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Crystal Structure of Tris(tetramethylammonium) μ-Bromo-bis[dibromocuprate(I)], $[N(CH_3)_4]_3[Cu_2Br_5]$

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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. $[N(CH_3)_4]_3[Cu_2Br_5]$ crystallizes in space group $C2/c$ with a=14.119(6), b=11.246(5), c=15.178(4) Å, β=95.12(3)°, at 170 K, and Z=4. Full-matrix least-squares refinement of 101 structural parameters gave R=0.057 for 1440 observed [$I>3.0\sigma(I)$] reflections. The $[Cu_2Br_5]^{3-}$ ion is a discrete, Br-bridged entity containing approximately trigonal-planar coordinated copper(I), the bridging bromide ligand being situated on a twofold axis. The angle subtended by the copper(I) atoms at the bridging ligand is 72.8(1)°; Cu···Cu=2.837(4) Å, Cu–$Br_{bridging}$=2.392(3) Å and Cu–$Br_{terminal}$=2.381(3) and 2.397(2) Å.

In tetrabutylammonium dibromocuprate(I) the anion is a linear monomer;[1] in the compounds obtained with tetrapropylammonium and tetraethylammonium as cations, *viz.* $[N(C_3H_7)_4]_2[Cu_4Br_6]$[2] and $[N(C_2H_5)_4]_2[Cu_2Br_4]$,[3] copper(I) is, however, three-coordinated. Unlike some of the tetraalkylammonium chlorocuprates(I)[4] and iodocuprates(I),[5–7] all the crystalline tetraalkylammonium bromocuprates(I) prepared hitherto contain discrete anions.[1–3] $(NH_4)_2[CuBr_3]$, however, contains chains of Cu(I)–Br tetrahedra sharing corners.[8] During investigation of the tetramethylammonium-bromocuprate(I) system, crystals of $[N(CH_3)_4]_3[Cu_2Br_5]$ have been prepared and a structural determination undertaken.

In crystalline tetraalkylammonium chlorocuprates(I) and iodocuprates(I), anions have been encountered as discrete species or as infinite chains: Whereas tetrabutylammonium dichlorocuprate(I) contains a linear monomeric anion,[1] in $[N(C_2H_5)_4]_3[Cu_7Cl_{10}]$ the anion is an infinite chain composed of two- and three-coordinated copper(I).[4] As far as the tetraalkylammonium-iodocuprate(I) system is concerned, a $[Cu_2I_4]^{2-}$ dimer occurs in the tetrabutylammonium compound,[9] and both a $[Cu_2I_4]^{2-}$ dimer[10] and a $[Cu_3I_4]^-$ chain[5] have been described with tetrapropylammonium as cation. A $[Cu_2I_3]^-$ chain has been reported for the tetraethylammonium compound[6] and also obtained with tetramethylammonium as cation.[7] In the $[Cu_2I_4]^{2-}$ dimer copper(I) is three-coordinated,[9,10] whereas both the $[Cu_3I_4]^-$ and $[Cu_2I_3]^-$ chains can be described in terms of shared Cu(I)–I tetrahedra.[5–7]

EXPERIMENTAL

Tris(tetramethylammonium) μ-bromo-bis[dibromocuprate(I)] was prepared by adding copper(I) bromide (5 mmol) to a solution of tetramethylammonium bromide (5 mmol) in

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boiling ethanol (150 ml). The mixture was boiled gently; the solution was filtered while hot to remove undissolved copper(I) bromide, cooled slowly to room temperature and allowed to stand. Colourless prisms of $[N(CH_3)_4]_3[Cu_2Br_5]$ were deposited after a few days.

Crystals of $[N(CH_3)_4]_3[Cu_2Br_5]$, M_r=749.0, are monoclinic, space group $C2/c$, (No. 15,[11a]) with a=14.119(6), b=11.246(5), c=15.178(4) Å, β=95.12(3)° at 170 K, Z=4, D_c=2.07 g cm^{-3} and μ(Mo$K\alpha$)=10.65 mm^{-1}. Diffracted intensities from a crystal, 0.05×0.16×0.04 mm, were measured at approximately 170 K for $2\theta < 50°$ on 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 2.0–12.0° 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 method[12] was used to calculate the intensities.[13] Of the 2134 independent reflections thus measured, 1440 had $I>3.0\sigma(I)$ and were used in subsequent calculations. Intensities were corrected for Lorentz and polarisation effects; an empirical correction[14] was made for the effects of absorption after solution of the structure. The unit-cell parameters were determined from diffractometer setting angles for 15 reflections.

STRUCTURE DETERMINATION AND REFINEMENT

The positions of the copper and bromine atoms were determined by direct methods (MULTAN 80).[15] The tetramethylammonium ions were located from the subsequent electron density map.[16] Full-matrix least-squares refinement[16] of positional and isotropic thermal parameters gave R=0.071; after an empirical correction[14] for the effects of absorption R=0.068. Inclusion of anisotropic thermal parameters for all atoms yielded a final R=0.057 (101 parameters; 1440 reflections). Comparable refinement based on the data uncorrected for absorption effects gave R=0.059. Hydrogen atoms were not located. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*[11b] and the F_o values were weighted according to $w=[\sigma^2(F_o)+0.0003F_o^2]^{-1}$. A final difference map[16] showed a maximum electron density of 1.1 eÅ^{-3}. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1. Structure factors and anisotropic thermal parameters may be obtained from the authors.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in $[N(CH_3)_4]_3[Cu_2Br_5]$. 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	0.0665(1)	0.2994(2)	0.6853(1)	2.38(5)
Br(1)	−0.0240(1)	0.2006(1)	0.5658(1)	2.19(4)
Br(2)	0.2279(1)	0.2399(1)	0.7164(1)	2.26(4)
Br(3)	0.0000	0.4707(2)	0.7500	2.69(6)
N(1)	0.0000	0.0951(13)	0.2500	0.9(4)
C(1)	0.0886(10)	0.0165(14)	0.2532(9)	2.4(4)
C(2)	0.0014(11)	0.1714(16)	0.3319(9)	2.9(5)
N(2)	0.2823(8)	0.0028(10)	0.0105(7)	1.7(3)
C(3)	0.2644(12)	0.0838(15)	0.0846(10)	3.1(5)
C(4)	0.2972(11)	0.0760(14)	−0.0718(10)	2.6(4)
C(5)	0.1996(11)	−0.0747(14)	−0.0087(9)	2.2(4)
C(6)	0.3727(12)	−0.0631(17)	0.0317(12)	4.0(5)

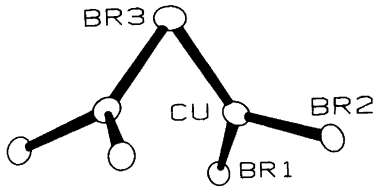

Fig. 1. The $[Cu_2Br_5]^{3-}$ion. Thermal ellipsoids enclose 50 % probability.[20]

Table 2. Interatomic distances (Å) and angles (°) within the $[Cu_2Br_5]^{3-}$ion. Estimated standard deviations are given in parentheses. Symmetry code: (*i*):$\bar{x},y,1\frac{1}{2}-z$.

Cu–Br(1)	2.397(2)	Br(1)–Cu–Br(2)	117.1(1)
Cu–Br(2)	2.381(3)	Br(1)–Cu–Br(3)	118.8(1)
Cu–Br(3)	2.392(3)	Br(2)–Cu–Br(3)	123.3(1)
Cu···Cu^i	2.837(4)	Cu–Br(3)–Cu^i	72.8(1)

DISCUSSION

There would appear to be no previous structural determination of a $[Cu_2Br_5]^{3-}$ ion. A planar μ-chloro-bis[dichloroargentate(I)] ion has, however, been determined in $(NH_4)_6[AuCl_4]_3[Ag_2Cl_5]$.[17] Unlike $[Ag_2Cl_5]^{3-}$, the $[Cu_2Br_5]^{3-}$ ion is folded about the bridging ligand (Fig. 1, Table 2), the planes through Br(1), Br(2) and Br(3) and Br(1^i), Br(2^i) and Br(3) being inclined at an angle of 76.28(6)° [Symmetry code: (*i*): $\bar{x},y,1\frac{1}{2}-z$]. The configuration of bromine atoms about copper(I) is approximately trigonal planar (Table 2) with Cu displaced 0.123(2) Å, towards Cu^i, from the plane through Br(1), Br(2) and Br(3). Terminal and bridging Cu–Br distances do not differ (Table 2); in the $[Cu_2Br_4]^{2-}$ [3,18] and $[Cu_2I_4]^{2-}$ dimers [9,10,19] determined hitherto, bridging copper(I)-ligand distances are significantly longer than terminal. Copper(I)-bromine distances in $[Cu_2Br_5]^{3-}$ are intermediate between terminal and bridging distances in $[Cu_2Br_4]^{2-}$, *e.g.* $Cu-Br_{terminal}$= 2.319(2) Å and $Cu-Br_{bridging}$=2.441(2) and 2.454(2) Å in $[N(C_2H_5)_4]_2[Cu_2Br_4]$.[3] In $[N(C_3H_7)_4]_2[Cu_4Br_6]$, which contains Cu–Br–Cu bridges only, distances range from 2.373(5) to 2.422(5) Å.[2]

The tetramethylammonium ions (Fig. 2, Table 3) show no unusual geometrical features. The closest contacts between anion and cation are: Br(2)···C(1^{ii})= 3.56(2) Å and Cu···C(1^{ii})= 3.70(2) Å [symmetry code: (*ii*): $x,\bar{y},\frac{1}{2}+z$]. The Br···C contact is comparable to the closest Br···C in $[N(C_3H_7)_4]_2[Cu_4Br_6]$, 3.61(5) Å,[2] whereas Cu···C is intermediate between the shortest distances of this kind determined in the tetrapropylammonium[2] and tetraethylammonium[3] compounds, *viz.* 3.52(5) and 3.56(1) Å, respectively, and that in tetrabutylammonium dibromocuprate(I), *viz.* 3.757(5) Å.

Some structural features of the crystalline tetraalkylammonium bromocuprates(I) investigated hitherto are summarized in Table 4. In the tetrabutylammonium compound, copper(I) exhibits linear coordination geometry, whereas in the compounds containing the smaller cations copper(I) is three-coordinated; all four anions are discrete entities. The copper(I)–copper(I) separation and the angles subtended by copper(I) at the bridging ligand are similar in $[Cu_4Br_6]^{2-}$, $[Cu_2Br_4]^{2-}$ and $[Cu_2Br_5]^{3-}$ even though $[Cu_2Br_5]^{3-}$ lacks the geometric constraints imposed by the bridges in $[Cu_4Br_6]^{2-}$ and $[Cu_2Br_4]^{2-}$.[2,3]

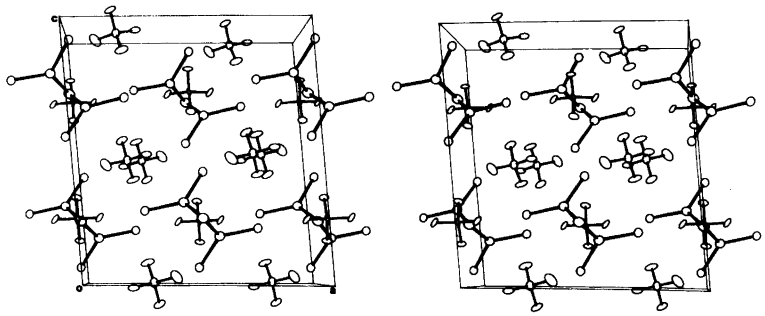

Fig. 2. Stereoscopic view[20] of the unit cell. Thermal ellipsoids enclose 50 % probability.

Previous structural investigations[1-4,9,10,19,21] would appear to indicate that large cations with low, well-screened positive charge tend to suppress −X−Cu−X−catenation (X=Cl,Br,I) in the solid state, favouring the formation of discrete anions. There would also seem to be a tendency towards increased coordination number of copper(I) with decreasing size of and less well-screened positive charge on the cation from two to three in the tetraalkylammonium chlorocuprates(I)[1,4] and bromocuprates(I) (Table 4) investigated hitherto. Hartl and Mahdjour-Hassan-Abadi have demonstrated 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

Table 3. Interatomic distances (Å) and angles (°) within the tetramethylammonium ions. Estimated standard deviations are given in parentheses. Symmetry code: (*i*): $\bar{x}$, $y,\frac{1}{2}-z$.

N(1)−C(1)	1.53(2)	N(2)−C(4)	1.53(2)
N(1)−C(2)	1.51(2)	N(2)−C(5)	1.46(2)
N(2)−C(3)	1.49(2)	N(2)−C(6)	1.49(2)
C(1)−N(1)−C(1^i)	109(1)	C(3)−N(2)−C(5)	109(1)
C(1)−N(1)−C(2)	111(1)	C(3)−N(2)−C(6)	110(1)
C(1)−N(1)−C(2^i)	108(1)	C(4)−N(2)−C(5)	109(1)
C(2)−N(1)−C(2^i)	111(2)	C(4)−N(2)−C(6)	106(1)
C(3)−N(2)−C(4)	110(1)	C(5)−N(2)−C(6)	114(1)

Table 4. Selected structural features of some crystalline tetraalkylammoniumbromocuprates(I). A bridging bromide ligand is denoted Br_b. Estimated standard deviations are given in parentheses.

Cation	Anion	Copper(I) coord. geometry	Cu···Cu (Å)	Cu−Br_b−Cu (°)	CuBr:Br^- ratio	Ref.
$N(C_4H_9)_4^+$	$[CuBr_2]^-$	linear	–	–	1:1	1
$N(C_3H_7)_4^+$	$[Cu_4Br_6]^{2-}$	trig. planar	2.718(7)−2.750(7)	69.0(2)−70.2(2)	1:0.5	2
$N(C_2H_5)_4^+$	$[Cu_2Br_4]^{2-}$	trig. planar	2.937(3)	73.7(1)	1:1	3
$N(CH_3)_4^+$	$[Cu_2Br_5]^{3-}$	trig. planar	2.837(4)	72.8(1)	1:1.5	present work

I^-:CuI ratio.[5] Smaller cations, on the other hand, tend to favour the formation of infinite chains of edge- and/or face-sharing Cu(I)–I tetrahedra with higher negative charge density.[5] As is seen from Table 4, the discrete three-coordinated bromocuprates(I) obtained with the tetrapropylammonium, tetraethylammonium and tetramethylammonium cations, respectively, would appear to follow a similar trend.

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