

Crystal Structure of Trimethylsulfonium *catena- μ_4 -Iodo-di- μ -iodo-dicuprate(I)*, $[\text{S}(\text{CH}_3)_3][\text{Cu}_2\text{I}_3]$

MILJA ASPLUND,^a SUSAN JAGNER^a and MARTIN NILSSON^b

^a Department of Inorganic Chemistry and ^b Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden

Iodocuprates(I) crystallizing with organic cations have been encountered as discrete anions containing three- or four-coordinated copper(I), *viz.* $[\text{CuI}_3]^{2-}$,¹ $[\text{Cu}_2\text{I}_4]^{2-}$,²⁻⁵ $[\text{Cu}_4\text{I}_6]^{2-}$,⁶ $[\text{Cu}_5\text{I}_7]^{2-}$,⁷ and $[\text{Cu}_6\text{I}_{11}]^{5-}$,⁸ or as infinite chains, composed of shared Cu(I)–I tetrahedra, of various geometrical configurations and stoichiometries: $[\text{CuI}_2]^-$,⁹ $[\text{Cu}_2\text{I}_3]^-$,¹⁰⁻¹⁴ and $[\text{Cu}_3\text{I}_4]^-$.¹² Since I–Cu(I)–I catenation appears to be promoted by smaller cations, trimethylsulfonium might be expected to crystallize with an infinite iodocuprate(I) chain rather than with a discrete iodocuprate(I) anion. With tetraethylammonium and tetramethylammonium as cations, infinite single $[\text{Cu}_2\text{I}_3]^-$ chains composed of edge- and face-sharing Cu(I)–I tetrahedra have been obtained.^{10,11} *N*-Methylpyridinium, which presumably has a less well-screened positive charge than tetraethylammonium or tetramethylammonium, crystallizes with a double $[\text{Cu}_2\text{I}_3]^-$ chain¹² and with a single $[\text{CuI}_2]^-$ chain,⁹ both composed of edge-sharing Cu(I)–I tetrahedra. The positive charge of the trimethylsulfonium cation would be expected to be less well-screened than that of *e.g.* tetramethylammonium and more localised than that of *e.g.* *N*-methylpyridinium. In an investigation of the trimethylsulfonium–iodocuprate(I) system, we have obtained crystals of $[\text{S}(\text{CH}_3)_3][\text{Cu}_2\text{I}_3]$ and undertaken a structural determination.

Trimethylsulfonium iodide was prepared from methyl iodide and dimethyl sulfide (molar ratio 1:1) and recrystallized from ethanol.^{15,16} $\text{S}(\text{CH}_3)_3\text{I}$ decomposed at *ca.* 209–211 °C. Trimethylsulfonium *catena- μ_4 -iodo-di- μ -iodo-dicuprate(I)* was prepared by dissolving trimethylsulfonium iodide and copper(I) iodide (molar ratio: 1:1) in acetonitrile. Colourless needles were deposited from the concentrated solution after a few days. $[\text{S}(\text{CH}_3)_3][\text{Cu}_2\text{I}_3]$ decomposed under vigorous gas evolution at *ca.* 215–220 °C.

Crystals of $[\text{S}(\text{CH}_3)_3][\text{Cu}_2\text{I}_3]$, $M_r=585.0$, are orthorhombic, space group *Pnma* (No. 62),^{17a} with $a=18.021(18)$, $b=6.526(4)$, $c=30.024(27)$ Å, $Z=12$, $D_c=3.30$ g cm⁻³ and $\mu(\text{MoK}\alpha)=11.80$ mm⁻¹. Diffracted intensities from a crystal, 0.18×0.33×0.13 mm, were measured at approximately 290 K for $2\theta\leq 50^\circ$ with a Syntex $P2_1$ diffractometer, using graphite-monochromated MoK α radiation and the ω scan mode with a variable 2θ scan rate of 2.5–29 °min⁻¹. A 19-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method¹⁸ was used to calculate the intensities.¹⁹ Of the 3419 independent reflections measured, 2006 had $I>3.0\sigma(I)$ and were considered to be observed. Correction was made for Lorentz and polarisation effects; an empirical correction²⁰ for the effects of absorption was made after solution of the structure. The unit-cell dimensions were determined from diffractometer setting angles for 15 reflections.

The positions of the copper and iodine atoms were determined by direct methods (MITHRIL)²¹ and those of the sulfur and carbon atoms from successive electron-density maps.²² All three crystallographically independent cations exhibit severe orientational disorder. The cation comprised of S(1), C(1), C(2) and C(3) has a disordered orientation with respect to the mirror plane in which the carbon atoms are situated; S(1) was therefore assigned an occupancy of 0.5 in the general position $8d$. In the second cation [S(2), C(4), C(5) and C(6)], C(6) was assigned an occupancy of 0.5 in $8d$ while the remaining atoms were constrained to lie in the mirror plane, attempts to resolve *e.g.* C(5) into partially occupied sites being unsuccessful. The third cation was located as two halves with C(7) as a common ordered atom. It was not, however, possible to resolve the positions of the partially occupied sites [S(3a), C(8a), S(3b), C(8b)] precisely. Full-matrix least-squares refinement²² of positional and isotropic thermal parameters gave $R=0.12$; after an empirical correction²⁰ for the effects of absorption $R=0.11$. Inclusion of anisotropic thermal parameters for the copper and iodine atoms yielded a final $R=0.068$ (125 parameters; 2006 reflections). Atomic

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (\AA^2) for the non-hydrogen atoms in $[\text{S}(\text{CH}_3)_3][\text{Cu}_2\text{I}_3]$. B_{eq} is defined as $8\pi^2/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$

For the sulfur and carbon atoms isotropic thermal parameters, B (\AA^2), where the temperature factor is $\exp(-B(\sin^2\theta)/\lambda^2)$, are given. An asterisk denotes an atom in $8d$ or $4c$ with occupancy 0.5 and 0.25, respectively. Estimated standard deviations are given in parentheses.

| Atom | x | y | z | B_{eq} or B |
|--------|------------|-----------|------------|------------------------|
| I(1) | 0.0937(1) | -0.2500 | 0.06288(6) | 3.94(5) |
| I(2) | 0.1720(1) | 0.2500 | 0.15457(8) | 4.76(7) |
| I(3) | -0.0498(1) | 0.2500 | 0.10264(6) | 3.60(5) |
| I(4) | 0.0339(1) | -0.2500 | 0.19796(6) | 3.75(5) |
| I(5) | -0.1849(1) | -0.2500 | 0.15349(7) | 4.06(6) |
| I(6) | -0.1076(2) | 0.2500 | 0.24212(7) | 5.93(8) |
| Cu(1) | 0.0655(2) | 0.0071(5) | 0.12825(9) | 5.20(9) |
| Cu(2) | -0.0790(2) | 0.0130(5) | 0.17462(9) | 5.11(9) |
| I(7) | 0.5926(1) | -0.2500 | 0.09027(7) | 4.26(6) |
| I(8) | 0.4240(1) | 0.2500 | 0.09829(8) | 4.92(7) |
| I(9) | 0.4104(1) | -0.2500 | 0.00281(6) | 3.67(5) |
| Cu(3) | 0.5031(2) | 0.0043(5) | 0.04893(9) | 5.18(9) |
| S(1)* | 0.3280(5) | -0.123(2) | 0.1714(3) | 3.1(2) |
| C(1) | 0.267(2) | -0.250 | 0.210(1) | 5.3(8) |
| C(2) | 0.295(2) | -0.250 | 0.121(1) | 3.3(5) |
| C(3) | 0.413(2) | -0.250 | 0.179(1) | 4.8(7) |
| S(2) | 0.2932(8) | -0.2500 | 0.4731(5) | 8.0(3) |
| C(4) | 0.399(2) | -0.250 | 0.484(1) | 5.6(8) |
| C(5) | 0.274(4) | -0.250 | 0.526(2) | 13(2) |
| C(6)* | 0.279(3) | -0.001(9) | 0.471(2) | 6(1) |
| S(3a)* | 0.174(2) | 0.250 | 0.302(1) | 9.0(7) |
| C(8a)* | 0.092(4) | 0.069(13) | 0.304(2) | 9(2) |
| S(3b)* | 0.113(2) | 0.250 | 0.325(1) | 9.9(8) |
| C(8b)* | 0.156(5) | 0.063(13) | 0.292(2) | 9(2) |
| C(7) | 0.188(2) | 0.250 | 0.364(1) | 6.4(9) |

scattering factors were taken from the *International Tables for X-Ray Crystallography*^{17b} and the F_o values were weighted according to $w = [\sigma^2(F_o) + 0.0005F_o^2]^{-1}$. A final difference map²² showed a maximum residual electron density of 2.2 e \AA^{-3} in the vicinity of I(8). Atomic coordinates, equivalent isotropic thermal parameters for the copper and iodine atoms and isotropic thermal parameters for the remaining atoms are listed in Table 1. Structure factors, anisotropic thermal parameters, distances and angles within the cations and angles within the anions may be obtained from the authors.

Discussion. In trimethylsulfonium *catena*- μ_4 -iodo-di- μ -iodo-dicuprate(I), the anion is an infinite double chain of edge-sharing Cu(I)-I tetrahedra (Fig. 1) similar to the anions in the cesium²⁴ and *N*-methylpyridinium¹² compounds. As in these compounds,^{12,24} there are two sets of Cu(I)-I distances (Table 2), the shorter involving the μ_2 -iodide ligands and the longer the μ_4 . Contrary to the chain comprised of Cu(3), I(7), I(8) and I(9), that comprised of Cu(1), Cu(2) and I(1)-I(6) lacks a centre of symmetry. The two crystallographically independent anions are, however, essentially similar (Table 2). The Cu...Cu separations (Table 2) are very similar to those in the cesium²⁴ and the *N*-methylpyridinium¹² compounds, the Cu...Cu distances perpendicular to the length of the chain being slightly shorter than those along the length of the chain.

Both $[\text{Cu}_2\text{I}_3]^-$ chains extend parallel to the b axis, the magnitude of this axis, $6.526(4) \text{ \AA}$, being closely similar to the corresponding distances in the *N*-methylpyridinium¹² and

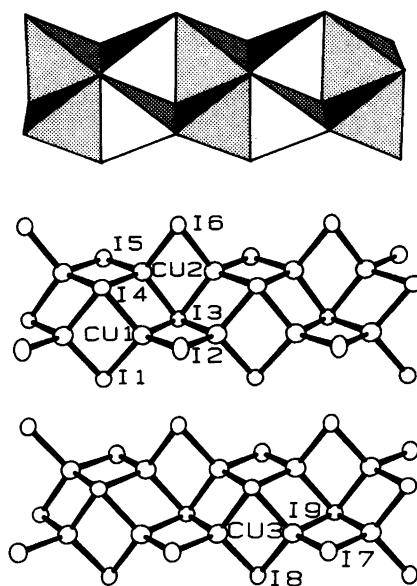


Fig. 1. Part of the infinite double $[\text{Cu}_2\text{I}_3]^-$ chain showing the edge-sharing of tetrahedra and the atomic numbering of the two crystallographically independent anions. The thermal ellipsoids enclose 50% probability.²³

cesium²⁴ compounds, viz. 6.288(2) and 6.073(2) Å, respectively. *N*-Methylpyridinium triiododicuprate(I) also crystallizes in space group *Pnma*, but with $Z=4$. The *a* axial length in this compound is practically identical to that in $[\text{S}(\text{CH}_3)_3][\text{Cu}_2\text{I}_3]$, i.e. 18.180(4) Å,¹² as compared with 18.021(18) Å, and the packing of the chains involving Cu(1), Cu(2) and I(1)–I(6) in $[\text{S}(\text{CH}_3)_3][\text{Cu}_2\text{I}_3]$ resembles the packing of the anions in $[\text{C}_6\text{H}_8\text{N}][\text{Cu}_2\text{I}_3]$.¹² It would, however, appear that $[\text{S}(\text{CH}_3)_3][\text{Cu}_2\text{I}_3]$ is slightly more compact than $[\text{C}_6\text{H}_8\text{N}][\text{Cu}_2\text{I}_3]$ but both structures are much less compact than CsCu_2I_3 .^{12,24}

The structure of $[\text{S}(\text{CH}_3)_3][\text{Cu}_2\text{I}_3]$ is illustrated in Fig. 2. S(1) exhibits three contacts of equal magnitude to iodide ligands situated in $y=\frac{1}{4}$, viz. $\text{S}(1)\cdots\text{I}(2)=3.75(1)$ Å, $\text{S}(1)\cdots\text{I}(6^i)=3.74(1)$ Å and $\text{S}(1)\cdots\text{I}(8)=3.71(1)$ Å. Identical contacts are provided by the alternative orientation of the cation, i.e. S(1) in $x, \frac{1}{2}-y, z$. S(2) has one contact < 4 Å to an iodide ligand: $\text{S}(2)\cdots\text{I}(5^i)=3.82(1)$ Å. For the third cation there are no S...I contacts shorter than 4 Å, which might account for the severe lack of orientational order associated with this cation. The shortest C...I distances are $\text{C}(4)\cdots\text{I}(1^i)=3.79(4)$, $\text{C}(8a)\cdots\text{I}(7^{ii})=3.80(7)$, $\text{C}(8b)\cdots\text{I}(5^i)=3.88(5)$ and $\text{C}(7)\cdots\text{I}(7^{ii})$ and $\text{C}(7)\cdots\text{I}(7^{iii})$ both 3.94(2) Å. [Symmetry code: (i): $\frac{1}{2}+x, y, \frac{1}{2}-z$; (ii): $x-\frac{1}{2}, y, \frac{1}{2}-z$; (iii): $x-\frac{1}{2}, 1+y, \frac{1}{2}-z$]. There are no Cu...S or Cu...C contacts significantly less than 4.5 Å. In $[\text{S}_2\text{C}_3(\text{SCH}_3)_3][\text{Cu}_2\text{I}_3]$,¹⁴ the shortest Cu...S distance is 3.600(4) Å, while in the cation radical salt of tetrathiotetracene with dibromocuprate(I)

Table 2. Interatomic distances (Å) within the $[\text{Cu}_2\text{I}_3]^-$ anions. Estimated standard deviations are given in parentheses. Symmetry code: (i): $1-x, -y, -z$; (ii): $x, -y-\frac{1}{2}, z$; (iii): $x, \frac{1}{2}-y, z$.

| | | | |
|------------|----------|-----------------------------|----------|
| Cu(1)–I(1) | 2.631(4) | Cu(3)–I(9) | 2.731(4) |
| Cu(1)–I(2) | 2.612(4) | Cu(3)–I(9 ⁱ) | 2.722(4) |
| Cu(1)–I(3) | 2.724(4) | Cu(1)⋯Cu(1 ⁱⁱ) | 3.356(7) |
| Cu(1)–I(4) | 2.742(4) | Cu(1)⋯Cu(1 ⁱⁱⁱ) | 3.170(7) |
| Cu(2)–I(3) | 2.709(4) | Cu(1)⋯Cu(2) | 2.954(5) |
| Cu(2)–I(4) | 2.753(4) | Cu(2)⋯Cu(2 ⁱⁱ) | 3.432(7) |
| Cu(2)–I(5) | 2.643(4) | Cu(2)⋯Cu(2 ⁱⁱⁱ) | 3.093(7) |
| Cu(2)–I(6) | 2.601(4) | Cu(3)⋯Cu(3 ⁱ) | 2.941(6) |
| Cu(3)–I(7) | 2.625(4) | Cu(3)⋯Cu(3 ⁱⁱ) | 3.319(7) |
| Cu(3)–I(8) | 2.608(4) | Cu(3)⋯Cu(3 ⁱⁱⁱ) | 3.207(7) |

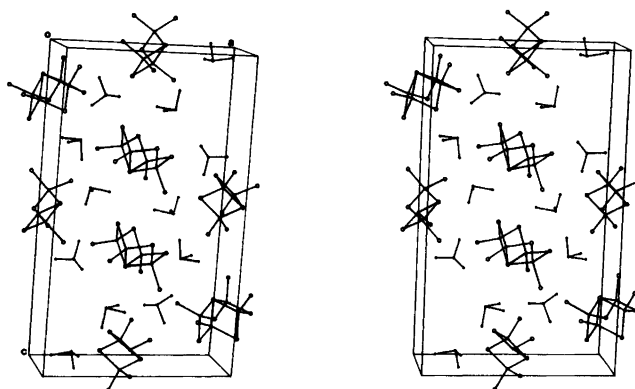


Fig. 2. Stereoscopic view²³ of the structure of $[\text{S}(\text{CH}_3)_3][\text{Cu}_2\text{I}_3]$. The iodine atoms are depicted as spheres of radius 0.10 Å and all other atoms as spheres of radius 0.05 Å. For clarity only one orientation of each cation is shown.

there are Cu–S contacts of 2.684 and 3.062 Å to adjacent cation radicals such that the configuration of ligands about copper(I) is approximately trigonal bipyramidal.²⁵

Unlike tetraethylammonium¹⁰ and tetramethylammonium,¹¹ trimethylsulfonium would appear to promote the formation of double $[\text{Cu}_2\text{I}_3]^-$ chains, and, in this respect, the cation shows similarity to both *N*-methylpyridinium and cesium. This might indicate that the formation of double *contra* single $[\text{Cu}_2\text{I}_3]^-$ chains is favoured by the presence of relatively small cations with exposed unipositive charge.

Acknowledgement. Financial support from the Swedish Natural Science Research Council (NFR) is gratefully acknowledged.

1. Bowmaker, G.A., Clark, G.R., Rogers, D.A., Camus, A. and Marsich, N. *J. Chem. Soc. Dalton Trans.* (1984) 37.
2. Asplund, M., Jagner, S. and Nilsson, M. *Acta Chem. Scand. A* 36 (1982) 751.
3. Asplund, M. and Jagner, S. *Acta Chem. Scand. A* 38 (1984) 297.
4. Asplund, M. and Jagner, S. *Acta Chem. Scand. A* 38 (1984) 411.
5. Mahdjour-Hassan-Abadi, F. and Hartl, H. *In preparation.*
6. Bowmaker, G.A., Clark, G.R. and Yuen, D.K.P. *J. Chem. Soc. Dalton Trans.* (1976) 2329.
7. Hartl, H. and Mahdjour-Hassan-Abadi, F. *Angew. Chem.* 96 (1984) 359.
8. Mahdjour-Hassan-Abadi, F., Hartl, H. and Fuchs, J. *Angew. Chem.* 96 (1984) 497.
9. Hartl, H., Brüdgam, I. and Mahdjour-Hassan-Abadi, F. *Z. Naturforsch. Teil. B* 38 (1983) 57.
10. Hartl, H. and Mahdjour-Hassan-Abadi, F. *Angew. Chem.* 93 (1981) 804.
11. Andersson, S. and Jagner, S. *Acta Chem. Scand. A* 39 (1985) 181.
12. Hartl, H. and Mahdjour-Hassan-Abadi, F. *Z. Naturforsch. Teil B* 39 (1984) 149.
13. Batsanov, A.S., Struchkov, Yu.T., Ukhin, L.Yu. and Dolgoplova, N.A. *Inorg. Chim. Acta* 63 (1982) 17.
14. Asplund, M. and Jagner, S. *Acta Chem. Scand. A* 38 (1984) 129.
15. Emeléus, H.J. and Heal, H.G. *J. Chem. Soc.* (1946) 1126.
16. Corey, E.J. and Chaykovsky, M. *J. Am. Chem. Soc.* 87 (1965) 1353.
17. a. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1952, Vol. 1, p. 151; b. *Ibid.* 1974, Vol. 4, p. 72.
18. Lehmann, M.S. and Larsen, F.K. *Acta Crystallogr. A* 30 (1974) 580.

19. Lindqvist, O. and Ljungström, E. *J. Appl. Crystallogr.* 12 (1979) 134.
20. Walker, N. and Stuart, D. *Acta Crystallogr. A* 39 (1983) 158.
21. Gilmore, C.J. *J. Appl. Crystallogr.* 17 (1984) 42.
22. Lindgren, O. *An Integrated Set of Crystallographic Programs*, In *On the Oxygen Coordination of Cerium in Some Sulfates and Chromates*, Thesis, Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, Göteborg 1977.
23. Johnson, C.K. *ORTEP*: Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge 1965.
24. Jouini, N., Guen, L. and Tournoux, M. *Rev. Chim. Miner.* 17 (1980) 486.
25. Shibaeva, R.P. and Kaminskii, V.F. *Kristallografiya* 26 (1981) 332.

Received February 15, 1985.