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Crystal Structure of Tetramethylammonium *catena*-Di-μ_3-iodo-[μ-iodo-dicuprate(I)], $[N(CH_3)_4][Cu_2I_3]$

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The crystal structure of the title compound has been determined from single-crystal X-ray diffractometer data collected at 170 K. $[N(CH_3)_4][Cu_2I_3]$ crystallizes in space group $P\bar{1}$ with a=9.443(3), b=24.993(10), c=8.105(5) Å, α=94.09(4), β=94.19(4), γ=100.12(3)°, at 170 K, and Z=6. Full-matrix least-squares refinement of 271 structural parameters gave R=0.034 for 5376 observed independent reflections. In $[N(CH_3)_4][Cu_2I_3]$ there are two crystallographically independent $[Cu_2I_3]^-$ chains, both composed of edge- and face-sharing Cu(I)–I tetrahedra. Cu(I)–I distances range from 2.517(3)–3.030(2) Å and Cu···Cu distances from 2.452(3)–2.648(3) Å.

Iodocuprates(I) crystallizing with tetraalkylammonium ions have been encountered as discrete entities or as infinite chains containing three- and/or four-coordinated copper(I): Bis(tetrabutylammonium) di-μ-iodo-diiododicuprate(I) contains a centrosymmetric $[Cu_2I_4]^{2-}$ dimer in which copper(I) exhibits trigonal-planar coordination geometry.[1] Tetrapropylammonium gives rise to a planar $[Cu_2I_4]^{2-}$ dimer,[2] to a $[Cu_3I_4]^-$ chain containing both three- and four-coordinated copper(I),[3] and to a discrete $[Cu_5I_7]^{2-}$ ion containing four-coordinated copper(I).[4] With tetraethylammonium a $[Cu_2I_3]^-$ chain[5] and a discrete $[Cu_6I_{11}]^{5-}$ ion,[6] both composed of shared Cu(I)–I tetrahedra, have been isolated, as well as a planar $[Cu_2I_4]^{2-}$ dimer containing three-coordinated copper(I).[6] In an investigation of the tetramethylammonium-iodocuprate(I) system, single crystals of $[N(CH_3)_4][Cu_2I_3]$ have been obtained and a structural determination undertaken.

EXPERIMENTAL

Tetramethylammonium *catena*-di-μ_3-iodo-[μ-iodo-dicuprate(I)] was prepared by dissolving copper (I) iodide and tetramethylammonium iodide (molar ratio 1:1) in acetonitrile. Colourless truncated octahedra were deposited from the concentrated solution after a few days. Crystals of $[N(CH_3)_4][Cu_2I_3]$, M_r=581.9, are triclinic, space group $P\bar{1}$, with a=9.443(3), b=24.993(10), c=8.105(5) Å, α=94.09(4), β=94.19(4), γ=100.12(3)° at approximately 170 K, Z=6, D_c=3.10 g cm^{-3}, μ(Mo$K\alpha$)=10.99 mm^{-1}. Diffracted intensities from a crystal, 0.35×0.33×0.30 mm, were measured at approximately 170 K for $2\theta < 55°$ with a Syntex $P2_1$ diffractometer, using graphite-monochromated Mo$K\alpha$ radiation and the ω–2θ scan mode with a variable 2θ scan rate of 2.5–20° min^{-1}. The temperature was maintained at approximately 170 K by a Syntex LT1 low-temperature device. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis

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Table 1. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in $[N(CH_3)_4][Cu_2I_3]$. 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}
Cu(1)	0.8810(2)	0.16973(7)	−0.1249(2)	3.32(4)
Cu(2)	0.6813(2)	0.15727(6)	0.0874(2)	3.14(4)
Cu(3)	0.7837(2)	0.20549(7)	0.3596(2)	3.16(4)
Cu(4)	0.8016(2)	0.13539(6)	0.5847(2)	3.16(4)
I(1)	1.04646(7)	0.10921(3)	−0.27861(8)	2.06(2)
I(2)	0.85114(7)	0.24716(2)	−0.34469(7)	1.85(2)
I(3)	0.99569(7)	0.21089(3)	0.15756(7)	1.88(2)
I(4)	0.56983(7)	0.23960(3)	0.19715(8)	2.07(2)
I(5)	0.69826(7)	0.08416(3)	0.31046(7)	1.87(2)
I(6)	0.60248(7)	0.10540(3)	−0.19202(7)	1.91(2)
Cu(5)	0.5373(2)	0.53573(7)	0.1292(2)	3.72(5)
Cu(6)	0.5953(2)	0.49673(7)	0.3895(2)	4.13(5)
I(7)	0.51812(7)	0.41911(3)	0.13060(8)	2.12(2)
I(8)	0.79550(7)	0.57288(3)	0.28884(8)	2.20(2)
I(9)	0.33552(7)	0.54376(3)	0.34734(8)	2.21(2)
N(1)	0.3619(9)	0.2677(4)	0.6826(10)	2.2(2)
C(11)	0.2565(12)	0.2605(5)	0.5306(13)	2.8(3)
C(12)	0.2838(12)	0.2760(5)	0.8361(12)	2.6(3)
C(13)	0.4245(12)	0.2171(4)	0.6921(14)	2.6(3)
C(14)	0.4774(12)	0.3155(4)	0.6733(17)	3.4(4)
N(2)	0.2210(9)	0.0590(3)	0.2346(11)	2.2(2)
C(21)	0.0599(11)	0.0548(5)	0.2213(14)	2.7(3)
C(22)	0.2929(13)	0.1157(5)	0.2502(20)	4.3(4)
C(23)	0.2673(14)	0.0292(6)	0.0825(14)	3.7(4)
C(24)	0.2675(12)	0.0304(5)	0.3870(14)	2.8(3)
N(3)	−0.0315(9)	0.3886(3)	0.1779(10)	2.1(2)
C(31)	−0.0362(16)	0.4481(5)	0.1697(23)	5.5(5)
C(32)	−0.1117(12)	0.3566(5)	0.0246(13)	2.8(3)
C(33)	0.1212(11)	0.3796(5)	0.1933(14)	3.0(3)
C(34)	−0.1030(13)	0.3683(6)	0.3268(13)	3.7(4)

method[7] was used to calculate the intensities.[8] Of the 6089 independent reflections measured, 5376 had $I>3.0\sigma(I)$ and were used in subsequent calculations. Intensities were corrected for Lorentz and polarisation effects; an empirical correction[9] was made for the effects of absorption after solution of the structure. The unit-cell parameters were determined at approximately 170 K from diffractometer setting angles for 15 reflections.

STRUCTURE DETERMINATION AND REFINEMENT

The positions of the copper and iodine atoms were determined by direct methods (MULTAN 80).[10] The tetramethylammonium ions were located from the subsequent electron density map.[11] Full-matrix least-squares refinement[11] of positional and isotropic thermal parameters gave $R=0.073$; after an empirical correction[9] for the effects of absorption $R=0.061$. Inclusion of anisotropic thermal parameters for all atoms yielded a final $R=0.034$ (271 parameters; 5376 reflections). Comparable refinement based on the data uncorrected for absorption effects gave $R=0.038$. No attempt was made to include the hydrogen atoms in the calculations. Atomic scattering factors were taken from the

Table 2. Interatomic distances (Å) and angles (°) within the $[Cu_2I_3]^-$ chains in $[N(CH_3)_4][Cu_2I_3]$. Estimated standard deviations are given in parentheses. Symmetry code: (*i*):$x,y,1+z$; (*ii*):$1-x,\ 1-y,-z$; (*iii*):$1-x,1-y,1-z$, (*iv*):$x,y,z-1$.

	Cu(1)–I(1)	2.670(2)		Cu(4)–I(1^i)	2.695(2)
	Cu(1)–I(2)	2.758(2)		Cu(4)–I(2^i)	2.761(2)
	Cu(1)–I(3)	2.527(2)		Cu(4)–I(5)	2.524(2)
	Cu(1)–I(6)	2.824(2)		Cu(4)–I(6^i)	2.750(2)
	Cu(2)–I(3)	3.030(2)		Cu(5)–I(7)	2.889(2)
	Cu(2)–I(4)	2.602(2)		Cu(5)–I(7^{ii})	2.523(2)
	Cu(2)–I(5)	2.677(2)		Cu(5)–I(8)	2.656(2)
	Cu(2)–I(6)	2.521(2)		Cu(5)–I(9)	2.715(2)
	Cu(3)–I(2^i)	2.534(2)		Cu(6)–I(7)	2.720(2)
	Cu(3)–I(3)	2.669(2)		Cu(6)–I(8)	2.654(2)
	Cu(3)–I(4)	2.630(2)		Cu(6)–I(9)	2.910(2)
	Cu(3)–I(5)	2.988(2)		Cu(6)–I(9^{iii})	2.517(2)
	Cu(1)···Cu(2)	2.637(2)		Cu(5)···Cu(5^{ii})	2.623(3)
	Cu(1)···Cu(4)	2.462(2)		Cu(5)···Cu(6)	2.452(3)
	Cu(2)···Cu(3)	2.481(2)		Cu(6)···Cu(6^{iii})	2.648(3)
	Cu(3)···Cu(4)	2.635(2)			
I(1)–	Cu(1)–I(2)	102.54(6)	I(1^i)–	Cu(4)–I(2^i)	101.79(6)
I(1)–	Cu(1)–I(3)	112.06(7)	I(1^i)–	Cu(4)–I(5)	116.36(7)
I(1)–	Cu(1)–I(6)	102.53(7)	I(1^i)–	Cu(4)–I(6^i)	103.85(6)
I(2)–	Cu(1)–I(3)	112.86(7)	I(2^i)–	Cu(4)–I(5)	126.13(7)
I(2)–	Cu(1)–I(6)	97.90(6)	I(2^i)–	Cu(4)–I(6^i)	99.61(6)
I(3)–	Cu(1)–I(6)	125.87(7)	I(5)–	Cu(4)–I(6^i)	105.97(7)
I(3)–	Cu(2)–I(4)	97.32(6)	I(7)–	Cu(5)–I(7^{ii})	122.50(7)
I(3)–	Cu(2)–I(5)	93.72(6)	I(7)–	Cu(5)–I(8)	101.81(7)
I(3)–	Cu(2)–I(6)	118.06(7)	I(7)–	Cu(5)–I(9)	95.83(6)
I(4)–	Cu(2)–I(5)	113.13(6)	I(7^{ii})–	Cu(5)–I(8)	115.56(7)
I(4)–	Cu(2)–I(6)	123.07(7)	I(7^{ii})–	Cu(5)–I(9)	110.87(7)
I(5)–	Cu(2)–I(6)	107.69(7)	I(8)–	Cu(5)–I(9)	107.91(7)
I(2^i)–	Cu(3)–I(3)	116.96(7)	I(7)–	Cu(6)–I(8)	106.52(7)
I(2^i)–	Cu(3)–I(4)	115.91(7)	I(7)–	Cu(6)–I(9)	95.27(6)
I(2^i)–	Cu(3)–I(5)	116.96(7)	I(7)–	Cu(6)–I(9^{iii})	111.76(8)
I(3)–	Cu(3)–I(4)	106.22(6)	I(8)–	Cu(6)–I(9)	102.53(7)
I(3)–	Cu(3)–I(5)	94.86(6)	I(8)–	Cu(6)–I(9^{iii})	115.90(8)
I(4)–	Cu(3)–I(5)	103.12(6)	I(9)–	Cu(6)–I(9^{iii})	122.14(7)
Cu(2)···	Cu(1)···Cu(4^{iv})	116.22(9)	Cu(3)···	Cu(4)···Cu(1^{iv})	119.29(9)
Cu(1)···	Cu(2)···Cu(3)	109.03(8)	Cu(5^{ii})···	Cu(5)···Cu(6)	114.78(11)
Cu(2)···	Cu(3)···Cu(4)	110.62(9)	Cu(5)···	Cu(6)···Cu(6^{iii})	113.74(11)
Cu(1)–	I(1)–Cu(4^{iv})	54.64(5)	Cu(1)–	I(6)–Cu(2)	58.80(6)
Cu(1)–	I(2)–Cu(3^{iv})	112.40(7)	Cu(1)–	I(6)–Cu(4^{iv})	52.41(5)
Cu(1)–	I(2)–Cu(4^{iv})	53.00(6)	Cu(2)–	I(6)–Cu(4^{iv})	110.41(6)
Cu(3^{iv})–	I(2)–Cu(4^{iv})	59.49(5)	Cu(5)–	I(7)–Cu(5^{ii})	57.50(7)
Cu(1)–	I(3)–Cu(2)	55.79(6)	Cu(5)–	I(7)–Cu(6)	51.74(6)
Cu(1)–	I(3)–Cu(3)	106.69(6)	Cu(5^{ii})–	I(7)–Cu(6)	109.24(7)
Cu(2)–	I(3)–Cu(3)	51.14(5)	Cu(5)–	I(8)–Cu(6)	55.01(6)
Cu(2)–	I(4)–Cu(3)	56.61(6)	Cu(5)–	I(9)–Cu(6)	51.55(5)
Cu(2)–	I(5)–Cu(3)	51.60(5)	Cu(5)–	I(9)–Cu(6^{iii})	109.41(7)
Cu(2)–	I(5)–Cu(4)	107.96(6)	Cu(6)–	I(9)–Cu(6^{iii})	57.86(7)
Cu(3)–	I(5)–Cu(4)	56.36(6)			

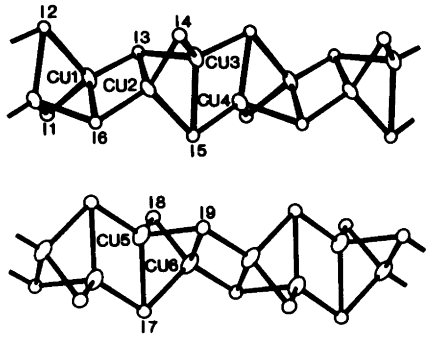

Fig. 1. The two crystallographically independent $[Cu_2I_3]^-$ chains showing the atomic numbering. The orientation of the anions is as in Fig. 2. Thermal ellipsoids enclose 50 % probability.[14]

International Tables for X-Ray Crystallography[12] and the F_o values were weighted according to $w=[\sigma^2(F_o)+0.000055F_o^2]^{-1}$. A final difference map[11] showed a maximum electron density of 1.1 eÅ^{-3}. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1. Structure factors, anisotropic thermal parameters, and distances and angles within the cations may be obtained from the authors.

DISCUSSION

In tetramethylammonium *catena*-di-μ_3-iodo-[μ-iodo-dicuprate(I)], the anion is an infinite chain of edge- and face-sharing Cu(I)–I tetrahedra, similar to those found for the tetraethylammonium,[5] the dimethyl(3-dimethylamino-2-aza-2-propenylidene)ammonium[5] and the 2,4,6-triphenylthiopyrylium[13] compounds. In the present compound there are two crystallographically independent $[Cu_2I_3]^-$ chains (Fig. 1) which differ slightly from one another with respect to both interatomic distances and angles (Table 2). In the chain comprising Cu(5), Cu(6), I(7), I(8) and I(9), each of the μ_3-iodide ligands [I(7) and I(9)] is involved in one short and two long bonds to copper (I) (Table 2) and I(7) lies 0.014(3) Å and I(9) 0.013(3) Å from the planes through the three copper(I) atoms to which they are bonded, similar to the case in $[C_{23}H_{17}S][Cu_2I_3]$.[13] In the other chain, which lacks a centre of symmetry, two of the μ_3-iodide ligands [I(2), I(6)] are involved in one short and two long bonds to copper (I) while the remaining two [I(3), I(5)] each participate in two bonds less than 2.7 Å and one close to 3.0 Å (Table 2). These iodide ligands, *viz.* I(2), I(3), I(5) and I(6), lie 0.153(3), 0.239(3), 0.013(3) and 0.444(3) Å, respectively, from the planes through the copper(I) atoms to which they are bonded. The μ_2-bridging Cu(I)–I distances are 2.670(2) and 2.695(2) Å for I(1), 2.602(2) and 2.630(2) Å for I(4) and 2.654(2) and 2.656(2) Å for I(8).

The copper(I) atoms are all surrounded by distorted tetrahedra of iodide ligands with Cu(I)–I distances ranging from 2.517(3)–3.030(2) Å, similar to the ranges found for the tetraethylammonium, 2.475(1)–2.961(1) Å,[5] the dimethyl(3-dimethylamino-2-aza-2-propenylidene)ammonium, 2.531(2)–2.916(2) Å,[5] and the 2,4,6-triphenylthiopyrylium, 2.522(2)–2.847(2) Å,[13] compounds. The longest Cu(I)–I bonds in $[N(CH_3)_4][Cu_2I_3]$, *viz.* Cu(2)–I(3)=3.030(2) Å and Cu(3)–I(5)=2.988(2) Å are both appreciably shorter than the distance, 3.452(3) Å, between the fourth nearest iodine neighbour and the copper(I) atom considered to be three-coordinated in the $[Cu_2I_3]^-$ chain in $[S_2C_3(SCH_3)_3][Cu_2I_3]$.[15]

As in the single $[Cu_2I_3]^-$ chains investigated hitherto,[5,13,15] the Cu···Cu contacts in $[N(CH_3)_4][Cu_2I_3]$ are all relatively short (Table 2). In both of the crystallographically

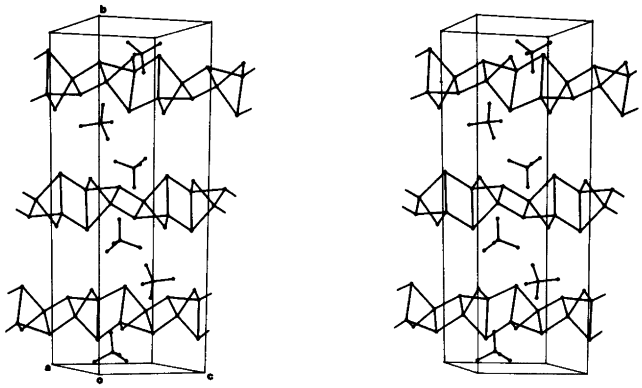

Fig. 2. Stereoscopic view[14] of the unit cell. For clarity, all atoms are represented as spheres of radius 0.05 Å.

independent $[Cu_2I_3]^-$ anions in tetramethylammonium *catena*-di-μ_3-iodo-[μ-iodo-dicuprate (I)], short and slightly longer Cu···Cu distances alternate, the copper(I) atoms involved in the shorter distances being bridged by three iodide ligands and those in the longer distances by two ligands.

The tetramethylammonium ions show no unusual geometrical features and the packing of cations and anions is illustrated in Fig. 2. The closest non-bonded approach distances between carbon and iodine are C(13)···I(6^i)=3.646(11) Å and C(14)···I(9^{ii})=3.670(11) Å [symmetry code: (*i*):$x,y,1+z$; (*ii*):$1-x,1-y,1-z$]. There are no Cu···C distances less than 4.0 Å.

It has been suggested[3] that large bulky cations with low polarizing ability tend to stabilize infinite iodocuprate(I) chains, composed of shared Cu(I)–I tetrahedra, with low negative charge density, expressed in terms of the I^-:CuI ratio, whereas smaller cations tend to favour the formation of infinite chains of edge- and/or face-sharing Cu(I)–I tetrahedra with higher negative charge density. That the tetramethylammonium cation gives rise to a $[Cu_2I_3]^-$ anion closely similar to that obtained with tetraethylammonium as cation[5] would seem to lend support to this hypothesis.

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