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The Crystal Structure of Bis(tetrabutylammonium) Di-μ-iodo-diiododicuprate(I), $[N(C_4H_9)_4]_2[Cu_2I_4]$

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The crystal structure of the title compound has been determined from single-crystal X-ray diffractometer data collected at 168 K. $[(C_4H_9)_4]_2[Cu_2I_4]$ crystallizes in space group $P2_1/n$ with $a=9.042(3)$, $b=21.231(9)$, $c=11.734(3)$ Å, $\beta=92.88(3)°$ and $Z=2$. Full-matrix least-squares refinement of the 181 structural parameters gave $R=0.058$ for 2088 observed $[I>3.0\sigma(I)]$ independent reflections. The $[Cu_2I_4]^{2-}$ anion is a discrete centrosymmetric dimer containing three-coordinated copper(I). The $Cu-I_{bridging}$ distances are 2.566(2) and 2.592(2) Å; $Cu-I_{terminal}$ is 2.514(2) Å and $Cu\cdots Cu$ 2.726(4) Å.

The structures assumed by dihalocuprate(I) ions appear to be strongly dependent on the nature of the cation, Cu(I) exhibiting linear, tetrahedral, or more seldom, trigonal coordination.[1] As yet, however, relatively little information is available on the geometry of the diiodocuprate(I) ion. Although monomeric $[CuI_2]^-$ ions have been shown to exist in solution,[2-4] there does not appear to be any conclusive evidence for the existence of discrete $[CuI_2]^-$ ions in the solid state. In tetraamminecopper(II) diiodocuprate(I)[5] and bis(1,2-diaminoethane)copper(II) diiodocuprate(I),[6] for example, the anions form infinite chains of edge-sharing Cu(I)–I tetrahedra. The iodocuprate(I) complex $[Cu_2I_3]^-$ has been found as infinite chains of edge- and face-sharing Cu(I)–I tetrahedra in the tetraethylammonium and dimethyl(3-dimethylamino-2-aza-2-propenylidene)ammonium compounds[7] and as double chains of edge-sharing tetrahedra in $Cs[Cu_2I_3]$.[8] With methyltriphenylphosphonium as cation, however, a $[Cu_4I_6]^{2-}$ cluster is obtained in which copper is trigonal-planar coordinated and pairs of copper atoms are bridged by iodine atoms.[9]

The recent preparation[10] of crystalline tetrabutylammonium diiodocuprate(I) has made an investigation of the crystal structure of this compound possible. Apart from providing information on the configuration of the anion and the nature of the copper(I) coordination, it was hoped that the investigation might be instrumental in the elucidation of the nucleophilicity of copper(I) and thus mechanisms of cuprate reactions.[10]

EXPERIMENTAL

Bis(tetrabutylammonium) di-μ-iodo-diiododicuprate(I) was prepared from copper(I) iodide and tetrabutylammonium iodide as described previously.[10] Rotation and Weissenberg photographs showed the crystals to be monoclinic with systematic absences consistent with space group $P2_1/n$.*

Intensities from a crystal, $0.25\times0.07\times0.08$ mm, were measured at 168 K with a Syntex $P2_1$ diffractometer, using graphite-monochromated Mo$K\alpha$ radiation and the $\omega-2\theta$ scan mode. The temperature was maintained by a Syntex LT1 low-temperature device and selected owing to the tendency of the crystals to disintegrate in the radiation at room temperature. Data were collected for $2\theta\leq50°$ with $h\geq0$ and $k\geq0$, the 2θ scan rate being varied between 3.5 and 18.0° min^{-1} depending on the intensity of the reflection. Periodical measurement of the intensities of two reflections showed that the crystal was not subject to decay. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method[12] was used to calculate the intensities.[13] A total of 3895 reflections were measured. Sym-

* Equipoints of general position of $P2_1/n$ (conventional setting,[11a] No. 14, $P2_1/c$): $\pm(x,y,z;\ \frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$.

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metry-related reflections were merged and systematically absent reflections excluded giving a unique set of 3337 reflections. Of these 2088 had $I > 3.0\sigma(I)$ and were considered to be observed. Data were corrected[14] for Lorentz and polarization effects but not for absorption. The unit-cell parameters at 168 K were determined by least squares from diffractometer setting angles for 15 reflections.

The low-temperature device was removed and unit-cell parameters were determined at 291 K. Intensities were then remeasured at this temperature, a total of 3618 values being obtained, owing to disintegration of the crystal.

CRYSTAL DATA

Bis(tetrabutylammonium) di-μ-iodo-diiododicuprate(I) $[N(C_4H_9)_4]_2[Cu_2I_4]$, $M_r = 1119.6$; monoclinic, space group $P2_1/n$ (No. 14, non-standard setting); $a = 9.042(3)$, $b = 21.231(9)$, $c = 11.734(3)$ Å, $\beta = 92.88(3)°$ at 168 K, $Z = 2$, $D_c = 1.65$ g cm^{-3}, $\mu(MoK\alpha) = 37.7$ cm^{-1}. The compound crystallizes as colourless prisms. At 291 K the unit-cell dimensions are: $a = 9.140(4)$, $b = 21.152(10)$, $c = 12.020(5)$ Å, $\beta = 95.25(3)°$.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved from Patterson and successive electron density maps.[14] Block-diagonal and finally full-matrix least-squares refinement[14] of the positional and anisotropic thermal parameters and a scale factor yielded $R = 0.058$ for 181 parameters (2088 reflections); when the 1249 unobserved reflections were included $R = 0.095$. The F_o values were weighted[15] according to $w = (32.0 + F_o + 0.010\,F_o^2)^{-1}$. The scattering factors were those of Doyle and Turner[16] for the uncharged atoms, those of I and Cu being corrected[11b] for the real part of the anomalous dispersion. Since C(12) had a rather large temperature factor, attempts were made to assign this atom to two partially occupied sites, but this did not improve the model. Atomic coordinates and thermal parameters are listed in Table 1. Structure factors can be obtained from the authors on request. A final difference map showed no unusual features and had diffuse peaks in probable hydrogen atom positions. No attempt was made to include the hydrogen atoms in the calculations.

The data collected at room temperature yielded essentially the same structural model but with

Table 1. Fractional coordinates and thermal parameters ($U_{ij} \times 10^3$). Estimated standard deviations are given in parentheses. The anisotropic temperature factor is $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \cdots + U_{23}b^*c^*kl)]$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	0.21778(11)	−0.00919(4)	0.08880(9)	52.0(6)	37.7(5)	59.8(6)	0.0(9)	−40.5(9)	−11.9(9)
I(2)	0.00424(10)	0.18162(4)	0.03164(8)	39.8(6)	36.8(5)	56.2(6)	0.1(8)	−16.5(8)	6.1(8)
Cu	0.0096(2)	0.0637(1)	0.0119(1)	49(1)	38(1)	43(1)	−2(2)	−8(2)	−2(1)
N	0.4869(12)	0.1722(5)	0.1790(9)	40(6)	46(7)	34(6)	−28(11)	14(9)	−14(10)
C(1)	0.4503(15)	0.1535(7)	0.0547(11)	40(7)	53(8)	29(7)	−20(13)	−5(11)	−19(12)
C(2)	0.5622(15)	0.1780(7)	−0.0294(11)	41(8)	79(11)	29(7)	3(16)	12(11)	9(14)
C(3)	0.5097(16)	0.1584(9)	−0.1510(12)	44(9)	102(13)	32(8)	−34(18)	14(13)	−16(16)
C(4)	0.3723(21)	0.1933(11)	−0.1968(15)	70(12)	141(19)	55(10)	−77(25)	−14(18)	−63(24)
C(5)	0.6335(17)	0.1420(7)	0.2226(13)	51(9)	57(9)	58(10)	5(15)	−58(16)	−5(15)
C(6)	0.6334(19)	0.0690(7)	0.2240(14)	75(12)	49(9)	68(11)	40(17)	−20(18)	16(16)
C(7)	0.7926(19)	0.0506(8)	0.2671(14)	70(12)	67(11)	61(11)	55(18)	−12(17)	15(17)
C(8)	0.7979(25)	−0.0254(11)	0.2673(17)	110(17)	97(15)	69(13)	58(27)	29(23)	72(23)
C(9)	0.3569(16)	0.1473(7)	0.2462(11)	60(9)	46(8)	28(7)	−31(14)	12(12)	−13(12)
C(10)	0.3703(20)	0.1591(9)	0.3740(14)	81(12)	78(11)	50(10)	−74(20)	13(17)	−47(17)
C(11)	0.2313(27)	0.1392(10)	0.4304(15)	135(19)	95(15)	43(10)	−59(27)	38(22)	−28(20)
C(12)	0.1870(37)	0.0748(14)	0.4217(18)	250(36)	177(27)	49(13)	−264(53)	115(34)	−79(29)
C(13)	0.5049(15)	0.2435(6)	0.1939(11)	41(8)	35(7)	41(8)	−31(12)	−10(12)	−21(12)
C(14)	0.3673(17)	0.2805(6)	0.1429(15)	54(10)	30(7)	84(12)	2(14)	0(17)	−13(15)
C(15)	0.3996(22)	0.3498(7)	0.1642(16)	99(14)	38(8)	74(12)	12(18)	−22(20)	4(16)
C(16)	0.2740(26)	0.3905(8)	0.1019(15)	151(19)	44(9)	53(10)	74(22)	16(22)	27(16)

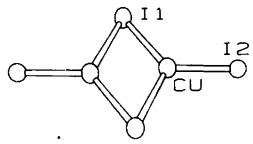

Fig. 1. The di-μ-iodo-diiododicuprate(I) anion showing the atomic numbering.[17]

large temperature factors for iodine and copper ($B \sim 6.5$ Å^2) and exceedingly large for some of the carbon atoms. It was not therefore considered profitable to refine the structure using this data set. The difference between the unit-cell parameters at the two temperatures can undoubtedly be ascribed to orientational disorder at room temperature of the tetrabutylammonium ion, in particular.

DISCUSSION

In bis(tetrabutylammonium) di-μ-iodo-diiododicuprate(I) the anion is a centrosymmetric dimer (Fig. 1) containing three-coordinated copper(I). The structure of the analogous $[Cu_2Br_4]^{2-}$ has recently been reported[18] but to our knowledge this is the first structural determination of $[Cu_2I_4]^{2-}$. The configuration of iodine atoms about copper(I) is approximately trigonal planar (Table 2), with the copper atom 0.03(3) Å from the plane defined by the three iodine atoms [I(1), I(1:$\bar{x},\bar{y},\bar{z}$) and I(2)]. As is seen from Table 2, the bridging Cu–I(1) distances differ slightly from one another and both are longer than the terminal Cu–I(2). The Cu–I(1) distances, the angle subtended at I(1) by the copper atoms [63.8(1)°], the Cu···Cu contact [2.726(4) Å] and the closest distance of approach of the bridging iodine atoms [I(1)···I(1)=4.380(3) Å] all agree closely with the corresponding values in the $[Cu_4I_6]^{2-}$ cluster, as determined in methyltriphenylphosphonium hexaiodotetracuprate(I).[9]

Table 2. Interatomic distances (Å) and angles (°) within the $[Cu_2I_4]^{2-}$ ion. Estimated standard deviations are given in parentheses. The superscript (*i*) denotes an atom in $-x,-y,-z$.

Cu–I(1)	2.566(2)	I(1)–Cu–I(2)	125.8(1)
Cu–I(1^i)	2.592(2)	I(1^i)–Cu–I(2)	117.9(1)
Cu–I(2)	2.514(2)	I(1)–Cu–I(1^i)	116.2(1)
Cu···Cu	2.726(4)	Cu–I(1)–Cu	63.8(1)

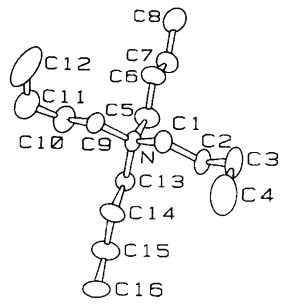

Fig. 2. The tetrabutylammonium ion showing the atomic numbering.

The configuration of $[Cu_2I_4]^{2-}$ is similar to that of $[Cu_2Br_4]^{2-}$ in the tetrathiotetracene salt.[18] There is, however, a somewhat larger difference between the copper(I)-terminal and copper(I)-bridging ligand distances in $[Cu_2Br_4]^{2-}$ than is the case for $[Cu_2I_4]^{2-}$, *i.e.* $Cu-Br_{terminal}=2.328(2)$ Å, $Cu-Br_{bridging}=2.490(2)$ and 2.472(3) Å. Moreover, $[Cu_2Br_4]^{2-}$ shows distortion from planarity, the copper atom lying 0.196 Å out of the plane through the three bromide ligands. There are also Cu–S contacts of 2.684 and 3.062 Å to tetrathiotetracene cations such that the copper(I) coordination can be described as being approximately trigonal bipyramidal.[18]

It would seem that the Cu···Cu distance is determined largely by the stereochemical demands of the bridging ligands[9,19] but that the value 2.726(4) Å in $[Cu_2I_4]^{2-}$ may indicate a weak attractive Cu(I)–Cu(I) interaction.[19] As expected, the Cu···Cu contact in $[Cu_2Br_4]^{2-}$, 2.660(3) Å,[18] is shorter than that in di-μ-iodo-diiododicuprate(I).

The cation is depicted[17] in Fig. 2 and a stereoscopic view[17] of the unit cell is shown in Fig. 3. The large thermal parameters of some of the carbon atoms, in particular those of the terminal atoms of the chains, would suggest some orientational disorder, which is also borne out by the data collected at room temperature. In consequence, bond distances and angles within the cation are associated with relatively large standard deviations (Table 3). The connectivity relationships show, however, good general agreement with values found in other tetrabutylammonium derivatives. Orientational disorder and/or large thermal parameters associated with the tetrabutylammonium ion appear to be not uncommon, *e.g.* $[N(C_4H_9)_4]IO_4$,[20] $[N(C_4H_9)_4]_2[Mo_2O_3S(C_4O_2S_2)_2]$,[21] $[N(C_4H_9)_4]$-

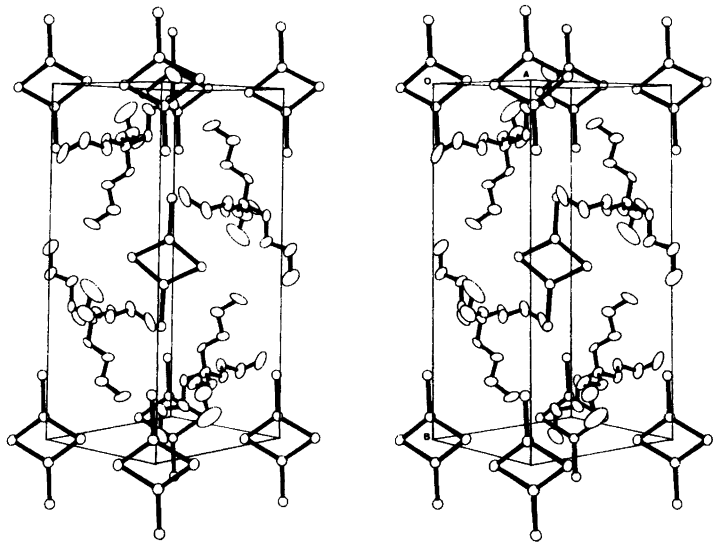

Fig. 3. Stereoscopic view of the unit cell.

Table 3. Bond lengths (Å) and angles (°) within the tetrabutylammonium ion. Estimated standard deviations are given in parentheses.

N–C(1)	1.53(2)	C(1)–N–C(5)	111(1)
C(1)–C(2)	1.54(2)	C(1)–N–C(9)	105(1)
C(2)–C(3)	1.54(2)	C(1)–N–C(13)	112(1)
C(3)–C(4)	1.52(2)	C(5)–N–C(9)	111(1)
N–C(5)	1.54(2)	C(5)–N–C(13)	107(1)
C(5)–C(6)	1.55(2)	C(9)–N–C(13)	111(1)
C(6)–C(7)	1.55(2)	N–C(1)–C(2)	114(1)
C(7)–C(8)	1.62(3)	C(1)–C(2)–C(3)	109(1)
N–C(9)	1.54(2)	C(2)–C(3)–C(4)	114(1)
C(9)–C(10)	1.52(2)	N–C(5)–C(6)	115(1)
C(10)–C(11)	1.51(3)	C(5)–C(6)–C(7)	105(1)
C(11)–C(12)	1.43(4)	C(6)–C(7)–C(8)	106(1)
N–C(13)	1.53(2)	N–C(9)–C(10)	115(1)
C(13)–C(14)	1.56(2)	C(9)–C(10)–C(11)	111(1)
C(14)–C(15)	1.52(2)	C(10)–C(11)–C(12)	118(2)
C(15)–C(16)	1.58(3)	N–C(13)–C(14)	112(1)
		C(13)–C(14)–C(15)	106(1)
		C(14)–C(15)–C(16)	109(1)

$[Ag_3I_4]$.[22] The closest non-bonded approach distances between carbon and copper(I) and carbon and iodide in $[N(C_4H_9)_4]_2[Cu_2I_4]$ are C(7)···Cu 3.67(2) Å and I(1)···C(9) 3.98(1) Å.

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