

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

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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 $\text{Cu}_4(\text{MT})_4$, **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 $\text{L}_2\text{M}_4(\text{MT})_4$; **2**, L = PPh_3 and M = Cu; **3**, L = AsPh_3 and M = Cu; **6**, L = PPh_3 and M = Ag; MT = $\text{C}_3\text{H}_4\text{NS}_2^-$, known as 2-mercaptothiazolinolate. The polymer $[\text{pyCu}_4(\text{MT})_4]_n$, **4**, formed by the addition of pyridine to **1**, was also characterized crystallographically. A mixed metal butterfly complex, $(\text{PPh}_3)_2\text{Ag}_2\text{Cu}_2(\text{MT})_4$, **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 $\text{M}_4(\text{MT})_4$. $^1\text{H-NMR}$ and $^{31}\text{P}\{^1\text{H}\}$ -NMR, both in solution and in the solid state are presented and interpreted. The solid state structures of these molecu-

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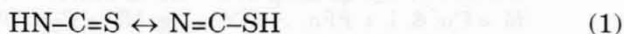
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lar complexes were determined by single crystal X-ray analysis. Four of them crystallize in the monoclinic space group $C2/c$ (No. 15) with $Z = 4$, and unit cell dimensions: **2**, $a = 15.558(6)$, $b = 11.945(5)$, $c = 27.927(9)$ Å, $\beta = 94.676(3)^\circ$;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

INTRODUCTION

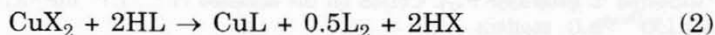
Self-assembly is the spontaneous formation of large molecules from smaller ones and is believed to be the process by which many biological molecules, like DNA, are formed.¹ A number of inorganic helical oligomers, models for DNA, have been obtained^{2,3} using long, flexible, N-containing ligands. The self-assembly of clusters has also been explored,⁴ and it is well established⁵ that inorganic cluster molecules of biological importance have been formed by this spontaneous assembly process. Recently, it has been reported⁶ 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 tautomerism⁷ between the thione and thiol forms:



The crystal structure⁸ 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 CuSO₄ or CuCO₃ salts were reduced to Cu^I N-bonded complexes⁹ by HMT. Some time later an intermolecularly linked polymeric structure was proposed, with the exocyclic sulfur atom and the endocyclic 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 established¹⁰ 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}X₂ 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:



where $X = \text{NO}_3^-$, BF_4^- , $1/2\text{SO}_4^{2-}$, Cl^- , or Br^- , and HX is the corresponding acid ($X = \text{Cl}$, Br) which was determined by base titration.¹⁰ The oxidation product of HMT is thought to be¹⁰ 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-benzothiazole)-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 $\text{M}_4(\text{MT})_4$ clusters¹² 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, $\text{Pt}_4(\mu_2\text{-CO})_5(\text{PMe}_2\text{Ph})_4$, was reported by Moor *et al.*¹³ The ^{195}Pt and $^{31}\text{P}\{^1\text{H}\}$ -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 $\text{M}_4(\text{MT})_4$ complexes, their detailed structures and fluxionality.

EXPERIMENTAL

Spectroscopy

^1H - and $^{31}\text{P}\{^1\text{H}\}$ -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 $^{31}\text{P}\{^1\text{H}\}$ -NMR. CP/MAS $^{31}\text{P}\{^1\text{H}\}$ -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-Mercaptobenzothiazole, 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

$\text{Cu}_4(\text{MT})_4$, **1**, is prepared by reaction of a solution of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (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 $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ into that of HMT, both in CH_3CN , inside a U shaped tube with a glass frit separator at the bottom.

$(\text{PPh}_3)_2\text{Cu}_4(\text{MT})_4$, **2** was synthesized by stoichiometric addition of PPh_3 (21.6 mg, 0.0824 mmoles) to a suspension of $[\text{Cu}(\text{MT})_4]$, **1**, (30.0 mg; 0.0413 mmoles) in 2 mL 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 $(\text{PPh}_3)_3\text{CuCl}$ and NaMT in a 1:1 molar ratio.¹⁵

$(\text{AsPh}_3)_2\text{Cu}_4(\text{MT})_4$, **3**, was prepared in a manner similar to that used for **2**, but a large excess of AsPh_3 had to be added to $\text{Cu}_4(\text{MT})_4$ (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.

$[\text{pyCu}_4(\text{MT})_4]_n$, **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.

$\text{Ag}_4(\text{MT})_4$, **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.

$(\text{PPh}_3)_2\text{Ag}_4(\text{MT})_4$, **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.

$\text{Ag}_2\text{Cu}_2(\text{MT})_4$, **7**, is prepared by adding AgOAc (30.0 mg; 0.1797 mmoles) to a solution of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (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%.

$(\text{PPh}_3)_2\text{Ag}_2\text{Cu}_2(\text{MT})_4$, **8**. Addition of four times the stoichiometric amount of PPh_3 (25.7 mg; 0.0981 mmoles) to a suspension of $\text{Ag}_2\text{Cu}_2(\text{MT})_4$, **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**.

