Notes

X-ray Crystallographic Structure of the Acetonitrile Solvate of Copper(I) Trifluoromethanethiolate: $(CF_3SCu)_{10}{\cdot}8CH_3CN$

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Introduction

Copper thiolate complexes (CuSR) are known in an extraordinarily broad range of structural types from discrete oligomers to multidimensional layered structures.[1] The complexity derives from the large number of possible combinations of the three commonly found Cu(I) coodination geometries, linear, trigonal planar, and tetrahedral, with both doubly and triply bridging thiolate ligands. In addition to their structural diversity, copper(I) thiolate clusters are of fundamental chemical interest due to their presence in redox-active metalloproteins.[2]

In neutral 1:1 metal:thiolate complexes, cluster size and tractability have been controlled either by steric manipulation of the R group (bulky R groups favor smaller clusters) or by partially blocking Cu(I) coordination sites with heteroligands. Thus, Block, Zubieta, and co-workers employing the former technique secured the dodecameric compound $[CuSC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$ (**I**),[3] and with a still larger R group Yang et al. obtained octameric $[CuSC_6H_2\text{-}(i\text{-}Pr)_3]_8$ (**II**).[4] Dance and co-workers used the latter method to prepare a tetrameric, distorted-step structure using PPh_3 to control cluster size, $Cu_4(SPh)_4(PPh_3)_4$ (**III**),[5a] a structure also seen in heteroligand Cu(I) halide complexes.[5b] Complexes related to **III** prepared from alkanedithiols have also been prepared.[5c]

From the direct reaction of bis(trifluoromethyl) disulfide, CF_3SSCF_3, with activated Cu metal in acetonitrile a colorless crystalline product (**IV**) was obtained which was originally described as containing a 1:1 $CuSCF_3$:CH_3CN ratio.[6] Herein we report the crystallographic structure of **IV**, which we now find to be $[CF_3SCu]_{10}{\cdot}8CH_3CN$. As such, it represents the first structurally characterized molecular copper thiolate complex without aryl substitution.

$$\mathrm{CF_3SSCF_3 + Cu \xrightarrow{CH_3CN} [CF_3SCu]_{10}{\cdot}8CH_3CN}$$

IV

Table 1. Crystal Data for $[CF_3SCu]_{10}{\cdot}8CH_3CN$ (IV)[a]

chem formula	$C_{11}0Cu_{10}F_{30}S_{10}{\cdot}C_{16}H_{24}N_8$	Z	2
fw	1974.5	D_x, g cm^{-3}	1.887
space group	$P2_1/n$	T, K	243
a, Å	12.595(3)	μ(Mo Kα), cm^{-1}	34.04
b,Å	18.821(4)	λ, Å	0.710 73
c, Å	15.202(3)	$R(F)$, %	9.79
β, deg	105.38(3)	$R_w(F)$, %	12.31
V, Å^3	3475(2)	Δ/ρ, e Å^{-3}	1.04

[a] The quantity minimized in the least-squares procedures is $\sum w(|F_o| - |F_c|)^2$. $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Table 2. Selected Bond Distances and Angles for **IV**

	(a) Bond Distances (Å)		
Cu(1)–S(1)	2.25(1)	Cu(1)–N(1)	1.95(3)
Cu(1)–S(2)	2.22(1)	Cu(4)–N(2)	1.91(3)
Cu(2)–S(1)	2.22(1)	Cu(5)–N(3)	1.98(4)
Cu(2)–S(3)	2.29(1)	Cu(5)–N(4)	2.05(3)
Cu(2)–S(5)	2.19(1)	S(1)–C(9)	1.82(5)
Cu(3)–S(2)	2.21(1)	S(2)–C(10)	1.74(6)
Cu(3)–S(3)	2.28(1)	S(3)–C(11)	1.82(5)
Cu(3)–S(4)	2.26(1)	S(4)–C(12)	1.71(6)
Cu(4)–S(4)	2.35(1)	S(5)–C(13)	1.79(4)
Cu(4)–S(5)	2.36(1)	Cu(5)–S(4a)	2.30(1)
Cu(4)–S(3a)	2.35(1)	Cu(2)···Cu(3)	2.898(7)
Cu(5)–S(5)	2.31(1)		
	(b) Bond Angles (deg)		
S(1)–Cu(1)–S(2)	122.7(5)	Cu(1)–S(1)–Cu(2)	92.4(6)
S(1)–Cu(2)–S(3)	113.5(5)	Cu(1)–S(2)–Cu(3)	94.8(5)
S(1)–Cu(2)–S(5)	140.6(4)	Cu(2)–S(3)–Cu(3)	78.7(3)
S(3)–Cu(2)–S(5)	105.9(4)	Cu(2)–S(3)–Cu(4a)	124.2(5)
S(2)–Cu(3)–S(3)	115.5(5)	Cu(3)–S(3)–Cu(4a)	125.1(6)
S(2)–Cu(3)–S(4)	138.7(5)	Cu(3)–S(4)–Cu(4)	111.0(5)
S(3)–Cu(3)–S(4)	105.8(4)	Cu(3)–S(4)–Cu(5a)	89.4(4)
S(4)–Cu(4)–S(3a)	105.1(4)	Cu(4)–S(4)–Cu(5a)	127.2(5)
S(5)–Cu(4)–S(3a)	106.3(4)	Cu(2)–S(5)–Cu(4)	114.5(4)
S(4)–Cu(4)–S(5)	109.8(4)	Cu(2)–S(5)–Cu(5)	107.8(5)
S(5)–Cu(5)–S(4a)	104.0(4)	Cu(4)–S(5)–Cu(5)	113.1(5)

Experimental Section

Crystallographic data are collected in Table 1. Crystals of **I** were obtained from batches prepared as a part of the original synthetic investigations[6] and were coated with mineral oil to prevent loss of solvent and were mounted in thin-walled Lindermann capillary tubes. All 12 of the specimens examined exhibited broad, diffuse X-ray diffraction. Such behavior is typical of compounds with numerous loosely bound solvent molecules and leads inevitably to a low fraction of observed data and high refinement residuals. Photographic characterization revealed $2/m$ Laue symmetry, and systematic absences in the diffraction data led to the unique assignment of the space group. A semi-empirical correction for absorption was applied to the data.

The five symmetry-independent Cu atoms were located by direct methods, and the remaining non-hydrogen atoms were obtained from subsequent difference Fourier syntheses. Anisotropic refinement of thermal parameters was restricted to Cu, S, F, and N atoms due to data limitations. Hydrogen atoms were placed in idealized locations (d(CH) = 0.96 Å). A void-space analysis revealed no volumes large enough to contain additional molecules of acetonitrile. Selected bond distances and angles are given in Table 2. All computations used the SHELXTL-PLUS library of programs.[7]

Results and Discussion

The structure of **IV** is shown in Figure 1. The cluster and its solvent entourage exist as discrete molecules without close intermolecular contacts in the crystal lattice. The cluster framework is composed of alternating copper–sulfur atoms in a centrosymmetric arrangement; half of the decamer forms the crystallographic symmetry-independent unit. Cu(2) and Cu(3)

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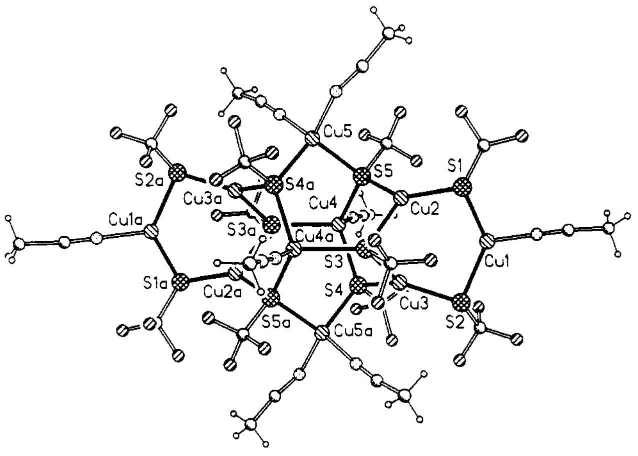

Figure 1. Molecular structure for $(CF_3SCu)_{10}\cdot 8CH_3CN$ (**IV**).

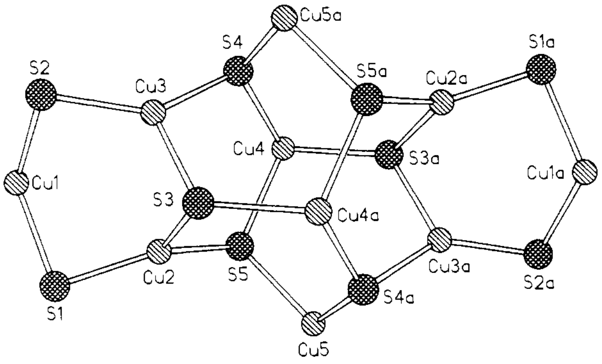

Figure 2. Copper-sulfur framework for **IV**.

make a close contact of 2.898(7) Å, but this is not a significant bonding interaction. The cluster framework, Figure 2, is without precedent. The central polycyclic 14-atom core, obtained by deleting atoms S(1), S(2), Cu(1), S(1a), S(2a), and Cu(1a), is described as a member of the tritwistane series of an all-carbon pentacyclic system.[8] This interior framework structure is completed by joining two $Cu(SCF_3)_2^{2-}$ spanning links to a central $Cu_8(SCF_3)_6^{4+}$ tritwistane core at Cu(2) and Cu(3).

In view of the low overall quality of the crystal structure, which is determined by the high thermal activity of the coordinated acetonitrile molecules, only a limited discussion of bond parameters is warranted. There are four distinctly different copper coordination environments. Cu(1) is trigonal planar with two μ_2-bridging thiolate groups and one acetonitrile molecule. The bond angles at Cu(1) are 120 ± 3°.

Cu(2) and Cu(3) are similar to each other and, like Cu(1), are also planar. Each is ligated by three bridging thiolate groups (one μ_2 and two μ_3), and these metal atoms are not solvated. The coordination geometries at Cu(2) and Cu(3) are highly distorted; the S–Cu–S angles are 113.5(5) (1,3), 140.6(4) (1,5), and 105.9(4)° (3,5) for Cu(2) and 115.5(5) (2,3), 138.7(5) (2,4), and 105.8(4)° (3,4) for Cu(3); the largest angle is at the attachment of the exterior link, which awkwardly fuses a chair-conformation six-membered ring to two with boat confirmations.

Cu(4) is tetrahedral with three μ_3-bridging thiolate groups and one acetonitrile molecule with bond angles at Cu(4) of 109 ± 4°. Cu(5) is also tetrahedral and is coordinated by two μ_3-briding thiolate groups and two acetonitrile molecules. The tetrahedral geometry is more distorted at Cu(5); the range of angles at Cu(5) is 104–120°.

The averages of the Cu–S bond distances in the three three-coordinate environments are statistically identical at 2.23 Å; those in the two tetrahedral environments are longer at 2.33 Å. Since linear, two-coordinate Cu–S bonds in both **I**[3] and **II**[4] average about 2.16 Å, a trend exists in which Cu(I)–S bond distances increase with increasing coordination numbers. A similar trend has also been observed in Cu–N bond distances in imidazole complexes.[9]

If the Cu–S frameworks in the four crystallographically characterized neutral copper–thiolate complexes, **I–IV**, are compared, several features are noteworthy. In structures **I**[3] and **II**,[4] in which large R groups must be accommodated, the average Cu-atom coordination number is low: 2.5 for **I** and 2.0 for **II** (all Cu environments are linear). In **III**[5] and **IV** with less bulky R groups and heteroligand substitution at Cu, the average coordination numbers are larger: 3.5 for **III** and 3.4 for **IV**. Space-filling molecular views of **IV** are helpful in understanding why four of the ten Cu atoms are unsolvated; Cu(2), Cu(3), and their symmetry equivalents are visibly sterically blocked.

The complexity of the structure suggests that a large number of competing factors including R-group electronic properties, solvation energy, steric favors, ring-strain energy, and lattice energy are at work in determining the final structure. Each of these factors will be examined in greater detail in our future work.

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Supplementary Material Available: Tables listing detailed experimental data for X-ray diffraction, fractional atomic coordinates and thermal parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen-atom coordinates and thermal parameters and a figure showing **IV** with thermal ellipsoids (8 pages). Ordering information is given on any current masthead page.

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