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Crystal Structure of Bis(tetraethylammonium) Di-μ-bromo-dibromodicuprate(I), $[N(C_2H_5)_4]_2[Cu_2Br_4]$

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The crystal structure of the title compound has been determined from single-crystal X-ray diffractometer data. $[N(C_2H_5)_4]_2[Cu_2Br_4]$ crystallizes in space group $P2_1/c$ with a=8.375(2), b=13.817(5), c=11.086(5) Å, β=97.03(3)° and Z=2. Full-matrix least-squares refinement of 109 structural parameters gave R=0.060 for 1328 observed [$I>3.0\sigma(I)$] independent reflections. The anion is a discrete centrosymmetric dimer, the configuration of bromide ligands about copper(I) being distorted trigonal planar. The $Cu-Br_{bridging}$ distances are 2.441(2) and 2.454(2) Å; $Cu-Br_{terminal}$ is 2.319(2) Å and Cu···Cu 2.937(3) Å.

Structural investigations of crystalline $[N(C_4H_9)_4][CuX_2]$, X=Cl, Br, I, CN[1–3] and $[N(C_4H_9)_4][CuBrCl]$[4] suggest that the tendency of the anion to catenation increases in the order X=Cl≈Br<I<CN and that the formation of discrete anions is favoured by the presence of large, bulky cations of low, well-screened charge. Thus tetrabutylammonium appears to stabilize linear monomeric $[CuCl_2]^-$, $[CuBr_2]^-$ and $[CuBrCl]^-$ in the solid state.[1,4] In the diiodocuprate(I)[2] the anion is a centrosymmetric dimer containing trigonal-planar coordinated copper(I), whereas the dicyanocuprate(I) contains a polymeric $[Cu(CN)_2]^-$ chain.[3] In order to ascertain which factors are decisive for the suppression of polymerization of $[CuX_2]^-$ and for the attainment of a particular configuration of ligands about copper(I) (*i.e.* linear, trigonal-planar, tetrahedral, trigonal-bipyramidal), dihalocuprates(I) with cations differing in size and geometry are presently being investigated.

Since tetrabutylammonium dibromocuprate(I) contains a discrete linear $[CuBr_2]^-$ anion, it would seem that a cation of similar geometry but smaller size ought to favour the formation of a polymeric $[CuBr_2]^-$ species. The far-infrared spectrum of polycrystalline tetraethylammonium dibromocuprate(I) has been interpreted[5] as indicating a polymeric structure for the anion; this structure appears to break down on dissolution of $[N(C_2H_5)_4][CuBr_2]$ in nitromethane giving a linear centrosymmetric $[CuBr_2]^-$ anion.[5] In order to determine the nature of the anion in crystalline tetraethylammonium dibromocuprate(I), the structure of the compound has been investigated.

EXPERIMENTAL

Bis(tetraethylammonium) di-μ-bromo-dibromodicuprate(I) was prepared from tetraethylammonium bromide and copper(I) bromide according to the method of Bowmaker, Brockliss and Whiting.[5] The product was recrystallized from ethyl formate giving colourless fibrous needles. After many attempts to grow crystals sufficiently large for single-crystal X-ray measurements, a variety of solvents being tested, a crystal of dimensions 0.30×0.06×0.08 mm was finally obtained from ethyl formate solution on seeding.

Intensities were measured with a Syntex $P2_1$ diffractometer, using graphite-monochromated Mo$K\alpha$ radiation and the ω–2θ scan mode. Data were collected for $2\theta \leq 55°$ with $h \geq 0$ and $k \geq 0$, the 2θ scan rate being varied between 3.0 and 20.0° min^{-1} depending on the intensity of the reflection. Periodical measurement of the intensity of two reflections showed no abnormal fluctuation. A 96-step profile was recorded for each reflection

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and the Lehmann and Larsen profile-analysis method[6] was used to calculate the intensities.[7] In all 3244 reflections were recorded, from which a unique set of 2929 reflections was obtained, systematically absent reflections being omitted. Of these 2929 reflections, those 1328 for which $I>3.0\sigma(I)$ were regarded as being observed and were used in the subsequent calculations. Data were corrected for Lorentz and polarisation effects but not for absorption. The unit cell parameters were refined from the setting angles of 15 reflections.

CRYSTAL DATA

Bis(tetraethylammonium) di-μ-bromo-dibromodicuprate(I), $[N(C_2H_5)_4]_2[Cu_2Br_4]$, M_r= 707.2; monoclinic, systematic absences $h0l$: $l=2n+1$, $0k0$: $k=2n+1$, space group $P2_1/c$; a=8.375(2), b=13.817(5), c=11.086(5) Å, β=97.03(3)°, Z=2, D_c=1.84 g cm^{-3}, μ(Mo$K\alpha$)= 8.38 mm^{-1}. The compound crystallizes as colourless fibrous needles.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved from Patterson and successive electron density maps.[8] Full-matrix least-squares refinement[8] of the positional and isotropic thermal parameters and a scale factor gave R=0.089 for 49 parameters; inclusion of anisotropic thermal parameters reduced R to 0.060 (1328 reflections; 109 parameters). The F_o values were weighted according to $w=[\sigma^2(F_o)+0.0015F_o^2]^{-1}$. Atomic scattering factors for the uncharged atoms were taken from the *International Tables for X-Ray Crystallography*.[9] A final difference map showed a maximum electron density of 0.8 e Å^{-3}. No attempt was made to include the hydrogen atoms in the calculations. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1. Structure factors and anisotropic thermal parameters can be obtained from the authors on request.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for $[N(C_2H_5)_4]_2[Cu_2Br_4]$. 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}
Br(1)	0.2337(1)	0.1009(1)	0.2862(1)	4.25(2)
Br(2)	0.1317(2)	−0.1174(1)	0.0183(1)	4.90(3)
Cu	0.0940(2)	0.0422(1)	0.1078(1)	5.18(4)
N	0.6803(10)	−0.0835(6)	0.2880(7)	3.0(2)
C(1)	0.6027(13)	−0.1688(8)	0.3492(10)	3.7(2)
C(2)	0.4186(13)	−0.1609(9)	0.3465(11)	4.6(3)
C(3)	0.8547(12)	−0.1099(9)	0.2732(11)	4.2(2)
C(4)	0.9615(14)	−0.1286(10)	0.3967(12)	5.4(3)
C(5)	0.5938(14)	−0.0618(8)	0.1616(9)	3.9(2)
C(6)	0.5862(17)	−0.1471(9)	0.0728(11)	5.3(3)
C(7)	0.6701(13)	0.0065(7)	0.3675(9)	3.5(2)
C(8)	0.7492(15)	0.0969(8)	0.3260(11)	4.7(3)

Table 2. Interatomic distances (Å) and angles (°) within the $[Cu_2Br_4]^{2-}$ ion. Estimated standard deviations are given in parentheses. The superscript (i) denotes an atom in $-x$, $-y$, $-z$.

Cu−Br(1)	2.319(2)	Br(1)−Cu−Br(2)	125.7(1)
Cu−Br(2)	2.454(2)	Br(1)−Cu−Br(2^i)	127.9(1)
Cu−Br(2^i)	2.441(2)	Br(2)−Cu−Br(2^i)	106.3(1)
Cu···Cu^i	2.937(3)	Cu−Br(2)−Cu^i	73.7(1)

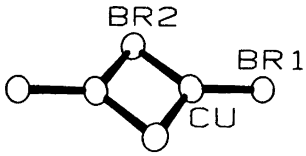

Fig. 1. The di-μ-bromo-dibromodicuprate(I) ion showing the atomic numbering. The thermal ellipsoids enclose 50 % probability.[17]

DISCUSSION

The anion in bis(tetraethylammonium) di-μ-bromodibromodicuprate(I) is a centrosymmetric dimer (Fig. 1) containing distortedly trigonal-planar coordinated copper(I). Interatomic distances and angles within the $[Cu_2Br_4]^{2-}$ ion are given in Table 2. Recently, the cation radical salt of tetrathiotetracene (TTT) with dibromocuprate(I) has been found to contain an analogous $[Cu_2Br_4]^{2-}$ anion.[10] In the latter compound there are, however, additional Cu–S contacts to the tetrathiotetracene cation radicals such that the configuration of ligands about copper(I) is approximately trigonal bipyramidal.[10] In bis(tetraethylammonium) di-μ-bromo-dibromodicuprate(I) the closest non-bonded approach distances between copper(I) and carbon and bromide and carbon are Cu···C(3^{ii})=3.56(1) Å, Br(2)···C(6)=3.80(1) Å and Br(1)···C(1^{iii})=3.84(1) Å. (Symmetry code: (*i*): $\bar{x},\bar{y},\bar{z}$; (*ii*): $x-1,y,z$; (*iii*): $1-x,\frac{1}{2}+y,\frac{1}{2}-z$.)

Copper(I) is three coordinated (Table 2) but the coordination geometry shows greater deviation from the ideal trigonal-planar configuration with respect to the Br(2)–Cu–Br(2^i) angle than is the case in the tetrathiotetracene compound[10] or in the analogous $[Cu_2I_4]^{2-}$ dimer in bis(tetrabutylammonium) di-μ-iodo-diiododicuprate(I).[2] The corresponding angles in $(TTT)_2[Cu_2Br_4]$[10] and $[N(C_4H_9)_4]_2[Cu_2I_4]$[2] are 115.4(1)° and 116.2(1)°, respectively. There is an accompanying increase in the Cu–Br(2)–Cu angle and the Cu···Cu distance (Table 2) compared to the corresponding values in $(TTT)_2[Cu_2Br_4]$, 64.7(1)° and 2.660(3) Å,[10] and in $[N(C_4H_9)_4]_2[Cu_2I_4]$, 63.8(1)° and 2.726(4) Å.[2] In bis(tetraethylammonium) di-μ-bromo-dibromodicuprate(I) the copper atom lies 0.06(1) Å from the plane defined by the three bromide ligands [Br(1), Br(2) and Br(2^i)]. In $(TTT)_2[Cu_2Br_4]$[10] and $[N(C_4H_9)_4]_2[Cu_2I_4]$[2] these distances are 0.196 Å and 0.03(3) Å, respectively.

Coordination geometry similar to that found in $[N(C_2H_5)_4]_2[Cu_2Br_4]$ has been found for the three-coordinated copper(I) in the $(CuBr)_4$ "step" structure, *e.g.* in $[P(C_6H_5)_3CuBr]_4 \cdot 2CHCl_3$ where the Br–Cu–Br angle is 110.81(8)°, Cu···Cu=2.991(2) Å and Br···Br=3.957(2) Å in the four-membered ring containing the trigonal-planar coordinated copper(I) atom.[11] Intramolecular X···X interactions have been demonstrated to be of importance for the magnitudes of the Cu–X–Cu angles and the Cu···Cu contacts in four-membered rings in the "step" (trigonal-planar and tetrahedrally coordinated copper(I))[11,12] and "cubane-like" (tetrahedrally coordinated copper(I)) structures of such compounds, *e.g.* the series $[P(C_2H_5)_3CuX]_4$, X=Cl, Br, I.[13,14,15] Thus, as X increases in size from Cl to I, the Cu···Cu distance and the Cu–X–Cu angle both decrease. The intramolecular Br(2)···Br(2) contact in bis(tetraethylammonium) di-μ-bromodibromodicuprate(I), 3.916(3) Å, is comparable with Br···Br contacts found in these compounds, *e.g.* 3.957(2) Å,[11] 3.932(1) Å.[14] It may thus be that the "more regular" copper(I) coordination geometry in $(TTT)_2[Cu_2Br_4]$ with respect to the Br–Cu–Br angle is a consequence of the steric requirements of the interactions between copper(I) and the tetrathiotetracene cation radicals.

The Cu–Br distances (Table 2) are in good general agreement with those found for $(TTT)_2[Cu_2Br_4]$, *i.e.* terminal: 2.328(2) Å, bridging: 2.472(3) and 2.490(2) Å,[10] although the bridging distances appear to be slightly shorter in the isolated dimer in the present compound. There would appear to be a somewhat larger difference between the copper(I)-terminal and

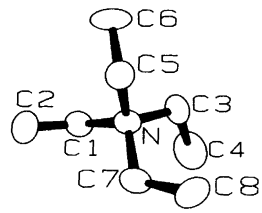

Fig. 2. The tetraethylammonium ion showing the atomic numbering. The thermal ellipsoids enclose 50 % probability.[17]

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

N–C(1)	1.54(1)	C(1)–N–C(3)	109(1)
C(1)–C(2)	1.54(2)	C(1)–N–C(5)	112(1)
N–C(3)	1.53(1)	C(1)–N–C(7)	108(1)
C(3)–C(4)	1.56(2)	C(3)–N–C(5)	108(1)
N–C(5)	1.53(1)	C(3)–N–C(7)	112(1)
C(5)–C(6)	1.53(2)	C(5)–N–C(7)	108(1)
N–C(7)	1.53(1)	N–C(1)–C(2)	114(1)
C(7)–C(8)	1.51(2)	N–C(3)–C(4)	113(1)
		N–C(5)–C(6)	115(1)
		N–C(7)–C(8)	116(1)

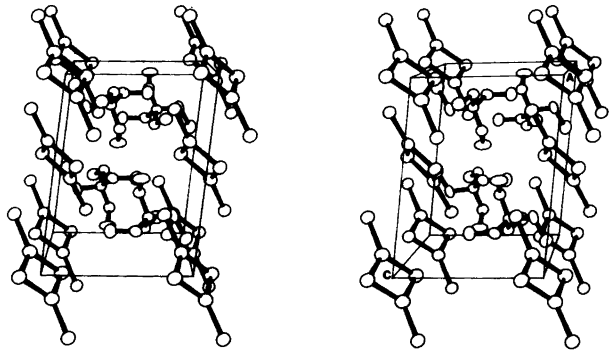

Fig. 3. Stereoscopic view[17] of the unit cell. The thermal ellipsoids enclose 50 % probability.

copper(I)-bridging ligand distances in $[Cu_2Br_4]^{2-}$ than is the case for $[Cu_2I_4]^{2-}$ (see Refs. 2, 10, this work). Both sets of Cu–Br distances, *i.e.* terminal and bridging, are intermediate between that found for linear Cu(I)–Br coordination, 2.226(1) Å,[1] and that in $[Cu(NH_3)_4][CuBr_2]_2$, 2.503(4) Å,[16] in which the anion is an infinite chain of edge-sharing Cu(I)–Br tetrahedra.

The tetraethylammonium ion (Fig. 2, Table 3) shows no unusual features. The packing of cations and anions is illustrated in Fig. 3. The closest contacts between bromide and carbon and, in particular, between copper(I) and carbon, *viz.* Cu···C(3)=3.56(1) Å, are somewhat shorter than those found in tetrabutylammonium dibromocuprate(I).[1]

The investigation would thus appear to confirm that bulky cations with low well-screened charge tend to stabilize formation of discrete $[CuX_2]^-$ ions in the solid state. Unlike tetrabutylammonium, tetraethylammonium appears to be insufficient for complete suppression of polymerization of $[CuBr_2]^-$, although it does appear to suppress catenation.

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