

Self Assembly of Isostructural Copper(I)–Silver(I) Butterfly Clusters with 2-Mercaptothiazoline: Syntheses and Structures of $(\text{PPh}_3)_2\text{Cu}_4(\text{C}_3\text{H}_4\text{NS}_2)_4$, $[(\text{C}_5\text{H}_5\text{N})\text{Cu}_4(\text{C}_3\text{H}_4\text{NS}_2)_4]_n$, $(\text{PPh}_3)_2\text{Ag}_4(\text{C}_3\text{H}_4\text{NS}_2)_4$ and $(\text{PPh}_3)_2\text{Ag}_2\text{Cu}_2(\text{C}_3\text{H}_4\text{NS}_2)_4$

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The crystal structures of tetranuclear butterfly clusters of Cu^{I} , Ag^{I} and the mixed metal $\text{Ag}^{\text{I}}_2\text{Cu}^{\text{I}}_2$ compound as obtained by reaction of the metal acetates with 2-mercaptothiazoline, and subsequent treatment of the insoluble polymeric clusters with organic bases are reported.

The self assembly of clusters¹ in inorganic systems is a subject of some interest. The self assembly of big molecules has been well established in biological systems, DNA being the best known example. In the last few years several groups have managed to prepare self-assembled helical inorganic complexes.^{2,3} Biological inorganic cluster molecules formed by self assembly also are well established.⁴ The recent report⁵ that the metalloregulatory protein CUP2 from yeast contains a Cu^{I} sulfur cluster with a 2.75 Å Cu–Cu distance adds interest

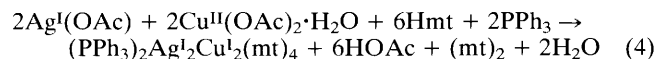
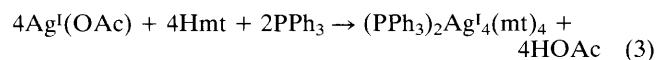
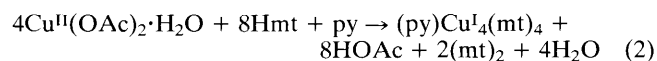
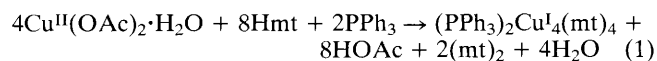
to the determination of structures of polynuclear Cu^{I} sulfur clusters. The Cu_8S_{12} cluster originally reported^{6,7} by one of us (J. P. F.) also has Cu–S and Cu–Cu distances similar to those reported by Hodgson⁵ for the protein.

Here, we report the synthesis of ‘butterfly-shaped’ tetranuclear clusters of Cu^{I} , Ag^{I} and the first mixed metal $\text{Cu}^{\text{I}}\text{Ag}^{\text{I}}$ tetranuclear cluster, using the bidentate ligand 2-mercaptothiazoline, Hmt. The structures reported here of $(\text{PPh}_3)_2\text{Cu}_4(\text{mt})_4$, **1** and $[(\text{py})\text{Cu}_4(\text{mt})_4]_n$, **2** (py = $\text{C}_5\text{H}_5\text{N}$) show that

the insoluble precipitate formed initially with Hmt and copper(II) acetate is polymeric, self-assembled, tetranuclear and butterfly-shaped. The structures of $(\text{PPh}_3)_2\text{Ag}^I_4(\text{mt})_4$, **3**, and the mixed metal species $(\text{PPh}_3)_2\text{Ag}^I_2\text{Cu}^I_2(\text{mt})_4$, **4**, have been determined to be essentially the same as for the tetranuclear $(\text{PPh}_3)_2\text{Cu}^I_4(\text{mt})_4$ complex.[†]

Both 2-mercaptothiazoline, Hmt, and its anion, mt, form various complexes with group 11 metals.⁸ Cu^{II} salts form insoluble 1:1 complexes with mt,⁹ and the related ligands pyridinethionate¹⁰ and 2-mercaptobenzothiazolate.¹¹

Reaction of copper(II) acetate monohydrate, silver(I) acetate, or a 1:1 mixture of the two acetates with Hmt gives an insoluble precipitate. Addition of PPh_3 to this precipitate gives a colourless solution from which crystals of $(\text{PPh}_3)_2\text{Cu}^I_4(\text{mt})_4$, **1**, $(\text{PPh}_3)_2\text{Ag}^I_4(\text{mt})_4$, **3**, or $(\text{PPh}_3)_2\text{Ag}^I_2\text{Cu}^I_2(\text{mt})_4$, **4**, are obtained (Fig. 1). The addition of pyridine[†] instead, gives a yellow solution from which crystals of $(\text{py})\text{Cu}^I_4(\text{mt})_4$, **2**, are obtained. The synthesis of both copper complexes requires two equivalents of Hmt to accommodate the reduction of Cu^{II} to Cu^{I} , presumably the $(\text{mt})_2$ disulfide product is the oxidation product obtained,¹² although it has not been isolated.



Compounds **1–4** have butterfly-shaped cores with the ligand on the wing-tip metal atoms, which are Ag in **4**. In **2**, the pyridine ligand is bonded to only one wing-tip copper atom. The other wing-tip copper atom interacts with the endocyclic sulfur atom of the next butterfly unit (Fig. 2) at the rather large Cu–S distance of 2.723(3) Å. (The sum of the van der Waals radii¹³ of Cu and S is 3.23 Å.) Each ligand is bonded to three metal atoms: nitrogen is bonded to one metal while the exocyclic sulfur atom bridges two other metal atoms. The wing-tip metal atoms, M, M_a are tetrahedrally NS_2L coordinated, where L = P, As,¹⁴ N or S; the body metal atoms, E, E_a are trigonally planar NS_2 coordinated. The wing-tip separation, ca. 3.6–4.2 Å for the clusters (Table 1), is considerably longer than the distance between wing-tip and body atoms, ca. 2.9–3.0 Å. The shortest metal–metal separation in each

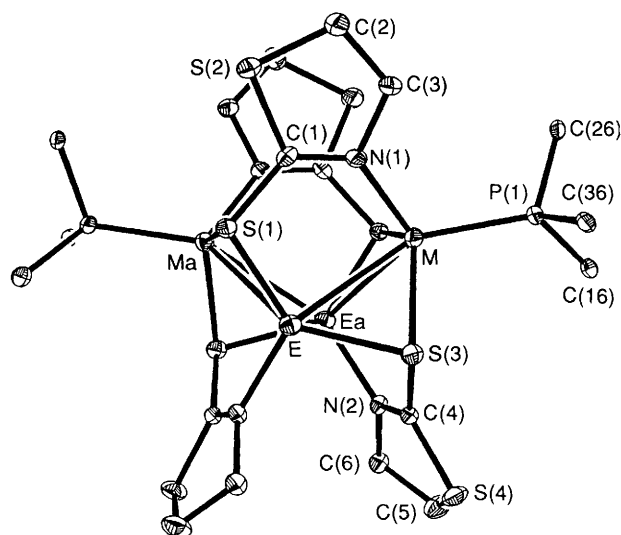


Fig. 1 Structure of $(\text{PPh}_3)_2\text{M}_2\text{E}_2(\text{mt})_4$ and $(\text{py})\text{Cu}_4(\text{mt})_4$, **2**, M = E = Cu, **1**; M = E = Ag, **3**; M = Ag, E = Cu, **4**

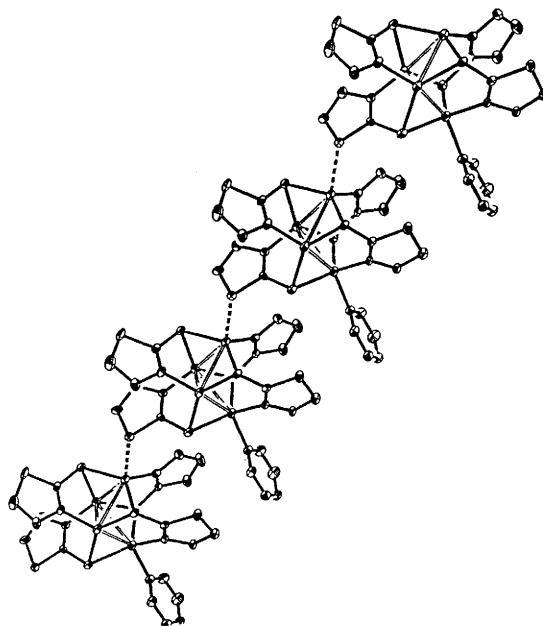


Fig. 2 A portion of the polymer of **2**, showing the Cu–S_{endo} interaction

[†] Crystal data for **1**: $\text{C}_{48}\text{H}_{46}\text{Cu}_4\text{N}_4\text{P}_2\text{S}_8$, monoclinic, $C2/c$ (No. 15), $Z = 4$ (molecule has crystallographic two-fold symmetry), $M = 1253.3$, $a = 15.558(6)$, $b = 11.945(5)$, $c = 27.927(9)$ Å, $\beta = 94.666(3)^\circ$, $V = 5137(3)$ Å³, $\mu(\text{Mo-K}\alpha) = 20.5$ cm⁻¹. Final $R = 0.0377$ and $R_w = 0.0335$ for 1977 unique reflections [$F_o^2 > 3\sigma(F_o)$]. For **2**: $\text{C}_{17}\text{H}_{21}\text{Cu}_4\text{N}_5\text{S}_8$, triclinic, $P\bar{1}$ (No. 2), $Z = 2$, $M = 806.1$, $a = 8.901(1)$, $b = 12.537(1)$, $c = 12.887(1)$ Å, $\alpha = 72.336(6)$, $\beta = 78.058(6)$, $\gamma = 88.230(6)^\circ$, $V = 1339.7(2)$ Å³, $\mu(\text{Mo-K}\alpha) = 20.61$ cm⁻¹. Final $R = 0.0541$ and $R_w = 0.0491$ for 3004 unique reflections. For **3**: $\text{C}_{48}\text{H}_{46}\text{Ag}_4\text{N}_4\text{P}_2\text{S}_8$, monoclinic, $C2/c$ (No. 15), $Z = 4$, $M = 1435.1$, $a = 14.6561(6)$, $b = 12.231(6)$, $c = 29.613(7)$ Å, $\beta = 97.71(3)^\circ$, $V = 5260(3)$ Å³, $\mu(\text{Mo-K}\alpha) = 18.3$ cm⁻¹. Final $R = 0.0525$ and $R_w = 0.0584$ for 3019 unique reflections. For **4**: $\text{C}_{48}\text{H}_{46}\text{Ag}_2\text{Cu}_2\text{N}_4\text{P}_2\text{S}_8$, monoclinic, $C2/c$ (No. 15), $Z = 4$, $M = 1340.1$, $a = 15.559(3)$, $b = 11.939(2)$, $c = 28.201(6)$ Å, $\beta = 94.71(3)^\circ$, $V = 5221(2)$ Å³, $\mu(\text{Mo-K}\alpha) = 19.45$ cm⁻¹. Final $R = 0.0470$ and $R_w = 0.0597$ for 3822 unique reflections. The structures were refined anisotropically with idealized phenyl rings, for **1**, **3** and **4**, and with hydrogen atoms in calculated positions, and for **1–4** using absorption corrected data. Data collection equipment and procedures (Nicolet R3m/E diffractometer, SHELXTL 5.1) are described elsewhere.²¹ Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1 Bond lengths for $[\text{M}_2\text{E}_2(\text{mt})_4(\text{PPh}_3)_2]$ and **2**, $[(\text{py})\text{Cu}_4(\text{mt})_4]_n$, M = E = Cu; **1**; M = E = Cu; **2**; M = E = Ag; **3**; M = Ag, E = Cu, **4**

	M = E = Cu; 1	M = E = Cu; 2	M = E = Ag; 3	M = Ag, E = Cu; 4
M–E	2.940(1)	2.672(2)	3.083(1)	2.948(1)
M–E _a	2.992(1)	2.828(2)	3.110(1)	3.005(1)
E–E _a	2.741(2)	2.780(2)	3.089(2)	2.817(1)
M–M _a	4.127(1)	3.645(2)	4.275(1)	4.188(1)
M–P ^a	2.293(2)	2.162(9)	2.523(3)	2.440(2)
M–S(3)	2.424(2)	2.349(4)	2.624(3)	2.571(2)
E–S(3)	2.265(2)	2.301(3)	2.546(3)	2.330(2)
E–S(1)	2.191(2)	2.231(3)	2.433(3)	2.225(2)
M _a –S(1)	2.394(2)	2.325(3)	2.728(3)	2.577(2)
M–N(1)	2.063(7)	2.025(9)	2.287(9)	2.242(5)
E–N(2A)	1.996(6)	2.021(1)	2.271(9)	2.049(5)

^a For **2**, P = N of py ligand.

compound is between the body atoms, *ca.* 2.7–3.1 Å, a distance similar to the distance found in tetrahedral tetranuclear and cubic octanuclear clusters. This distance is slightly less than the sum of metallic van der Waals radii¹³ in each case.

The fact that an excess of pyridine converts the insoluble precipitate formed upon reaction of Hmt with Cu(OAc)₂·H₂O into a polymeric chain (Fig. 2) with only one pyridine per butterfly unit suggests that this ligand does 'half of the job' compared to PPh₃ (or AsPh₃¹⁴). The softer group 15 ligands break all the M–S_{endo} interactions. These M–S_{endo} interactions presumably exist in the insoluble precipitate producing a polymer of tetranuclear units. The *endo*-cyclic S atoms then form the polymer cross linking by attachment to both wing-tip metal atoms.

The nature of the Lewis base determines the distance between the wing-tip atoms in the butterfly core. The phosphine causes the wing-tip atoms in the Cu₄ cluster to separate further by 0.58 Å than found in the pyridine containing polymer.

The 200 MHz ¹H NMR spectrum of **1** in CDCl₃ at room temperature shows two triplets at δ 3.26 and 3.94, corresponding to the two neighbouring methylene groups present in the five-membered ring. At –50 °C there is partial resolution of the methylene groups as predicted by the solid-state structure. The ³¹P{¹H} NMR spectrum of the silver(I) and mixed copper(I)–silver(I) clusters further suggests fluxional behaviour in solution, presumably rendered by dissociation of the wing-tip ligands thereby making all four mt ligands equivalent (pseudo *D*_{2d} symmetry). Details of these studies will be described elsewhere.

The nature of the insoluble precipitates, obtained from the reaction between the metal acetates and the free ligand, has not yet been completely determined crystallographically although preliminary interpretation of the data suggests that tetranuclear butterfly clusters are formed. They polymerize through *endo* sulfur atoms with one cluster bonding to wing-tip atoms of another cluster. Field desorption mass spectrometric (FD–MS) studies corroborate the tetranuclear cluster premise. The spectrum shows intense signals for the cluster units: *m/z* 362, ⁶³Cu₂(mt)₂⁺, and *m/z* 724, ⁶³Cu₄(mt)₄⁺. The mononuclear unit, *m/z* 181, ⁶³Cu(mt)⁺, is not observed. The FD–MS of **4** shows an intense cluster ion signal at *m/z* 406–408–410, which is assigned to ^{107,109}Ag^{63,65}Cu(mt)₂⁺. The existence of this mixed metal cluster in the gas phase establishes that the (PPh₃)₂Ag₂Cu₂(mt)₄ is not a mixture of homonuclear copper and silver butterfly clusters. While the crystallography was interpreted sensibly without disorder, the structural similarities between the copper and silver clusters did not absolutely remove the possibility. The FD–MS data also suggests that the mixed metal cluster primarily breaks apart along the C₂ axis by separating the body atoms, thus forming the ¹⁰⁷Ag⁶³Cu(mt)₂⁺ species of nominal mass 406. Mass spectrometric data were obtained with a Finnigan MAT 95Q system (The BFGoodrich Co.).

While complexes **1–4** are the first examples of isostructural silver and copper–silver butterfly structures constructed with the same three-atom bridging ligands, similar copper butterfly complexes have been obtained with other ligands: [(CuNEt)₄]₄,¹⁵ [Cu(PrⁱO)₂PS₂]₄,¹⁶ [Cu₄(mhp)₄]₄,¹⁷ (mhp = 6-methyl-2-oxypyridine), and Cu₄(mdap)₄,¹⁸ {mdap = 5-methyl-2-[(dimethylamino)methyl]phenyl}. Similar structures for the silver complex are found for (α-naphthalene-dithioato-*S,S,S'*)₄Ag₄(py)₄¹⁹ and (toluenedithioato-*S,S,S'*)₄Ag₄(py)₄.²⁰

This work was supported by the National Science Foundation, CHE8708625, and the Robert A. Welch Foundation, A-0960.

Received, 24th June 1991; Com. 1/03134A

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