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Insertion of CS_2 into Cu–S Bonds (II). Preparation and Crystal Structure of Insertion Product with CS_2 $[Cu_6(S_2CSC_6H_2Pr^i{}_3\text{-}2,4,6)_4(SC_6H_2Pr^i{}_3\text{-}2,4,6)_2]\cdot 2CHCl_3\cdot 4CH_3OH$

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ABSTRACT

Complex $[Cu(SC_6H_2Pr^i{}_3\text{-}2,4,6)]_8$ *(**1**) reacts with a small amount of* CS_2 *to give red crystals* $[Cu_6(S_2CSC_6H_2Pr^i{}_3\text{-}2,4,6)_4(SC_6H_2Pr^i{}_3\text{-}2,4,6)_2]\cdot 2CHCl_3\cdot 4CH_3OH$ *(**2**), and* CS_2 *is inserted into two-thirds of the Cu–S bonds of complex (**1**). The unusual structure of complex (**2**) consists of six copper atoms linked through arenethiolate* (RS^-) *and aryl trithiocarbonate* ($RSCS_2{}^-$) *ligands, exhibiting a number of interesting features. Crystal data: triclinic, space group* $P\bar{1}$, $a = 14.298(4)$, $b = 14.282(5)$, $c = 17.745(7)$Å, $\alpha = 109.92(3)$, $\beta = 111.88(3)$, $\gamma = 90.42(2)°$, $Z = 1$, $R = 7.83\%$, *for 4118 observed reflections.*

INTRODUCTION

The insertion of CS_2 into M–X bonds (M = transition metal; X = H, N, O, S, halide, alkyl, amine, alkoxide, etc.) has been widely studied [1]. However, few reports on the insertion of CS_2 into Cu–S or Ag–S bonds have been made. In 1931, Dunean et al. reported that CS_2 reacts with copper mercaptides (CuSR) to give trithiocarbonates (CuS_2CSR) [2], but their structures had not been determined until 1975, when Avdeef determined the first structure of the insertion product of CS_2 into a Cu–S bond, $Cu(PPh_3)_2(S_2CSEt)$ [3]. Later, a similar structure of the complex $Cu(PPh_3)_2(S_2CSPh)$ [4] was determined. In 1986, Chadha et al. reported an unusual copper-sulfur cage (Cu_8S_{12}) complex $Cu_8(S_2CSCMe_2Et)_4(SCMe_2Et)_4$ [5]. Since 1987, we have found two insertion products of CS_2 into Ag–S bonds: $Ag(PPh_3)_2(S_2CSBu^t)$ [6] and $[\{Ag(S_2CSC_6H_2Pr^i{}_3\text{-}2,4,6)\}_2\{Ag(SC_6H_2Pr^i{}_3\text{-}2,4,6)\}_6]\cdot 8CHCl_3$ [7]. We are especially interested in the structures of products formed by CS_2 insertion into a part of a set of Cu–S or Ag–S bonds in polynuclear compounds. In this article, we present the preparation and crystal structure of the insertion product $[Cu_6(S_2CSC_6H_2Pr^i{}_3\text{-}2,4,6)_4(SC_6H_2Pr^i{}_3\text{-}2,4,6)_2]\cdot 2CHCl_3\cdot 4CH_3OH$ (**2**), involving insertion of CS_2 into two-thirds of the Cu–S bonds of complex (**1**).

EXPERIMENTAL

Infrared spectra of KBr pellets were recorded with a Perkin-Elmer 983G spectrometer.

Preparation of Complex (**2**)—synthesis of complex (**1**) $[Cu(SC_6H_2Pr^i{}_3\text{-}2,4,6)]_8$ followed our previous article [8]. The yellow crystals effloresced and turned into a yellow powder when they were collected by filtration and then dried in vacuo. IR (KBr): 2952 vs, 2864 m, 2476 m, 1753 w, 1594 m, 1555 m, 1457 s, 1419 s, 1395 m, 1378 s, 1356 s, 1306 m, 1256 m, 1244 m, 1165 m, 1153 m, 1098 m, 1067 m, 1055 s, 1029 s, 935 m, 920 w, 874 s, 838 w, 804 w, 752 m, 646 m, 630 m, 520 w, 474 w, 417 w, 344 w cm^{-1}.

Carbon disulfide (0.20 cm^3) was added to a solution of complex (**1**) powder (350 mg) in chloroform (20 cm^3), and the pale yellow solution turned black-red in 1.5 hour. After 4 hours, the solution was condensed and dried in vacuo, a black-red solid being obtained. This solid is soluble in CH_2Cl_2,

1042-7163/92/$3.50 + .25

TABLE 1 Summary of Crystal Data and Experimental Details for Complex (**2**)

Formula	$C_{100}H_{148}Cl_6Cu_6O_4S_{14}$
M	1228.4
Color/Habit	Red Prismatic
Crystal System	Triclinic
Space Group	$P\bar{1}$
a/Å	14.298(4)
b/Å	14.282(5)
c/Å	17.745(7)
α/°	109.92(3)
β/°	111.88(3)
γ/°	90.42(2)
V/Å^3	3124(2)
Z	1
Dc/g cm^{-3}	1.306
λ(Mo-K_α)/Å	0.71073
F(000)	1280
Crystal Dimension/mm^3	0.3 × 0.5 × 0.6
Scan Mode	2θ
2θ Range	$3.0 < 2\theta < 45.0$
Scan Rate/min^{-1}	4.0–29.3
Scan Range/°	1.2
No. of Reflections Measured	8224
No. Observed [$F > 8\sigma(F)$]	4118
R	0.0783
Rw	0.0830

TABLE 2 Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	y	z	$U(eq)$
Cu(1)	9229(1)	4789(1)	5378(1)	54(1)
Cu(2)	8870(1)	4675(1)	3387(1)	57(1)
Cu(3)	9400(1)	6541(1)	5085(1)	54(1)
S(1)	5922(3)	5078(3)	3671(3)	62(2)
S(2)	9810(3)	7912(3)	3473(2)	61(2)
S(3)	9996(3)	6391(2)	6389(2)	53(2)
S(4)	7871(3)	4452(2)	4068(2)	53(2)
S(5)	7737(3)	6674(2)	4464(2)	55(2)
S(6)	9465(2)	3241(2)	5462(2)	49(2)
S(7)	8722(3)	5817(3)	2776(2)	57(2)
C(1)	5308(10)	6147(11)	3588(11)	58(8)
C(2)	4750(13)	6140(12)	2759(11)	75(9)
C(3)	4171(14)	6881(16)	2699(13)	87(11)
C(4)	4119(13)	7638(14)	3425(15)	90(11)
C(5)	4645(13)	7621(12)	4259(13)	81(10)
C(6)	5257(11)	6876(12)	4349(11)	65(8)
C(7)	4803(15)	5356(15)	1940(12)	93(11)
C(8)	3769(27)	4892(26)	1263(20)	376(36)
C(9)	5493(26)	5700(25)	1660(18)	248(28)
C(10)	3654(40)	8614(29)	3444(38)	353(77)
C(11)	2939(29)	8629(24)	3737(28)	424(65)
C(12)	3934(30)	9152(21)	3022(25)	261(37)
C(13)	5816(12)	6886(12)	5245(10)	74(9)
C(14)	6458(14)	7930(14)	5919(11)	93(11)
C(15)	5058(14)	6495(15)	5539(13)	102(12)
C(16)	12772(9)	4491(9)	5889(8)	45(6)
C(21)	8686(11)	7938(10)	2584(10)	58(7)
C(22)	8667(12)	7555(10)	1739(10)	66(8)
C(23)	7828(14)	7682(12)	1062(11)	78(9)
C(24)	7032(13)	8134(13)	1231(11)	85(9)
C(25)	7118(12)	8496(12)	2086(11)	76(9)
C(26)	7948(13)	8401(11)	2790(11)	69(9)
C(27)	9479(15)	7073(12)	1512(10)	81(9)
C(28)	9134(21)	6164(13)	641(11)	136(17)
C(29)	10272(17)	7766(19)	1569(13)	126(14)
C(30)	6181(15)	8235(14)	500(13)	114(12)
C(31)	6211(20)	9343(14)	575(14)	176(19)
C(32)	5180(17)	7702(31)	405(24)	330(42)
C(33)	7940(13)	8795(13)	3697(11)	80(9)
C(34)	6884(14)	8748(14)	3740(13)	94(11)
C(35)	8489(15)	9883(13)	4182(10)	98(10)
C(36)	9627(10)	6744(9)	3552(8)	48(6)
C(41)	10662(11)	3018(11)	2920(9)	58(7)
C(42)	11246(11)	3551(11)	2671(10)	58(7)
C(43)	11665(13)	2956(15)	2110(13)	84(11)
C(44)	11585(14)	1935(14)	1825(10)	77(10)
C(45)	11058(13)	1458(12)	2097(10)	75(8)
C(46)	10569(11)	1940(9)	2660(8)	56(7)
C(47)	11424(13)	4669(12)	2975(12)	74(10)
C(48)	12463(15)	5120(14)	3649(13)	103(12)
C(49)	11159(15)	5013(14)	2183(12)	99(12)
C(50)	12117(17)	1479(16)	1202(13)	137(19)
C(51)	12724(27)	696(24)	1507(20)	320(46)
C(52)	11273(19)	957(23)	280(12)	181(22)
C(53)	9975(12)	1316(10)	2908(10)	68(8)
C(54)	9171(13)	504(12)	2150(11)	92(9)
C(55)	10722(15)	850(14)	3539(12)	109(12)
Cl(1)	7436(6)	1716(6)	2883(7)	203(7)
Cl(2)	5676(9)	1087(7)	3052(10)	253(11)

Continued

$CHCl_3$, THF, acetone, ether, EtOH, *n*-pentane, benzene, pyridine, and ethyl acetate but insoluble in MeOH. Red prismatic crystals were obtained by diffusion of MeOH into a $CHCl_3$ solution over several days.

The red prismatic crystal is the title complex (**2**). It effloresced in the air and turned into a red powder. IR (KBr): 2956 vs, 2864 s, 1758 w, 1595 m, 1561 m, 1515 w, 1458 s, 1422 m, 1380 s, 1359 s, 1311 m, 1252 w, 1167 w, 1153 m, 1101 m, 1069 m, 1056 m, 1024 s, 937 m, 875 s, 751 m, 652 w, 520 w, 486 m, 226 w cm^{-1}.

X-ray Crystal Structural Determination of Complex (**2**)—the crystal data for complex (**2**) are summarized in Table 1 together with some experimental details. The diffraction intensities were collected at room temperature on a Siemens R3 diffractometer with Mo-K_α (λ = 0.71073 Å) radiation. The crystal was sealed in a glass capillary. The structure was solved by a direct method with the SHELXTL PLUS program. Blocked full-matrix least-squares refinement of all positional parameters, anisotropic thermal parameters for the copper, sulfur, and carbon atoms in the ligands, and individual isotropic thermal parameters for the atoms of solvent molecules were obtained. The hydrogen atoms were located in calculated positions, and a value of 0.08 was assigned for isotropic thermal parameters of hydrogen atoms. A weighting scheme of the form $w = [\sigma^2(F) + 0.0001F^2]^{-1}$ was

TABLE 2 Continued

Cl(3)	*5486(10)*	*2229(9)*	*2000(7)*	*281(9)*
C(61)	*6308(6)*	*2126(8)*	*2998(7)*	*130(14)*
C(62)	*7470(23)*	*3689(21)*	*859(20)*	*173(11)*
C(63)	*2182(28)*	*8250(33)*	*−295(31)*	*262(21)*
O(1)	*7697(20)*	*2905(19)*	*1263(17)*	*228(10)*
O(2)	*1152(25)*	*7737(25)*	*−478(21)*	*278(12)*

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

applied. The atomic coordinates for the nonhydrogen atoms of complex (**2**) are presented in Table 2.

Additional material available from the author comprises H-atom coordinates, thermal parameters, and bond lengths and angles.

RESULTS AND DISCUSSION

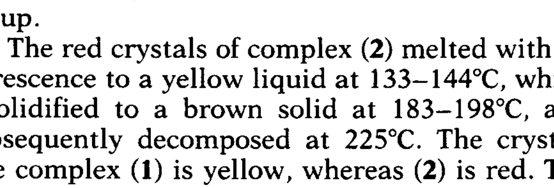
Structure of complex (2)—the molecular structure of complex (2) consists of six copper atoms linked through arenethiolate (RS^-) and aryl trithiocarbonate ($RSRS_2^-$) ligands. Figures 1 and 2 give the molecular configuration and the structure of the core, respectively. There are some interesting features of this structure.

Four out of six copper atoms Cu(**1**), (**3**), (**1a**), (**3a**) are in one plane, forming a parallelogram. The other two copper atoms Cu(**2**) and Cu(**2a**) link to the Cu(**1a**) and Cu(**1**) atoms, respectively. There is a symmetry center at the centerpoint of the parallelogram. This Cu_6 framework is then capped by sulfur atoms which may be terminal, dibridging, or tribridging. Each of the sulfur atoms S(**3**), S(**3a**) of the arenethiolate ligands bridges three copper atoms. The ligating sulphur atoms of the aryl trithiocarbonate are of two kinds: S(**5**), (**5a**), (**7**), and (**7a**) are terminal, while S(**4**), (**4a**), (**6**), and (**6a**) are dibridging. The Cu–Cu distances bridged by the dibridging sulfur atoms are longer (e.g., Cu(**1**)–Cu(**3a**) 2.885 Å) than those bridged by the tribridging sulfur atoms (e.g., Cu(**1**)–Cu(**3**) 2.794 Å). Every copper atom is coordinated by three sulfur atoms. Because the sum of three S-Cu-S angles is 360 ± 1°, the CuS_3 segment has a slightly distorted trigonal planar geometry. The average length of the Cu–S bonds is 2.264 Å (2.219–2.316 Å).

An interesting feature of complex (**2**) is that only two-thirds of the (CuSR) units of the starting material have been inserted with CS_2, forming a copper cluster with mixed ligands. The CS_3 group of the new ligands ($RSCS_2^-$) is planar (the sum of three S–C–S angle is 360 ± 1°). The C–S distances of the CS_3 segment average 1.712 Å (1.616–1.779 Å), shorter than the length of a C–S single bond 1.812 Å, longer than that of a C=S double bond 1.607 Å [9], and close to the mean C–S distance 1.691 Å observed in the CS_3 group of the complex $[\{Ag(S_2CSC_6H_2Pr^i_3)_2\}\cdot\{Ag(SC_6H_2Pr^i_3)_6\}]\cdot 8CHCl_3$ [7]. The C–S distances of the CS_3 segment are not equal. The distance of C–S_t (Av.1.631 Å, 1.616–1.647 Å) is obviously shorter than those of the other two C–S bonds (Av.1.752 Å, 1.738–1.779 Å). The S–C–S bond angles of the CS_3 segment are not equal either. Angle S_t–C–S (av 124.1°, 122.4–125.9°) is larger than that of S_{db}–C–S (av 108.1°, 107.6–108.6°); the R group is on the side of the larger S_t–C–S bond angle.

Compared with the starting material of complex (**1**) [8], the structure of the insertion product has changed remarkably. The Cu_8S_8 core of complex (**1**) consists of a discrete twisted 16-membered ring of alternating Cu and S atoms. However, the structure of the insertion product is based on an unusual Cu_6S_{10} core. The CuS_3 trigonal planar geometry of the insertion complex is different from that of the CuS_2 linear coordination of complex (**1**).

Up until now, we have found three coordination types of Cu or Ag atoms with trithiocarbonate ($RSCS_2^-$) ligands which were produced by insertion of CS_2 into Cu–S or Ag–S bonds. (i) In the complexes with heteroligand triphenylphosphine, the type of monometallic insertion products $(PPh_3)_2M(S_2CSR)$ (M=Cu [3] [4], Ag[6]) is similar to that of other transition-metal trithiocarbonate complexes (e.g., $CpW(CO)_2S_2CSCH_2Ph$ [10], Ni $(S_2CSC_4H_9)_2\cdot$bpy [11], etc.). (ii) In the novel moiety $(AgS_2CSR)_2$ of $(AgS_2CSC_6H_2Pr^i_3)_2$ $(AgSC_6H_2Pr^i_3)_6$, two Ag atoms are linked to the same ($RSCS_2^-$) ligands. (iii) Each ($RSCS_2^-$) ligand coordinates to three Cu atoms in complexes $Cu_8(SR)_4(S_2CSR)_4$ (R=CMe_2Et [5], $CMeEt_2$ [12]). The coordination type of complex (**2**) is type (iii), the same as that of $Cu_8(SR)_4(S_2CSR)_4$ and different from that of $(AgS_2CSC_6H_2Pr^i_3)_2(AgSC_6H_2Pr^i_3)_6$, even though they have the same ligand 2,4,6-$Pr^i_3C_6H_2S^-$.



The IR spectrum of complex (**2**), compared with that of complex (**1**), exhibits two extra peaks at 1024 and 826 cm^{-1}, which are characteristic of the CS_3 group.

The red crystals of complex (**2**) melted with efflorescence to a yellow liquid at 133–144°C, which resolidified to a brown solid at 183–198°C, and subsequently decomposed at 225°C. The crystalline complex (**1**) is yellow, whereas (**2**) is red. The change of color is common in CS_2 insertion reactions into Cu–S or Ag–S bonds. This may be regarded as a characteristic of the insertion of CS_2.

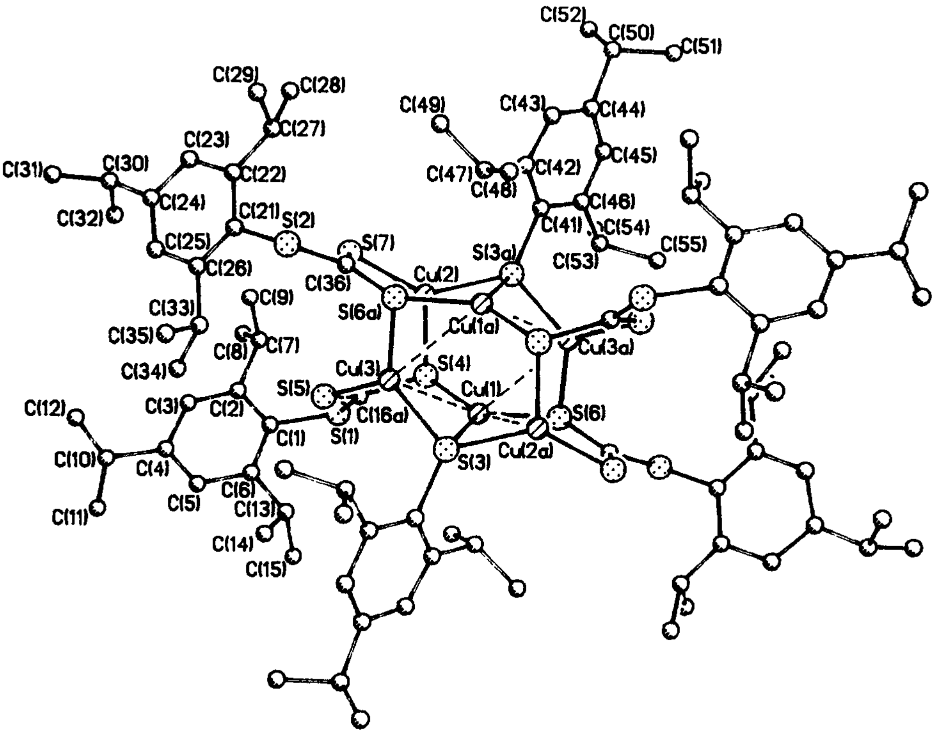


FIGURE 1 The Molecular Structure of $Cu_6(S_2CSC_6H_2Pr^i_3\text{-}2,4,6)_4(SC_6H_2Pr^i_3\text{-}2,4,6)_2$

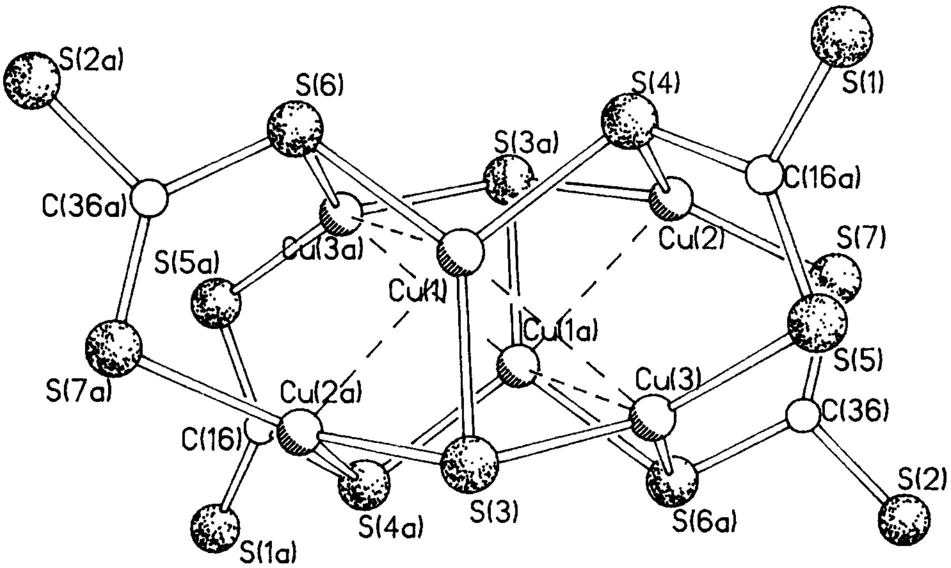


FIGURE 2 The Core Structure of $Cu_6(S_2CSC_6H_2Pr^i_3\text{-}2,4,6)_4(SC_6H_2Pr^i_3\text{-}2,4,6)_2$

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