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Notes

Crystal and Molecular Structures of a Neutral Pentanuclear Copper(I)−Iodide Complex

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Introduction

The coordination chemistry of divalent copper stands among the most studied topics in inorganic chemistry. In contrast, cuprous derivatives have been much less extensively studied.[1] However, the realization that copper(I) species are involved in the structure of type III copper proteins[2] has resulted in an increased interest in the field, to the extent that the space devoted to copper(I) in the fourth edition of Cotton and Wilkinson's text[3] was larger than that dedicated to copper(II), a trend that has been maintained in the fifth edition of the book.

The chemistry of copper(I) is characterized by the wide diversity of crystal structures reported. A comprehensive survey has been made, and a brief summary of the situation would be that while in the solid state this chemistry is dominated by 4-coordination, significant numbers of 3- and 2-coordinated complexes are also known.[1] The factors that determine the coordination numbers and stereochemistries about the metal are still subjects of study, with electronic and steric effects being found important in the final outcome. Thus 2-coordination has been attributed to electronic effects in a series of neutral complexes of copper(I) with nitrogen donors.[4] Sterics seems to play the most important role in complexes that bear phosphorus as donor. This has been demonstrated through the use of the sterically demanding ligands tris(2,4,6-trimethoxyphenyl)phosphine[5] and tribenzylphosphine.[6]

Relevant aspects of the ligating properties of thiuram disulfides $R_2NC(S)S{-}SC(S)NR_2$ have been reviewed in a previous paper of this series, where the significance of these compounds in the field of agriculture and medicine has been remarked upon.[7] Particularly striking has been the application of these materials as inhibitors of human immunodefficiency viral infections such as AIDS.[8] Explanations have been recently offered as to the reasons for this wide range of biological activity.[9]

Complexes of metals with thiuram monosulfides, $R_2NC(S)SC(S)NR_2$ (henceforth abbreviated R_4tms) have not been studied as extensively, and the reader is referred to previous work for a more general review of this particular topic.[7] Only the most important details will be outlined here.

Straightforward 1:1 adducts have resulted from the interaction of tetraalkylthiuram monosulfides, abbreviated R_4tms, and some metal halides. Some but not all of the examples reported are MR_4tmsX_2 ($M = Zn^{10}$ and Hg^{11}) and $M'R_4tmsX$ ($M' = Ag^{12}$ and Cu^{13}). C−S bond scission of monosulfides in many cases leads to dithiocarbamate−metal−thiocarboxamido[14] or metal−dithiocarbamato[15] complexes. The ligand may also undergo a 2-electron oxidation to the cyclic organic dication 3,5-bis(*N*,*N*-dialkylimonium)-1,2,4-trithiolane, which has been isolated as a metal−halogen anionic complex.[7,16]

In a recent publication, we reported the crystal and molecular structures of halogenobis(*N*,*N*-dimethylthiocarbamoyl)sulfidocopper(I) complexes $CuMe_4tmsX$ (X = Cl, Br, I; $Me_4tms = Me_2NC(S)SC(S)NMe_2$). In all three structural studies it was found that the basic $XCuS_2$ units undergo more extensive association to afford dimers (X = Cl, I) or a polymer (X = Br). The nature and extent of the association seemed to be determined by packing in the solid as much as by steric and electronic effects inherent to the halogen involved in each case.[7]

The diversity of structures in the solid state and availability of good crystalline material prompted an extension of these studies to include compounds in the ethyl series.

Experimental Section

Reagents, Spectroscopy, and Analyses. Handling of reagents, instrumentation, methods of analyses, and preparation of the cuprous

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Table 1. Crystallographic Data and Refinement Details for $(Et_4Tms)_2Cu_5I_5$

empirical formula	$C_{20}H_{40}Cu_5I_5N_4S_6$
a/Å	17.917(5)
b/Å	13.911(3)
c/Å	20.207(4)
α/deg	90
β/deg	103.85(2)
γ/deg	90
V/Å^3	4890(2)
Z	4
crystal dimens/mm	0.14 × 0.28 × 0.36
fw	1481.12
space group (No.)	$C2/c$ (15)
D_c/g cm^{-3}	2.01
μ/cm^{-1}	55.7
R^a	0.058
$R_w{}^{b,c}$	0.197

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{0.5}$. ^{c} $s = [\sum[w(F_o{}^2 - F_c{}^2)^2]/(n - p)]^{0.5}$.

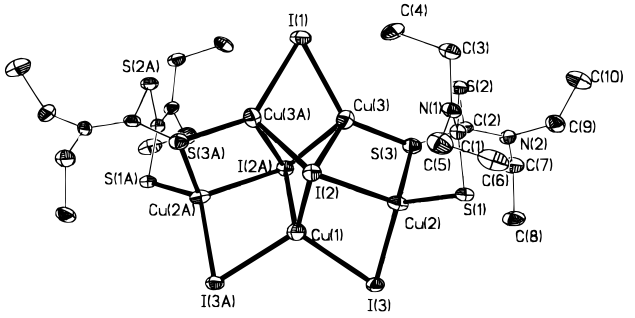

Figure 1. Structure of $Cu_5(Et_4tms)_2I_5$ (**1**) and numbering scheme with 50% displacement ellipsoids for non-hydrogen atoms.

halides have been described previously.[7] Tetraethylthiuram monosulfide was prepared by a published procedure.[17]

Preparation of the Complex. The monosulfide (0.79 g, 3.0 mmol) was dissolved in acetonitrile (15 mL), and the solution was added dropwise to a stirred, cooled (ice−salt bath) solution of cuprous halide (3.0 mmol) in the same solvent (25 mL). The resulting red solution was treated with diethyl ether (15 mL), which was layered on top of the acetonitrile solution. A crop of black needles of the known bis(*N*,*N*-diethyldithiocarbamato)copper(II)$Cu(Et_2NCS_2)_2$, mp 198 °C, was produced after the solution had stood in a freezer for 3 h. This undesired product was filtered, the solution was treated with additional ether (5 mL) and returned to the freezer overnight, and large orange-red prismatic crystals separated. These were isolated by decanting the solvent, washing with fresh ether, and drying in air.

$Cu_5(Et_4tms)_2I_5$ (1). Dark red prisms; mp 135−145 °C (d). (Found: Cu, 21.8; I, 43.0; C, 16.5; H, 2.7. Calcd for $C_{20}H_{40}N_4S_6Cu_5I_5$: Cu, 21.5; I,42.8; C,16.2; H, 2.7.) IR: 2973 m, 2927 w, 2857 w, 1519 s, 1440 s, 1361 m, 1275 s, 1203 m, 1157 m, 1071 w, 999 w, 907 w, 834 w, 755 w. $\delta_H(CDCl_3)$: 4.03 (q, 7 Hz, 4), 3.63 (q, 7 Hz, 4), 1.46 (t, 7 Hz, 6), 1.35 (t, 7 Hz, 6). μ_{EFF}: 0.00 μ_B. Λ_M: 17−22 ohm^{-1} cm^2 mol^{-1} (10^{-3}−10^{-4} M).

Crystal Structure Determinations. Diffraction intensities were collected on a Siemens P3 diffractometer, which included a beam monochromator. Two standard reflections checked after every 98 reflections showed no significant crystal decay. Intensities were corrected for Lorentz and polarization effects. The structures were solved by direct methods using the program package SHELXTL PLUS[18] (personal computer version) and refined by full-matrix least-squares on F^2 using SHELXL93 program.[19] H atoms were included in their idealized positions with the isotropic thermal parameter fixed at 0.08 Å^2. Additional material comprises H atom coordinates and thermal parameters.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $(Et_4Tms)_2Cu_5I_5$

Cu(1)−I(2)	2.743(3)	Cu(2)−S(1)	2.292(10)
Cu(1)−I(3)	2.623(3)	Cu(2)−S(3)	2.413(8)
Cu(2)−I(2)	2.846(3)	Cu(3)−S(3)	2.256(6)
Cu(2)−I(3)	2.540(3)	C(2)−S(2)	1.81(3)
Cu(3)−I(1)	2.574(3)	C(2)−S(3)	1.69(3)
Cu(3)−I(2)	2.772(5)	C(1)−S(1)	1.69(2)
Cu(3)−I(2)a	2.989(7)	C(1)−S(2)	1.79(3)
I(3)−Cu(1)−I(3)a	112.04(14)	I(3)−Cu(1)−I(2)	107.31(7)
I(3)a−Cu(1)−I(2)	113.20(5)	I(2)−Cu(1)−I(2)a	102.59(14)
S(3)−Cu(2)−I(3)	111.4(3)	S(1)−Cu(2)−I(3)	122.4(2)
S(1)−Cu(2)−S(3)	105.5(3)	S(1)−Cu(2)−I(2)	101.0(2)

^{a} $-x + 1, y, -z + {}^3/_2$.

Results and Discussion

A summary of the crystal data for the complex is given in Table 1. Additional experimental details are found in the Supporting Information. Figure 1 shows the structural diagram and the atomic numbering scheme. Selected bond distances and angles are given in Table 2.

The reaction of acetonitrile solutions of cuprous iodide and Et_4tms leads to a crystalline phase of composition $(CuI)_5(Et_4tms)_2$. The solid-state structure of this aggregate may be described as formed by a central $(CuI)_3$ distorted octahedral element and two additional $CuEt_4tmsI$ units fused to the central $(CuI)_3$ cage by means of sulfur and iodine bridges. The molecule displays a 2-fold crystallographic axis through Cu1 and I1, coincident with the long axial position of the "octahedron". The severely bent equatorial plane of the octahedron is defined by I2, Cu3A, I2A, and Cu3. Each CuEt4tmsI unit contains one tetrahedral copper (Cu2), a bidentate sulfur ligand (S1 and S3), and one iodine atom (I3). These units are fused to two faces of the octahedron by means of two iodine bridges (I3 to Cu1 and I2 to Cu2) and one sulfur bridge (S3 to Cu3).

So far, discrete pentanuclear copper(I) complexes have been reported for $Cu_5(SPh)_72^-$ and $Cu_5X_7{}^{2-}$ (X = Br, I). The anion $Cu_5(SPh)_7{}^{2-}$ displays a molecular structure where four copper(I) atoms are found in a pseudo-cubane arrangement, with the supernumerary metal atom sitting in one of the diagonals of the face from the reference cube. Copper in this case shows two types of coordination, namely, trigonal planar and linear,[20] a situation which deviates considerably from the case reported here.

The anion $Cu_5I_72^-$ has been described as a pentagonal bipyramid of seven iodine atoms, where only slight deviations from C_{5h} symmetry occur. The anion may be viewed as five face-sharing copper(I) iodide tetrahedra.[21] In the bromo derivative, the pentagonal bipyramid of ligand atoms is more severely distorted.[22] With the hindsight afforded by the previous models we may now view the structure of (1) as consisting of the same basic structural unit, viz., a pentagonal bipyramid conformed by the apical I2 and I2A and by a distorted basal plane I1−S3−I3−I3A−S1A. All copper atoms display tetrahedral coordination and appear as three distinct sets. Cu3 and Cu3A are coordinated to three iodines and to one sulfur atom, while

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the ligand entourage for Cu2 and Cu2A consists of two sulfurs and two iodines. The unique Cu1 is coordinated to four iodines. The shortest metal−metal distance found (2.533(8) Å for Cu3−Cu3a) rules out any possible metal−metal bonding. The iodine atoms are either μ_2- or μ_4-bridged and the shortest I···I contact (4.261 Å for I1−I2) compares well with the one found in $[Cu_2I_4^{2-}]$[23] and other related systems.[24]

The structure of the pentanuclear derivative (1) is unique within a series of thiuram monosulfide-copper(I) complexes known thus far. The molecular structures of the complexes $CuMe_4tmsX$ (X = Cl, Br, I), described in a previous paper, display features which may be summarized as follows.[7] All three compounds consist of a basic metal−bidentate ligand six membered chelate ring, with the halogen atom occupying a third coordination position on copper. Tetracoordination about the metal is achieved by bridging. The chloro and iodo derivatives are dimers and bridging is effected by sulfur from the thiuram unit and by iodine, respectively. The bromo derivative is similar to the chloro compound in that sulfur atoms from the thiuram ligand serve as bridges between copper units, but in this case a polymer is formed. The variety of structures thus obtained may be understood on the basis of the relative abilities of the available bases to form bridges. The complex $(CuR_4tmsI)_2$ (R_4-tms = pentamethylenethiuram monosulfide) displays a solid-state structure similar to the iodo derivative found in the methyl series.[13] Complexes $CuEt_4tmsX$ (X = Cl, Br)[25] and $CuPr_4tmsBr$ (Pr = *n*-propyl, *i*-propyl)[26] feature monomeric structures incorporating tricoordinate copper(I).

A variety of experimental conditions have failed to yield a mononuclear copper complex in combinations of copper(I) iodide and tetraethylthiuram monosulfide. Also, all efforts to isolate a species of higher nuclearity using combinations of different copper(I) halides and methyl, ^{n}Pr, or ^{i}Pr substituents on the ligand have not met with any success. It is speculated that the kinetics of complexation might be slow in the case of CuI/Et_4tms, so that the available free CuI competes with the monomeric $CuEt_4tmsI$ for extension of the association.

Characteristic IR frequencies are reported under the protocol for the complex. While the data do not add to the features found by the crystal structure determination, coordination of the chelate to the metal is confirmed. Particularly noteworthy is the shift of the $C-NR_2$ frequency compared to that of the free ligand.[27] At room temperature the ^1H NMR spectra of the free ligand as well as those of the copper complex consist of two sets of resonances for the alkyl groups (R = Me; Et). This must be interpreted in terms of hindered rotation about the $C-NR_2$ bond, which causes nonequivalence of the alkyl groups.[28]

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Supporting Information Available: Listings of full crystallographic data with refinement details, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacements for **1** (4 pages). Ordering information is given on any current masthead page.

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