Crystal Structure of Bis(tetraphenylarsonium) Di-μ-iododiiododicuprate(I), [As(C₆H₅)₄]₂[Cu₂I₄]

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The crystal structure of the title compound has been determined from single-crystal X-ray diffractometer data. $[As(C_6H_5)_4]_2[Cu_2I_4]$ crystallizes in space group $P2_1/c$ with $a=12.040(6)$, $b=18.046(10)$, $c=22.683(12)$ Å, $\beta=102.73(4)°$ and $Z=4$. Full-matrix least-squares refinement of 505 structural parameters gave $R=0.058$ for 4345 observed $[I>3.0\sigma(I)]$ reflections. The two crystallographically independent copper(I) atoms of the $[Cu_2I_4]^{2-}$ anion have approximately trigonal-planar coordination. The dimer is not, however, planar but is folded about the bridging I$\cdots$I contact, the planes through the two ligand triangles thus being inclined at 147°. Cu$-$I$_{bridging}$ ranges from 2.578(3) to 2.610(3) Å; Cu$-$I$_{terminal}$=2.490(3) and 2.491(3) Å; Cu$\cdots$Cu=2.663(4) Å.

The structures assumed by diiodocuprate(I) ions in the solid state appear to be strongly dependent on the nature of the cation. In the tetraamminecopper(II),[1] the bis(1,2-diaminoethane)copper(II),[2] the N-methylpyridinium[3] and the dimethyl(3-dimethylamino-2-aza-2-propenylidene)ammonium[3] diiodocuprates(I), the anions form infinite chains of edge-sharing Cu(I)$-$I tetrahedra. Bis(tetrabutylammonium) di-μ-iodo-diiododicuprate(I),[4] on the other hand, contains a discrete centrosymmetric $[Cu_2I_4]^{2-}$ dimer in which copper(I) has trigonal-planar coordination. Although monomeric $[CuI_2]^-$ has been shown to exist in solution (see, for example, Refs. 5$-$9) there does not yet appear to be any conclusive evidence for the existence of a discrete monomeric $[CuI_2]^-$ ion in the solid state.

Previous structural studies on dihalocuprates(I),[4,10,11] $[CuX_2]^-$, and related anions[12–14]

appear to indicate that the tendency of the anion to catenation increases in the order X=Cl$\approx$Br<I<CN and that the formation of discrete anions in the solid state is favoured by the presence of large cations with low, well-screened charge. Tetraphenylarsonium and tetrabutylammonium are similar in size and shape but would be expected to differ with respect to the delocalisation of the positive charge, the positive charge presumably being less well-screened in the former cation. In order to ascertain the nature of the copper(I) coordination and the geometry of the anion in tetraphenylarsonium diiodocuprate(I) crystals of this compound have been prepared and a structural investigation undertaken.

EXPERIMENTAL

The compound was prepared by dissolving copper(I) iodide and excess tetraphenylarsonium iodide (molar ratio 1:2) in acetonitrile. Colourless truncated octahedra were deposited from the concentrated solution after a few hours.

Crystals of $[As(C_6H_5)_4]_2[Cu_2I_4]$, $M_r=1401.4$, are monoclinic, $P2_1/c$, with $a=12.040(6)$ Å, $b=18.046(10)$ Å, $c=22.683(12)$ Å, $\beta=102.73(4)°$, $Z=4$, $D_c=1.96$ g cm⁻³, $\mu(MoK\alpha)=5.04$ mm⁻¹. Diffracted intensities from a crystal, $0.27\times0.26\times0.27$ mm, were measured for $2\theta\leqslant49°$ with a Syntex $P2_1$ diffractometer, using graphite-monochromated MoKα radiation and the ω scan mode with a variable scan rate of 1.5$-$15.0°min⁻¹. A 19-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method[15] was used to calculate the intensities.[16] After merging of symmetry-

Table 1. Fractional coordinates and equivalent isotropic thermal parameters ($Å^2$) for $[As(C_6H_5)_4]_2[Cu_2I_4]$. 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)	0.1857(1)	0.1198(1)	0.1670(1)	6.23(3)
I(2)	0.1490(1)	0.2984(1)	0.2908(1)	6.56(3)
I(3)	0.3870(1)	0.1095(1)	0.3559(1)	6.99(3)
I(4)	−0.1509(1)	0.2277(1)	0.1452(1)	6.07(3)
Cu(1)	0.2436(2)	0.1735(1)	0.2763(1)	6.01(6)
Cu(2)	0.0503(2)	0.2150(1)	0.2020(1)	5.88(6)
As(1)	0.2060(1)	0.0678(1)	0.5882(1)	3.99(3)
C(1)	0.3428(12)	0.1088(9)	0.6385(7)	4.5(4)
C(2)	0.4443(12)	0.0717(11)	0.6423(8)	5.8(4)
C(3)	0.5421(16)	0.1042(15)	0.6793(11)	8.3(6)
C(4)	0.5372(16)	0.1728(12)	0.7062(9)	6.2(5)
C(5)	0.4351(17)	0.2075(13)	0.7021(10)	7.7(6)
C(6)	0.3370(15)	0.1770(11)	0.6677(8)	6.0(4)
C(7)	0.2483(15)	−0.0141(9)	0.5431(7)	4.9(4)
C(8)	0.1988(14)	−0.0834(9)	0.5458(8)	5.3(4)
C(9)	0.2339(18)	−0.1409(11)	0.5133(9)	6.3(5)
C(10)	0.3113(18)	−0.1301(11)	0.4775(9)	6.3(5)
C(11)	0.3583(16)	−0.0600(12)	0.4762(9)	6.8(5)
C(12)	0.3307(15)	−0.0003(10)	0.5082(8)	5.5(4)
C(13)	0.1314(11)	0.1407(9)	0.5323(7)	4.1(4)
C(14)	0.1226(13)	0.1289(10)	0.4694(8)	5.0(4)
C(15)	0.0659(11)	0.1856(13)	0.4296(8)	5.9(5)
C(16)	0.0253(12)	0.2476(10)	0.4545(9)	5.0(4)
C(17)	0.0374(15)	0.2585(11)	0.5147(11)	6.4(5)
C(18)	0.0904(15)	0.2053(9)	0.5527(9)	5.6(4)
C(19)	0.1039(14)	0.0356(9)	0.6361(7)	4.5(4)
C(20)	0.1462(15)	−0.0004(13)	0.6898(9)	6.7(5)
C(21)	0.0742(19)	−0.0303(15)	0.7242(10)	8.3(6)
C(22)	−0.0420(20)	−0.0146(12)	0.7054(10)	7.5(6)
C(23)	−0.0876(16)	0.0256(14)	0.6519(10)	7.7(6)
C(24)	−0.0135(13)	0.0499(11)	0.6177(9)	6.1(5)
As(2)	0.3887(1)	−0.0958(1)	0.0824(1)	4.13(3)
C(25)	0.4922(14)	−0.0264(9)	0.1322(7)	4.5(4)
C(26)	0.4571(15)	0.0049(11)	0.1799(9)	6.0(5)
C(27)	0.5320(18)	0.0599(12)	0.2132(9)	6.6(5)
C(28)	0.6310(15)	0.0779(11)	0.1970(8)	5.6(4)
C(29)	0.6620(14)	0.0428(12)	0.1499(8)	6.0(5)
C(30)	0.5951(13)	−0.0120(11)	0.1162(8)	5.6(4)
C(31)	0.2742(12)	−0.0406(9)	0.0278(7)	4.2(3)
C(32)	0.2830(13)	0.0373((10)	0.0237(8)	4.9(4)
C(33)	0.1986(16)	0.0737(11)	−0.0174(10)	6.8(5)
C(34)	0.1084(17)	0.0340(13)	−0.0545(9)	6.7(5)
C(35)	0.1004(15)	−0.0423(11)	−0.0505(9)	6.2(5)
C(36)	0.1833(13)	−0.0808(10)	−0.0085(8)	5.4(4)
C(37)	0.3123(10)	−0.1581(10)	0.1297(7)	4.6(4)
C(38)	0.2292(12)	−0.1271(11)	0.1534(7)	5.4(4)
C(39)	0.1681(13)	−0.1747(15)	0.1868(9)	6.9(5)
C(40)	0.1941(19)	−0.2494(14)	0.1919(9)	7.1(6)
C(41)	0.2753(18)	−0.2792(13)	0.1669(8)	6.6(5)
C(42)	0.3391(16)	−0.2340(11)	0.1343(8)	6.0(5)
C(43)	0.4740(12)	−0.1545(9)	0.0386(7)	4.1(3)
C(44)	0.4339(14)	−0.1610(10)	−0.0245(8)	5.4(4)
C(45)	0.4985(17)	−0.2031(12)	−0.0568(9)	6.4(5)
C(46)	0.5975(20)	−0.2398(11)	−0.0265(12)	7.5(6)
C(47)	0.6330(16)	−0.2353(12)	0.0359(11)	6.9(6)
C(48)	0.5693(14)	−0.1918(10)	0.0691(8)	5.7(4)

equivalent and exclusion of systematically absent reflections, 7965 independent reflections were obtained. Of these the 4345 for which $I>3.0\sigma(I)$ were used in the subsequent calculations. Correction was made 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.

Fig. 1. The $[Cu_2I_4]^{2-}$ ion showing the atomic numbering. The thermal ellipsoids enclose 50 % probability.[21]

STRUCTURE DETERMINATION AND REFINEMENT

The positions of the copper and iodine atoms were determined by direct methods (MULTAN 80)[17] and those of the arsenic and carbon atoms from successive electron density maps.[18] Full-matrix least-squares refinement[18] of positional, isotropic thermal and, finally, anisotropic thermal parameters and a scale factor gave $R=0.058$ (505 parameters; 4345 observed reflections); $R=0.116$ based on all 7965 measured independent reflections. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*[19] and the F_o values were weighted[20] according to $w=(250+F_o+0.0001F_o^2)^{-1}$. A final difference map showed a maximum electron density of 1.2 e Å^{-3}. Hydrogen atoms were not included in the calculations. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1 and interatomic distances and angles within the anion in Table 2. Structure factors, anisotropic thermal parameters and distances and angles within the tetraphenylarsonium ions may be obtained from the authors.

DISCUSSION

In bis(tetraphenylarsonium) di-μ-iodo-diiodo-dicuprate(I) the anion is a $[Cu_2I_4]^{2-}$ dimer (Fig. 1)

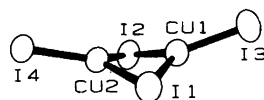but differs from that in the tetrabutylammonium compound in that it is neither centrosymmetric nor planar. Each copper(I) atom is approximately trigonal-planar coordinated by iodide (Table 2) with Cu(1) displaced 0.04(1) Å from the plane through I(1), I(2) and I(3), and Cu(2) 0.07(1) Å from that through I(1), I(2) and I(4). The anion is folded about the I(1)···I(2) contact such that the planes through I(1), I(2) and I(3) and through I(1), I(2) and I(4) are inclined at 147°. The folding and the slight displacement of the copper(I) atoms from the ligand planes towards one another results in a relatively short Cu(1)···Cu(2) contact, *i.e.* 2.663(4) Å; the corresponding distance in $[N(C_4H_9)_4]_2[Cu_2I_4]$ is 2.726(4) Å.[4] The Cu−I terminal and bridging distances and the angles subtended at I(1) and I(2) by the copper(I) atoms (Table 2) are all similar to those found for $[N(C_4H_9)_4]_2[Cu_2I_4]$, *viz.* Cu−I$_{terminal}$=2.514(2) Å, Cu−I$_{bridging}$=2.566(2) and 2.592(2) Å, Cu−I(1)−Cu=63.8(1)°.[4] Whereas in $[N(C_4H_9)_4]_2[Cu_2I_4]$ opposite Cu−I$_{bridging}$ distances are exactly equal, due to the crystallographic symmetry, while adjacent distances differ, the reverse is true in the present case, adjacent Cu−I$_{bridging}$ distances, *viz.* Cu(1)−I(1), Cu(2)−I(1) and Cu(1)−I(2), Cu(2)−I(2) being of equal length (Table 2). The closest distance of approach of the bridging iodine atoms [I(1)···I(2)=4.360(3) Å] is closely similar to that,

Table 2. Interatomic distances (Å) and angles (°) within the $[Cu_2I_4]^{2-}$ ion. Estimated standard deviations are given in parentheses.

Cu(1)−I(1)	2.610(3)	Cu(2)−I(1)	2.609(3)
Cu(1)−I(2)	2.578(3)	Cu(2)−I(2)	2.584(3)
Cu(1)−I(3)	2.490(3)	Cu(2)−I(4)	2.491(3)
Cu(1)···Cu(2)	2.663(4)		
I(1)−Cu(1)−I(2)	114.4(1)	I(1)−Cu(2)−I(2)	114.2(1)
I(1)−Cu(1)−I(3)	120.9(1)	I(1)−Cu(2)−I(4)	120.3(1)
I(2)−Cu(1)−I(3)	124.6(1)	I(2)−Cu(2)−I(4)	125.3(1)
Cu(1)−I(1)−Cu(2)	61.4(1)	Cu(1)−I(2)−Cu(2)	62.1(1)

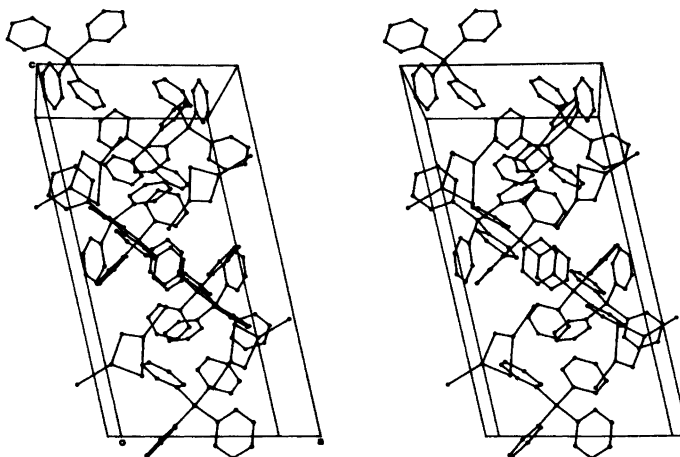*Fig. 2.* Stereoscopic view [21] of the unit cell. For clarity all atoms are represented as spheres of radius 0.05 Å.

4.380(3) Å, found in $[N(C_4H_9)_4]_2[Cu_2I_4]$.[4]

It would seem likely that the folding of the anion has its origin primarily in electrostatic and steric interactions between the iodide ligands and the phenyl rings, since the trigonal-planar coordination of copper(I) is very similar in both the planar[4] and the bent $[Cu_2I_4]^{2-}$ dimer. The packing of cations and anions in the unit cell is illustrated in Fig. 2. The closest approach distances between iodide and carbon are $I(1)\cdots C(26)=3.83(2)$ Å, $I(2)\cdots C(6^i)=3.99(2)$ Å, $I(2)\cdots C(39^{ii})=3.99(2)$ Å, $I(3)\cdots C(47^{iii})=3.77(2)$ Å, $I(4)\cdots C(40^{iii})=3.87(2)$ Å. Symmetry code: (*i*): $x, \frac{1}{2}-y, z-\frac{1}{2}$; (*ii*): $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; (*iii*): $1-x, \frac{1}{2}+y, \frac{1}{2}-z$. Some of these distances are somewhat shorter than the shortest such distance in $[N(C_4H_9)_4]_2[Cu_2I_4]$, *viz* 3.98(1) Å.[4] The shortest $Cu\cdots C$ contacts, *i.e.* $Cu(1)\cdots C(5^i)=3.80(2)$ Å, $Cu(2)\cdots C(18^i)=3.80(2)$ Å are both longer than the corresponding distance in $[N(C_4H_9)_4]_2[Cu_2I_4]$, 3.67(2) Å.[4] The tetraphenylarsonium ions (Fig. 2) show no anomalous features.

Apart from in $[N(C_4H_9)_4]_2[Cu_2I_4]^4$ and $[As(C_6H_5)_4]_2[Cu_2I_4]$, $[Cu_2X_4]^{2-}$ dimers have been found to occur for X=Br in $(TTT)_2[Cu_2Br_4]$,[22] where TTT=tetrathiotetracene, and in $[N(C_2H_5)_4]_2[Cu_2Br_4]$.[11] In $(TTT)_2[Cu_2Br_4]$,[22] there are additional Cu−S contacts to the tetrathiotetracene cation radicals such that the configuration of ligands about copper(I) is approximately trigonal bipyramidal. In $[N(C_2H_5)_4]_2$-

$[Cu_2Br_4]$,[11] the anion is an isolated centrosymmetric dimer containing distortedly trigonal-planar coordinated copper(I), the angle subtended at copper(I) by the bridging bromide ligands being 106.3(1)°. The Cu−Br(2)−Cu angle, 73.7(1)°, and the Cu$\cdots$Cu contact, 2.937(3) Å,[11] within the $[Cu_2Br_4]^{2-}$ dimer in $[N(C_2H_5)_4]_2[Cu_2Br_4]$ are both appreciably larger than in either of the known $[Cu_2I_4]^{2-}$ dimers (see Ref. 4, this work). There would thus appear to be considerable flexibility in the geometry assumed by the $[Cu_2X_4]^{2-}$ moiety under different steric and electrostatic constraints in the solid state.

Despite the presumably less well-screened positive charge on tetraphenylarsonium as compared to tetrabutylammonium, tetraphenylarsonium would appear to be as effective as tetrabutylammonium in the suppression of −I−Cu−I−catenation and the stabilization of a discrete dimeric $[Cu_2I_4]^{2-}$ configuration in the solid state. Although it would seem likely that the folding of the dimer is due primarily to packing forces, the paucity of information concerning the structure of the $[Cu_2I_4]^{2-}$ anion precludes a firm conclusion on this point.

REFERENCES

1. Baglio, J. A., Weakliem, H. A., Demelio, F. and Vaughan, P. A. *J. Inorg. Nucl. Chem. 32* (1970) 795.
2. Freckmann, B. and Tebbe, K.-F. *Z. Naturforsch. Teil B 35* (1980) 1319.
3. Hartl, H., Brüdgam, I. and Mahdjour-Hassan-Abadi, F. *Z. Naturforsch. Teil B 38* (1983) 57.
4. Asplund, M., Jagner, S. and Nilsson, M. *Acta Chem. Scand. A 36* (1982) 751.
5. Specker, H. and Pappert, W. *Z. Anorg. Allg. Chem. 341* (1965) 287.
6. Mahfooz Khan, M., Zaidi, S. A. A. and Malik, A. U. *Z. Anorg. Allg. Chem. 375* (1970) 291.
7. Waters, D. N. and Basak, B. *J. Chem. Soc. A* (1971) 2733.
8. Ahrland, S., Bläuenstein, P., Tagesson, B. and Tuhtar, D. *Acta Chem. Scand. A 34* (1980) 265.
9. Ahrland, S., Nilsson, K. and Tagesson, B. *Acta Chem. Scand. A 37* (1983) 193.
10. Asplund, M., Jagner, S. and Nilsson, M. *Acta Chem. Scand. A 37* (1983) 57.
11. Asplund, M. and Jagner, S. *Acta Chem. Scand. A 38* (1984) 135.
12. Asplund, M., Jagner, S. and Nilsson, M. *Acta Chem. Scand. A 37* (1983) 165.
13. Asplund, M., Jagner, S. and Nilsson, M. *Acta Chem. Scand. A 38* (1984) 57.
14. Asplund, M. and Jagner, S. *Acta Chem. Scand. A 38* (1984) 129.
15. Lehmann, M. S. and Larsen, F. K. *Acta Crystallogr. A 30* (1974) 580.
16. Lindqvist, O. and Ljungström, E. *J. Appl. Crystallogr. 12* (1979) 134.
17. Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P. and Woolfson, M. M. *MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data,* Univs. of York, England and Louvain, Belgium 1980.
18. 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.
19. *International Tables for X-Ray Crystallography,* Kynoch Press, Birmingham 1974, Vol IV, p. 72.
20. Cruickshank, D. W. J. *Crystallographic Computing,* Munksgaard, Copenhagen 1970, p. 195.
21. Johnson, C. K. *ORTEP,* Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge 1965.
22. Shibaeva, R. P. and Kaminskii, V. F. *Kristallografiya 26* (1981) 332.

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