# Structure of 3,4,5-Tris(methylthio)-1,2-dithiolium

## *catena*-μ-Iodo-μ₃-iodo-(μ-iodo-dicuprate(I)),

## [S₂C₃(SCH₃)₃][Cu₂I₃]

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The structure of the title compound has been determined from single-crystal X-ray diffracto-meter data. The compound crystallizes, as lus-trous black prisms, in space group $P2_1/c$ with $a=10.856(7)$, $b=18.992(5)$, $c=8.630(2)$ Å, $\beta=106.74(3)°$ and $Z=4$. Full-matrix least-squares refinement of 145 structural parameters gave $R=0.060$ for 2932 observed $[I>3.0\sigma(I)]$ reflec-tions. The $[Cu_2I_3]^-$ anion consists of an infinite I-bridged chain along **c**, I(1) and I(2) each bridging two copper(I) atoms while I(3) bridges three copper(I) atoms. One copper atom, Cu(1), is distortedly trigonal-planar coordinated by iodide whereas Cu(2) is surrounded by an approximately tetrahedral arrangement of iodide ligands. Cu-I bond lengths range from 2.523(3)−2.730(3) Å for Cu(1) and from 2.597(2)−2.781(3) Å for Cu(2). Cu⋯Cu contacts of 2.551(3) and 2.657(3) Å alternate within the chains, forming a zig-zag pattern along **c**. The cations lie between the $[Cu_2I_3]^-$ chains with their molecular planes approximately perpendicular to **b** and the dithio groups orientated towards the chains. There are, however, no exceptionally short Cu⋯S contacts.

From results of structural investigations of crys-talline [N(C₄H₉)₄][CuX₂], X=Cl, Br, I, CN,[1−3] and [N(C₄H₉)₄][CuBrCl][4], it would appear that the tendency of the anion to catenation increases in the order X=Cl≈Br<I<CN. Moreover, it would seem that the formation of discrete ions is favoured by the presence of large bulky cations of low, well-screened charge. Thus tetrabutylam-monium stabilizes discrete monomeric [CuCl₂]⁻,

[CuBr₂]⁻ and [CuBrCl]⁻ in the solid state,[1,4] dimeric [Cu₂I₄]²⁻,[2] but a [Cu(CN)₂]⁻ chain.[3] Infinite chains of edge-sharing Cu(I)−X tetra-hedra, X=Cl, Br, I, occur, on the other hand, in *e.g.* the tetraamminecopper(II) dihalocup-rates(I)[5,6] and bis(1,2-diaminoethane)copper(II) diiododicuprate(I).[7]

In order to ascertain which factors are decisive for the formation of discrete [CuX₂]⁻ ions *contra* chains in the solid state, dihalocuprates(I) with cations of different sizes and geometry are presently being investigated. In an attempt to prepare [S₂C₃(SCH₃)₃][CuI₂], [S₂C₃(SCH₃)₃][Cu₂I₃] was obtained, whose structure was also considered relevant for this study. The iodocup-rate(I) complex [Cu₂I₃]⁻ has been found to form various types of infinite chain, *e.g.* chains of edge- and face-sharing Cu(I)−I tetrahedra in the tetraethylammonium and dimethyl(3-dimethyl-amino-2-aza-2-propenylidene)ammonium com-pounds[8] and in 2,4,6-triphenylthiopyrylium triiododicuprate(I),[9] and double chains of edge-sharing tetrahedra in Cs[Cu₂I₃].[10] A discrete [Cu₄I₆]²⁻ cluster, in which copper is trigonal-planar coordinated and pairs of copper atoms are bridged by iodide, is, however, obtained with methyltriphenylphosphonium as cation.[11]

## EXPERIMENTAL

[S₂C₃(SCH₃)₃][Cu₂I₃] was obtained in an attempt to prepare [S₂C₃(SCH₃)₃][CuI₂]. Excess 3,4,5-tris(methylthio)-1,2-dithiolium iodide[12]

and copper(I) iodide [molar ratio 2:1] were dissolved in acetonitrile. Black crystals with a metallic lustre were deposited after a few hours.

Diffracted intensities from a crystal, 0.14×0.11×0.36 mm, were measured with a Syntex $P2_1$ diffractometer, using graphite-monochromated Mo$K\alpha$ radiation and the $\omega$–$2\theta$ scan mode. Data were collected for $2\theta \leq 55$ °, the $2\theta$ scan rate being varied between 2.5 and 25.0 min$^{-1}$, depending on the intensity of the reflection. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method[13] was used to calculate the intensities.[14] A total of 4263 reflections were measured from which a unique set of 3949 reflections was obtained, systematically absent reflections being omitted. Of these 3949 reflections, those 2932 for which $I > 3.0\sigma(I)$ were used in the subsequent calculations. Data were corrected for Lorentz and polarisation effects but not for absorption. The unit cell parameters were determined by least squares from diffractometer setting angles for 15 reflections.

## CRYSTAL DATA

3,4,5-Tris(methylthio)-1,2-dithiolium *catena-μ-* iodo-$\mu_3$-iodo-($\mu$-iodo-dicuprate(I)),    [S$_2$C$_3$ (SCH$_3$)$_3$][Cu$_2$I$_3$], $M_r$=749.2; monoclinic, space group $P2_1/c$, $a$=10.856(7), $b$=18.992(5), $c$= 8.630(2) Å, $\beta$=106.74(3)°, $Z$=4, $D_c$=2.92 g

cm$^{-3}$, $\mu$(Mo$K\alpha$)=8.64 mm$^{-1}$. The compound crystallizes as lustrous black prisms, elongated along **c**.

## STRUCTURE DETERMINATION AND REFINEMENT

The positions of the copper and iodine atoms were obtained by direct methods (MULTAN 80)[15] and those of the sulfur and carbon atoms from a subsequent electron density map.[16] Block-diagonal least-squares refinement[16] of positional and isotropic thermal parameters yielded $R$=0.125 for 65 parameters. Full-matrix least-squares refinement[16] with inclusion of anisotropic thermal parameters terminated at $R$=0.060 [145 parameters; 2932 reflections]; when the 1017 unobserved reflections were included $R$=0.078. The $F_o$ values were weighted[17] according to $w$=(30.0+$F_o$+0.010 $F_o^2$)$^{-1}$. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.[18] No attempt was made to include the hydrogen atoms in the calculations. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1. Structure factors and anisotropic thermal parameters can be obtained from the authors on request.

*Table 1.* Fractional coordinates and equivalent isotropic thermal parameters (Å$^2$) for [S$_2$C$_3$(SCH$_3$)$_3$][Cu$_2$I$_3$]. $B_{eq}$ is defined as $8\pi^2/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. Estimated standard deviations are given in parentheses.

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| I(1) | 0.05337(8) | 0.10575(4) | 0.52974(10) | 3.61(2) |
| I(2) | 0.13980(9) | 0.17727(5) | 1.04512(11) | 4.55(2) |
| I(3) | −0.20647(7) | 0.25798(4) | 0.65803(9) | 3.49(2) |
| Cu(1) | 0.0271(3) | 0.1923(2) | 0.7475(3) | 8.22(7) |
| Cu(2) | −0.0571(2) | 0.2300(1) | 0.4520(2) | 5.25(4) |
| S(1) | −0.1875(3) | 0.0455(2) | 0.7235(4) | 3.47(6) |
| S(2) | −0.2871(3) | 0.0713(2) | 0.4911(4) | 3.39(5) |
| S(3) | −0.5646(3) | 0.1142(2) | 0.3866(4) | 3.27(5) |
| S(4) | −0.5699(3) | 0.0933(2) | 0.7559(4) | 3.65(6) |
| S(5) | −0.2988(3) | 0.0448(2) | 1.0042(4) | 3.71(6) |
| C(1) | −0.4296(10) | 0.0876(5) | 0.5342(13) | 2.7(2) |
| C(2) | −0.4284(10) | 0.0788(5) | 0.6970(13) | 2.6(2) |
| C(3) | −0.3141(10) | 0.0576(5) | 0.8021(13) | 2.8(2) |
| C(4) | −0.5670(17) | 0.1891(9) | 0.7766(22) | 5.6(4) |
| C(5) | −0.1288(13) | 0.0278(9) | 1.0904(16) | 4.7(3) |
| C(6) | −0.5054(14) | 0.1179(8) | 0.2111(16) | 4.4(3) |

*Table 2.* Interatomic distances (Å) and angles (°) within the [Cu$_2$I$_3$]$^-$ chain. Symmetry code: (*i*) $x$, $\frac{1}{2}-y$, $z-\frac{1}{2}$, (*ii*) $x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$.

| | | | |
|---|---|---|---|
| Cu(1)−I(1) | 2.573(3) | Cu(2)−I(3) | 2.781(3) |
| Cu(1)−I(2) | 2.523(3) | Cu(2)−I(3$^i$) | 2.597(2) |
| Cu(1)−I(3) | 2.730(3) | Cu(1)···Cu(2) | 2.551(3) |
| Cu(2)−I(1) | 2.644(2) | Cu(1)···Cu(2$^{ii}$) | 2.657(3) |
| Cu(2)−I(2$^i$) | 2.708(3) | | |
| I(1)−Cu(1)−I(2) | 123.2(1) | I(3)−Cu(2)−I(3$^i$) | 107.0(1) |
| I(1)−Cu(1)−I(3) | 112.0(1) | Cu(2)···Cu(1)···Cu(2$^{ii}$) | 114.5(1) |
| I(2)−Cu(1)−I(3) | 118.6(1) | Cu(1)···Cu(2)···Cu(1$^i$) | 136.6(2) |
| I(1)−Cu(2)−I(2$^i$) | 104.1(1) | Cu(1)−I(1)−Cu(2) | 58.5(1) |
| I(1)−Cu(2)−I(3) | 108.3(1) | Cu(1)−I(2)−Cu(2$^{ii}$) | 60.9(1) |
| I(1)−Cu(2)−I(3$^i$) | 115.9(1) | Cu(1)−I(3)−Cu(2) | 55.1(1) |
| I(2$^i$)−Cu(2)−I(3) | 104.0(1) | Cu(1)−I(3)−Cu(2$^{ii}$) | 59.8(1) |
| I(2$^i$)−Cu(2)−I(3$^i$) | 116.7(1) | Cu(2)−I(3)−Cu(2$^{ii}$) | 109.1(1) |
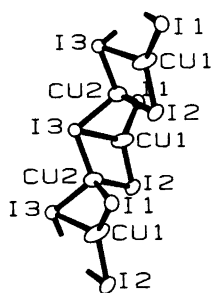


*Fig. 1.* Part of the *catena*-μ-iodo-μ$_3$-iodo-(μ-iodo-dicuprate(I)) anion, showing the atomic numbering.

## DISCUSSION

In [S$_2$C$_3$(SCH$_3$)$_3$][Cu$_2$I$_3$] the anion consists of an infinite I-bridged chain along **c** (Figs. 1−2). Interatomic distances and angles within the chain are given in Table 2. The two crystallographically independent copper atoms have different environments: Cu(1) is coordinated by three iodide ligands in a distorted trigonal planar arrangement, while Cu(2) is surrounded by an approximately tetrahedral arrangement of ligands (Table 2). The distances between Cu(1) and the two next nearest neighbouring atoms, *viz.* Cu(1)···I(2: $x,\frac{1}{2}-y,z-\frac{1}{2}$) = 3.452(3)   Å   and Cu(1)···S(1)=3.600(4) Å, preclude consideration of Cu(1) as other than trigonal planar coordinated. Two of the iodine atoms, I(1) and I(2), each bridge two copper atoms whereas I(3) bridges three copper atoms, *viz.* Cu(1), Cu(2) and Cu(2: $x,\frac{1}{2}-y,\frac{1}{2}+z$). The chain thus differs from those found for the tetraethylammonium,[8] the dimethyl(3-dimethylamino-2-aza-2-propenyl-idene)ammonium[8] and the 2,4,6-triphenylthio-pyrylium[9] compounds, and would appear to be the first [Cu$_2$I$_3$]$^-$ chain reported to contain both three- and four-coordinated copper(I).
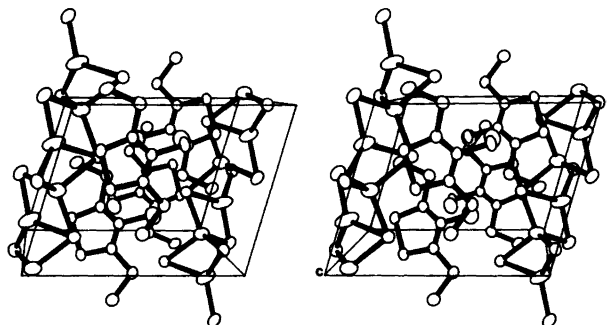


*Fig. 2.* Stereoscopic view[20] of the unit cell.

The chains in the three compounds mentioned above[8,9] contain tetrahedrally coordinated copper(I) only, each Cu(I)−I tetrahedron having a common face with one of its neighbours and a common edge with the other.

Apart from Cu(1)−I(3), the Cu(I)−I distances (Table 2) lie within the ranges of distances reported for trigonal and tetrahedral coordination, see e.g. Refs. 2,6,7,8,9,11. Cu(1) has two shorter bonds [2.523(3) and 2.573(3) Å] to the iodide ligands which bridge two copper atoms and a longer, 2.730(3) Å, to the $\mu_3$-iodide, I(3). There is, however, no such correlation for the Cu(2)−I bond lengths (Table 2). The rather large thermal parameters for the copper atoms suggest that there may be some disorder associated with these sites. There were, however, no obvious signs of partial occupancy. The angles subtended at I(1), I(2) and I(3) by the copper atoms agree closely with those reported for $[C_{23}H_{17}S][Cu_2I_3]$.[9] In the latter compound, each $\mu_3$-bridging iodine atom lies almost in the plane through the copper atoms to which it is bonded; this is not the case in $[S_2C_3(SCH_3)_3][Cu_2I_3]$.

The two Cu···Cu contacts, 2.551(3) and 2.657(3) Å, alternate forming a zig-zag pattern along c (Figs. 1–2). Short Cu···Cu distances have been observed both in I-bridged chains[8,9] and in I-bridged clusters.[2,11] It would seem that Cu···Cu is determined largely by the stereochemical demands of the ligands and that short Cu···Cu contacts in themselves need not necessarily presuppose metal–metal bonds.[19] On the other hand, the colour and metallic lustre of the crystals and the displacement [0.376(3) Å] of Cu(1) from the plane through the three iodide ligands in a direction towards the neighbouring Cu(2) atoms could indicate attractive Cu(I)−Cu(I) interactions along the length of the chain. A preliminary SEM study suggests that $[S_2C_3(SCH_3)_3][Cu_2I_3]$ is not an insulator.

Despite structurally similar $[Cu_2I_3]^-$ chains in the three compounds, the tetraethylammonium and dimethyl(3-dimethylamino-2-aza-2-propenylidene)ammonium salts are white[8] whereas $[C_{23}H_{17}S][Cu_2I_3]$ is black.[9] Batsanov et al. attribute the difference in colour between the 2,4,6-triphenylthiopyrylium and 2,4,6-triphenylpyrylium salts (both black) and the N-methylpyridinium salt (light yellow) to the presence of short Cu···Cu distances realized largely through differences in the degree of delocalization of the

positive charge on the cation.[9] Only the structure of the 2,4,6-triphenylthiopyrylium compound was reported; it would appear that the N-methylpyridinium salt contains double chains of edge-sharing Cu(I)−I tetrahedra.[21] The Cu···Cu contacts in the three compounds known to contain chains of edge- and face-sharing Cu(I)−I tetrahedra[8,9] are comparable with those in $[S_2C_3(SCH_3)_3][Cu_2I_3]$, despite differences in colour, i.e. 2.479(2) and 2.634(2) Å in the 2,4,6-triphenylthiopyrylium (black),[9] 2.507(1) and 2.679(1) Å in the tetraethylammonium (white)[8] and 2.491(2) and 2.699(1) Å in the dimethyl(3-dimethylamino-2-aza-2-propenylidene)ammonium (white)[8] salts.

Apart from C(4), the cation is planar, to within $4\sigma$ for S(4) and S(5) and $3\sigma$ for the remaining atoms. C(4) is situated 1.76(2) Å from the least-squares molecular plane. The geometry of the cation (Fig. 3, Table 3) is consistent with that reported for 3,4,5-tris(methylthio)-1,2-dithiolium iodide.[12] The closest contacts between S(1), S(2) and iodide are S(1)···I(1)=3.669(3) Å and S(2)···I(1)=3.672(4) Å, which are somewhat longer than those observed in the iodide,[12] viz. 3.442(6) and 3.394(6) Å. The cations pack with their molecular planes approximately perpendicular to b and the dithio groups orientated towards the chains (Fig. 2). There are, however, no exceptionally short Cu···S contacts; the shortest such distances are Cu(1)···S(1)=3.600(4) Å and Cu(2)···S(2)=3.988(4) Å.

In contrast to methyltriphenylphosphonium,[11] the essentially planar 3,4,5-tris(methylthio)-1,2-dithiolium appears to promote −Cu−I−Cu− catenation. This is in agreement with the hypothesis that a bulky cation with a low, well-screened charge will tend to suppress polymerization, leading to the formation of discrete halocuprate(I) anions. That different types of chains consisting of Cu(I)−I tetrahedra can be obtained
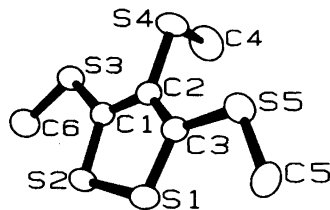


Fig. 3. The 3,4,5-tris(methylthio)-1,2-dithiolium cation showing the atomic numbering.

*Table 3.* Bond distances (Å) and angles (°) within the 3,4,5-tris(methylthio)-1,2-dithiolium cation.

| | | | |
|---|---|---|---|
| S(1)−S(2) | 2.045(4) | S(3)−C(6) | 1.809(14) |
| S(2)−C(1) | 1.720(11) | C(2)−S(4) | 1.772(11) |
| C(1)−C(2) | 1.412(15) | S(4)−C(4) | 1.828(17) |
| C(2)−C(3) | 1.370(15) | C(3)−S(5) | 1.721(11) |
| C(3)−S(1) | 1.713(11) | S(5)−C(5) | 1.810(14) |
| C(1)−S(3) | 1.718(11) | | |
| C(3)−S(1)−S(2) | 95.7(4) | C(1)−S(3)−C(6) | 101.5(6) |
| S(1)−S(2)−C(1) | 94.9(4) | C(1)−C(2)−S(4) | 120.5(8) |
| S(2)−C(1)−C(2) | 116.3(8) | S(4)−C(2)−C(3) | 123.4(8) |
| C(1)−C(2)−C(3) | 116.0(10) | C(2)−S(4)−C(4) | 101.0(7) |
| C(2)−C(3)−S(1) | 117.1(8) | C(2)−C(3)−S(5) | 121.1(8) |
| S(2)−C(1)−S(3) | 121.4(6) | S(1)−C(3)−S(5) | 121.9(6) |
| S(3)−C(1)−C(2) | 122.2(8) | C(3)−S(5)−C(5) | 103.3(6) |

with cations differing in size, form and charge distribution has been noted previously.[21] Whether or not the versatility of copper(I) with respect to three- and fourfold coordination in [Cu$_2$I$_3$]$^-$ chains (*cf.* Refs. 8,9, this work) can also be attributed, at least in part, to the properties of the cation is as yet uncertain.

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