimers. As confirmed by computer modeling using the program Insight II,[17] increasing the Cu–S–Cu angles by sliding the dimers along one of the axes results in unfavorably large Cu–S distances and a comparable decrease in two other Cu–S–Cu angles. Thus the acute angles are a necessary consequence of the cluster formation dictated by the topology of the tetramer.

The above analysis of the geometric effects in the oligomeric structures is consistent with available chemical evidence. In general, the hexameric cluster is found to be more stable than the corresponding tetramer, reflecting the optimum nature of metal–ligand bonding in the former. Experimentally, attempts to break down the hexameric structure after it is formed using ancillary ligands such as $PPh_3$ fail. On the other hand, the bridges of the tetramer are considerably strained. This is reflected in its reactivity with $PPh_3$ resulting in the formation of the monomer (eq 1).

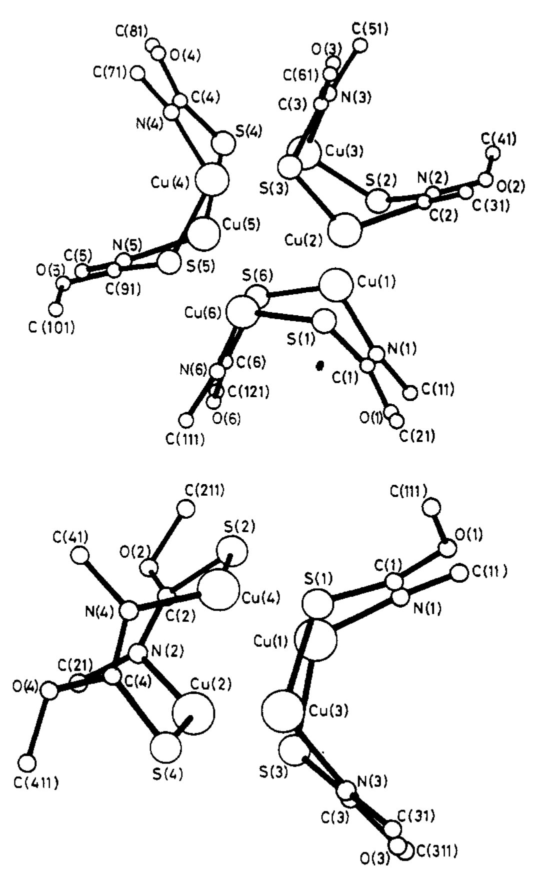
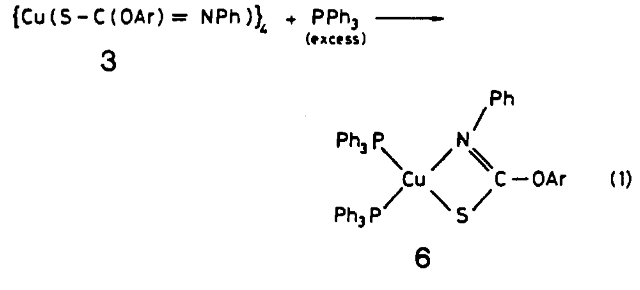


**Figure 5.** Orientation of the tubs forming the tetramer **3** (bottom) and the hexamer **4** (top).



(1)

Interestingly, in the synthesis of these copper clusters, oligomerization stops at the tetramer stage if bulky aryloxy groups are used. This result is consistent with the absence of steric repulsions in the orthogonally disposed tubs in the tetramer and the unavoidably large repulsion in the hexamer.

The geometric control of bridge angles should also exist in other tetrahedral arrays of copper where S and ligand bridges span the copper atoms, independent of the size of the bridge. The observed Cu–S–Cu angles in clusters $[Cu\{S{=}C(N(C_2H_5)_2)S\}]_4$,[18] $[Cu\{S{=}P((i\text{-}C_3H_7O)_2)S\}]_4$,[19] $(PPh_4)_2[Cu_4(o\text{-}(SCH_2)_2C_6H_4)_3]$[20], and $[Cu\{(S)SC(C_7H_7){=}S\}]_4$[21] are indeed acute (74.5, 73.5, 76.5, and 71.5°, respectively), as expected from the above analysis. Unfortunately the corresponding hexameric species are not

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available for comparison. Such comparisons of structures of different cluster sizes with identical ligand and coordination geometries would be valuable for confirming the oligomerization control of Cu–S–Cu angles and Cu–Cu distances.

## Conclusions

Two Cu(I) clusters with identical ligand and coordination geometries have widely varying metal–metal distances. Using EHT calculations, the corresponding $Cu_4^{4+}$ and $Cu_6^{6+}$ cores are shown to have little direct attractive interactions. Introduction of the ligands lowers the reduced overlap populations between the metals further. Hence the ligands are not indicated to induce attractive metal–metal interactions. The bite angle requirements of the ligand, as determined using MNDO calculations, are shown to be adequately met in both the tetramer and the hexamer. The key geometric feature distinguishing **3** and **4** is the Cu–S–Cu angle involving the bridging $S^-$ unit. Acute angles are found in the tetramer, which in turn lead to a greater contribution from a closed three-center bond and a correspondingly short Cu–Cu distance. Wider angles are computed to be energetically favored in view of the more optimum metal–ligand bonding. However, these geometries are characterized by an open three-center bond and a long Cu–Cu distance. We suggest that the main structural differences are primarily constrained by the mode of oligomerization. The dimeric units can be brought together in a parallel manner to form optimum hexamers. However, a similar orientation of dimers to form the tetramer results in an unfavorable coordination geometry around the metal atoms. The dimeric units have to be brought into a mutually orthogonal alignment, which leads to unavoidably acute Cu–X–Cu angles and short Cu–Cu distances. It would be of considerable interest to evaluate this proposal with additional structures of copper clusters having related ligand and coordination geometries.

## Computational Details

Extended Huckel calculations[22] were performed with standard parameters on the structures **1**–**4** using crystallographically determined geometries.[7–10] However the Ph and the Ar groups were replaced by hydrogens at the corresponding angles and estimated distances. Semiempirical MO calculations on ligand models were carried out using the MNDO method.[23] Crystal structure geometries of the tetramer (**3**) were used for the (N(Ph)═C(OAr)S⁻) ligand framework.

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