Acta Chemica Scandinavica A 38 (1984) 411–421

Short Communications

Crystal Structure of Bis(tetrapropylammonium) Di-μ-iodo-diiododicuprate(I), $[N(C_3H_7)_4]_2[Cu_2I_4]$

MILJA ASPLUND and SUSAN JAGNER

Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden.

Diiodocuprate(I) ions have been encountered in the solid state as infinite chains of edge-sharing Cu(I)–I tetrahedra [1–3] and as discrete $[Cu_2I_4]^{2-}$ dimers containing trigonal-planar coordinated copper(I).[4,5] Although monomeric $[CuI_2]^-$ has been shown to exist in solution (see, *e.g.* Refs. 6–10) there does not yet appear to be any crystallographic evidence for the existence of a discrete $[CuI_2]^-$ monomer.

Previous structural studies on dihalocuprates(I),[4,5,11,12] $[CuX_2]^-$, and related anions [13–15] would seem to indicate that the tendency of the anion to polymerization increases in the order X=Cl≈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. In $[N(C_2H_5)_4][Cu_2I_3]$ the anion forms an infinite chain of edge- and face-sharing Cu(I)–I tetrahedra.[16] Tetrapropylammonium, intermediate in size between tetrabutylammonium and tetraethylammonium, might be expected to promote –Cu–I–Cu– catenation, leading to a larger entity than $[Cu_2I_4]^{2-}$. In order to determine the nature of the copper(I) coordination and the geometry of the anion in tetrapropylammonium diiodocuprate(I), crystals of this compound have been prepared and a structural investigation undertaken.

The compound was prepared by dissolving copper(I) iodide and tetrapropylammonium iodide (molar ratio 1:1) in acetonitrile. Colourless prisms were deposited from the concentrated solution after a few days.

Crystals of $[N(C_3H_7)_4]_2[Cu_2I_4]$, M_r=1007.4, are monoclinic, space group $P2_1/n$ (No. 14,[17a] non-standard setting.) Equipoints of general position of $P2_1/n$: $\pm(x,y,z;\ \frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$; a=9.017(3), b=12.683(3), c=16.140(5) Å, β=93.15(3)°, Z=2, D_c=1.82 g cm^{-3}, μ(Mo$K\alpha$)=4.60 mm^{-1}. Diffracted intensities from a crystal, 0.25×0.12×0.11 mm, were measured at approximately 290 K for $2\theta \leq 55°$ 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 2.5–29.3° min^{-1}. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method [18] was used to calculate the intensities.[19] After merging of symmetry-equivalent and exclusion of systematically absent reflections, 4269 independent reflections were obtained. Of these the 2905 for which $I > 3.0\,\sigma(I)$ were regarded as observed and used to solve the structure. 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.

The structure was solved from Patterson and successive electron density maps.[20] Full-matrix least-squares refinement [20] of positional and anisotropic thermal parameters for the non-hydrogen atoms and positional for the hydrogen atoms gave R=0.044 for 2899 reflections, six reflections notably affected by extinction being excluded from the final cycles (R=0.066 based on all 4269 measured independent reflections). The isotropic temperature factors of the hydrogen atoms were set equal to the equivalent isotropic values of the carrying carbon atoms. The F_o values were weighted according to $w=[\sigma^2(F_o)+0.00065\,F_o^2]^{-1}$. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.[17b] A final difference map showed a maximum electron density of 0.9 eÅ^{-3}. Atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are listed in Table 1. Structure factors, anisotropic thermal parameters, hydrogen atom coordinates and carbon-hydrogen distances may be obtained from the authors.

In bis(tetrapropylammonium) di-μ-iodo-diiododicuprate(I) the anion is a centrosymmetric dimer (Fig. 1) similar to that in bis(tetrabutyl-

0302-4377/84 $2.50

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in $[N(C_3H_7)_4]_2[Cu_2I_4]$. 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}
Cu	−0.00702(9)	0.08425(6)	0.05063(5)	5.54(2)
I(1)	−0.02034(5)	0.23644(4)	0.14826(3)	6.48(1)
I(2)	0.12113(6)	0.09529(3)	−0.08751(3)	6.91(1)
N	0.4877(5)	0.0869(3)	0.2464(3)	4.1(1)
C(1)	0.3909(7)	0.0521(5)	0.3161(4)	4.7(1)
C(2)	0.3905(10)	0.1258(7)	0.3904(5)	6.6(2)
C(3)	0.2871(10)	0.0836(8)	0.4517(5)	7.1(2)
C(4)	0.4947(7)	−0.0034(5)	0.1857(4)	5.0(1)
C(5)	0.3497(9)	−0.0402(7)	0.1434(5)	6.8(2)
C(6)	0.3760(12)	−0.1254(10)	0.0823(7)	8.5(2)
C(7)	0.6426(7)	0.1149(5)	0.2784(4)	5.2(1)
C(8)	0.7243(8)	0.0312(6)	0.3289(5)	6.6(2)
C(9)	0.8668(12)	0.0775(11)	0.3681(7)	9.2(3)
C(10)	0.4182(7)	0.1831(5)	0.2048(4)	5.2(1)
C(11)	0.4914(11)	0.2217(8)	0.1288(6)	8.1(2)
C(12)	0.4163(13)	0.3182(13)	0.0957(11)	11.4(4)

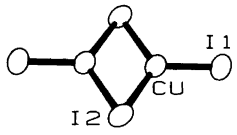

Fig. 1. The $[Cu_2I_4]^{2-}$ ion showing the atomic numbering. The thermal ellipsoids enclose 50 % probability.[21]

ammonium) di-μ-iodo-diiododicuprate(I).[4] The configuration of ligands about copper(I) is approximately trigonal planar (Table 2) with the copper atom situated 0.013(1) Å from the plane defined by the three ligand atoms [I(1), I(2) and I(2^i)]. Symmetry code: (*i*) $-x, -y, -z$; (*ii*) $1-x, -y, -z$. As in $[N(C_4H_9)_4]_2[Cu_2I_4]$[4] and in $[As(C_6H_5)_4]_2[Cu_2I_4]$,[5] the $Cu-I_{bridging}$ distances differ slightly from one another; the difference is, however, somewhat less in the present compound. In $[N(C_4H_9)_4]_2[Cu_2I_4]$, $Cu-I_{bridging}$=2.566(2) and 2.592(2) Å;[4] in the bent dimer in $[As(C_6H_5)_4]_2[Cu_2I_4]$, $Cu-I_{bridging}$= 2.578(3), 2.584(3) and 2.609(3), 2.610(3) Å, opposite distances rather than adjacent differing. The Cu···Cu^i contact in $[N(C_3H_7)_4]_2[Cu_2I_4]$, 2.698(1) Å, is intermediate between that in $[As(C_6H_5)_4]_2[Cu_2I_4]$, 2.663(4) Å,[5] and that in $[N(C_4H_9)_4]_2[Cu_2I_4]$, 2.726(1) Å.[4] The I(2)···I(2^i) distance, 4.390(1) Å, and the angle subtended at I(2) by Cu and Cu^i, 63.14(3)°, are both close to the values obtained for bis(tetrabutylammonium) di-μ-iodo-diiododicuprate(I).[4]

The packing of cations and anions in the unit cell is illustrated in Fig. 2, the tetrapropylammonium ions showing no anomalous geometrical features (Table 3). The closest approach distances between iodide and carbon are I(2)···C(4^{ii})=4.059(6) Å and I(1)···C(10)= 4.066(7) Å and between copper(I) and carbon Cu···C(5)=3.815(8) Å, all slightly longer than the shortest such distances in $[N(C_4H_9)_4]_2[Cu_2I_4]$, *viz.* 3.98(1) and 3.67(2) Å, respectively.[4] It would thus seem likely that the inequality between the $Cu-I_{bridging}$ distances in $[Cu_2I_4]^{2-}$ is primarily steric in origin. In $[As(C_6H_5)_4]_2[Cu_2I_4]$ electrostatic and steric interactions between the iodide ligands and the phenyl rings would appear

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)	2.499(1)	I(1)−Cu−I(2)	122.98(4)
Cu−I(2)	2.571(1)	I(1)−Cu−I(2^i)	120.15(4)
Cu−I(2^i)	2.582(1)	I(2)−Cu−I(2^i)	116.86(3)
Cu···Cu^i	2.698(2)	Cu−I(2)−Cu^i	63.14(3)

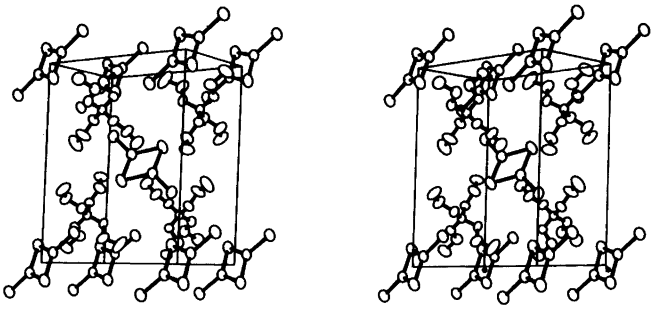

Fig. 2. Stereoscopic view[21] of the unit cell. The thermal ellipsoids enclose 50 % probability.

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

N–C(1)	1.526(7)	N–C(7)	1.505(7)
C(1)–C(2)	1.521(10)	C(7)–C(8)	1.505(10)
C(2)–C(3)	1.495(12)	C(8)–C(9)	1.519(14)
N–C(4)	1.511(8)	N–C(10)	1.512(8)
C(4)–C(5)	1.514(10)	C(10)–C(11)	1.506(12)
C(5)–C(6)	1.490(15)	C(11)–C(12)	1.484(19)
C(1)–N–C(4)	107.7(4)	C(4)–N–C(7)	109.3(4)
C(1)–N–C(7)	111.9(4)	C(4)–N–C(10)	110.8(4)
C(1)–N–C(10)	108.7(4)	C(7)–N–C(10)	108.5(4)
N–C(1)–C(2)	115.4(5)	N–C(7)–C(8)	115.9(5)
C(1)–C(2)–C(3)	109.3(7)	C(7)–C(8)–C(9)	109.3(7)
N–C(4)–C(5)	117.4(5)	N–C(10)–C(11)	115.8(6)
C(4)–C(5)–C(6)	110.9(7)	C(10)–C(11)–C(12)	110.4(9)

to cause more severe distortion, the anion being folded about the bridging I···I contact such that the planes through the two ligand triangles are inclined at 147°.[5]

Despite the smaller size of the tetrapropylammonium ion and the presumably less well-screened positive charge as compared with tetrabutylammonium, tetrapropylammonium would seem 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. Attempts to prepare the tetraethylammonium diiodocuprate(I) by dissolving tetraethylammonium iodide and copper(I) iodide in acetonitrile have hitherto resulted in crystals identical with those described by Hartl and Mahdjour-Hassan-Abadi,[16] *i.e.* $[N(C_2H_5)_4][Cu_2I_3]$. This suggests that, whereas tetraethylammonium is capable of suppressing –Br–Cu–Br-catenation and stabilizing a $[Cu_2Br_4]^{2-}$ dimer in the solid state,[12] it is insufficient for the suppression of –I–Cu–I– catenation.

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

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. Asplund, M. and Jagner, S. *Acta Chem. Scand. A 38* (1984) 297.
6. Specker, H. and Pappert, W. *Z. Anorg. Allg. Chem. 341* (1965) 287.
7. Mahfooz Khan, M., Zaidi, S. A. A. and Malik, A. U. *Z. Anorg. Allg. Chem. 375* (1970) 291.
8. Waters, D. N. and Basak, B. *J. Chem. Soc. A* (1971) 2733.

9. Ahrland, S., Bläuenstein, P., Tagesson, B. and Tuhtar, D. *Acta Chem. Scand. A 34* (1980) 265.
10. Ahrland, S., Nilsson, K. and Tagesson, B. *Acta Chem. Scand. A 37* (1983) 193.
11. Asplund, M., Jagner, S. and Nilsson, M. *Acta Chem. Scand. A 37* (1983) 57.
12. Asplund, M. and Jagner, S. *Acta Chem. Scand. A 38* (1984) 135.
13. Asplund, M., Jagner, S. and Nilsson, M. *Acta Chem. Scand. A 37* (1983) 165.
14. Asplund, M., Jagner, S. and Nilsson, M. *Acta Chem. Scand. A 38* (1984) 57.
15. Asplund, M. and Jagner, S. *Acta Chem. Scand. A 38* (1984) 129.
16. Hartl, H. and Mahdjour-Hassan-Abadi, F. *Angew. Chem. 93* (1981) 804.
17. a. *International Tables for X-Ray Crystallography,* Kynoch Press, Birmingham 1952, Vol. I, p. 99; b. *Ibid.* 1974, Vol. IV, 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. 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.
21. Johnson, C. K. *ORTEP,* Report ORNL-3794. Oak Ridge National Laboratory, Oak Ridge 1965.

Received January 16, 1984.