CROATICA CHEMICA ACTA CCACAA **68** (4) 793–823 (1995)

ISSN 0011-1643
CCA–2272 *Original Scientific Paper*

Self Assembly of Copper(I) and Silver(I) Butterfly Clusters with 2-Mercaptothiazoline

César A. López, John P. Fackler, Jr.[*], *Richard J. Staples, Suning Wang*[a], *and Richard E. P. Winpenny*[b]

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843-3255, USA

Received January 25, 1995; accepted February 3, 1995

X-ray data obtained from poor crystals which formed from the reaction of copper(II) acetate with 2-mercaptothiazoline reveal the formation of a product that is a polymer formed of tetranuclear, butterfly shaped $Cu_4(MT)_4$, **1**, clusters. Preparation, isolation and structural characterization of a series of isostructural butterfly complexes was accomplished by addition of a Lewis base (pyridine, PPh_3, or $AsPh_3$) to the precipitate obtained from the reaction of copper(II) and/or silver(I) acetate with the appropriate stoichiometric amount of 2-mercaptothiazoline. The general formula of these clusters is $L_2M_4(MT)_4$; **2**, L = PPh_3 and M = Cu; **3**, L = $AsPh_3$ and M = Cu; **6**, L = PPh_3 and M = Ag; MT = $C_3H_4NS_2^-$, known as 2-mercaptothiazolinate. The polymer $[pyCu_4(MT)_4]_n$, **4**, formed by the addition of pyridine to **1**, was also characterized crystallographically. A mixed metal butterfly complex, $(PPh_3)_2Ag_2Cu_2(MT)_4$, **8**, is formed by addition of PPh_3 to a suspension of the precipitate formed upon reaction of the free HMT ligand with a 1:1 mixture of copper(II) and silver(I) acetates in CH_2Cl_2. FD-MS results of each of the precipitates obtained from the metal acetates and the free ligand indicate that the monomeric unit is $M_4(MT)_4$. ^{1}H-NMR and $^{31}P\{^1H\}$-NMR, both in solution and in the solid state are presented and interpreted. The solid state structures of these molecu-

---

[a] Present address: Department of Chemistry, University of Windsor, Windsor, Ontario, Canada.

[b] Present address: Department of Chemistry, University of Edinburgh, Edinburgh, Scotland.

[*] Author to whom correspondence should be addressed.

Dedicated to Professor F. A. Cotton on the occasion of his 65th birthday and the graduation of his 100th Ph.D. student.

lar complexes were determined by single crystal X-ray analysis. Four of them crystallize in the monoclinic space group $C2/c$ (No. 15) with $Z = 4$, and unit cell dimensions: **2**, $a = 15.558(6)$, $b = 11.945(5)$, $c = 27.927(9)$ Å, $\beta = 94.676(3)°$ **3**, $a = 15.632(8)$, $b = 11.951(6)$, $c = 28.156(16)$ Å, $\beta = 94.04(4)°$; **6**, $a = 14.656(6)$, $b = 12.231(6)$, $c = 29.613(7)$ Å, $\beta = 97.71(3)°$; **8**, $a = 15.559(3)$, $b = 11.939(2)$, $c = 28.201(6)$ Å, $\beta = 94.71(3)°$. Polymer **4** crystallizes in the space group $P1$ (No. 2) with $Z = 2$ and unit cell dimensions: $a = 8.900(6)$, $b = 12.537(9)$, $c = 12.887(9)$ Å, $\alpha = 72.34(5)°$, $\beta = 78.06(5)°$, $\gamma = 88.23(6)°$.

INTRODUCTION

Self-assembly is the spontaneous formation of large molecules from smaller ones and is believed to be the process by which many biological molecules, like DNA, are formed.[1] A number of inorganic helical oligomers, models for DNA, have been obtained[2,3] using long, flexible, N-containing ligands. The self-assembly of clusters has also been explored,[4] and it is well established[5] that inorganic cluster molecules of biological importance have been formed by this spontaneous assembly process. Recently, it has been reported[6] that the metalloregulatory protein CUP2 from yeast metallothionein may contain a cluster of eight Cu(I) ions, bridged most likely by thiolate sulfur atoms, with a copper-copper distance of about 2.75 Å, and with the copper atoms in a three-coordinate environment of atoms; thus, large Cu(I) sulfur clusters also appear subject to the process of self assembly.

1,3-Thiazolidine-2-thione, commonly known as 2-mercaptothiazoline, HMT, is a N,S-containing ligand. This compound contains the thioamido group which undergoes tautomerism[7] between the thione and thiol forms:

$$\text{HN–C=S} \leftrightarrow \text{N=C–SH} \qquad (1)$$

The crystal structure[8] of HMT shows it is a dimer with a strong N-HS$_{exo}$ interaction. The structure also shows the HMT in its thione form.

In 1973, it was reported for the first time that $CuSO_4$ or $CuCO_3$ salts were reduced to Cu^I N-bonded complexes[9] by HMT. Some time later an intermolecularly linked polymeric structure was proposed, with the *exo*cyclic sulfur atom and the *endo*cyclic nitrogen atom simultaneously bonded to the metal ion, as the best fit for the IR spectrum and the insolubility of the product.[7] It was later established[10] that the thioamido group is in part responsible for the reduction of Cu(II) salts to Cu(I) complexes based upon reduction of $Cu^{II}X_2$ salts with other ligands containing the thioamido group. No reduction takes place when the N atom has been alkylated.[10b] The reduction has been proposed (see Discussion, however) to occur according to the following equation:

$$CuX_2 + 2HL \rightarrow CuL + 0.5L_2 + 2HX \qquad (2)$$

where X = NO_3^-, BF_4^-, $1/2SO_4^{2-}$, Cl^-, or Br^-, and HX is the corresponding acid (X = Cl, Br) which was determined by base titration.[10] The oxidation product of HMT is thought to be[10] the disulfide, L_2, namely bis(1,3-thiazol-2-yl) disulfide, but this compound has not been structurally characterized. A disulfide has been structurally characterized from the oxidation of 2-mercaptobenzothiazole, namely bis(1,3-benzothizole)-2,2'-disulfide,[11] using SeO_2 as the oxidant. It has a S-S distance of 2.030(2) Å. A preliminary communication on the formation of these $M_4(MT)_4$ clusters[12] has appeared.

Fluxionality of these butterfly complexes was first observed when ^1H-NMR studies were carried out at various temperatures. Fluxionality in a platinum butterfly cluster, $Pt_4(\mu_2\text{-}CO)_5(PMe_2Ph)_4$, was reported by Moor *et al.*[13] The ^{195}Pt and $^{31}P\{^1H\}$-NMR of this later cluster shows only one environment for each ^{195}Pt and ^{31}P nucleus, rather than the two different environments suggested by the solid state structure. We report here the chemistry associated with several groups $M_4(MT)_4$ complexes, their detailed structures and fluxionality.

EXPERIMENTAL

Spectroscopy

^1H- and $^{31}P\{^1H\}$-NMR spectra were obtained in $CDCl_3$ with a Varian XL-200, 200 MHz instrument, at 23 °C. Internal standards were $SiMe_4$ for ^1H-NMR, and external 85% H_3PO_4 for $^{31}P\{^1H\}$-NMR. CP/MAS $^{31}P\{^1H\}$-NMR spectra were run on a 300 MHz Chemagnetics machine, and on a Bruker MSL 300, 300 MHz. All IR spectra were obtained in KBr (infrared grade, Aldrich) with either a Perkin Elmer 783 or a Perkin Elmer 531 infrared spectrophotometer. The Raman spectra were obtained at the Shell Development Company, Westhollow Research Center, Houston, Texas, 77251, by Dr. Patrick Killough, on an ISA Ramanor 2000 M double monochromator, by excitation with the 647.1 nm line from a krypton ion laser (red). All Field Desorption Mass Spectroscopy (FD-MS) data were recorded at the BFGoodrich Research and Development Center, Brecksville Rd., Brecksville, Ohio 41441, using a Finnigan MAT 95Q instrument. For **1**, **2**, **3** and **6**, a 50/50 matrix of glycerol/thioglycerol was used while for **8** the matrix was CH_2Cl_2. Elemental analyses were performed by Galbraith Laboratories, Inc., P.O. Box 51610, Knoxville, TN 37950.

Unless otherwise stated, all reactions were carried out under an inert atmosphere of either dry argon or nitrogen in oven-dried glassware using standard Schlenk techniques.[14] All reaction solvents were distilled and kept over molecular sieves prior to use. The diethylether used in crystal growth was of anhydrous reagent grade. 2-Mercaptothiazoline, HMT, was purchased from Fluka AG. Copper(II) acetate monohydrate was purchased from J. T. Baker. PPh_3 and $AsPh_3$ were both purchased from Aldrich Chemical Company, Inc. Silver(I) acetate was purchased from Mallinckrodt. All reagents were used as received.

Syntheses

$Cu_4(MT)_4$, **1**, is prepared by reaction of a solution of $Cu(OAc)_2{\cdot}H_2O$ (0.50 g; 2.503 mmoles) in CH_3CN with the protonated ligand, HMT, (0.7463 g; 6.261 mmoles) in a 2:5 molar ratio. The precipitate was washed with CH_3CN (3 × 5 mL), and dried. This reaction was carried out in an open atmosphere (see Discussion). Yield: 0.273 g; 60%.

Crystals of **1** were obtained by diffusion of a solution of $Cu(OAc)_2{\cdot}H_2O$ into that of HMT, both in CH_3CN, inside a U shaped tube with a glass frit separator at the bottom.

$(PPh_3)_2Cu_4(MT)_4$, **2** was synthesized by stoichiometric addition of PPh_3 (21,6 mg, 0.0824 mmoles) to a suspension of $[Cu(MT)]_4$, **1**, (30.0 mg; 0.0413 mmoles) in 2 2mL of CH_2Cl_2, giving a colorless solution which was stirred overnight. The solution was filtered and crystals were obtained by slow diffusion of diethylether into the CH_2Cl_2 solution. Yield: 34.0 mg; 66%; m.p. 210 °C (the color changes at 150 °C) with decomposition.

A different crystalline modification of compound **2** can be obtained by direct reaction between $(PPh_3)_3CuCl$ and NaMT in a 1:1 molar ratio.[15]

$(AsPh_3)_2Cu_4(MT)_4$, **3**, was prepared in a manner similar to that used for **2**, but a large excess of $AsPh_3$ had to be added to $Cu_4(MT)_4$ (30.0 mg; 0.0413 mmoles) in order to obtain a homogeneous solution. The solution was stirred overnight, settled, filtered, and set aside for crystallization. Crystals grew after 3–4 days by slow diffusion of diethylether into the CH_2Cl_2 solution.

$[pyCu_4(MT)_4]_n$, **4**, is formed when a large excess of pyridine is added stepwise (in 1 to 2 mL portions) to a suspension of **1** (30.0 mg, 0.0413 mmole) in 10 mL THF, at room temperature, forming a yellow solution.

$Ag_4(MT)_4$, **5**, is obtained by reaction of a suspension of AgOAc (40.0 mg; 0.2399 mmoles) in 5 mL of THF with the free ligand HMT (28.6 mg; 0.2399 mmoles), giving an insoluble material.

$(PPh_3)_2Ag_4(MT)_4$, **6**. Stepwise addition of a large excess of PPh_3 to the insoluble **5** (35.6 mg; 0.0394 mmoles) suspended in THF yields a colorless solution. The use of excess PPh_3 for the dissolution of silver compounds is well established.[16] Crystals were obtained after 3–4 days by slow diffusion of diethylether into the CH_2Cl_2 solution. M.p. 173–175 °C.

$Ag_2Cu_2(MT)_4$, **7**, is prepared by adding AgOAc (30.0 mg; 0.1797 mmoles) to a solution of $Cu(OAc)_2{\cdot}H_2O$ (35.9 mg; 0.1798 mmoles) in 10 mL of CH_3CN, giving a mixture which is vigorously stirred for 5–10 minutes to allow complete mixing. To this mixture a small excess of HMT is added (96.4 mg; 0.8087 mmoles) giving an insoluble yellowish precipitate with stirring continued overnight. This precipitate is washed with CH_3CN (2 × 5 mL), and dried under reduced pressure. Yield: 45.0 mg; 30.7%.

$(PPh_3)_2Ag_2Cu_2(MT)_4$, **8**. Addition of four times the stoichiometric amount of PPh_3 (25.7 mg; 0.0981 mmoles) to a suspension of $Ag_2Cu_2(MT)_4$, **7**, (20.0 mg; 0.0245 mmoles) in CH_2Cl_2 gave a clear, yellow solution which was stirred overnight. Crystals were obtained as described for **6**.

X-Ray Crystallography

X-ray diffraction studies were carried out using a Nicolet R3m/E automated 4-circle diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å), except for $(PPh_3)_2Ag_2Cu_2(MT)_4$, **8**, which was carried out on a Nicolet R3m/V automated 4-circle diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å), using SHELXTL Plus, version 3.4.

All crystals used for X-ray studies were mounted atop glass fibers in a random orientation.

Unit cell determination, reduction and data collection procedures were performed using the P3 program. SHELXTL, versions 4.1 and 5.1, was used to solve and refine all structures. A Data General Eclipse S140 mini-computer was used for all calculations. All structures were solved by direct methods. Corrections for Lorentz and polarization effects were applied. Empirical absorption correction based on azimuthal (ψ) scans of reflections with χ between 70° and 90°, and 270° and 290°, and 10° increment on φ, covering a wide 2θ range, were recorded for all crystals. Corrections for crystal decay or fluctuation in X-ray beam intensity, were monitored by 3 standard reflections measured every 97 reflections.

$Cu_4(MT)_4$, **1**. Colorless crystals were sent to Crystallitics Company for data collection. Although the most appropriate space group based upon axial photographs is $P2_12_12_1$, the structure was not solved. Another crystal was used to obtain the data presented here. These data refined poorly in the monoclinic $P2_1/n$ space group. Cell constants obtained are a = 18.870(3); b = 11.290(2); c = 24.270(5); β = 110.12(3)°; V = 4341(1) Z = 8. The model used defined a polymer of butterfly clusters of copper(I) atoms bridged by MT units through endocyclic N and exocyclic S atoms. The clusters are polymerized through the wing-tip copper(I) atoms and sulfur atoms of adjacent clusters.

$(PPh_3)_2Cu_4(MT)_4$, **2**. White, well formed crystals of **2** grew after 3 days by slow diffusion of diethylether into a CH_2Cl_2 solution. The initial unit cell and matrix orientation parameters were obtained from 23 reflections from a rotation photograph. The final unit cell and matrix orientation parameters were obtained from 14 reflections. The space group $C2/c$ is uniquely defined from the systematic absences. A total of 4222 data were collected for $2° \leq 2\theta \leq 45°$. All non-hydrogen atoms were treated anisotropically. Phenyl rings were treated as rigid bodies and hydrogen atoms were placed at calculated positions for phenyl and methylene groups. Final R = 0.0357, R_w = 0.0357. The molecule contains a C_2 symmetry axis passing midway the body Cu-Cu vector. Data collection and structure solution parameters are listed in Table I. Atomic coordinates and isotropic thermal parameters, bond distances, and angles for compound **2** are listed in Tables II and III, respectively. Figure 1 shows a representative structural diagram for complexes **2**, **6** and **8**.

$(AsPh_3)_2Cu_4(MT)_4$, **3**. White crystals grew after 6–7 days by slow diffusion of diethylether into a CH_2Cl_2 solution. A total of 1891 data were collected for $0 \leq 2\theta \leq 32$. Since this molecule turned out to be isostructural with **2**, and the crystal quality was not outstanding, the remaining atom positions were determined from the structure of **2**. The space group $C2/c$ is uniquely defined from the systematic absences. The final refinement was R = 0.0554 and R_w = 0.1059. Phenyl rings were treated as rigid bodies (C-C 1.40 Å) with the hydrogen atoms placed in fixed positions (C-H 0.96 Å).

TABLE I

Table of crystallographic data for complexes **2**, **3**, **4**, **6** and **8**

	2	**3**	**4**	**6**	**8**
Formula	$C_{48}H_{46}Cu_4N_4P_2S_8$	$C_{48}H_{46}As_2Cu_4N_4S_8$	$C_{17}H_{21}Cu_4N_5S_8$	$C_{48}H_{46}Ag_4N_4P_2S_8$	$C_{48}H_{46}Ag_2Cu_2N_4P_2S_8$
Formula weight	1251.57	1339.48	806.0	1428.8	1340.1
Space group	$C2/c$ (no. 15)	$C2/c$ (no. 15)	$P1$ (no. 2)	$C2/c$ (no. 15)	$C2/c$ (no. 15)
a/Å	15.558(6)	15.632(8)	8.900(6)	14.656(6)	15.559(3)
b/Å	11.945(5)	11.951(6)	12.537(9)	12.231(6)	11.939(2)
c/Å	27.927(9)	28.156(16)	12.887(9)	29.613(7)	28.201(6)
α/°	90.000	90.000	72.34(5)	90.000	90.000
β/°	94.676(3)	94.04(4)	78.06(5)	97.71(3)	94.71(3)
γ/°	90.000	90.000	88.23(6)	90.000	90.000
Volume/Å^3	5173(3)	5247(4)	1340(2)	5260(3)	5221(2)
Z	4	4	2	4	4
$d_{calc.}$/g cm^{-3}	1.61	1.70	2.00	1.80	1.705
Crystal size/mm	0.1 × 0.15 × 0.25	0.2 × 0.2 × 0.2	0.20 × 0.25 × 0.30	0.2 × 0.3 × 0.35	0.21 × 0.26 × 0.41
F(000) e	2544	2688	657.9	2832	2016
μ Mo Kα /cm^{-1}	20.9	31.98	20.61	18.26	14.6
Radiation/Å graphite monochromated Mo Kα (0.71073)					
Orientation refl., no., range (2θ)	23, 20–30	12, 5–10	25, 2–7	25, 1–8	24,13–30
Temperature/K	293	293	295	293	293
Scan method	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ
Data collection range, 2θ/°	2–45	0–32	0–45	0–45	4–50
Total reflections measured	4222	1892	3902	3921	5110
No. unique reflections	4167	1666	3780	3768	4603
No. with $F_o^2 > 3\sigma(F_o^2)$	1977	1169	3004	3019	3822
No. of parameters refined	262	178	307	262	298
Trans. factor: max., min.	1.00, 0.95	N/A	N/A	0.906, 0.06	1.00, 0.50
R^a,R_w^b	0.0357, 0.357	0.0554, 0.1059	0.0656, 0.0756	0.0567, 0.0684	0.0470, 0.0598
S, GOOF^c	1.216	1.15	1.31	2.56	1.09
Largest shift/esd	0.008	0.000	0.039	0.024	0.002
Largest peak, e/Å^3	0.329	0.523	0.939; –1.446	0.759	1.85
g	0.000012	0.007	0.006400	0.001067	0.005065

$^a R = \Sigma \mid \mid F_o\mid - \mid F_c\mid \mid / \Sigma \mid F_o\mid$ $^b R_w = [\Sigma w(\mid F_o\mid - \mid F_c\mid)^2 / \Sigma w\mid F_o\mid^2]^{1/2}$, $w^{-1} = [\sigma^2(\mid F_o\mid) + g\mid F_o\mid^2]$ ^{c}goodness-of-fit $= [\Sigma w(\mid F_o\mid - \mid F_c\mid)^2 / (N_o - N_p)]^{1/2}$

TABLE II

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($U \times 10^3/\text{Å}^2$) for $(PPh_3)_2Cu_4(MT)_4$, **2**

	x	y	z	U^a
Cu1	4476(1)	1441(1)	1792(1)	36(1)
Cu2	5803(1)	75(1)	2330(1)	35(1)
N1	5363(4)	2704(6)	1936(2)	36(2)
N2	4061(4)	–1291(5)	2257(2)	29(2)
P1	3664(1)	1771(2)	1078(1)	32(1)
S1	6476(1)	1608(2)	2576(1)	34(1)
S2	6552(2)	4020(2)	2328(1)	61(1)
S3	5061(1)	–384(2)	1620(1)	36(1)
S4	4267(2)	–2684(2)	1560(1)	52(1)
C1	6024(5)	2722(7)	2242(3)	31(3)
C2	5794(7)	4676(8)	1908(3)	65(4)
C3	5160(6)	3805(7)	1725(3)	43(3)
C4	4413(5)	–1390(7)	1875(3)	33(3)
C5	3473(7)	–3071(8)	1967(3)	62(4)
C6	3683(5)	–2344(7)	2401(3)	38(3)
C11	1905(6)	1329(8)	772(3)	50(3)
C12	1217(6)	632(10)	642(3)	59(4)
C13	1319(7)	–499(10)	657(4)	64(4)
C14	2102(8)	–944(9)	802(4)	75(5)
C15	2789(7)	–260(8)	948(4)	58(4)
C16	2705(6)	893(7)	927(3)	39(3)
C21	3441(6)	3922(7)	651(3)	47(3)
C22	3123(7)	5005(9)	642(3)	66(4)
C23	2606(7)	5374(9)	987(4)	65(4)
C24	2411(6)	4670(8)	1356(4)	52(4)
C25	2729(5)	3578(7)	1368(3)	40(3)
C26	3236(5)	3195(7)	1015(3)	35(3)
C31	5155(5)	1693(7)	600(3)	43(3)
C32	5639(6)	1623(8)	203(3)	56(4)
C33	5241(7)	1427(8)	–248(3)	56(4)
C34	4360(7)	1302(8)	–299(3)	50(4)
C35	3865(5)	1393(8)	92(3)	44(3)
C36	4265(5)	1593(7)	543(3)	34(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Only the Cu and S atoms were refined anisotropically due to the limited data set. The molecule has a C_2 symmetry axis located perpendicular to the body Cu-Cu vector. Table I contains the data collection and structure solution parameters and Table IV the atomic coordinates. Selected bond distances and angles for compound **3** can be found in Table V. Figure 2 shows the molecular drawing with labeling scheme.

TABLE III

Bond lengths/Å and angles/° for $(PPh_3)_2Cu_4(MT)_4$, **2**

Cu1-Cu2	2.940(1)	Cu1-Nl	2.063(7)
Cu1-P1	2.293(2)	Cu1-S3	2.424(2)
Cu1-Cu2A	2.992(1)	Cu1-S1A	2.394(2)
Cu2-S1	2.191(2)	Cu2-S3	2.265(2)
Cu2-Cu1A	2.992(1)	Cu2-Cu2A	2.741(2)
Cu2-N2A	1.996(6)	N1-C1	1.28(1)
N1-C3	1.46(1)	N2-C4	1.24(1)
N2-C6	1.46(1)	N2-Cu2A	1.996(6)
P1-C16	1.844(9)	P1-C26	1.829(8)
P1-C36	1.830(8)	S1-C1	1.737(8)
S1-Cu1A	2.394(2)	S2-C1	1.761(8)
S2-C2	1.77(1)	S3-C4	1.754(8)
S4-C4	1.781(8)	S4-C5	1.80(1)
C2-C3	1.49(1)	C5-C6	1.50(1)
Cl1-C12	1.38(1)	C11-C16	1.38(1)
Cl2-C13	1.36(2)	C13-C14	1.36(2)
Cl4-C15	1.38(1)	C15-C16	1.38(1)
C21-C22	1.38(1)	C21-C26	1.39(1)
C22-C23	1.37(2)	C23-C24	1.38(1)
C24-C25	1.39(1)	C25-C26	1.38(1)
C31-C32	1.39(1)	C31-C36	1.38(1)
C32-C33	1.37(1)	C33-C34	1.37(1)
C34-C35	1.38(1)	C35-C36	1.37(1)
Cu2-Cu1-N1	82.9(2)	Cu2-Cu1-P1	148.0(1)
N1-Cu1-P1	110.7(2)	Nl-Cul-S3	116.1(2)
P1-Cu1-S3	100.1(1)	Cu2-Cu1-Cu2A	55.0(1)
Nl-Cu1-Cu2A	112.4(2)	P1-Cu1-Cu2A	133.7(1)
S3-Cu1-Cu2A	75.6(1)	Cu2-Cul-S1A	97.2(1)
N1-Cu1-S1A	104.0(2)	P1-Cu1-S1A	106.7(1)
S3-Cu1-S1A	118.9(1)	Cu2A-Cu1-S1A	46.4(1)
Cul-Cu2-S1	89.6(1)	S1-Cu2-S3	132.1(1)
Cul-Cu2-CulA	88.2(1)	S1-Cu2-CulA	52.3(1)
S3-Cu2-Cu1A	137.9(1)	Cu1-Cu2-Cu2A	63.5(1)
S1-Cu2-Cu2A	108.6(1)	6S3-Cu2-Cu2A	83.4(1)
Cu1A-Cu2-Cu2A	61.5(1)	Cu1-Cu2-N2A	141.5(2)
S1-Cu2-N2A	118.6(2)	S3-Cu2-N2A	108.9(2)
Cu1A-Cu2-N2A	89.6(2)	Cu2A-Cu2-N2A	81.9(2)
Cu1-N1-C1	129.0(6)	Cu1-N1-C3	117.5(5)
C1-N1-C3	112.7(7)	C4-N2-C6	111.7(6)
C4-N2-Cu2A	122.4(5)	C6-N2-Cu2A	125.0(5)
Cu1-P1-C16	118.5(3)	Cu1-P1-C26	114.5(3)
C16-P1-C26	103.0(4)	Cu1-P1-C36	113.4(3)
C16-P1-C36	101.9(4)	C26-P1-C36	103.6(4)
Cu2-S1-C1	108.2(3)	Cu2-S1-Cu1A	81.3(1)

TABLE III (continued)

C1-S1-Cu1A	101.9(3)	C1-S2-C2	91.3(4)
Cu1-S3-Cu2	77.6(1)	Cu1-S3-C4	107.4(3)
Cu2-S3-C4	94.9(3)	C4-S4-C5	88.9(4)
N1-C1-S1	127.5(6)	N1-C1-S2	116.4(6)
S1-C1-S2	116.1(4)	S2-C2-C3	107.5(6)
N1-C3-C2	112.1(7)	N2-C4-53	126.1(6)
N2-C4-S4	117.2(6)	S3-C4-S4	116.8(5)
S4-C5-C6	103.8(6)	N2-C6-CS	110.2(7)
C12-C11-C16	120.8(9)	C11-C12-C13	120.3(9)
C12-C13-C14	120.(1)	C13-C14-C15	121.(1)
C14-C15-C16	120.6(9)	P1-C16-C11	123.2(7)
P1-C16-C15	119.0(7)	C11-C16-C15	117.8(8)
C22-C21-C26	119.7(9)	C21-C22-C23	121.(1)
C22-C23-C24	120.(1)	C23-C24-C25	119.4(9)
C24-C25-C26	120.9(8)	P1-C26-C21	123.3(6)
P1-C26-C25	117.6(6)	C21-C26-C25	119.0(8)
C32-C31-C36	120.5(8)	C31-C32-C33	120.0(9)
C32-C33-C34	119.0(9)	C33-C34-C35	121.7(8)
C34-C35-C36	119.1(8)	P1-C36-C31	118.0(6)
P1-C36-C35	122.4(6)	C31-C36-C35	119.6(7)

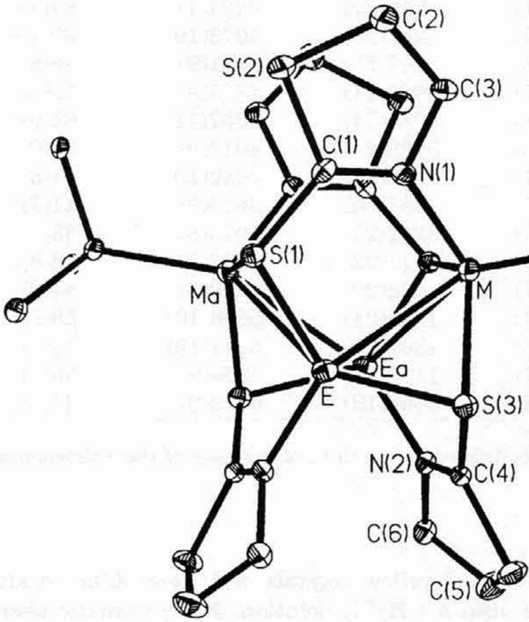

Figure 1. General drawing of $(PPh_3)_2M_2E_2(MT)_4$, **2** M = E = Cu, **6** M = E = Ag, **8** M = Ag E = Cu.

TABLE IV

Atomic coordinates (× 10^4) and isotropic thermal parameters ($U \times 10^3/\text{Å}^2$) for $(AsPh_3)_2Cu_4(MT)_4$, **3**

	x	y	z	U^a
Cul	5466(2)	1371(3)	3162(1)	41(1)
Cu2	4190(2)	47(2)	2668(1)	38(1)
As	6339(2)	1762(2)	3903(1)	38(1)
S1	3531(4)	1584(5)	2429(2)	37(3)
S2	3437(5)	4006(6)	2687(3)	63(3)
S3	4933(4)	–414(6)	3369(2)	37(3)
S4	5716(5)	–2715(6)	3431(3)	56(3)
Nl	4643(11)	2659(14)	3058(7)	29(8)
N2	5905(11)	–1327(14)	2741(7)	28(8)
C1	3938(16)	2695(18)	2774(8)	26(7)
C2	4186(17)	4627(22)	3096(10)	59(9)
C3	4834(18)	3759(22)	3270(10)	60(9)
C4	5549(14)	–1403(18)	3130(8)	17(6)
C5	6487(18)	–3087(25)	3018(9)	68(9)
C6	6336(15)	–2382(19)	2594(9)	34(7)
C11	8092(17)	1292(21)	4233(9)	46(8)
C12	8901(18)	668(23)	4384(10)	62(9)
C13	8712(20)	–494(26)	4384(10)	68(9)
C14	7948(21)	–938(29)	4221(11)	84(11)
C15	7284(20)	–267(26)	4073(10)	69(10)
C16	7312(16)	867(23)	4081(9)	46(8)
C21	6574(17)	3961(21)	4335(9)	50(8)
C22	6901(18)	5085(24)	4357(11)	64(9)
C23	7431(18)	5429(24)	4017(9)	57(9)
C24	7639(17)	4730(22)	3642(10)	51(8)
C25	7330(15)	3667(20)	3649(9)	41(7)
C26	6785(15)	3242(21)	3974(8)	35(7)
C31	4780(16)	1711(22)	4437(9)	48(8)
C32	4297(17)	1628(20)	4820(8)	44(8)
C33	4837(19)	1434(21)	5269(10)	58(9)
C34	5642(18)	1307(21)	5311(10)	53(8)
C35	6189(17)	1438(22)	4924(9)	55(8)
C36	5657(15)	1602(19)	4463(8)	31(7)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor

$[pyCu_4(MT)_4]_n$, 4. Well formed yellow crystals of **4** were obtained after 4 days by diffusion of diethylether into a CH_2Cl_2 solution. No systematic absences suggested a space group of $P1$ or $P\text{–}1$. The structure was solved in $P1$, giving a final refinement value of $R = 0.0510$ and $R_w = 0.0489$, Figure 3. The initial unit cell and orientation matrix were obtained from 25 centered reflections from the rotation pho-

TABLE V

Bond lengths/Å and angles/° for $(AsPh_3)_2Cu_4(MT)_4$, **3**

Cu1-Cu2	2.834(4)	Cu1-Asl	2.456(4)
Cu1-S3	2.378(7)	Cu1-Nl	2.01(2)
Cu1-Cu2A	2.904(4)	Cul-S1A	2.380(8)
Cu2-S1	2.189(7)	Cu2-S3	2.285(7)
Cu2-Cu1A	2.904(4)	Cu2-Cu2A	2.763(6)
Cu2-N2A	2.00(2)	Asl-C16	1.90(3)
Asl-C26	1.91(2)	As1-C36	1.98(2)
S1-C1	1.74(2)	S1-Cu1A	2.380(8)
S2-C1	1.76(2)	S2-C2	1.75(3)
S3-C4	1.69(2)	S4-C4	1.79(2)
S4-CS	1.79(3)	N1-C1	1.32(3)
N1-C3	1.47(3)	N2-C4	1.27(3)
N2-C6	1.50(3)	N2-Cu2A	2.00(2)
C2-C3	1.51(4)	C5-C6	1.47(4)

Cu2-Cu1-As1	148.6(2)	As1-Cu1-S3	98.4(2)
Cu2-Cu1-N1	86.2(5)	As1-Cu1-N1	106.9(5)
S3-Cu -N1	119.3(5)	Cu2-Cu1-Cu2A	57.6(1)
As1-Cu1-Cu2A	131.6(2)	S3-Cu1-Cu2A	78.2(2)
Nl-Cu1-Cu2A	116.8(5)	Cu2-Cu1-S1A	101.0(2)
Asl-Cul-SlA	102.7(2)	S3-Cu1-S1A	121.7(3)
Nl-Cu1-SlA	105.2(6)	Cu2A-Cu1-S1A	47.7(2)
Cul-Cu2-S1	89.0(2)	S1-Cu2-S3	131.8(3)
Cu-Cu2-Cu1A	85.8(1)	S1-Cu2-CulA	53.5(2)
S3-Cu2-CulA	135.6(2)	Cu1-Cu2-Cu2A	62.5(1)
S1-Cu2-Cu2A	108.6(2)	S3-Cu2-Cu2A	82.7(2)
Cu1A-Cu2-Cu2A	59.9(1)	Cu1-Cu2-N2A	139.6(5)
S1-Cu2-N2A	119.8(5)	S3-Cu2-N2A	108.1(5)
Cu1A-Cu2-N2A	89.8(5)	Cu2A-Cu2-N2A	80.6(5)
Cu1-As1-C16	120.3(8)	Cu1-As1-C26	116.3(7)
C16-As1-C26	102.(1)	Cu1-As1-C36	111.2(7)
C16-As1-C36	102.(1)	C26-As1-C36	103.(1)
Cu2-S1-C1	108.9(8)	Cu2-S1-CulA	78.8(2)
Cu1-S1-Cu1A	103.8(9)	C1-S2-C2	91.(1)
Cu1-S3-Cu2	74.8(2)	Cu1-S3-C4	108.1(8)
Cu2-S3-C4	95.4(8)	C4-S4-C5	90.(1)
Cu1-Nl-C1	128.(1)	Cu1-N1-C3	121.(1)
C1-N1-C3	111.(2)	C4-N2-C6	114.(2)
C4-N2-Cu2A	122.(1)	C6-N2-Cu2A	123.(1)
S1-C1-S2	117.(1)	S1-C1-N1	125.(2)
S2-C2-N2	117.(2)	S2-C2-C3	109.(2)
N1-C3-C2	112.(2)	S3-C4-S4	119.(1)
S3-C4-N2	126.(2)	S4-C4-N2	114.(2)
S4-C5-C6	108.(2)	N2-C6-C5	108.(2)
Asl-C16-C11	124.(2)	As1-C16-C15	122.(2)
Asl-C26-C21	123.(2)	As1-C26-C25	120.(2)
Asl-C36-C31	123.(2)	As1-C36-C35	114.(2)

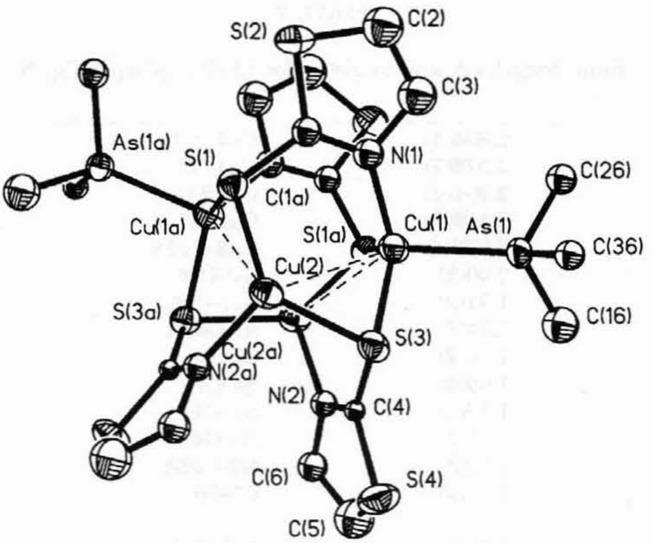

Figure 2. Drawing of $(AsPh_3)_2Cu_4(MT)_4$, **3**, showing the labeling scheme.

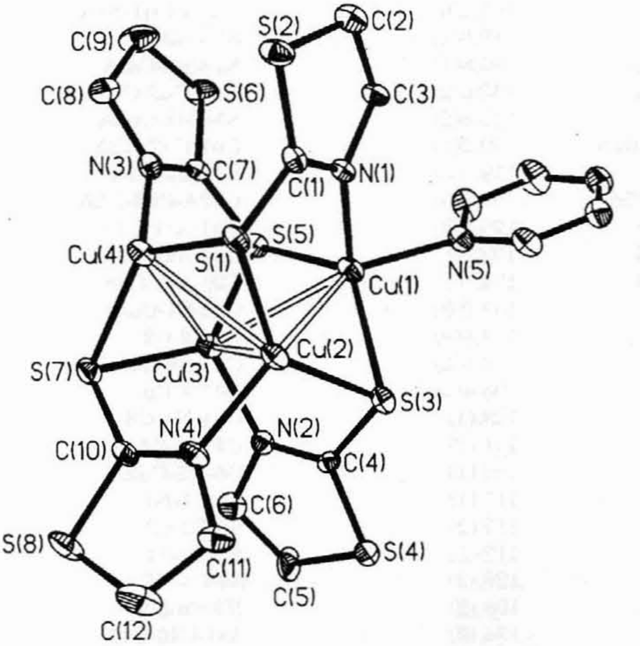

Figure 3. The structure of the cluster in $[pyCu_4(MT)_4]_n$, **4**.

TABLE VI

Atomic coordinates (× 10^4) and isotropic thermal parameters ($U \times 10^3$/Å^2) for [pyCu$_4$(MT)$_4$]$_n$, **4**

	x	y	z	U^{a}
Cul	2223(2)	8560(1)	2442(1)	49(l)
Cu2	3366(2)	7245(1)	1199(1)	47(l)
Cu3	2510(2)	6250(1)	3488(1)	47(1)
Cu4	5504(2)	6746(1)	2576(1)	48(1)
C1	5470(13)	9205(8)	1313(8)	40(4)
C2	6040(15)	10969(10)	1776(11)	62(6)
C3	4405(13)	10497(9)	2169(10)	47(5)
C4	29(12)	6471(9)	2350(9)	40(4)
C5	−1762(18)	4771(11)	3300(16)	94(8)
C6	−247(16)	4759(10)	3661(11)	62(5)
C7	4428(13)	7757(9)	4354(9)	43(4)
CS	7052(15)	7673(11)	4068(12)	61(6)
C9	6728(17)	8409(15)	4797(15)	90(8)
C10	3696(13)	4846(9)	1960(10)	45(5)
C11	2695(14)	5266(11)	382(11)	58(5)
C12	2878(22)	4015(12)	580(13)	87(8)
C21	614(15)	10677(10)	1541(10)	52(5)
C22	−67(17)	11689(11)	1448(12)	65(6)
C23	−564(17)	12008(12)	2381(14)	70(7)
C24	−347(19)	11306(12)	3356(14)	83(7)
C25	353(16)	10299(11)	3414(10)	64(6)
N1	4200(11)	9499(7)	1810(7)	41(3)
N2	591(11)	5833(7)	3164(7)	45(4)
N3	5623(11)	7450(8)	3769(8)	48(4)
N4	3357(12)	5647(8)	1157(8)	50(4)
N5	798(11)	9975(8)	2509(8)	50(4)
S1	5698(3)	8049(2)	826(2)	43(1)
S2	7126(4)	10004(3)	1131(3)	62(1)
S3	848(4)	7765(2)	1472(2)	50(1)
S4	−1641(4)	5966(3)	2070(3)	54(1)
S5	2504(3)	7570(2)	4297(2)	46(1)
S6	4739(4)	8453(3)	5287(3)	68(2)
S7	4355(4)	5000(2)	3095(3)	52(1)
S8	3422(5)	3477(3)	1920(4)	80(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

tograph. A total of 3902 reflections were collected for 0° ≤ 2θ ≤ 45°. The hydrogen atoms of the pyridine ring and methylene group were placed at calculated positions (C-H 0.96 Å). All non-hydrogen atoms were refined anisotropically. Data collection and structure solution parameters are listed in Table I. Atomic coordinates and isotropic thermal parameters, bond distances and angles are listed in Tables VI and VII.

TABLE VII

Bond lengths/Å and angles/° for $[pyCu_4(MT)_4]_n$, **4**

Cu1-Cu2	2.672(2)	Cul-Cu3	2.828(2)
Cu1-Nl	2.025(9)	Cul-N5	2.16(1)
Cu-1S3	2.349(4)	Cu1-S5	2.396(3)
Cu2-Cu3	2.780(2)	Cu2-Cu4	2.795(2)
Cu2-N4	2.021(1)	Cu2-S1	2.231(3)
Cu2-S3	2.301(3)	Cu3-Cu4	2.689(2)
Cu3-N2	1.96(1)	Cu3-S5	2.207(4)
Cu3-S7	2.320(3)	Cu4-N3	2.01(1)
Cu4-S 1	2.325(3)	Cu4-S7	2.292(3)
Cu4-S4A	2.718(3)	C1-N1	1.28(1)
C1-S1	1.74(1)	C1-S2	1.74(1)
C2-C3	1.51(2)	C2-S2	1.82(1)
C3-N1	1.49(2)	C4-N2	1.29(1)
C4-S3	1.75(1)	C4-S4	1.78(1)
C5-C6	1.51(2)	C5-S4	1.81(1)
C6-N2	1.46(1)	C7-N3	1.29(1)
C7-S5	1.75(1)	C7-S6	1.75(1)
C8-C9	1.49(3)	C8-N3	1.46(2)
C9-S6	1.76(1)	C10-N4	1.28(1)
C10-S7	1.75(1)	C10-S8	1.76(1)
C11-C12	1.52(2)	C11-N4	1.46(2)
C12-S8	1.81(2)	C21-C22	1.37(2)
C21-N5	1.33(1)	C22-C23	1.37(2)
C23-C24	1.35(2)	C24-C25	1.38(2)
C25-N5	1.33(2)	S4-Cu4A	2.718(3)
Cu2-Cu1-Cu3	60.7(1)	Cu2-Cul-Nl	88.1(3)
Cu3-Cul-Nl	116.6(2)	Cu2-Cu1-N5	144.4(3)
Cu3-Cu1-N5	143.6(2)	Nl-Cu1-N5	94.3(3)
Cu3-Cu1-S3	78.9(1)	N1-Cu1-S4	126.9(3)
N5-Cu1-S3	98.4(3)	Cu2-Cu1-S5	105.9(1)
Nl-Cu1-S5	102.4(3)	N5-Cu1-S5	108.2(3)
S3-Cu1-S5	121.5(1)	Cul-Cu2-Cu3	62.4(1)
Cu1-Cu2-Cu4	83.6(1)	Cu1-Cu2-N4	143.0(3)
Cu3-Cu2-N4	83.6(3)	Cu4-Cu2-N4	90.7(3)
Cu1-Cu2-S1	91.1(1)	Cu3-Cu2-S1	108.2(1)
N4-Cu2-S1	114.7(3)	Cu3-Cu2-S3	80.7(1)
Cu4-Cu2-S3	132.8(1)	N4-Cu2-S3	107.1(3)
S1-Cu2-S3	137.9(1)	Cu1-Cu3-Cu4	82.7(1)
Cul-Cu3-Cu4	61.4(1)	Cu1-Cu3-N2	93.3(3)
Cu2-Cu3-N2	84.9(2)	Cu4-Cu3-N2	142.3(3)
Cu2-Cu3-S5	108.0(1)	Cu4-Cu3-S5	88.9(1)
N2-Cu3-S5	119.3(3)	Cu1-Cu3-S7	131.5
Cu2-Cu3-S7	81.6(1)	N2-Cu3-S7	108.0(3)
S5-Cu3-S7	132.2(1)	Cu2-Cu4-Cu3	60.9(1)
Cu2-Cu4-N3	125.(3)	Cu3-Cu4-N3	88.9(3)

TABLE VII (continued)

Cu3-Cu4-S1	108.4(1)	N3-Cu4-S1	113.1(3)
Cu2-Cu4-S7	81.8(1)	N3-Cu4-S7	118.5(2)
S1-Cu4-S7	124.2(1)	Cu2-Cu4-S4A	125.9(1)
Cu3-Cu4-S4A	147.2(1)	N3-Cu4-S4A	104.5(3)
S1-Cu4-S4A	93.9(1)	S7-Cu4-S4A	92.9.(1)
N1-C1-S1	125.4(9)	N1-C1-S2	118.0(9)
S1-C1-S2	116.6(6)	C3-C2-S2	106.(1)
C2-C3-N1	112.(1)	N2-C4-S3	124.4(9)
N2-C4-S4	117.5(8)	S3-C4-S4	118.0(6)
C6-C5-S4	106.3(9)	C5-C6-N2	112.(1)
N3-C7-S5	127.(1)	N3-C7-S6	117.(1)
S5-C7-S6	116.1(7)	C9-C8-N3	109.(1)
C8-C9-S6	111.(1)	N4-C10-S7	126.(1)
N4-C10-S8	117.(1)	S7-C10-S8	117.7(6)
C12-C11-N4	111.(1)	C11-C12-S8	106.(1)
C22-C21-N5	123.(1)	C21-C22-C23	119.(1)
C22-C23-C24	118.(1)	C23-C24-C25	121.(2)
C24-C25-N5	121.(1)	Cu1-Nl-C1	126.4(8)
Cu1-Nl-C3	119.5(7)	C1-N1-C3	112.2(9)
Cu3-N2-C4	121.3(7)	Cu3-N2-C6	126.5(8)
C4-N2-C6	112.(1)	Cu4-N3-C7	123.1(9)
Cu4-N3-C8	124.3(8)	C7-N3-C8	113.(1)
Cu2-N4-C10	121.(1)	Cu2-N4-C11	124.7(7)
Cu10-N4-C11	114.(1)	Cul-N5-C21	116.8(8)
Cu1-N5-C25	124.0(8)	C21-N5-C25	118.(1)
Cu2-S1-Cu4	75.7(1)	Cu2-S1-Cu1	106.4(4)
Cu4-S1-C1	95.0(3)	C1-S2-C2	91.5(6)
Cu1-S3-Cu2	70.2(1)	Cu1-S3-C4	109.2(4)
Cu2-S3-C4	97.8(4)	C4-S4-C5	89.8(7)
C4-S4-Cu4A	123.7(4)	C5-S4-Cu4A	98.4(5)
Cu1-S5-Cu3	75.7(1)	Cu1-S5-C7	107.2(4)
Cu3-S5-C7	105.3(4)	C7-S6-C9	89.0(8)
Cu3-S7-Cu4	71.3(l)	Cu3-S7-C10	95.5(4)
Cu4-S7-C10	108.2(4)	C10-S8-C12	90.9(7)

$(PPh_3)_2Ag_4(MT)_4$, **6**. White crystals of compound **6** grew after 2-3 days by slow diffusion of diethylether over a THF solution of **6**. Crystals became brownish after a few days on the diffractometer but did not loose quality. A total of 3921 reflections were collected for $0 \leq 2\theta \leq 45$. The space group *C*2/*c* was uniquely defined from the observed systematic absences. The initial unit cell and orientation matrix parameters were obtained from 25 centered reflections taken from the rotation photograph. Final parameters were obtained from 25 reflections for $24 \leq 2\theta \leq 30$. The final refinement value is $R = 0.0535$ and $R_w = 0.0598$. All non-hydrogen atoms were refined anisotropically. Phenyl rings were refined as rigid groups (C-C 1.40 Å). The hydro-

TABLE VIII

Atomic coordinates (× 10^4) and isotropic thermal parameters ($U \times 10^3/\text{Å}^2$) for $(PPh_3)_2Ag_4(MT)_4$, **6**

	x	*y*	*z*	U^a
Ag1	5241(1)	11610(1)	8228(1)	42(1)
Ag2	3953(1)	10282(1)	7523(1)	45(1)
S1	3288(2)	12001(2)	7224(1)	39(1)
S2	3185(2)	14370(2)	7453(1)	44(1)
S3	4514(2)	9683(3)	8336(1)	47(1)
S4	5217(3)	7399(3)	8462(1)	67(1)
N1	4285(6)	13005(7)	7954(3)	38(3)
N2	5868(6)	8781(8)	7908(3)	42(3)
P1	6129(2)	11964(3)	9005(1)	38(1)
C1	3654(7)	13049(9)	7593(4)	44(4)
C2	3673(9)	14896(10)	8001(4)	51(4)
C3	4487(8)	14114(9)	8144(4)	48(4)
C4	5254(7)	8694(8)	8193(3)	33(3)
C5	6061(15)	6865(14)	8133(7)	102(8)
C6	6381(10)	7768(11)	7867(5)	65(5)
C11	7068(9)	9994(10)	9056(5)	52(5)
C12	7800(11)	9301(12)	9125(5)	67(6)
C13	8658(10)	9696(12)	9250(5)	63(5)
C14	8797(8)	10808(12)	9302(5)	61(5)
C15	8036(9)	11534(12)	9228(4)	58(5)
C16	7169(8)	11107(11)	9113(3)	43(4)
C21	7087(9)	13860(11)	8811(4)	53(5)
C22	7344(9)	14934(12)	8855(5)	58(5)
C23	7085(10)	15582(11)	9221(5)	66(5)
C24	6565(11)	15130(11)	9506(4)	65(5)
C25	6285(9)	14024(10)	9464(4)	53(4)
C26	6540(7)	13357(9)	9107(3)	34(4)
C31	6004(10)	11372(13)	9923(4)	62(5)
C32	5580(11)	11251(13)	10315(5)	66(6)
C33	4688(13)	11437(13)	10280(5)	75(6)
C34	4138(9)	11804(13)	9836(5)	64(5)
C35	4613(8)	11895(11)	9469(4)	54(5)
C36	5551(8)	11661(10)	9507(4)	41(4)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

gen atoms were placed in idealized positions for the phenyl and methylene groups (C-H 0.96 Å). Table I lists the data collection and structure solution parameters. Atomic coordinates and isotropic thermal parameters, bond distances, and angles for compound **6** can be found in Tables VIII and IX, respectively.

TABLE IX

Bond lengths/Å and angles/° for $(PPh_3)_2Ag_4(MT)_4$, **6**

Ag1-Ag2	3.083(1)	Ag1-S3	2.624(3)
Agl-Nl	2.287(9)	Ag1-P1	2.523(3)
Agl-Ag2A	3.110(1)	Ag1-S1A	2.728(3)
Ag2-S1	2.433(3)	Ag2-S3	2.546(3)
Ag2-Ag1A	3.110(1)	Ag2-Ag2A	3.089(2)
Ag2-N2A	2.271(9)	S1-C1	1.72(1)
S1-AglA	2.728(3)	S2-C1	1.78(1)
S2-C2	1.80(1)	S3-C4	1.72(1)
S4-C4	1.77(1)	S4-C5	1.80(2)
N1-C1	1.32(1)	N1-C3	1.48(1)
N2-C4	1.32(1)	N2-C6	1.46(2)
N2-Ag2A	2.271(9)	P1-C16	1.84(1)
P1-C26	1.82(1)	P1-C36	1.85(1)
C2-C3	1.54(2)	C5-C6	1.47(2)
C11-C12	1.36(2)	C11-C16	1.38(2)
C12-C13	1.35(2)	C13-C14	1.38(2)
C14-C15	1.42(2)	C15-C16	1.37(2)
C21-C22	1.37(2)	C21-C26	1.41(2)
C22-C23	1.43(2)	C23-C24	1.33(2)
C24-C25	1.41(2)	C25-C26	1.42(2)
C31-C32	1.39(2)	C31-C36	1.37(2)
C32-C33	1.32(2)	C33-C34	1.51(2)
C34-C35	1.37(2)	C35-C36	1.39(2)
Ag2-Ag1-Nl	82.1(2)	S3-Ag1-Nl	118.3(2)
Ag2-Ag1-P1	154.4(1)	S3-Ag1-P1	102.2(1)
Nl-Ag1-P1	114.3(2)	Ag2-Ag1-Ag2A	59.8(1)
S3-Ag1-Ag2A	79.5(1)	N1-Ag1-Ag2A	114.1(2)
P1-Ag1-Ag2A	122.9(1)	Ag2-Agl-S1A	102.3(1)
S3-Ag1-S1A	125.3(1)	N1-Ag1-S1A	100.5(2)
P1-Ag1-S1A	94.2(1)	Ag2A-Ag1-S1A	48.7(1)
Ag1-Ag2-S1	88.3(1)	S1-Ag2-S3	131.0(1)
Ag1-Ag2-Ag1A	87.3(1)	S1-Ag2-Ag1A	57.4(1)
S3-Ag2-Ag1A	136.2(1)	Ag1-Ag2-Ag2A	60.5(1)
S1-Ag2-Ag2A	109.7(1)	S3-Ag2-Ag2A	81.1(1)
AglA-Ag2-Ag2A	59.7(1)	Ag1-Ag2-N2A	134.4(2)
S1-Ag2-N2A	124.4(2)	S3-Ag2-N2A	104.6(2)
AglA-Ag2-N2A	86.4(2)	Ag2A-Ag2-N2A	77.6(2)
Ag2-S1-C1	109.6(4)	Ag2-S1-Ag1A	73.9(1)
C1-S1-Ag1A	104.0(4)	C1-S2-C2	91.1(6)
Agl-S3-Ag2	73.2(1)	Ag1-S3-C4	108.8(4)
Ag2-S3-C4	96.0(3)	C4-S4-C5	91.0(7)
Ag1-N1-C1	130.4(7)	Ag1-Nl-C3	117.8(6)
C1-N1-C3	110.7(9)	C4-N2-C6	113.(1)
C4-N2-Ag2A	124.4(7)	C6-N2-Ag2A	122.6(8)

TABLE IX (continued)

Ag1-P1-C16	112.0(3)	Ag1-P1-C26	115.5(3)
C16-P1-C26	104.8(5)	Ag1-P1-C36	117.7(3)
C16-P1-C36	101.7(5)	C26-P1-C36	103.4(5)
S1-C1-S2	116.6(6)	S1-C1-N1	127.6(9)
S2-C1-N1	115.7(8)	S2-C2-C3	102.9(8)
N1-C3-C2	110.8(9)	S3-C4-S4	117.4(6)
S3-C4-N2	127.5(8)	S4-C4-N2	115.0(8)
S4-C5-C6	108.(1)	N2-C6-C5	113.(1)
C12-C11-C16	122.(1)	C11-C12-C13	120.(1)
C12-C13-C14	120.(1)	C13-C14-C15	120.(1)
C14-C15-C16	119.(1)	P1-C16-C11	117.9(9)
P1-C16-C15	123.(1)	C11-C16-C15	119.(1)
C22-C21-C26	122.(1)	C21-C22-C23	121.(1)
C22-C23-C24	119.(1)	C23-C24-C25	122.(1)
C24-C25-C26	121.(1)	P1-C26-C21	120.7(9)
P1-C26-C25	123.0(9)	C21-C26-C25	116.(1)
C32-C31-C36	124.(1)	C31-C32-C33	118.(1)
C32-C33-C34	122.(1)	C33-C34-C35	116.(1)
C34-C35-C36	121.(1)	P1-C36-C31	124.0(9)
P1-C36-C35	116.5(8)	C31-C36-C35	119.(1)

$(PPh_3)_2Ag_2Cu_2(MT)_4$, **8**. Colorless crystals of **8** grew after 4-5 days by slow diffusion of diethylether into a CH_2Cl_2 solution of **7**. A total of 5110 reflections were collected for $4 \leq 2\theta \leq 50$. The space group $C2/c$ (No. 15) is uniquely defined from the systematic absences. The molecule contains a C_2 axis perpendicular to the Cu-Cu and Ag-Ag axes. All non-hydrogen atoms were anisotropically refined. Phenyl rings were refined as rigid bodies (C-C 1.40 Å). All hydrogen atoms were placed in idealized positions for phenyl and methylene groups (C-H 0.96 Å). The final refinement gave $R = 0.0470$ and $R_w = 0.0598$. The positions of the Cu and Ag atoms were interchanged to check for possible disorder. By doing this, the refinement indices increase to $R = 0.1509$ and $R_w = 0.1654$. When the two heavy atoms in the asymmetric unit are both assumed to be Ag, the refinement values become $R = 0.0709$ and $R_w = 0.0865$. When the two heavy atoms are assumed to be Cu, the refinement values are $R = 0.0802$ and $R_w = 0.0949$. Table I lists the data collection and structure solution parameters. Atomic coordinates and isotropic thermal parameters, bond distances, angles, and anisotropic thermal parameters, can be found in Tables X and XI, respectively, for compound **8**.

RESULTS

The thiol-thione equilibrium of 2-mercaptothiazoline is shown by ^{1}H-NMR spectroscopy in solution where both N-H and S-H peaks are observed at ~ 10 ppm and ~ 1.8 ppm, respectively.[17,18] The ^{1}H-NMR spectrum of HMT also shows two triplets corresponding to the methylene groups.[18] A closer

TABLE X

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($U \times 10^3/\text{Å}^2$) for $(PPh_3)_2Ag_2Cu_2(MT)_4$, **8**

	x	y	z	U^a
Ag1	5503(1)	1399(1)	3212(1)	43(1)
Cu1	4167(1)	77(1)	2662(1)	27(1)
N1	4560(3)	2797(4)	3054(2)	41(2)
N2	5908(3)	−1322(4)	2761(2)	34(1)
P1	6352(1)	1784(1)	3960(1)	33(1)
S1	3453(1)	1634(1)	2445(1)	41(1)
S2	3365(1)	4078(2)	2649(1)	64(1)
S3	4846(1)	−518(1)	3385(1)	43(1)
S4	5704(1)	−2768(2)	3430(1)	52(1)
C1	3906(4)	2789(5)	2757(2)	33(2)
C2	4099(8)	4751(7)	3072(3)	79(4)
C3	4754(5)	3925(6)	3240(3)	53(2)
C4	5528(4)	−1459(5)	3138(2)	40(2)
C5	6550(5)	−3082(6)	3035(3)	55(2)
C6	6314(5)	−2363(6)	2604(2)	48(2)
C11	6557(5)	3940(5)	4377(2)	42(2)
C12	6844(6)	5039(6)	4390(3)	60(3)
C13	7366(5)	5424(6)	4036(3)	52(2)
C14	7565(4)	4697(6)	3679(3)	48(2)
C15	7262(4)	3623(5)	3661(2)	42(2)
C16	6750(4)	3226(5)	4019(2)	35(2)
C21	8115(4)	1356(6)	4244(2)	47(2)
C22	8815(5)	651(7)	4363(2)	53(2)
C23	8710(5)	−482(6)	4341(3)	52(2)
C24	7900(6)	−928(6)	4186(3)	61(3)
C25	7209(5)	−233(6)	4061(3)	48(2)
C26	7320(4)	917(5)	4101(2)	36(2)
C31	4853(4)	1733(5)	4423(2)	40(2)
C32	4376(5)	1655(6)	4807(2)	47(2)
C33	4772(5)	1424(6)	5261(2)	47(2)
C34	5638(5)	1272(5)	5315(2)	44(2)
C35	6143(4)	1367(5)	4934(2)	39(2)
C36	5753(4)	1608(5)	4478(2)	32(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

examination of the peaks reveals that they are in fact triplets of doublets, each peak of each triplet is split into a doublet. Solid state IR spectra, however, do not show a ν(S-H) peak in the 2500 cm^{-1} region, nor a ν(C=N) peak in the 1700 to 1590 cm^{-1} region, but do show a strong absorption band around 3400 cm^{-1}, corresponding to the N-H stretching frequency. Hence, the thione form is preferred in the solid state.[7,19]

TABLE XI

Bond lengths/Å and angles/° for $(PPh_3)_2Ag_2Cu_2(MT)_4$, **8**

Ag1-Cu1	2.948(1)	Ag1-N1	2.242(5)
Ag1-P1	2.440(2)	Ag1-S3	2.571(2)
Ag1-Cu1A	3.005(1)	Ag1-S1A	2.577(2)
Cu1-S1	2.225(2)	Cu1-S3	2.330(2)
Cu1-Ag1A	3.005(1)	Cu1-Cu1A	2.817(1)
Cu1-N2A	2.049(5)	N1-C1	1.264(7)
N1-C3	1.467(9)	N2-C4	1.270(8)
N2-C6	1.478(9)	N2-Cu1A	2.049(5)
P1-C16	1.832(6)	P1-C26	1.844(6)
P1-C36	1.807(6)	S1-C1	1.752(6)
S1-Ag1A	2.577(2)	S2-C1	1.768(6)
S2-C2	1.77(1)	S3-C4	1.732(7)
S4-C4	1.777(6)	S4-C5	1.832(8)
C2-C3	1.47(1)	C5-C6	1.51(1)
C11-C12	1.39(1)	C11-C16	1.374(9)
C12-C13	1.41(1)	C13-C14	1.38(1)
C14-C15	1.37(1)	C15-C16	1.417(9)
C21-C22	1.39(1)	C21-C26	1.374(9)
C22-C23	1.36(1)	C23-C24	1.40(1)
C24-C25	1.38(1)	C25-C26	1.387(9)
C31-C32	1.37(1)	C31-C36	1.404(9)
C32-C33	1.403(9)	C33-C34	1.36(1)
C34-C35	1.386(9)	C35-C36	1.406(8)
Cu1-Ag1-N1	82.7(1)	Cu1-Ag1-P1	149.8(1)
N1-Ag1-P1	109.3(1)	N1-Ag1-S3	115.9(1)
P1-Ag1-S3	101.5(1)	Cu1-Ag1-Cu1A	56.5(1)
N1-Ag1-Cu1A	112.4(1)	P1-Ag1-Cu1A	133.7(1)
S3-Ag1-Cu1A	77.6(1)	Cu1-Ag1-S1A	98.0(1)
N1-Ag1-S1A	102.5(1)	P1-Ag1-S1A	105.8(1)
S3-Ag1-S1A	121.2(1)	Cu1A-Ag1-S1A	46.2(1)
Ag1-Cu1-S1	90.7(1)	S1-Cu1-S3	132.5(1)
Ag1-Cu1-Ag1A	89.4(1)	S1-Cu1-Ag1A	56.7(1)
S3-Cu1-Ag1A	141.5(1)	Ag1-Cu1-Cu1A	62.8(1)
S1-Cu1-Cu1A	111.3(1)	S3-Cu1-CulA	85.5(1)
Ag1A-Cu1-Cu1A	60.7(1)	Ag1-Cu1-N2A	138.3(1)
S1-Cu1-N2A	121.2(1)	S3-Cu1-N2A	105.1(1)
Ag1A-Cu1-N2A	87.6(1)	Cu1A-Cu1-N2A	79.8(1)
Ag1-N1-C1	127.1(4)	Ag1-N1-C3	120.0(4)
C1-N1-C3	112.1(5)	C4-N2-C6	112.5(5)
C4-N2-Cu1A	125.7(4)	C6-N2-Cu1A	121.1(4)
Ag1-P1-C16	114.2(2)	Ag1-P1-C26	117.1(2)
C16-P1-C26	104.1(3)	Ag1-P1-C36	113.5(2)
C16-P1-C36	103.2(3)	C26-P1-C36	103.1(3)
Cu1-S1-C1	110.4(2)	Cu1-S1-Ag1A	77.1(1)
C1-S1-Ag1A	101.3(2)	C1-S2-C2	90.4(4)

TABLE XI (continued)

Ag1-S3-Cu1	73.8(1)	Ag1-S3-C4	103.6(2)
Cu1-S3-C4	95.4(2)	C4-S4-C5	89.3(3)
N1-C1-S1	127.4(5)	N1-C1-S2	116.9(4)
S1-C1-S2	115.6(3)	S2-C2-C3	107.7(5)
N1-C3-C2	112.5(6)	N2-C4-S3	126.7(5)
N2-C4-S4	115.9(5)	S3-C4-S4	117.4(4)
S4-C5-C6	103.6(5)	N2-C6-C5	108.6(6)
C12-C11-C16	121.3(6)	C11-C12-C13	119.4(7)
C12-C13-C14	119.1(7)	C13-C14-C15	121.2(7)
C14-C15-C16	120.1(6)	P1-C16-C11	123.9(5)
P1-C16-C15	117.2(4)	C11-C16-C15	118.9(6)
C22-C21-C26	120.5(6)	C21-C22-C23	119.9(7)
C22-C23-C24	119.5(7)	C23-C24-C25	120.8(7)
C24-C25-C26	119.0(6)	P1-C26-C21	123.3(5)
P1-C26-C25	116.3(5)	C21-C26-C25	120.3(6)
C32-C31-C36	120.4(6)	C31-C32-C33	120.7(6)
C32-C33-C34	119.1(6)	C33-C34-C35	121.7(6)
C34-C35-C36	119.7(6)	P1-C36-C31	118.2(4)
P1-C36-C35	123.4(5)	C31-C36-C35	118.3(6)

$Cu_4(MT)_4$, **1**. Although the crystal structure of this complex has not been solved completely, the positions of the copper atoms and a cluster appear in the best model. The cluster has a distorted tetrahedral butterfly shape. The four MT ligands bond through their nitrogen atoms and exocyclic sulfur atoms, these latter being η,^{2} so that each MT ligand binds to three copper atoms. Interaction between an exocyclic sulfur atom and a copper atom of a neighboring butterflay unit is found at a distance of 2.62 Å. The Cu-Cu distances in the copper core vary between 2.76 Å and 3.62 Å. Since the Cu-Cu separation in metallic copper is 2.56 Å, a weak interaction is expected at the shortest distance observed within the core.

Since compound **1** contains four uninegative MT ligands and four copper atoms, the copper atoms have undergone reduction from the initial Cu(II) oxidation state. The IR spectrum of **1** shows no N-H bond (no band around the 3400 cm^{-1}) but does show the thioamido bands at 1530, 1255, and 970 cm^{-1}, indicating that the C=S double bond has lost part od its double bond character, and that the C=N double bond is being formed.[7] (See Ref. 19 for solid state IR of HMT).

The FD-MS spectrum of **1** shows two peaks: one at m/z 726, for $[Cu_4(MT)_4]^+$ and the other at m/z 363, for $[Cu_2(MT)_2]^+$.

$(PPh_3)_2Cu_4(MT)_4$, **2**. A faintly yellow, butterfly shaped complex is obtained by stoichiometric addition of PPh_3 to the insoluble $[Cu(MT)]_4$, **1**. The four MT ligands each bind three copper atoms through their N and S_{exo} atoms. Two MTs bind the »wing-tip« copper atoms *via* the exocyclic sulfur, and the copper »body« atoms *via* the N atom. The other two MT ligands binding the reverse way, *i.e.*, the wing-tip copper atoms are bonded to the N atom, and the body copper atoms to the exocyclic S atom. Each S_{exo} atom binds one wing-tip and one body copper atom at a time. The geometry for the wing-tip copper atoms is pseudo-tetrahedral while the copper atoms in the body are coordinated trigonally planar.

The average C-S_{exo} distance is 1.745 Å, slightly longer than in the free ligand[8] (C-S_{exo} 1.68 Å). The average C-N distance in **2** is 1.255 Å, slightly shorter than in the free ligand (C-N 1.32 Å), meaning that the ligand has a C-S_{exo} single bond and a C=N double bond, corresponding to the thiol form. The shortest metal-metal separation in **2** is between the body copper atoms: 2.741(1) Å, which is slightly less than the sum of the copper van der Waals radius,[20] 2.86 Å, and therefore short enough to suggest some metal-to-metal interaction. The copper distances between wing tip and body atoms are 2.940(1) and 2.99(1) Å. The longest copper-to-copper distance in **2** is 4.127(1) Å, corresponding to the wing tip separation.

The ^{1}H-NMR spectrum shows two triplets, one at 3.26 ppm, and the other at 3.94 ppm, corresponding to the two adjacent CH_2 groups. The $^{31}P\{^1H\}$-NMR spectrum shows a broad peak at –8.1 ppm. The peak slowly shifts up to –4.9 ppm as more and more PPh_3 is added. The CP/MAS ^{31}P-NMR of **2** shows a quadruplet at 4.8, –4.5, –14.9, and –25.821 ppm (I = 3/2 for Cu). There is also a peak at 41.3 ppm which has been tentatively assigned to the T-shaped $(PPh_3)_2Cu(MT)$ molecule. This result is consistent with $^{31}P\{^1H\}$-NMR solution spectrum obtained at low temperatures (–40 to –70 °C), where two peaks are observed at –7.6 and –9.4 ppm. However, even at –70 °C, the PPh_3 molecules of $(PPh_3)_2(MT)_4$ still exchange very rapidly, so the P-Cu interaction produces a singlet, rather than the quartet expected, at –11.7 ppm. This singlet shifts to –8.2 ppm at room temperature.

The IR spectrum does not show a ν(N-H) peak but like **1**, it shows the thioamido bands at 1520, 1260 and 970 cm^{-1}, somewhat shifted with respect to **1** by the incorporation of PPh_3. FD-MS studies show two peaks corresponding to the tetranuclear $[^{63}Cu_4(MT)_4]^+$, *m/z* 726.4 and the dinuclear $[^{63}Cu_2(MT)_2]^+$, *m/z* 362.3, fragment ions. The Raman spectrum shows a peak at 90 cm^{-1}, which is assigned to the body Cu-Cu interaction.

$(AsPh_3)_2Cu_4(MT)_4$, **3**. This compound is structurally nearly the same as $(PPh_3)_2Cu_4(MT)_4$, **2**. The most important structural differences between **3** and **2** are the copper-to-copper distances. The shortest one is 2.753(4) Å, in **3**, essentially the same as the body Cu-Cu distance in **2**. The wing tip to body distances are 2.825(3) Å and 2.900(3) Å, shorter than those observed in **2**. The wing tip separation is 3.898(3) Å. This suggests that the nature of the Lewis base affects the separation of the wing tip copper atoms and the distances inside the butterfly core.

The distances inside the five-membered ring ligand are opposite to what is observed in the free ligand,[8] *i.e.*, the C-N average distance is 1.272 Å and the C-S_{exo} average distance is 1.747 Å, establishing once more the thiol-like structure in the solid state. The Cu-S and Cu-N average distances (2.312 and 2.023 Å) are similar to those observed in $(PPh_3)_2Cu_4(MT)_4$, **2.**

The solid state IR of **3** shows its thioamido bands at 1532, 1260, and 970 cm^{-1}, which are very close or identical to the positions of the bands in **2**.

$[pyCu_4(MT)_4]_n$, **4**. This complex contains four core copper(I) atoms arranged in a butterfly shape (Figure 3), like **2** and **3**, but it has only one Lewis base bonded to it. The way the four MT ligands bind to the copper core is exactly the same as for **2** and **3**. The pyridine is bonded to only one of the wing tip copper atoms. The other wing tip copper atom interacts with the *endo*cyclic sulfur atom of the next butterfly unit at a distance of 2.72 Å. This complex was obtained by excess addition of py to a suspension of the insoluble material $[Cu(MT)]_4$, **1**.

The Cu-Cu distances in the core are all non-bonding distances, but they are shorter than the sum of the copper atom van der Waals radius.[9] They range from 2.67 Å to 2.83 Å. The longest Cu-Cu distance corresponds to the wing-tip separation, 3.645 (2) Å.

The copper-sulfur_{exo} distance averages 2.303 Å and the Cu-N distance averages 2.001 Å (without considering the Cu-$N_{pyridine}$ bond), both being in the same range as for **2** and **3**.

$(PPh_3)_2Ag_4(MT)_4$, **6**. This tetranuclear butterfly complex is isostructural with $(PPh_3)_2Cu_4(MT)_4$, **2**, and $(AsPh_3)_2Cu_4(MT)_4$, **3**. The wing tip separation in **6** is 4.275 Å. The other metal-metal distances in **6** are less than the sum of the silver atom van der Waals radius,[20] 3.44 Å. The wing tip to body distances are 3.083(1) and 3.110(1) Å, and the separation between body atoms is 3.089(2) Å.

Unlike the copper butterfly analogues, the silver butterfly complex does not show big variations in the distances within the five-membered ring. The C-S_{exo} average distance is 1.723 Å, slightly longer than that found in the free ligand (1.68 Å).[8] Surprisingly, the C-N average distance, 1.312 Å, is essentially the same as in the free ligand, 1.32 Å. This indicates that the C-S_{exo} bond has a less double bond character while the C-N bond order remains about the same as for the free ligand.

The ^1H-NMR spectrum shows two triplets, 3.05 and 3.72 ppm, corresponding to the adjacent ring CH_2 groups. The ^{31}P-NMR solid state spectrum shows a singlet at –3.1 ppm with two side bands symmetrically located at each side of the main peak. The $^{31}P\{^1H\}$-NMR solution spectrum shows a singlet at –5.8 ppm when run at –60 °C with a broadline of about 50 Hz. Two other singlets also appear at 5.1 ppm and 1.5 ppm, which have not been assigned.

The FD-MS of **6** shows quite a different spectrum from that of $(PPh_3)_2Cu_4(MT)_4$. Here, the heaviest peak observed corresponds to the $(PPh_3)_2Ag_3(MT)_2^+$ species, *m/z* 1084.3. Other species observed include: $(PPh_3)_2Ag_2(MT)^+$, *m/z* 858,9; $Ag(PPh_3)_2^+$, *m/z* 633.8; $OPPh_3^+$, *m/z* 278.2 and PPh_3^+, 262.3. Thus, PPh_3 appears to be more strongly bonded in $(PPh_3)_2Ag_4(MT)_4$, **6**, than in $(PPh_3)_2Cu_4(MT)_4$, **2**.

$(PPh_3)_2Ag_2Cu_2(MT)_4$, **8**. This mixed metal cluster has the Ag atoms in the wing tip positions, the distance between the wing tips being 4.188(1) Å. The silver-to-copper distances are 2.948(1) and 3.005(1) Å, values less than the sum of the copper and silver van der Waals radii,[19] 3.15 Å. The distance between the copper atoms is 2.817(1) Å, a distance 0.07 Å longer than the body Cu-Cu distance in the homonuclear Cu^I cluster, $(PPh_3)_2Cu_4(MT)_4$, **2**. The structure shows no disorder. The Ag^I atoms exist as four coordinate species while the bridging Cu^I atoms are 3-coordinate. A preference of Ag^I over Cu^I for the tetrahedral MS_2NP coordination geometry is suggested. The coordination mode of the MT ligand is the same as for the other MT butterfly clusters. The average $C\text{-}S_{exo}$ distance in **8** is 1.743 Å, slightly longer than in the free ligand, 1.68 Å. The average C-N distance in **8** is 1.267 Å, shorter than in the free ligand, 1.32 Å. These distances are in agreement with the previous observations that MT can adopt the thiol-like form in solid state, provided that both the endocyclic sulfur atom and the endocyclic nitrogen atom participate in bond formation.

The ^1H-NMR spectrum shows two triplets centered at 3.24 and 3.89 ppm. The CP/MAS ^{31}P-NMR shows two signals at –3.1 and –6.1 ppm. The $^{31}P\{^1H\}$-NMR in solution, however, shows a singlet at room temperature at 1.6 ppm and two signals at –50 °C, one at 0.03 ppm and the other at 4.9 ppm. There is also a broad peak centered at about –9 ppm, which may be assigned to the $^{31}P\text{–}^{63,65}Cu$ interaction. The solid state IR of **8** shows its thioamido bands at 1525, 1253, and 970 cm^{-1}, all shifted with respect to the free HMT ligand.[19] FD-MS shows a peak at *m/z* 408, which corresponds to the mixed metal $[AgCu(MT)_2]^+$ species.

DISCUSSION

The reaction of Cu(II) or Ag)I) acetate with 2-mercaptothiazoline, HMT, leads to the formation of an insoluble prepicitate with the formula $M_4(MT)_4$ under the conditions reported in this paper. However, Preti and Tosi[24] reported that $Cu(OAc)_2$ with HMT gives $CuMT(OAc)\cdot 2H_2O$, a compound soluble in methanol, ethanol, and various other organic solvents, when ethanol is used for the synthesis. Thus the reduction of Cu(II) to Cu(I) and the ligand coupling indicated in Eq. (2) appears to be solvent dependent. In acetonitrile, as reported here, the reduction of Cu(II) is complete and an insoluble precipitate forms.

The addition of a Lewis base, PPh_3 or $AsPh_3$, causes attachment to both wing tip metal atoms and breaks up interactions that exist between clusters in the insoluble $[M_4(MT)_4]_n$ materials, causing dissolution of the materials and subsequent crystallization of the adducts **2**, **3**, and **6**. If pyridine is used as the base with the Cu(I) cluster, only partial base adduct formation occurs and the crystalline polymer $[pyCu_4(MT)_4]_n$, **4**, is isolated and characterized. This material, a polymer[12] formed from the butterfly shaped tetranuclear $[Cu_4(MT)_4]$ units, Figure 3, presumably reflects the butterfly structure of the initial cluster precipitate which could not be characterized adequately by X-ray crystallography. However, the polymerization in this adduct is through *endo*cyclic sulfur atoms on adjacent units. The FD-MS results which show a *m/z* peak at 727, as expected for $[Cu_4(MT)_4]^+$, further confirm the existence of cluster units in the solid.

The molecular clusters $(PPh_3)_2Cu_4(MT)_4$, **2**, $(AsPh_3)_2Cu_4(MT)_4$, **3**, and $(PPh_3)_2Ag_4(MT)_4$ are isostructural, butterfly shaped complexes. The wing tip metal atoms are pseudo-tetrahedrally coordinated, and the body atoms are trigonally planar coordinated. Other examples of mixed coordination geometries for Cu(I) include "step" shaped species, which also have tetrahedrally and trigonally coordinated Cu(I) atoms in the same complex.[21,22] We have not identified similar Ag(I) systems and the butterfly shape for silver clusters is relatively uncommon. It has been reported in only two other Ag complexes, $(\alpha$-naphthalenedithionato-S,S,S'$)_4Ag_4py_4$,[30] and (toluenedithionato-S,S,S'$)_4Ag_4py_4$,[31] (py = pyridine).

Cu(I) complexes similar to **2** and **3** have been described in the literature: $[Cu(NEt)]_4$,[25] where the N atom is alternating with the Cu atom, forming a butterfly shape. $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$,[25] has a tetrahedral core formed by the four Cu(I) atoms with the $(i\text{-}C_3H_7O)_2PS_2$ ligands using one sulfur as a monodentate atom, bonding one copper atom, and the other sulfur atom as bidentate ligand, bonding two copper atoms. The complex formed from MHP, 6-methyl-2-oxypyridine, $[Cu_4(MHP)_4]$[27] has been described by its authors as "four copper atoms arranged approximately in a square, which is subject to a considerable puckering or 'butterfly' distortion".[27] Each copper atom in this molecule binds one nitrogen and one oxygen atom. A "butterfly arrangement, intermediate between a square planar and a tetrahedral situation"[28] is found in $Cu_4(MDAP)_4$,[28] (MDAP = 5-methyl-2-[(dimethylamino)methyl]phenyl).

If the two PPh_3 ligands are removed in these MT clusters from the wing tip atom positions and these atoms are brought closer while the metal-metal distance is stretched in the body metal positions, a tetrahedron of metal atoms is produced. Under such conditions all four MT ligands become equivalent and only two ^{1}H-NMR triplets are to be expected for the four equivalent MT ligands, not four as suggested from the solid state structures where the MT ligands exist in pairs. In fact, the ^{1}H-NMR solution spectrum of **2** shows two triplets (C-H 3.26, and 3.94 ppm) corresponding to the two methylene groups and for **6**, triplets are observed at 3.05 and 3.72 ppm. These results demonstrate the lability of the bases in these molecules in solution.

The $^{31}P\{^1H\}$-NMR spectrum of **2** and **6** does not reveal fluxionality directly because, as the PPh_3 group moves between the wing tip and body positions, the body atoms become wingtips indistinguishable from the original wing tip positions. If excess PPh_3 is added to a solution containing $(PPh_3)_2Cu_4(MT)_4$, **2**, the singlet observed as a broad peak at –8.1 ppm smoothly moves downfield, becoming sharper to –4.9 ppm after which it no longer shifts position, averaging near the free PPh_3 position of –5.0 ppm. Thus rapid exchange occurs between the free and coordinated phosphine ligands.

The IR spectrum of $(PPh_3)_2Cu_4(MT)_4$, **2**, shows some slight shifts of its bands (about 10 cm^{-1}) compared to the IR of $[Cu(MT)]_4$, **1**, and verifies the absence of a N-H bond in the solid, a band which is at 3130 cm^{-1} in the free ligand.[19] These shifts are consistent with the observed shortening of the C-N distance and the lengthening of the $C\text{-}S_{exo}$ distance in the five-membered ring suggested by X-ray crystallography. The IR spectrum of $(AsPh_3)_2Cu_4(MT)_4$, **3**, shows the same behavior as observed for **2**.

The parent ion peak expected at *m/z* 1251.6 is not observed in **2**, reflecting again the lability of the PPh_3 ligands. The peaks corresponding to the tetranuclear cluster unit $[^{63}Cu(MT)]_4^+$, and the dinuclear $[^{63}Cu(MT)]_2^+$ or doubly charged tetranuclear species appear at *m/z* 726.4 and 363.2, respectively. No fragmentation of the tetranuclear species into the mononuclear unit $^{63}Cu(MT)^+$, *m/z* 181, is observed.

The Raman spectrum of **2** shows a peak at 90 cm^{-1}, which was initially assigned to the body Cu-Cu interaction. However, using Woodruff's rule,[23] the peak is to be expected at 185 cm^{-1}, about two times higher in energy. Thus, the assignment of this band to a Cu-Cu stretch of the body Cu atoms either becomes questionable or the Cu-Cu stretch is weakened substantially by other constraints in this cluster.

As the ligand attached to the wing tip Cu atom in the $[Cu_4(MT)_4]$ clusters varies, the wing tip to wing tip distance within the butterfly clusters increases in the order: weak cluster bridge < pyridine < $AsPh_3$ < PPh_3. The stronger the Lewis base, the further apart the wing tip copper atoms become. The wing tip to body distance also increases in the same order. The metal-metal distances inside the butterfly core are shortest in the polymers. The "softer" bases[29] apparently increase electron density in the antibonding orbitals of the metal atoms.

The FD-MS spectrum of the insoluble Ag material is very different from $[Cu_4(MT)_4]_n$, **1**. The products observed correspond to ligand components R-S-R, *m/z* 204; and $R\text{-}S\text{-}C_2H_4\text{-}S\text{-}R$, *m/z* 264, where R is the thiazoline ring (C_3H_4NS-). Apparently, the silver cluster is not as robust as the copper species.

The interesting, novel butterfly shaped mixed metal cluster $(PPh_3)_2Ag_2Cu_2(MT)_4$, **8**, is isostructural with **2**, **3**, and **6**. It is formed surprisingly free from disorder with the silver atoms located in the tetrahedral wing tip positions. The copper atoms are located in the trigonally planar coordination of the body positions. The PPh_3 groups in **8** are bonded exclusively to the Ag atoms, demonstrating a preference of Ag(I) over Cu(I) for the tetrahedral site. If one assumes that PPh_3 dissociation and exchange can occur with little or no barrier, as indicated by the ^{1}H-NMR results for **8**, which shows only two triplets at 3.24 and 3.89 ppm corresponding to the equivalent methylene groups, the preference of Ag(I) over Cu(I) for the wing-tip positions must be a result of electronic factors associated with the bonding. The structural features of the homometallic clusters do not predict this outcome. Assuming that M-M interactions do not contribute significantly to the structure, we conclude that a tetrahedral MS_2NP coordination in this system is favored by Ag(I) over Cu(I). The stoichiometry for the synthesis of the mixed metal cluster involves reduction of the Cu(II) species:

$$\begin{gathered} 2Ag^{I}(OAc) + 2Cu^{II}(OAc)_2{\cdot}H_2O + 6HMT + 2PPh_3 \rightarrow \\ (PPh_3)_2Ag_2{}^{I}Cu_2{}^{I}(MT)_4 + 6HOAc + (MT)_2 + 2H_2O \end{gathered} \tag{3}$$

The $^{31}P\{^1H\}$-NMR at variable temperatures of **8** in solution shows a singlet at 1.6 ppm at 30 °C. Upon lowering the temperature a doublet starts to appear and becomes evident at –40 °C, with the peak centered at about 2 ppm. At –50 °C, the broad doublet is clear and centered at about 1.8 ppm. The coupling is $J = 390.7$ Hz, in good agreement with the values reported by Muetterties[32] for $J_{Ag\text{-}P}$, but the isotopic distinction for ^{109}Ag and ^{107}Ag remains unresolved. The $^{31}P\{^1H\}$-NMR solid state spectrum shows two broad signals with a coupling constant od $J = 379$ Hz, Table XII.

The $J_{Ag\text{-}P}$ coupling constant decreases roughly linearly with an increase in the Ag-P distance in the data reported by Clayden.[30] Using Clayden's numbers and extrapolating them, a Ag-P separation of 2.47 Å is predicted (observed, 2.44 Å) from the coupling of 379 Hz for the $Ag_2Cu_2(MT)_4$ cluster. The broad unresolved peak observed in the homonuclear Ag_4 cluster reflects the long 2.523(3) Å Ag-P distance found here, Table XII.

The FD-MS spectrum of **8** shows an important peak at *m/z* 406, corresponding to the $AgCu(MT)_2{}^+$ fragment. Breakup of the mixed metal butterfly cluster across the Cu-Cu' vector gives this fragment, confirming that **8** is not a mixture of $(PPh_3)_2Cu_4(MT)_4$, **2**, and $(PPh_3)_2Ag_4(MT)_4$, **6**. As observed crystallographically, it is a mixed metal cluster having no major disordering of the metal atoms.

TABLE XII

CP/MAS $^{31}P\{^1H\}$-NMR results of ^{31}P – Ag complexes

Compound	$J_{P\text{-}Ag}$/Hz	$d_{(P\text{-}Ag)}$/Å	Reference
$Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(\mu\text{-dmpm})$	509	2.382	38
$Ag(PPh_3)_2NO_3$	470	2.443(1) 2.440(1)	39
$Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(\mu\text{-dmpm})$	448	2.412	38
$Ag_2Cu_2(MT)_4(PPh_3)_2$	379	2.440(2)	this work
$Ag(PPh_3)_3NO_3$	310	2.525(1) 2.545(2) 2.630(2)	39
$Ag_4(MT)_4(PPh_3)_2$	broad (*ca.* 295)	2.523(3)	this work
$Ag(PPh_3)_2NO_3$	190	2.643(3) 2.672(4)	39

The FD-MS of the insoluble precursor to the mixed metal butterfly cluster, $Ag_2Cu_2(MT)_4$, **7**, is also very interesting. While the parent ion peak $Ag_2Cu_2(MT)_4^+$ is not observed, a peak at *m/z* 406 for $^{107}Ag^{63}Cu(MT)_2^+$ is seen. This suggests that even the insoluble precursor to the characterized cluster **8** is not a mixture of $Cu_4(MT)_4$, **1**, and $Ag_4(MT)_4$, **5**, but is probably also a polymer formed from the mixed metal clusters.

As in the copper butterfly, **2**, this mixed copper-silver butterfly, **8**, has the body copper atoms at the closest distance. Also, as for **2**, the Raman spectrum of $(PPh_3)_2Ag_2Cu_2(MT)_4$, **8**, shows a peak much lower in frequency than predicted by Woodruff's rule at 92 cm^{-1}. We suspect that Woodruff's rules are not adequate for describing the force constants between the two copper atoms in these tetranuclear complexes which have heavy neighboring metal atoms.

The butterfly clusters reported here have all been obtained in the same manner, by reaction of the free ligand, 2-mercaptothiazoline, with a stoichiometric amount of the copper(II) or silver(I) acetate and further addition of a Lewis base (PPh_3, $AsPh_3$, or py) to the suspension of the product. Excess quantities of the Lewis base do not break up the cluster. However, strong oxidizing agents and some electrophiles do, forming a variety of mononuclear, sulfur-bonded species that will be discussed elsewhere.

Supplementary Materials. – Crystallographic data (excluding structure factors which are available from the authors) for the structure of compound **3** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-109/68-793. Copies of the data can be obtained on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: 44 (0) 1223-336033; E-mail: teched@chemcrys.cam.ac.uk).

Acknowledgements. – We acknowledge with thanks the help of Patrick Killough, at Shell Development, Houston, Texas, for running the Raman spectra and Robert P. Lattimer of the BFGoodrich Co., Brecksville, Ohio for obtaining the FD-MS spectra reported here. We also want to thank the National Science Foundation CHE-9300107 and the Welch Foundation of Houston, Texas, for financial support.

REFERENCES

1. J. D. Watson and F. C. Crick, *Nature* **171** (1956) 737.
2. a) C. J. Cathey, E. C. Constable, M. J. Hannon, D. A. Tocher, and M. D. Ward, *J. Chem. Soc. Chem. Commun.* (1990) 621. b) E. C. Constable, S. M. Elder, J. Healy, and M. D. Ward, *J. Amer. Chem. Soc.* **112** (1990) 1256. c) E. C. Constable, M. D. Ward, M. G. B. Drew, and G. Forsyth, *Polyhedron* **8** (1989) 2551. d) E. C. Constable, M. G. B. Drew, G. Forsyth, and M. D. Ward, *J. Chem. Soc. Chem. Commun.* (1988) 1450. e) M. Barley, E. C. Constable, S. A. Corr, R. C. J. McQueen, J. C. Nutkins, M. D. Ward, and M. G. B. Drew, *J. Chem. Soc. Dalton Trans.* (1988) 2655. f) E. C. Constable, M. G. D. Drew, and M. D. Ward, *J. Chem. Soc. Chem. Commun.* (1987) 1600.
3. a) U. Koert, M. M. Harding, and J. -M. Lehn, *Nature* **346** (1990) 339. b) T. M. Garrett, U. Koert, J. -M. Lehn, A. Rigault, D. Meyer, and J. Fischer, *J. Chem. Soc. Chem. Commun.* (1990) 557. c) J. -M. Lehn, M. Mascal, A. DeCian, and J. Fischer, J. Chem. Soc. Chem. Commun. (1990) 479. d) J. -M. Lehn and A. Rigault, *Angew. Chem. Int. Ed. Engl.* **27** (1988) 1085. e) J. -M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier, and D. Moras, *Proc. Natl. Acad. Sci. USA* **84** (1987) 2565.
4. F. A. Cotton, P. A. Kibala, and W. J. Roth, *J. Amer. Chem. Soc.* **110** (1988) 298.
5. R. H. Holm and J. M. Berg, *Acc. Chem. Res.* **19** (1986) 363.
6. K. H. Nakagawa, C. Inouye, B. Hedman, M. Karin, T. D. Tullius, and K. O. Hodgson, *J. Amer. Chem. Soc.* **113** (1991) 3621.
7. C. Preti and G. Tosi, *Can. J. Chem.* **54** (1976) 1558.
8. E. S. Raper, R. E. Oughtred, and I. W. Nowell, *Inorg. Chim. Acta* **77** (1983) L89.
9. D. De Filippo, F. Devillanova, E. F. Trogu, G. Verani, C. Preti, and P. Viglino, *Can. J. Chem.* **51** (1973) 1172.
10. a) F. A. Devillanova, F. Isaia, and G. Verani, *J. Inorg. Nucl. Chem.* **43** (1981) 2749. b) F. A. Devillanova, and G. Verani, *Transition Met. Chem.* **3** (1978) 42. c) F. A. Devillanova, and G. Verani, *Transition Met. Chem.* **2** (1977) 120.
11. R. A. Zingaro, and E. A. Meyers, *Crystal Struc. Commun.* **9** (1980) 1167.
12. J. P. Fackler, C. A. López, R. J. Staples, S. Wang, R. E. P. Winpenny, and R. P. Lattimer, *J. Chem. Soc. Chem. Commun.* (1992) 146.
13. A. Moor, P. S. Pregosin, L. M. Venanzi, and A. J. Welch, *Inorg. Chim. Acta* **85** (1984) 103.
14. D. F. Shriver, and M. A. Drezdzon, *The Manipulation of Air-Sensitive Compounds*, 2nd Ed., Wiley, New York, 1986.
15. The reaction of NaMT (4.8 mg; 0.034 mmoles) with $(PPh_3)_3CuCl$ (30.0 mg; 0.034 mmoles) in 6–8 mL of THF gave a colorless solution which was stirred overnight, filtered, and set for crystallization by diethylether diffusion. Colorless crystals were obtained after two days. The space group is $C2/c$ with $a = 27.561(1)$, $b = 11.715(4)$, $c = 16.050(8)$ Å, $\beta = 91.59(4)^\circ$, $V = 5179(3)$ Å^3, $Z = 4$. The refinement gave $R = 0.1120$

for the cluster which appears to be a polymorph of **2**. However, the solvent may be in the lattice. Crystal quality precluded further characterization.

16. I. G. Dance, L. J. Fitzpatrick, D. G. Craig, and M. L. Scudder, *Inorg. Chem.* **28** (1989) 1853.
17. E. S. Raper, *Coord. Chem. Rev.* **61** (1985) 115.
18. The ^{1}H-NMR spectrum of HMT gives two singlets (δ S-H 1.8 ppm, δ N-H 8.25 ppm), and two triplets (δ C-H 3.69 ppm and 4.00 ppm) corresponding to the methylene groups.
19. The experimental solid state IR spectrum of the free ligand HMT shows a ν(N-H) band at 3130 cm^{-1} and the thioamido bands^{35} (H-N-C=S) at 1500, 1250, and 995 cm^{-1}.
20. W. W. Porterfield, *Inorganic Chemistry*, Addison Wesley, Reading, Mass., 1984, Ch. 4, p. 168.
21. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th Ed., John Wiley & Sons, New York, 1988, pp 755–7.
22. B. J. Hathaway, in: G. Wilkinson, R. P. Guillard and J. A. McCleverty (Eds.) *Comprehensive Coordination Chemistry*, Pergamon, Oxford, England, 1987, Vol. 5, Ch. 53, pp 533–774.
23. a) Woodruff has developed the empirical *s* which relates the force constant, F, with the distance between two elements, r. The parameters depend on the period the metal belongs to; for 3d elements is: $r = 1.81 + 1.22e^{-F/2.37}$. These *s* have been proven to be effective for transition metal dimer complexes. See J. D. Conradson, A. P. Sattelberger, and W. H. Woodruff, *J. Amer. Chem. Soc.* **110** (1988) 1309.
    b) To calculate the wavenumber, the following is used:
    $\bar{\nu} = (1/2\pi c)(F\text{x}10^5/1.66\text{x}10^{-24}\mu)^{1/2}$, where $\mu = m_1m_2/(m_1 + m_2)$.
24. C. Preti and G. Tosi, *Can J. Chem.* **53** (1975) 177.
25. H. Hope and P. P. Power, *Inorg. Chem.* **23** (1984) 936.
26. S. L. Lawton, W. L. Rohrbaugh, and G. T. Kokotailo, *Inorg. Chem.* **11** (1972) 612.
27. M. Bery, W. Clegg, C. D. Garner, and I. H. Hiller, *Inorg. Chem.* **21** (1982) 1342.
28. a) G. Van Koten and J. G. Noltes, *J. Organomet. Chem.* **84** (1975) 129. b) J. M. Guss, R. Mason, I. Søtofte, G. Van Koten, and J. G. Noltes, *J. Chem. Soc. Chem. Commun.* (1972) 446.
29. J. E. Huheey, *Inorganic Chemistry*, 3rd Ed., Harper & Row, New York, 1983, p. 312.
30. T. Kaluo, J. Xianglin, S. Yun, and T. Youqi, *Sci Sin. Ser. B.* (Chinese Ed.) (1986) 485.
31. T. Kaluo, J. Xianglin, S. Qunong, S. Jianguang, and T. Youqi, *J. Struct. Chem.* **7** (1988) 245.
32. E. L. Muetterties and C. W. Alegranti, *J. Amer. Chem. Soc.* **94** (1972) 6386.
33. J. Beck and J. Strähle, *Angew. Chem. Int. Ed. Engl.* **24** (1985) 409.
34. K. M. Merz and R. Hoffmann, *Inorg. Chem.* **27** (1988) 2121, and references therein.
35. a) B. Singh and K. P. Thakur, *Inorg. Nucl. Chem.* **36** (1974) 1735. b) K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.* **20** (1966) 597. c) C. N. R. Rao and R. Ven-Kataraghavan, *Spectrochim. Acta* **18** (1962) 541.
36. L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler Jr., and K. Knox, *J. Amer. Chem. Soc.* **90** (1988) 7357.
37. a) G. N. George, J. Byrd, and D. R. Winge, *J. Biol. Chem.* **263** (1988) 8199. b) J. R. Casas-Finet, S. Hu, D. Hamer, and R. L. Karpel, *Biochemistry* **31** (1992) 6617.
38. N. J. Clayden, *Chemica Scripta* **28** (1987) 211.
39. P. F. Barron, J. C. Dyson, P. C. Healy, L. M. Engelhardt, B. W. Skelton, and A. H. White, *J. Chem. Soc. Dalton Trans.* (1986) 1965.

SAŽETAK

Mješoviti klusteri bakra(I) i srebra(I) s 2-merkaptotiazolinom

César A. López, John P. Fackler, Jr., Richard J. Staples, Suning Wang
i Richard E. P. Winpenny

Analiza podataka dobivenih difrakcijom rentgenskih zraka na slabo kristalnom spoju koji nastaje reakcijom bakrova(II)acetata s 2-merkaptotiazolinom otkrila je polimerni produkt koji se sastoji od tetranuklearnog klustera $Cu_4(MT)_4$, **1**, oblika "leptira". Niz izostrukturnih kompleksa priređen je dodatkom Lewis-ovih baza (piridin, PPh_3, $AsPh_3$) talogu dobivenom reakcijom bakrova(II) i/ili srebrova(I) acetata sa stehiometrijskom količinom 2-merkaptotiazolina. Opća formula tih klustera jest $L_2M_4(MT)_4$: **2**, L = PPh_3, M = Cu; **3**, L = $AsPh_3$, M = Cu; **6**, L = PPh_3 , M = Ag; MT = $C_3H_4NS_2^-$, poznat kao 2-merkaptotiazolinat. Za polimer $[pyCu_4(MT)_4]_n$ **4**, koji nastaje dodatkom piridina spoju **1**, određena je kristalna struktura. Mješoviti metalni kompleks oblika "leptira" $(PPh_3)_2Ag_2Cu_2(MT)_4$ **8**, nastaje dodatkom PPh_3 suspenziji taloga dobivenoga reakcijom slobodnog liganda HMT i smjese bakrova(II) i srebrova(I) acetata (1:1) u CH_2Cl_2. Maseni spektri (FD-MS) taloga dobivenih iz metalnih acetata i slobodnog liganda ukazuju na postojanje monomerne jedinice $M_4(MT)_4$. Prikazani su i raspravljeni spektroskopski podaci, ^{1}H-NMR i ^{31}P{^{1}H}-NMR, dobiveni snimanjem spojeva u otopini i krutom stanju. Strukture ovih molekulskih kompleksa određene su rentgenskom difrakcijom na monokristalu. Od priređenih spojeva četiri kristaliziraju u monoklinskoj prostornoj grupi $C2/c$ (Br. 15) sa $Z = 4$ i parametrima jediničnih ćelija: **2**, a = 15.558(6), b = 11.945(5), c = 27.927(9) Å, β = 94.676(3)° **3**, a = 15.632(8), b = 11.951(6), c = 28.156(16) Å, β = 94.04(4)° **6**, a = 14.656(6), b = 12.2312(6), c = 29.613(7) Å, β = 97.71(3)°; **8**, a = 15.559(3), b = 11.939(2), c = 28.201(6) Å, β = 94.71(3)°. Polimer **4** kristalizira u prostornoj grupi $P1$ (Br. 2) sa $Z = 2$ i parametrima jedinične ćelije a = 8.900(6), b = 12.537(9), c = 12.887(9) Å, α = 72.34(5)°, β = 78.06(5)°, γ = 88.23(6)°.