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Di-μ-iodo-bis{[methyltris(methylthiomethyl)silane-κ^2S,S']copper(**I**)}

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Key indicators

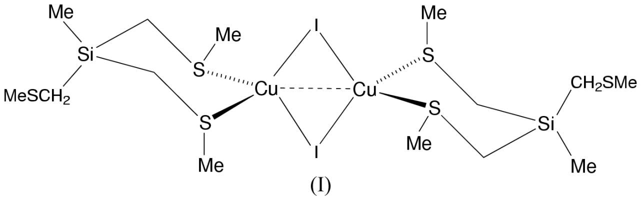
Single-crystal X-ray study
T = 173 K
Mean σ(Si–C) = 0.008 Å
Disorder in main residue
R factor = 0.042
wR factor = 0.090
Data-to-parameter ratio = 20.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The molecule of the title compound, $[Cu_2I_2(C_7H_{18}S_3Si)_2]$, is dimeric. It lies on an inversion center and contains roughly tetrahedral copper centers surrounded by two thioether groups and two bridging iodo ligands. The Cu···Cu separation, 2.862 (2) Å, is indicative of a weak interaction between the two metal atoms and is not unusual for this type of compound.

Comment

The coordination chemistry of polythioethers, with the exception of the many studies carried out with macrocyclic thioethers such as 1,4,7-trithiacyclononane (9S3) (Cooper & Rawle, 1990; Blake & Schröder, 1990), is underdeveloped relative to that of simple monodentate (RSR') and bidentate [$RS(CH_2)_nSR'$] thioethers (Murray & Hartley, 1981). Prompted by our interest in a systematic investigation of tripodal thioethers of general formula $MeSi(CH_2SR)_3$, we recently reported the preparation of $MeSi(CH_2SMe)_3$ and the synthesis and structural characterization of its group 6 metal tricarbonyl derivatives $\{MeSi(CH_2SMe)_3\}M(CO)_3$ (M = Cr, Mo, W) (Yim, Tran, Dobbin *et al.*, 1999). In contrast to the mononuclear nature of these complexes, the reactions of $MeSi(CH_2SMe)_3$ with the copper(I) halides CuX (X = Cl, Br) yielded one-dimensional coordination polymers of stoichiometry $Cu_3\{MeSi(CH_2SMe)_3\}X_3$ (Yim, Tran, Pullen *et al.*, 1999). Unexpectedly, the corresponding reaction of CuI, under similar conditions, produced a 1:1:1 species of composition $\{MeSi(CH_2SMe)_3\}CuI$, which we initially assumed to be analogous to the mononuclear crown thioether derivative (9S3)CuI (Küppers *et al.*, 1987). Unlike the latter, however, iodo[methyltris(methylthiomethyl)silane]copper(I) turned out to be dimeric in the solid state and we describe here the synthesis, characterization, and structure of $[\{MeSi(CH_2SMe)_3\}CuI]_2$, (I).



(I)

The structure of (I) was determined by single-crystal X-ray diffraction (Fig. 1). Each of the two Cu atoms in the centrosymmetric dimer is in a distorted tetrahedral environment, coordinated by two of the three thioether groups present in $MeSi(CH_2SMe)_3$ and by two bridging iodo ligands, with the angles subtended at each metal center in the approximate range 104–118°. The metrical parameters of the planar

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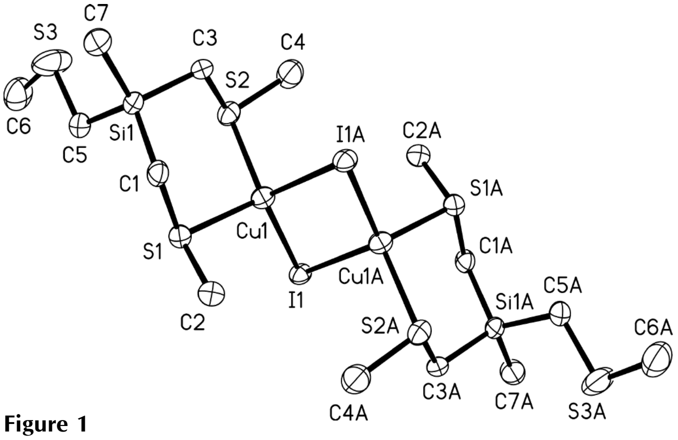

Figure 1
The molecular structure of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms and the minor disorder component have been omitted for clarity.

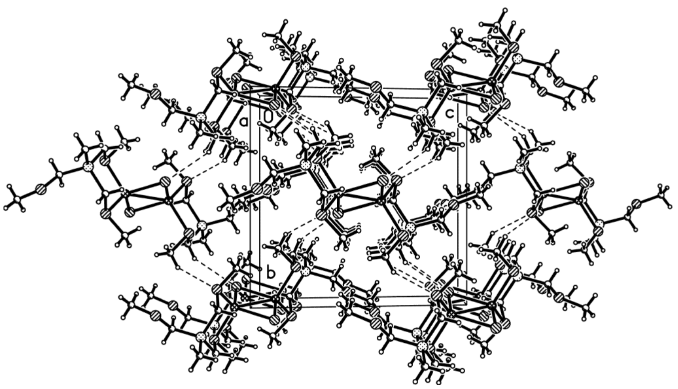

Figure 2
Packing diagram of the dimer molecules. The view is along the *a* axis. Short intermolecular H···I contacts are shown as dashed lines.

rhomboidal Cu_2I_2 core in (I) [Cu—I = 2.5798 (11) and 2.6904 (12) Å; Cu—I—Cu and I—Cu—I = 65.75 (4) and 114.25 (4)°, respectively] are typical of such moieties (Holloway & Melnik, 1995). The Cu—S bond lengths in (I), 2.304 (2) and 2.322 (2) Å, are very close to the mean value found in the Cambridge Structural Database (CSD; Version 5.24, November 2002; Allen, 2002) for tetracoordinate Cu^I bound to single thioether (SR_2) functionalities (2.322 Å). The Cu···Cu separation in (I), 2.862 (2) Å, reflects a weak interaction between the two metal atoms and is not unusual for this type of compound; the mean value found in the CSD for such distances in a variety of [Cu(μ-I)$_2$Cu] complexes is *ca* 2.76 Å (Allen, 2002). Weak intermolecular interactions are noted for atoms I1 and S2 with H atoms H1*B* and H2*A*, respectively, at 3.19 and 2.79 Å.

Experimental

A stirred pale-yellow solution of CuI (1.00 g, 5.25 mmol) in acetonitrile (40 ml) was treated with $MeSi(CH_2SMe)_3$ (1.40 ml, 7.05 mmol), resulting in the immediate formation of an off-white precipitate. The suspension was stirred for 15 min and concentrated under reduced pressure to *ca* 10 ml. After addition of diethyl ether (30 ml), the product was isolated by filtration, washed with diethyl ether (30 ml) and pentane (30 ml), and dried *in vacuo* for 1 h (1.37 g, 63%). NMR data (in CD_3CN): ^1H δ 0.23 (*s*, 3H, CH_3Si), 2.05 (*s*, 6H, CH_2), 2.23 (*s*, 9H, SCH_3); $^{13}C\{^1H\}$ δ −4.2 (*s*, 1C, CH_3Si), 19.8 (*s*, 3C, CH_2), 22.7 (*s*, 3C, SCH_3). IR data (cm^{-1}): 2912 (*m*), 2868 (*m*), 1427 (*m*), 1412 (*m*),1368 (*m*), 1309 (*m*), 1249 (*m*), 1121 (*w*), 1084 (*w*), 1059 (*w*), 974 (*m*), 960 (*s*), 820 (*vs*), 777 (*s*), 732 (*m*). Analysis calculated for $C_7H_{18}CuIS_3Si$: C 20.2, H 4.4%; found: C 20.2, H 4.2%.

Crystal data

$[Cu_2I_2(C_7H_{18}S_3Si)_2]$
$M_r = 833.85$
Monoclinic, $P2_1/c$
$a = 9.3372\ (1)$ Å
$b = 12.8346\ (3)$ Å
$c = 13.0991\ (3)$ Å
$\beta = 103.316\ (1)°$
$V = 1527.58\ (5)$ Å^3
$Z = 2$
$D_x = 1.813$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 540 reflections
$\theta = 2$–$25°$
$\mu = 3.90$ mm^{-1}
$T = 173\ (2)$ K
Block, colorless
0.20 × 0.10 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.509$, $T_{max} = 0.745$
5836 measured reflections
2641 independent reflections
2191 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 25.0°$
$h = -10 \rightarrow 11$
$k = -15 \rightarrow 14$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.090$
$S = 1.28$
2641 reflections
128 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0168P)^2 + 4.7233P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

I1—Cu1	2.5796 (9)	S1—C1	1.803 (7)
I1—Cu1^i	2.6916 (10)	S2—C4	1.794 (8)
Cu1—S2	2.304 (2)	S2—C3	1.801 (7)
Cu1—S1	2.322 (2)	Si1—C1	1.872 (7)
Cu1—Cu1^i	2.8633 (17)	Si1—C3	1.882 (7)
S1—C2	1.798 (8)		
Cu1—I1—Cu1^i	65.76 (3)	C3—S2—Cu1	102.5 (3)
S2—Cu1—S1	104.08 (7)	S1—C1—Si1	113.8 (4)
C1—S1—Cu1	102.5 (2)	S2—C3—Si1	113.3 (4)

Symmetry code: (i) $1-x, 1-y, 1-z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*B*···I1^{ii}	0.99	3.15	4.027 (6)	149
C2—H2*A*···S2^{ii}	0.98	2.79	3.639 (8)	146

Symmetry code: (ii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$.

All H atoms were placed in calculated positions with U_{iso} set at 1.2 or 1.5 times U_{eq} of the parent atom, and were refined as riding atoms. Atom S3 was found to be disordered over two sites in a 75:25% occupancy ratio.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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