Coordination of Copper(I) in Bis(tetramethylphosphonium) Tribromocuprate(I) and Bis(tetraethylphosphonium) Di-μ-bromo-dibromodicuprate(I); Comparison of Anionic Configurations in Bromocuprates(I) Crystallizing with Symmetrical Tetraalkylammonium and Related Cations

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The title compounds have been prepared and their structures have been determined from single-crystal X-ray diffraction data. $[P(CH_3)_4]_2[CuBr_3]$ crystallizes in space group $R32$ with $a = 7.878(8)$ Å, $\alpha = 79.08(8)°$ and $Z = 1$. Full-matrix least-squares refinement of 23 structural parameters gave $R = 0.040$ for 374 observed $[I > 3.0\sigma(I)]$ independent reflections, measured at 170 K. The anion is a discrete $[CuBr_3]^{2-}$ entity with D_{3h} symmetry and a Cu–Br distance of 2.365(3) Å. $[P(C_2H_5)_4]_2[Cu_2Br_4]$ crystallizes in space group $P2_1/n$ with $a = 12.545(13)$, $b = 8.300(4)$, $c = 14.629(11)$ Å, $\beta = 110.76(6)°$ and $Z = 2$. Full-matrix least-squares refinement of 109 structural parameters gave $R = 0.068$ for 956 observed $[I > 3.0\sigma(I)]$ independent reflections measured at 290 K. The $[Cu_2Br_4]^{2-}$ anion is a centrosymmetric dimer containing approximately trigonal-planar coordinated copper(I). The Cu–Br(terminal) distance is 2.263(4) Å, the Cu–Br(bridging) distances are 2.423(4) and 2.436(3) Å and the Cu···Cu separation 2.870(5) Å. The anionic configurations in tetraphenylphosphonium and symmetrical tetraalkylammonium and tetraalkylphosphonium bromocuprates(I) are compared and the coordination number of copper(I) discussed in terms of the degree of dilution imposed on the bromide ligands by the cations in the crystalline phase.

Bromocuprates(I) crystallizing with tetraphenylphosphonium and with symmetrical tetraalkylammonium cations have been found to contain discrete anions in which copper(I) is two- or three-coordinated.[1–5] Correlation of the concentration of halide ligand in crystalline halocuprates(I), containing such cations, with the coordination number of copper(I) in the anion formed suggests that dilution of the ligands by the cations is a determinative factor for the attainment of a particular copper(I) coordination number and thus for the resulting anionic configuration.[6] In order to examine this effect further, bromocuprates(I) have been prepared using the tetraethylphosphonium and tetramethylphosphonium cations, intermediate in size between tetrapropylammonium and tetraethylammonium and between tetraethylammonium and tetramethylammonium, respectively. Both cations were expected to yield three-coordinated bromocuprate(I) species (cf. Ref. 6); it was, however, considered of interest to determine the structures of

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the resulting anions in order to investigate possible trends in the stoichiometry of the three-coordinated bromocuprate(I) species as a function of cation size.

Experimental

Bis(tetramethylphosphonium) tribromocuprate(I) was prepared by dissolving 0.1 mmol of tetramethylphosphonium bromide [Alfa (Ventron)] in 45 ml of ethanol under nitrogen, by stirring and heating gently. 0.1 mmol of copper(I) bromide [Aldrich 99.999 % Gold Label] was then added and stirring and heating were continued until all the solid had dissolved. The resulting solution was filtered and allowed to evaporate slowly at room temperature under nitrogen. Colourless, irregular-shaped plates, m.p. 220–221 °C, were obtained after 1–3 days. Bis(tetramethylphosphonium) di-μ-bromo-dibromodicuprate(I) was prepared in a similar manner, using 0.075 mmol of tetramethylphosphonium bromide [Alfa (Ventron)], 0.075 mmol of copper(I) bromide and 45 ml of ethanol. Colourless striated needles, m.p. 169–170 °C, were obtained after approximately 3 days.

Crystal and experimental data for the two compounds are given in Table 1. Space groups and preliminary unit cell dimensions were determined from rotation and Weissenberg photographs. Diffracted intensities were measured with a Syntex $P2_1$ diffractometer, using graphite-monochro-

Table 1. Crystal and experimental data for bis(tetramethylphosphonium) tribromocuprate(I) and bis(tetraethylphosphonium) di-μ-bromo-dibromodicuprate(I).

	$[P(CH_3)_4]_2[CuBr_3]$	$[P(C_2H_5)_4]_2[Cu_2Br_4]$
M_r	485.5	741.1
Unit cell dimensions/Å,°	a=7.878(8), α=79.08(8)	a=12.545(13), b=8.300(4), c=14.629(11), β=110.76(6)
Space group[a]	$R\bar{3}2$ (No. 155)	$P2_1/n$ (No. 14, non-standard setting)
Z	1	2
D_c/g cm^{-3}	1.73	1.73
Habit	Colourless irregular-shaped plates	Colourless needles
m.p./°C	220–221	169–170
μ(Mo$K\alpha$)/mm^{-1}	8.18	7.60
Crystal size/mm	0.24 × 0.19 × 0.23	0.18 × 0.31 × 0.10
Temperature (data collection)/K	170	290
$2\theta_{max}$/°	55	50
Scan mode	ω-2θ	ω-2θ
2θ scan rate /°min^{-1}	2.5–15.0	2.5–20.0
Total No. of reflections measured	2310	2820
No. of independent reflections excluding those systematically absent	426	2514
No. of observed independent reflections [$I > 3.0\sigma(I)$]	374	956
Correction for absorption	Empirical[b]	Empirical[b]
Method used to solve structure	Patterson; successive electron density maps	Direct methods (MITHRIL;[c] DIRDIF[d]); successive electron density maps
No. of parameters refined	23	109
Weights calculated according to	$w = [\sigma^2(F_o)+0.0003\ F_o^2]^{-1}$	$w = [\sigma^2(F_o)+0.0004\ F_o^2]^{-1}$
R	0.040	0.068
R_w	0.046	0.075
Maximum residual electron density/e Å^{-3}	0.38	0.84

[a]Ref. 12a. [b]Ref. 9. [c]Ref. 10. [d]Ref. 11.

mated Mo$K\alpha$ radiation. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method[7] was used to calculate the intensities.[8] Correction was made for Lorentz and polarisation effects. Unit cell dimensions were determined from diffractometer angles for 15 reflections.

Structure determination and refinement

Bis(tetramethylphosphonium) tribromocuprate(I). The structure was solved from a Patterson and a subsequent electron density map based on data collected at room temperature. Full-matrix least-squares refinement yielded a final R = 0.055 for 298 observed [$I > 3.0\sigma(I)$] independent reflections and 23 parameters, an empirical correction having been made for the effects of absorption.[9] Large thermal parameters were, however, obtained for all atoms, e.g. B_{eq} for Cu and Br of 5.08(3) and 9.67(9) Å^2, respectively. Refinement of the structure was therefore based on a set of F_0-values for a new crystal, intensities from which were measured at 170 K. Full-matrix least-squares refinement of positional and isotropic thermal parameters gave R = 0.18 for 1948 observed unaveraged reflections, and after an empirical correction for the effects of absorption,[9] R = 0.11. Inclusion of anisotropic thermal parameters yielded a final R = 0.040 for 23 parameters and 374 observed independent reflections. A comparable refinement based on data uncorrected for absorption gave R = 0.068. It was not possible to locate the hydrogen atoms from the final difference map.

Bis(tetramethylphosphonium) di-μ-bromo-dibromodicuprate(I). The atomic coordinates of the anion and, subsequently, those of the cation were determined by direct methods (MITHRIL;[10] DIRDIF[11]), the positions of some of the carbon atoms being obtained from an electron density map. Full-matrix least-squares refinement of positional and isotropic thermal parameters gave R = 0.16, and after an empirical correction for the effects of absorption,[9] R = 0.13. Inclusion of anisotropic thermal parameters gave R = 0.068 for 956 reflections and 109 parameters. Comparable refinement based on the data uncorrected for absorption gave R = 0.086. Hydrogen atoms were not included in the refinement. Attempts made to collect data at 170 K failed owing to immediate cleavage of the striated crystals. Nor was it possible to obtain a more satisfactory set of intensity data at room temperature, despite many attempts using crystals from different batches.

Further details concerning the refinement of both structures are summarised in Table 1. Atomic scattering factors were taken from Ref. 12b. The computer programs employed are described in Refs. 13 and 14. Atomic coordinates and equivalent isotropic thermal parameters are given in Tables 2 and 3. Structure factors, anisotropic thermal parameters and connectivity relationships within the cations may be obtained from the authors on request.

Discussion

As expected, copper(I) is three-coordinated in both anions. The anion in bis(tetramethylphosphonium) tribromocuprate(I) is a discrete mononuclear entity with perfect D_{3h} symmetry and a Cu–Br distance of 2.365(3) Å (Fig. 1). Bis(methyltriphenylphosphonium) triiodocuprate(I) has been shown to contain a mononuclear trigonal $[CuI_3]^{2-}$ anion with Cu–I = 2.537(2), 2.559(2) and 2.566(2) Å, and, from spectroscopic

Table 2. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for $[P(CH_3)_4]_2[CuBr_3]$. 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*a*	0.0000	0.0000	0.0000	2.19(2)
Br	3*d*	0.0000	0.2358(1)	−0.2358	4.25(4)
P	2*c*	0.2606(2)	0.2606	0.2606	2.64(2)
C(1)	2*c*	0.3730(8)	0.3730	0.3730	3.5(1)
C(2)	6*f*	0.0354(11)	0.3654(11)	0.2700(11)	3.6(2)

Table 3. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for $[P(C_2H_5)_4]_2[Cu_2Br_4]$. 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	*x*	*y*	*z*	B_{eq}
Cu	0.4083(2)	0.0270(3)	0.5353(2)	8.1(1)
Br(1)	0.2622(2)	0.0552(3)	0.5905(2)	10.3(1)
Br(2)	0.5937(2)	0.1557(3)	0.5956(2)	10.0(1)
P	−0.0001(4)	0.0875(6)	0.7555(4)	7.3(2)
C(11)	0.114(1)	0.025(3)	0.867(2)	12(1)
C(12)	0.229(2)	0.042(3)	0.873(2)	14(1)
C(21)	0.042(2)	0.253(3)	0.702(2)	12(1)
C(22)	−0.054(2)	0.311(3)	0.610(2)	15(1)
C(31)	−0.075(3)	−0.064(3)	0.683(2)	16(1)
C(32)	0.003(2)	−0.193(4)	0.658(2)	14(1)
C(41)	−0.112(2)	0.201(5)	0.807(2)	19(1)
C(42)	−0.156(2)	0.117(3)	0.863(2)	12(1)

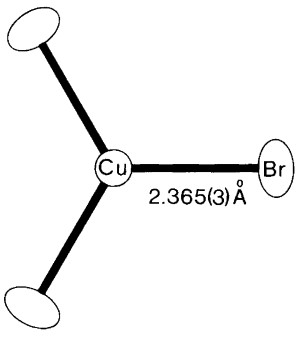

Fig. 1. The tribromocuprate(I) ion in $[P(CH_3)_4]_2[CuBr_3]$. The estimated standard deviation in the Cu−Br distance is given in parenthesis. The thermal ellipsoids enclose 50 % probability.[15]

studies, the tribromocuprate(I) analogue was shown to contain a similar anion.[16] There does not, however, appear to be a previous crystallographic determination of a mononuclear tribromocuprate(I) anion.

The anion in bis(tetraethylphosphonium) di-μ-bromo-dibromocuprate(I) is a centrosymmetric dimer containing approximately trigonal-planar coordinated copper(I) (Fig. 2; Table 4), the copper(I) atom lying 0.032(3) Å from the plane defined by the three bromide ligands: Br(1), Br(2) and Br(2^i) [symmetry code: (*i*): 1-*x*, -*y*, 1-*z*]. Comparison with other structures containing discrete $[Cu_2Br_4]^{2-}$ anions determined hitherto (Table 4) shows considerable variation in the geometry of the four-membered $(Cu-Br)_2$ ring, particularly with respect to the magnitude of the Cu···Cu separation, the present anion showing closest similarity to that in bis(tetraethylammonium) di-μ-bromo-dibromodicuprate(I).[4]

The structures of the compounds are illustrated in Figs. 3 and 4. Neither compound exhibits any unusually short cation-anion distances. In bis(tetramethylphosphonium) tribromocuprate(I) the shortest such distances are Br···C(2^{ii}) and Br···C(2^{iii}) = 3.803(9) Å, whereas the shortest cation-anion distance in bis(tetraethylphosphonium) di-μ-bromo-dibromodicuprate(I) is Cu···C (42^{iv}) = 3.78(3) [symmetry code: (*ii*): *x*, *y*, *z*-1; (*iii*): -*x*, 1-*z*, -*y*; (*iv*): $\frac{1}{2}+x$, $\frac{1}{2}-y$, $z-\frac{1}{2}$].

The variation in the coordination number of copper(I) with cation size and concentration of bromide ligand in crystalline bromocuprates(I) containing symetrical tetraalkylammonium and related cations is illustrated in Table 5. Copper(I)

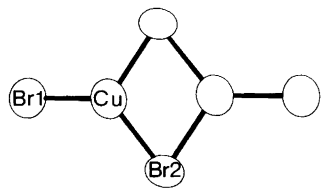

Fig. 2. The di-μ-bromo-dibromodicuprate(I) ion in $[P(C_2H_5)_4]_2[Cu_2Br_4]$. The thermal ellipsoids enclose 50 % probability.[15]

Table 4. Comparison of connectivity relationships in discrete $[Cu_2Br_4]^{2-}$ anions. Distances are in Å and angles in °. A terminal bromide ligand is denoted Br_t and a bridging ligand Br_b; *d* is the distance of Cu from the plane through the three bromide ligands by which it is coordinated. For $[P(C_2H_5)_4]_2[Cu_2Br_4]$, the second distance or angle cited for Br_b refers to Br(2) in 1–*x*, *ȳ*, 1–*z*.

Compound	Cu–Br_t	Cu–Br_b	Cu···Cu	Cu-Br_b-Cu	Br_b-Cu-Br_b	Br_b–Cu-Br_t	*d*	Br_b···Br_b	Ref.
$[P(C_2H_5)_4]_2[Cu_2Br_4]$	2.263(4)	2.423(4) 2.436(3)	2.870(5)	72.4(1)	107.6(1)	128.2(1) 124.1(1)	0.032(3)	3.921(5)	This work
$[N(C_2H_5)_4]_2[Cu_2Br_4]$	2.319(2)	2.441(2) 2.454(2)	2.937(3)	73.7(1)	106.3(1)	125.7(1) 127.9(1)	0.06(1)	3.916(3)	4
$[N(C_6H_5)(CH_3)_3]_2[Cu_2Br_4]$	2.310(1)	2.417(1) 2.421(1)	2.738(2)	68.95(4)	111.05(4)	124.70(4) 124.12(4)	0.049(1)	3.988(2)	17
$[P(CH_3)(C_6H_5)_3]_2[Cu_2Br_4]$	2.337(2)	2.426(2) 2.455(1)	2.697(2)	67.09(5)	112.91(5)	124.60(6) 122.47(5)	0.012(1)	4.068(2)	18
$(TTT)_2[Cu_2Br_4]$[a]	2.328(3)	2.472(3) 2.490(2)	2.660(3)	64.7(1)	115.4(1)	125.0(1) 117.9(1)	0.196	4.188(4)[b]	19

[a]TTT = tetrathiotetracene; two additional Cu–S distances, 2.684 and 3.062 Å, to the tetrathiotetracene cation radicals. [b]Estimated.

is seen to assume digonal, trigonal and, finally, tetrahedral coordination as the size of the cation decreases. The concentration of bromide ligand also shows a general increase with cation size. That tetraphenylphosphonium yields a slightly lower concentration than tetrabutylammonium is probably ascribable to the greater rigidity of the phenyl rings than the butyl chains, leading to a larger effective volume for the former cation. Similar trends have been noted for the chlorocuprate(I) and iodocuprate(I) counterparts (cf. Ref. 6 and references therein). A further discontinuity in the correlation between cation size and ligand concentration is observed for $[N(C_3H_7)_4]_2[Cu_4Br_6]$ and $[P(C_2H_5)_4]_2[Cu_2Br_4]$.

As noted previously,[6] large cations appear to hinder a high overall ligand concentration, thus favouring the formation of small, discrete anions in which copper(I) exhibits a low coordination number. Conversely, the relatively small ammonium cation permits a high ligand concentration (Table 5), resulting in a polynuclear species[20] in which copper(I) is tetrahedrally coordinated. If dilution of the ligands by the cations is a determinative factor for the attainment of a particular copper(I) coordination number, one might envis-

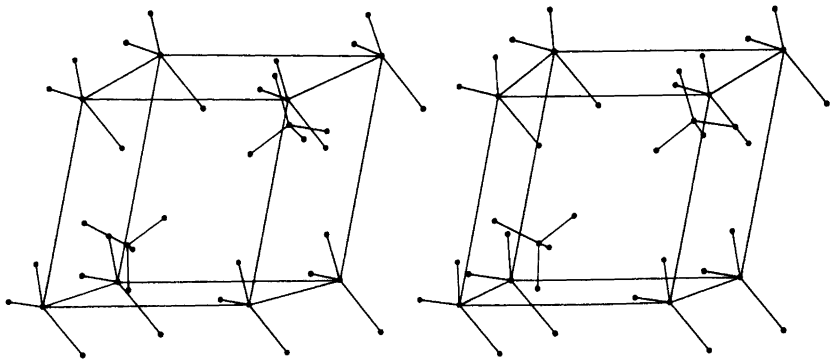

Fig. 3. Stereoscopic view[15] of the structure of $[P(CH_3)_4]_2[CuBr_3]$. All atoms are represented as spheres of radius 0.05 Å.

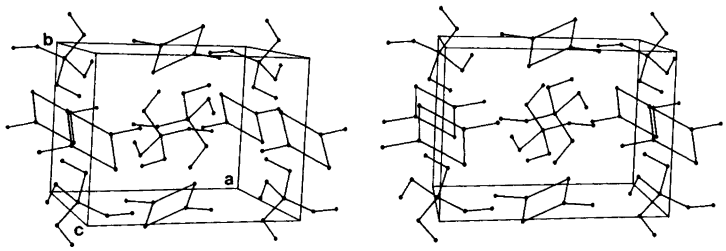

Fig. 4. Stereoscopic view[15] of the structure of $[P(C_2H_5)_4]_2[Cu_2Br_4]$. All atoms are represented as spheres of radius 0.05 Å.

Table 5. Bromocuprate(I) ions characterised by crystal-structure determination of compounds containing symmetrical tetraalkylammonium and related cations. An infinite chain is denoted as such; the remaining anions are discrete species. C.N. is the coordination number of copper(I) in the anion and [Br] the concentration of bromide ligand (mol dm^{-3}) in the crystalline phase, calculated from structural data.

Cation	Anion	C.N.	[Br]	Ref.
$[N(C_4H_9)_4]^+$	$[CuBr_2]^-$	2	6.4	2
$[P(C_6H_5)_4]^+$	$[CuBr_2]^-$	2	5.9	1
$[N(C_3H_7)_4]^+$	$[Cu_4Br_6]^{2-}$	3	10.3	3
$[P(C_2H_5)_4]^+$	$[Cu_2Br_4]^{2-}$	3	9.3	This work
$[N(C_2H_5)_4]^+$	$[Cu_2Br_4]^{2-}$	3	10.4	4
$[P(CH_3)_4]^+$	$[CuBr_3]^{2-}$	3	10.7	This work
$[N(CH_3)_4]^+$	$[Cu_2Br_5]^{3-}$	3	11.1	5
NH_4^+	$(CuBr_3^{2-})_\infty$	4	24.7	20

age cation-bromide packing as being the primary process at the solution-crystal interface during crystal growth, copper(I) then occupying available interstices. Apart from the anion crystallizing with the smallest tetraalkylammonium cation, viz. $[Cu_2Br_5]^{3-}$, all the three-coordinated bromocuprate(I) anions are dinegative. Within the latter series, the Cu:Br ratio decreases with decreasing cation size and increasing concentration of bromide in the crystalline phase, perhaps suggesting decreased availability of interstices in the cation-bromide framework.

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