A New Bromocuprate(I) Cluster: Structure of Tris(methyltriethylammonium) Octa-μ-bromo-μ_4-bromo-hexacuprate(I), $[N(CH_3)(C_2H_5)_3]_3[Cu_6Br_9]$

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A new bromocuprate(I) cluster has been prepared as the title compound and its structure determined from single-crystal X-ray diffraction data, measured at 290 K. $[N(CH_3)(C_2H_5)_3]_3[Cu_6Br_9]$ crystallizes in space group *Cmcm* with a = 11.591(8), b = 16.640(13), c = 21.250(11) Å and Z = 4. Full-matrix least-squares refinement of 111 structural parameters gave R = 0.052 for 1164 observed $[I > 3.0\sigma(I)]$ independent reflections. Tris(methyltriethylammonium) octa-μ-bromo-μ_4-bromo-hexacuprate(I) contains a discrete $[Cu_6Br_9]^{3-}$ cluster containing four four-coordinated and two two-coordinated copper(I) centres. The anion has C_{2v} symmetry and can be visualized in terms of four edge-sharing Cu-Br tetrahedra, two pairs of such tetrahedra each being further connected by a two-coordinated copper(I) atom situated between vertices. The Cu–Br distances associated with the four-coordinated copper(I) centre are 2.386(3), 2.472(3), 2.528(2) and 2.697(3) Å. The two-coordinated copper(I) atom is situated on a mirror plane and has a Cu–Br distance of 2.285(2) Å and a Br–Cu–Br angle of 162.6(1)°, with an additional bromide ligand at 2.866(4) Å. This copper(I) centre can thus alternatively be considered as being (2+1) coordinated. The closest Cu···Cu separations are 2.650(3) and 2.862(4) Å.

In bromocuprates(I) crystallizing with unsymmetrically substituted quaternary ammonium and phosphonium cations, the coordination number of copper(I) in the anion has been found to increase with increasing concentration of bromide ligand in the crystalline phase and with decreasing overall size of the cation.[1-6] This trend would, however, appear to be somewhat less marked than that observed for bromocuprates(I) crystallizing with symmetrically substituted ammonium and phosphonium cations (Ref. 7 and references therein). Thus a $[Cu_4Br_6]^{2-}$ aggregate, containing trigonal-planar coordinated copper(I), has been isolated with butyltriphenylphosphonium as cation, crystals containing a linear, monomeric $[CuBr_2]^-$ anion being deposited towards the end of the crystallization.[1] Monomeric $[CuBr_2]^-$ anions have also been obtained in the propyltriphenylphosphonium and ethyltriphenylphosphonium compounds.[2,3] Three different compounds have been prepared from copper(I) bromide and methyltriphenylphosphonium bromide, viz. $[P(CH_3)(C_6H_5)_3]_2[CuBr_3]$, containing a mononuclear anion in which copper(I) is trigonal-planar coordinated, $[P(CH_3)(C_6H_5)_3]_2[CuBr_2]Br$ containing a discrete $[CuBr_2]^-$ monomer, and a compound of stoichiometry $[P(CH_3)(C_6H_5)_3][CuBr_2]$ whose far-IR spectrum indicated that the compound did not contain a monomeric anion.[8] Recently, the anion in this last compound has been shown to be a dinuclear $[Cu_2Br_4]^{2-}$ species, containing three-coordinated copper(I).[4] A similar $[Cu_2Br_4]^{2-}$ ion is present in bis(phenyltrimethylammonium) di-μ-bromo-dibromodicuprate(I),[5] whereas the methyltributylammonium compound contains a discrete $[Cu_5Br_7]^{2-}$ cluster which can be described as a distorted pentagonal bipyramidal cage of bromide ions, containing two (2+2)-coordinated and three (3+1)-coordinated copper(I) atoms.[6] We now wish to report the preparation and crystal structure determination of a new bromocuprate(I) species isolated with the methyltriethylammonium cation.

Experimental

Preparation of tris(methyltriethylammonium) octa-μ-bromo-μ_4-bromo-hexacuprate(I). All operations were carried out under nitrogen. Methyltriethylammonium bromide (0.098 g; 0.50 mmol) [Alfa (Ventron)] was dissolved in a mixture of 40 ml of ethanol and 20 ml of dichloromethane by stirring and heating gently. Copper(I) bromide (0.072 g; 0.50 mmol) [Aldrich 99.999 % Gold Label] was added, and stirring and heating were continued until all the solid had dissolved. The resulting solution was allowed to evaporate slowly, colourless, truncated pyramidal prisms of $[N(CH_3)(C_2H_5)_3]_3[Cu_6Br_9]$, m.p. 109–110°C, being obtained after 1–4 days. At the commencement of crystallization, colourless, irregular-shaped plates were deposited. These were shown, by means of Weissenberg and rotation photographs, to be identical with the prisms, a crystal with

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Table 1. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in $[N(CH_3)(C_2H_5)_3]_3[Cu_6Br_9]$. B_{eq} is defined as $\frac{8\pi^2}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$. Estimated standard deviations are given in parentheses.

Atom	Site	*x*	*y*	*z*	B_{eq}
Cu(1)	16*h*	0.1380(2)	0.1406(1)	0.6827(1)	6.01(6)
Cu(2)	8*f*	0.0000	0.0681(2)	0.6010(1)	5.45(7)
Br(1)	4*c*	0.0000	0.0424(1)	0.7500	3.56(6)
Br(2)	16*h*	0.1949(1)	0.0512(1)	0.59168(6)	4.59(4)
Br(3)	8*f*	0.0000	0.2352(1)	0.63387(8)	3.83(5)
Br(4)	8*g*	0.2874(1)	0.1890(1)	0.7500	4.07(5)
N(1)	4*c*	0.0000	0.4505(12)	0.7500	4.8(6)
C(10)	8*g*	0.1023(13)	0.3930(10)	0.7500	3.9(5)
C(11)[a]	8*g*	0.2162(21)	0.4346(13)	0.7500	4.5(7)
C(12)	8*f*	0.0000	0.5073(10)	0.6929(10)	4.9(5)
C(13)[a]	8*f*	0.0000	0.4671(17)	0.6299(15)	6.4(9)
N(2)	8*f*	0.0000	0.2000(8)	0.4098(6)	3.9(4)
C(20)	16*h*	0.1040(10)	0.1690(8)	0.4489(6)	5.0(4)
C(21)	16*h*	0.2220(11)	0.1944(10)	0.4213(7)	6.8(5)
C(22)	8*f*	0.0000	0.2883(11)	0.4017(9)	5.0(5)
C(23)	8*f*	0.0000	0.3347(12)	0.4651(10)	6.5(7)
C(24)	8*f*	0.0000	0.1616(12)	0.3429(8)	5.2(6)

[a]Site occupancy 0.375.

the latter form being selected for the measurement of intensity data.

Crystal data and data collection. $[N(CH_3)(C_2H_5)_3]_3[Cu_6Br_9]$, M_r = 1449.1, $F(000)$ = 2760, orthorhombic, space group *Cmcm* (No. 63),[9a] a = 11.591(8), b = 16.640(13), c = 21.250(11) Å, Z = 4, D_c = 2.35 g cm^{-3}, μ(Mo*K*α) = 12.48 mm^{-1}, λ(Mo*K*α) = 0.71069 Å. Preliminary unit-cell dimensions and possible space groups [viz. *Cmcm* (No. 63), $Cmc2_1$, (No. 36), *Ama*2 (No. 40)][9a] were determined from rotation and Weissenberg photographs. Diffracted intensities from a crystal, 0.19×0.19×0.18 mm, were measured at approximately 290 K for $2\theta \leq 50°$ with a Syntex $P2_1$ diffractometer, using graphite-monochromated Mo*K*α radiation and the ω-2θ scan mode, with a variable 2θ scan rate of 2.0–15.0° min^{-1}. A 96-step profile was recorded for each reflection, and the intensities were calculated[10] using the Lehmann and Larsen profile-analysis method.[11] Of the 1959 independent reflections measured, excluding those systematically absent, 1164 had $I > 3\sigma(I)$ and were considered observed. Correction was made for Lorentz and polarisation effects; an empirical correction for the effects of absorption[12] was made after solution of the structure (min., max. and average absorption correction factors = 0.79, 1.46 and 0.98, respectively). Unit-cell dimensions were determined from diffractometer setting angles for 15 reflections.

Structure determination and refinement. The structure was solved by direct methods (MITHRIL,[13] DIRDIF[14]) in space group *Cmcm* (No. 63),[9a] which implies orientational disorder of one of the cations [N(1), C(10)–C(13)] with respect to the methyl group and an ethyl group. C(11) and C(13) were therefore assigned site occupancy factors of 0.375 in 8*g* and 8*f*, respectively. Since intensity statistics[13] were clearly consistent with the presence of a centre of

Table 2. Interatomic distances (Å) and angles (°) within the $[Cu_6Br_9]^{3-}$ cluster. Symmetry code: (*i*): -*x*, *y*, *z*; (*ii*): *x*, *y*, 1½-*z*; (*iii*): -*x*, *y*, 1½-*z*.

Cu(1)–Br(1)	2.697(3)	Cu(2)···Br(3)	2.866(4)
Cu(1)–Br(2)	2.528(2)	Cu(2)···Br(1)	3.195(3)
Cu(1)–Br(3)	2.472(3)	Cu(1)···Cu(1^i)	3.199(4)
Cu(1)–Br(4)	2.386(3)	Cu(1)···Cu(1^{ii})	2.862(4)
Cu(2)–Br(2)	2.285(2)	Cu(1)···Cu(2)	2.650(3)
Br(1)–Cu(1)–Br(2)	101.7(1)	Br(2)–Cu(2)···Br(3)	98.1(1)
Br(1)–Cu(1)–Br(3)	103.0(1)	Cu(1)–Br(1)–Cu(1^i)	72.7(1)
Br(1)–Cu(1)–Br(4)	108.5(1)	Cu(1)–Br(1)–Cu(1^{ii})	64.1(1)
Br(2)–Cu(1)–Br(3)	102.9(1)	Cu(1)–Br(1)–Cu(1^{iii})	105.4(1)
Br(2)–Cu(1)–Br(4)	117.9(1)	Cu(1)–Br(2)–Cu(2)	66.6(1)
Br(3)–Cu(1)–Br(4)	120.4(1)	Cu(1)–Br(3)–Cu(1^i)	80.6(1)
Br(2)–Cu(2)–Br(2^i)	162.6(1)	Cu(1)–Br(4)–Cu(1^{ii})	73.7(1)

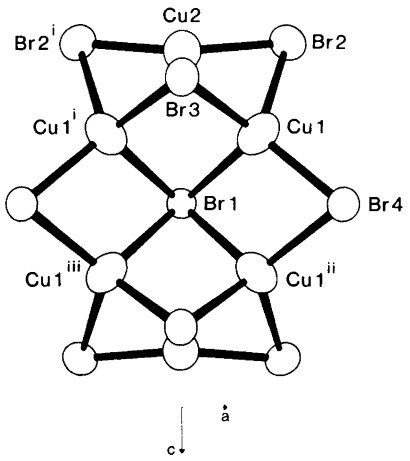

Fig. 1a

Fig. 1. (a) The $[Cu_6Br_9]^{3-}$ ion in $[N(CH_3)(C_2H_5)_3]_3[Cu_6Br_9]$, showing the crystallographic numbering. For symmetry code, see Table 2. The thermal ellipsoids enclose 50 % probability.[17] (b) View of the anion in Fig. 1a, seen approximately along the *a* axis with the *b* axis vertical.

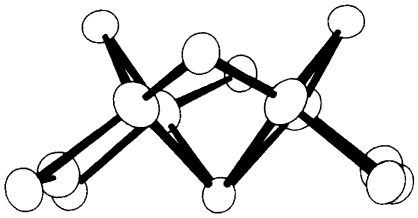

Fig. 1b

symmetry, it was not considered profitable to attempt to refine the structure in either of the acentric space groups (*Ama*2, No. 40, or $Cmc2_1$, No. 36)[9a] which might permit an ordered description of this cation. Full-matrix least-squares refinement of positional and isotropic thermal parameters gave $R = 0.089$; after an empirical correction for the effects of absorption,[12] $R = 0.083$. Inclusion of anisotropic thermal parameters gave a final $R = 0.052$, $R_w = 0.060$, for 111 parameters and 1164 observed, independent reflections; $(\Delta/\sigma)_{max} = 0.005$. If C(13) [$B_{eq} = 6.4(9)$ Å^2] was assigned an occupancy factor of 0.25 in 8*f* and C(11) was considered to be ordered, a value of $R = 0.054$ was obtained, which indicated further that the model based on *Cmcm* provides the most satisfactory description of the structure. Refinement of this model based on data uncorrected for absorption gave $R = 0.057$. Hydrogen atoms were not included in the refinement. A final difference map showed a maximum residual electron density of 0.98 e Å^{-3}. Atomic scattering factors were taken from Ref. 9b, and the F_o values were weighted according to $w = [\sigma^2(F_o) + 0.0005F_o^2]^{-1}$. The computer programs employed are described in Refs. 15 and 16. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1. Lists of structure factors, anisotropic thermal parameters and connectivity relationships within the cations may be obtained from the authors on request.

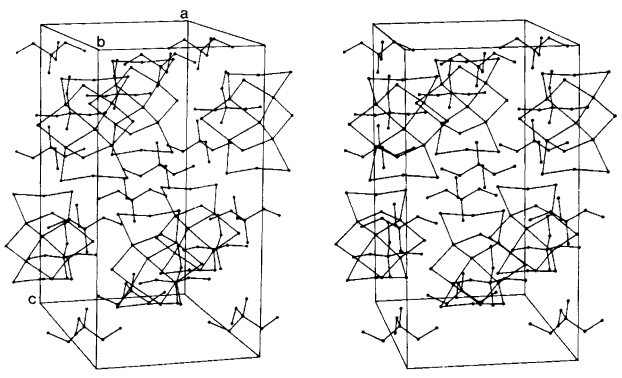

Fig. 2. Stereoscopic view[17] of the structure of $[N(CH_3)(C_2H_5)_3]_3[Cu_6Br_9]$. All atoms are represented as spheres of radius 0.05 Å. The disordered cation [N(1), C(10)–C(13)] has been drawn in one of the possible ordered orientations.

Discussion

The $[Cu_6Br_9]^{3-}$ cluster in tris(methyltriethylammonium) octa-μ-bromo-μ_4-bromo-hexacuprate(I) is depicted in Fig. 1, and interatomic distances and angles within the anion are given in Table 2. Cu(1) is seen to be approximately tetrahedrally coordinated, while Cu(2) can be described as being two- or, alternatively, (2+1)-coordinated. The anion has C_{2v} (*m*2*m*) symmetry and can be visualized as being composed of four edge-sharing Cu-Br tetrahedra, two pairs of tetrahedra each also being linked by a two-coordinated copper(I) atom situated between vertices. Apart from the Cu(1)–Br(4) distance (2.386(3) Å), which is similar to the distance determined for the mononuclear trigonal $[CuBr_3]^{2-}$ ion in $[P(CH_3)_4]_2[CuBr_3]$ (2.365(3) Å),[7] the Cu–Br distances associated with the four-coordinated copper(I) centre (Table 2) are comparable with those determined for bromocuprates(I) containing tetrahedrally coordinated copper(I).[18–22] The two-coordinated copper(I) atom, Cu(1), exhibits a coordination geometry closely resembling that of the copper(I) atom in the bent monomer in [TSeT][$CuBr_2$] (TSeT = tetraselenotetracene), in which the Cu–Br distances are 2.267(2) and 2.282(3) Å and the Br–Cu–Br angle is 153.8(1)°, there being an additional Cu···Br contact of 2.829(2) Å to a neighbouring $[CuBr_2]^-$ ion.[23] The shortest Cu···Cu contact in $[Cu_6Br_9]^{3-}$, viz. 2.650(3) Å, is similar to that in the dinuclear $[Cu_2Br_4]^{2-}$ ion in $[TTT]_2[Cu_2Br_4]$, 2.660(3) Å,[24] (TTT = tetrathiotetracene), but longer than the Cu···Cu contacts in the $[Cu_5Br_7]^{2-}$ cluster [2.566(7)–2.637(6) Å].[6]

The structure is illustrated in Fig. 2, the disordered cation having been drawn in one of the possible ordered orientations. Bond distances and angles within both cations

Table 3. Coordination of copper(I) in bromocuprates(I) crystallizing with unsymmetrically substituted ammonium and phosphonium cations. [Br] is the concentration (mol dm^{-3}) of bromide ligand in the crystalline phase.

Cation	Anion	Coord. No. of Cu(I)	[Br]	Ref.
$P(C_4H_9)(C_6H_5)_3^+$	$[Cu_4Br_6]^{2-}$	3	7.8	1
	$[CuBr_2]^-$	2	5.7	1
$P(C_3H_7)(C_6H_5)_3^+$	$[CuBr_2]^-$	2	6.2	2
$P(C_2H_5)(C_6H_5)_3^+$	$[CuBr_2]^-$	2	6.5	3
$P(CH_3)(C_6H_5)_3^+$	$[CuBr_3]^{2-}$	3		8
	$[CuBr_2]^-$	2		8
	$[Cu_2Br_4]^{2-}$	3	6.8	4
$N(CH_3)(C_4H_9)_3^+$	$[Cu_5Br_7]^{2-}$	2x(2+2) 3x(3+1)	11.2	6
$N(C_6H_5)(CH_3)_3^+$	$[Cu_2Br_4]^{2-}$	3	10.8	5
$N(CH_3)(C_2H_5)_3^+$	$[Cu_6Br_9]^{3-}$	2x(2+1) 4x4	14.6	This work

are normal. The shortest distances between bromide and carbon are Br(3)···C(21^{iv}) and Br(3)···C(21^{v}) = 3.62(1) Å [symmetry code: (*iv*): *x*-½, ½-*y*, 1-*z*; (*v*): ½-*x*, ½-*y*, 1-*z*]. There are no copper(I)-carbon distances less than 3.8 Å.

The coordination number of copper(I) in bromocuprate(I) anions, documented hitherto in compounds containing unsymmetrically substituted quaternary ammonium and phosphonium cations, is shown in Table 3 as a function of decreasing overall cation size, estimated from volume increments for the various substituents.[25] As in bromocuprates(I) crystallizing with symmetrically substituted quaternary ammonium and phosphonium ions,[7] the coordination number of copper(I) increases with increasing concentration of bromide ligand in the crystalline phase (Table 3). Correlation between the copper(I) coordination number and decreasing overall volume of the cation, seems, however, to be somewhat less pronounced. By comparison of volume increments for the relevant substituents,[25] the methyltriethylammonium cation is estimated to have an overall volume approximately 4 $Å^3$ less than that of phenyltrimethylammonium. Despite the similarity in overall size, the cations differ, however, considerably in shape, and form compounds containing very different bromocuprate(I) species. The symmetrically substituted quaternary ammonium cation closest in size to methyltriethylammonium, and, moreover, of similar shape, i.e. tetraethylammonium, crystallizes with a dinuclear $[Cu_2Br_4]^{2-}$ ion containing three-coordinated copper(I),[26] analogous to that obtained with phenyltrimethylammonium (Table 3), the concentration of bromide ligand in crystalline bis(tetraethylammonium) di-μ-bromo-dibromodicuprate(I) being 10.4 mol dm^{-3}. In this context, it is, perhaps, somewhat surprising that the methyltriethylammonium bromocuprate (I) contains a $[Cu_6Br_9]^{3-}$ cluster.

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