

# Anionic Configurations and Ligand Concentrations in Butyltriphenylphosphonium Dibromocuprate(I) and Bis(butyltriphenylphosphonium) hexa- $\mu$ -bromo-tetrahedro-tetracuprate(I)

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The anionic configurations in the title compounds were determined from single-crystal X-ray diffractometer data and are discussed in terms of ligand concentration in the crystalline phases.  $[\text{P}(\text{C}_4\text{H}_9)(\text{C}_6\text{H}_5)_3][\text{CuBr}_2]$  crystallizes in space group  $P2_1/c$  with  $a = 8.798(2)$ ,  $b = 17.282(7)$ ,  $c = 15.292(7)$  Å,  $\beta = 92.40(3)^\circ$  and  $Z = 4$ . Full-matrix least-squares refinement of 235 structural parameters gave  $R = 0.043$  for 1875 observed [ $I > 3.0 \sigma(I)$ ] reflections. The anion is monomeric with  $\text{Cu}-\text{Br} = 2.213(2)$  and  $2.220(1)$  Å and  $\text{Br}-\text{Cu}-\text{Br} = 177.67(6)^\circ$ .  $[\text{P}(\text{C}_4\text{H}_9)(\text{C}_6\text{H}_5)_3]_2[\text{Cu}_4\text{Br}_6]$  crystallizes in space group  $Pa\bar{3}$  with  $a = 17.229(16)$  Å and  $Z = 4$ . Full-matrix least-squares refinement of 93 structural parameters gave  $R = 0.043$  for 523 observed [ $I > 3.0 \sigma(I)$ ] independent reflections. The  $[\text{Cu}_4\text{Br}_6]^{2-}$  anion is an aggregate composed of an octahedron of bromide ligands containing a tetrahedron of trigonal-planar coordinated copper(I) atoms. The orientation of the copper(I) tetrahedron is disordered, there being two equivalent copper(I) tetrahedra related by inversion through the centre of the ligand octahedron.  $\text{Cu}-\text{Br}$  distances range from 2.358(4)–2.443(4) Å and  $\text{Cu}\cdots\text{Cu}$  are 2.719(6) and 2.755(6) Å. The butyl group of the cation exhibits severe orientational disorder with respect to a three-fold axis.

Bromocuprates(I) crystallizing with tetraphenylphosphonium and symmetrical tetraalkylammonium cations have been shown to be discrete species containing two- or three-coordinated copper(I).<sup>1-5</sup> Calculation of the ligand concentrations in these and related compounds indicates that the anionic configuration is dependent on the degree of dilution imposed on the ligands by the cations.<sup>6</sup> In order to examine the effect of dissymmetry in this type of cation, with respect both to size and to exposure of the positive charge, on the configuration assumed by the anion, attempts are being made to prepare crystalline bromocuprates(I) containing unsymmetrically substituted quaternary aryl or alkylammonium and phospho-

nium cations. A discrete planar  $[\text{Cu}_2\text{Br}_4]^{2-}$  dimer, similar to that in the tetraethylammonium compound,<sup>4</sup> has been obtained with the phenyltrimethylammonium cation.<sup>7</sup> Both ethyltriphenylphosphonium<sup>8</sup> and propyltriphenylphosphonium<sup>9</sup> crystallize, however, with monomeric dibromocuprate(I) anions. It was therefore expected that the anion in butyltriphenylphosphonium dibromocuprate(I) would also prove to be a monomer.

## Experimental

Butyltriphenylphosphonium bromide and copper(I) bromide (molar ratio 1:1) were dissolved in ethanol. Colourless octahedra (m.p. 123–124 °C) were deposited from the concentrated so-

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Table 1. Crystal and experimental data for butyltriphenylphosphonium dibromocuprate(I) and bis(butyltriphenylphosphonium) hexa- $\mu$ -bromo-tetrahedro-tetracuprate(I).

	[P(C <sub>4</sub> H <sub>9</sub> )(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ][CuBr <sub>2</sub> ]	[P(C <sub>4</sub> H <sub>9</sub> )(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> [Cu <sub>4</sub> Br <sub>6</sub> ]
<i>M<sub>r</sub></i>	542.8	1372.4
Unit-cell dimensions	<i>a</i> =8.798(2), <i>b</i> =17.282(7) <i>c</i> =15.292(7) Å, $\beta$ =92.40(3)°	<i>a</i> =17.229(16) Å
Space group <sup>10a</sup>	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>Pa</i> 3 (No. 205)
<i>Z</i>	4	4
<i>D<sub>c</sub></i>	1.55 g cm <sup>-3</sup>	1.78 g cm <sup>-3</sup>
Habit	Colourless needles	Colourless octahedra
m.p.	137–138 °C	123–124 °C
$\mu$ (MoK $\alpha$ )	4.69 mm <sup>-1</sup>	6.76 mm <sup>-1</sup>
Crystal size	0.31 × 0.13 × 0.18 mm	0.31 × 0.31 × 0.31 mm
Temperature	290 K	290 K
2 $\theta$ <sub>max</sub>	50°	50°
Scan mode	$\omega$ – 2 $\theta$	$\omega$ – 2 $\theta$
2 $\theta$ scan rate	2.5 – 15.0° min <sup>-1</sup>	3.0 – 15.0° min <sup>-1</sup>
Total no. of reflections measured	4569	5047
No. of independent reflections excluding those systematically absent	4160	1523
No. of observed independent reflections [ <i>I</i> >3.0 $\sigma$ ( <i>I</i> )]	1875	523
Correction for absorption	Empirical <sup>13</sup>	–
Method used to solve structure	Direct methods (MITHRIL; <sup>14</sup> DIRDIF <sup>15</sup> )	Direct methods (MITHRIL; <sup>14</sup> DIRDIF <sup>15</sup> ); successive electron density maps
No. of parameters refined	235	93
Weights calculated according to	$w = [\sigma^2(F_o) + 0.0005 F_o^2]^{-1}$	$w = [\sigma^2(F_o) + 0.0005 F_o^2]^{-1}$
<i>R</i>	0.043	0.043
<i>R<sub>w</sub></i>	0.047	0.062
Maximum residual electron density	0.35 e Å <sup>-3</sup>	0.44 e Å <sup>-3</sup>

lution after approximately 24 h and colourless needles (m.p. 137–138 °C) after a few days. The former phase is bis(butyltriphenylphosphonium) hexa- $\mu$ -bromo-tetrahedro-tetracuprate(I) and the latter butyltriphenylphosphonium dibromocuprate(I).

Crystal and experimental data for the two compounds are given in Table 1. Diffracted intensities were measured with a Syntex *P*2<sub>1</sub> diffractometer, using graphite-monochromated MoK $\alpha$  radiation. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method<sup>11</sup> was used to calculate the intensities.<sup>12</sup> Correction was made for Lorentz and polarisation effects. Unit-cell dimensions were determined from diffractometer setting angles for 15 reflections.

### Structure determination and refinement

*Butyltriphenylphosphonium dibromocuprate(I)*. The atomic coordinates of the anion and subsequently those of the cation were determined by direct methods (MITHRIL;<sup>14</sup> DIRDIF<sup>15</sup>). Full-matrix least-squares refinement<sup>16</sup> of positional and isotropic thermal parameters gave *R* = 0.094; after an empirical correction<sup>13</sup> for the effects of absorption *R* = 0.073. Inclusion of anisotropic thermal parameters gave *R* = 0.053 for 235 parameters and 1875 reflections. Comparable refinement based on the data uncorrected for absorption yielded *R* = 0.059. Finally, the hydrogen atoms associated with the phenyl rings and the  $\alpha$ -,  $\beta$ - and  $\gamma$ -carbon atoms of the butyl group were included as a fixed contribution [*C*–*H* = 1.0

Table 2. Fractional coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for the non-hydrogen atoms in  $[\text{P}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5)_3][\text{CuBr}_2]$ .  $B_{\text{eq}}$  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	$B_{\text{eq}}$
Cu	0.7929(1)	0.14456(6)	0.81400(6)	5.12(3)
Br(1)	0.9652(1)	0.15210(6)	0.71301(6)	7.28(3)
Br(2)	0.6148(1)	0.14081(5)	0.91256(6)	6.54(3)
P	0.3547(2)	0.1654(1)	0.2281(1)	3.65(5)
C(11)	0.2539(6)	0.1513(4)	0.3269(4)	3.4(2)
C(12)	0.2251(8)	0.0755(4)	0.3530(5)	4.8(2)
C(13)	0.1526(9)	0.0618(5)	0.4309(6)	6.1(3)
C(14)	0.1069(9)	0.1230(6)	0.4817(5)	5.8(3)
C(15)	0.1339(9)	0.1982(5)	0.4553(5)	6.0(3)
C(16)	0.2077(8)	0.2129(4)	0.3780(5)	5.1(2)
C(21)	0.2416(7)	0.1292(4)	0.1368(4)	3.9(2)
C(22)	0.0841(8)	0.1376(4)	0.1390(5)	5.0(2)
C(23)	-0.0062(9)	0.1167(5)	0.0646(6)	5.9(3)
C(24)	0.0571(12)	0.0891(5)	-0.0081(6)	6.6(3)
C(25)	0.2153(12)	0.0812(5)	-0.0098(5)	6.4(3)
C(26)	0.3057(9)	0.1011(4)	0.0631(5)	4.7(2)
C(31)	0.5315(7)	0.1138(4)	0.2415(4)	3.4(2)
C(32)	0.6529(8)	0.1522(4)	0.2852(5)	4.5(2)
C(33)	0.7860(8)	0.1126(5)	0.3040(6)	6.1(3)
C(34)	0.8016(8)	0.0359(5)	0.2802(6)	5.8(3)
C(35)	0.6825(9)	-0.0015(4)	0.2367(5)	5.4(3)
C(36)	0.5467(8)	0.0362(4)	0.2178(5)	4.5(2)
C(41)	0.3910(7)	0.2656(4)	0.2095(4)	4.0(2)
C(42)	0.4839(8)	0.2801(4)	0.1277(5)	4.8(2)
C(43)	0.5066(9)	0.3660(4)	0.1075(5)	5.7(3)
C(44)	0.5950(10)	0.3774(5)	0.0234(5)	7.2(3)

$\text{\AA}$  and  $B = B_{\text{eq}}$  of the carrying carbon atom], an  $R$  value of 0.043 being obtained (235 parameters; 1875 reflections). It was not possible to locate the hydrogen atoms bonded to C(44).

*Bis(butyltriphenylphosphonium) hexa- $\mu$ -bromotetrahydro-tetracuprate(I)*. The main features of the structure were obtained by direct methods (MITHRIL;<sup>14</sup> DIRDIF<sup>15</sup>). Initially the orthorhombic space group  $Pbca$  (No. 61)<sup>10a</sup> was employed, as an ordered butyl group is not compatible with occupation of  $8c$  in the cubic space group  $Pa3$ , *i.e.* the butyl group cannot lie along a three-fold axis. Since, however, the carbon atoms of the butyl chain could not be located in  $Pbca$  and the rest of the structure could be described equally well in  $Pa3$ , the latter space group was adopted in refinement. The copper(I) atoms were distributed over a general site ( $24d$ ) and a

special site ( $8c$ ) and were assigned occupancies  $\frac{1}{2}$  and  $\frac{1}{6}$ , respectively. Three of the carbon atoms of the butyl group were located in  $24d$  and assigned occupancy  $\frac{1}{3}$ , whereas the fourth, C(9), was assumed to occupy  $8c$ . Full-matrix least-squares refinement<sup>16</sup> of positional and isotropic thermal parameters gave  $R = 0.10$  (51 parameters; 523 reflections). Inclusion of anisotropic thermal parameters for all atoms except C(7)–C(10) gave  $R = 0.047$  (93 parameters; 523 reflections). Finally, the hydrogen atoms of the phenyl group were included as a fixed contribution [C–H = 1.0  $\text{\AA}$  and  $B = B_{\text{eq}}$  of the carrying carbon atom] yielding  $R = 0.043$ . It was obvious that the disorder associated with the butyl group had not been resolved satisfactorily since refinement led to too long a value for the P–C(7) bond and too short a value for C(9)–C(10). We were, however, unable to obtain better resolution of this group.

Table 3. Fractional coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for the non-hydrogen atoms in  $[\text{P}(\text{C}_4\text{H}_9)(\text{C}_6\text{H}_5)_3]_2[\text{Cu}_4\text{Br}_6]$ .  $B_{\text{eq}}$  is defined as  $8\pi^2/3\Sigma\Sigma U_j a_j^* a_j \cdot a_j$ . For the carbon atoms of the butyl group isotropic thermal parameters,  $B$  ( $\text{\AA}^2$ ), are given, the temperature factor being  $\exp\{-B(\sin^2\theta)/\lambda^2\}$ . Atoms in partially occupied sites are indicated by asterisks: \*occupancy  $\frac{1}{6}$ , \*\*occupancy  $\frac{1}{2}$  and \*\*\*occupancy  $\frac{1}{3}$ . Estimated standard deviations are given in parentheses.

Atom	Site	x	y	z	$B_{\text{eq}}$ or $B$
Cu(1)*	8c	0.0558(2)	0.0558	0.0558	5.9(1)
Cu(2)**	24d	0.0406(2)	-0.0132(2)	-0.0877(2)	5.9(1)
Br	24d	0.15127(8)	0.06515(9)	-0.04601(8)	7.01(5)
P	8c	0.2271(2)	0.2271	0.2271	7.8(1)
C(1)	24d	0.2061(9)	0.2736(7)	0.1383(8)	6.8(5)
C(2)	24d	0.1307(10)	0.2718(9)	0.1063(10)	8.7(6)
C(3)	24d	0.1145(11)	0.3061(12)	0.0365(11)	10.4(7)
C(4)	24d	0.1729(15)	0.3448(11)	-0.0039(12)	10.6(7)
C(5)	24d	0.2473(15)	0.3489(10)	0.0264(14)	10.4(8)
C(6)	24d	0.2648(9)	0.3119(10)	0.0968(13)	9.2(7)
C(7)***	24d	0.265(2)	0.294(3)	0.314(2)	7(1)
C(8)***	24d	0.352(2)	0.310(3)	0.296(3)	7(1)
C(9)	8c	0.367(1)	0.367	0.367	12(1)
C(10)***	24d	0.433(3)	0.376(4)	0.357(4)	7(2)

Further details concerning the refinement of both structures are summarised in Table 1. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.<sup>10b</sup> Atomic coordinates and equivalent isotropic thermal parameters are given in Tables 2 and 3. Structure factors, anisotropic thermal parameters, hydrogen-atom coordinates and angles within the cation may be obtained from the authors.

## Discussion

As expected, the anion in butyltriphenylphosphonium dibromocuprate(I) is monomeric (Fig. 1). The Cu-Br distances and Br-Cu-Br angle are in close agreement with values determined previously (*cf.* Refs. 8 and 9 and references therein). The ligand concentration in the crystalline phase is  $5.72 \text{ mol dm}^{-3}$ , slightly lower than that in tetraphenylphosphonium dibromocuprate(I),<sup>1</sup> *i.e.*  $5.87 \text{ mol dm}^{-3}$ . Ligand concentrations in the solid state obtained hitherto for monomeric dibromocuprates(I) crystallizing with tetraalkylammonium and related unipositive cations lie within the range  $5.87\text{--}6.50 \text{ mol dm}^{-3}$ .<sup>9</sup>

The butyltriphenylphosphonium cation also

crystallizes with a  $[\text{Cu}_4\text{Br}_6]^{2-}$  anion, similar to that obtained in bis(tetrapropylammonium) hexa- $\mu$ -bromo-tetrahedro-tetracuprate(I).<sup>3</sup> The  $[\text{Cu}_4\text{Br}_6]^{2-}$  anion is an aggregate composed of an octahedron of bromide ligands containing a tetrahedron of trigonal-planar coordinated copper(I) atoms. As in  $[\text{N}(\text{C}_3\text{H}_7)_4]_2[\text{Cu}_4\text{Br}_6]$ ,<sup>3</sup> the copper(I) tetrahedron in the anion in  $[\text{P}(\text{C}_4\text{H}_9)(\text{C}_6\text{H}_5)_3]_2[\text{Cu}_4\text{Br}_6]$  can assume either of two equivalent orientations with respect to inversion through the centre of the ligand octahedron, (see Figs. 2a and 2b). Distances and angles within the anion are given in Table 4, the orientation being that of Fig. 2a. As in  $[\text{N}(\text{C}_3\text{H}_7)_4]_2[\text{Cu}_4\text{Br}_6]$ ,<sup>3</sup> the copper atoms were assigned site occupancies corresponding to equal

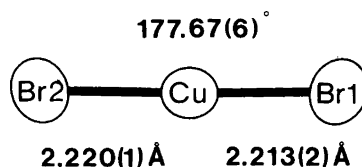


Fig. 1. The dibromocuprate(I) ion in  $[\text{P}(\text{C}_4\text{H}_9)(\text{C}_6\text{H}_5)_3][\text{CuBr}_2]$ . Estimated standard deviations in the distance and angle are given in parentheses. The thermal ellipsoids enclose 50% probability.<sup>17</sup>

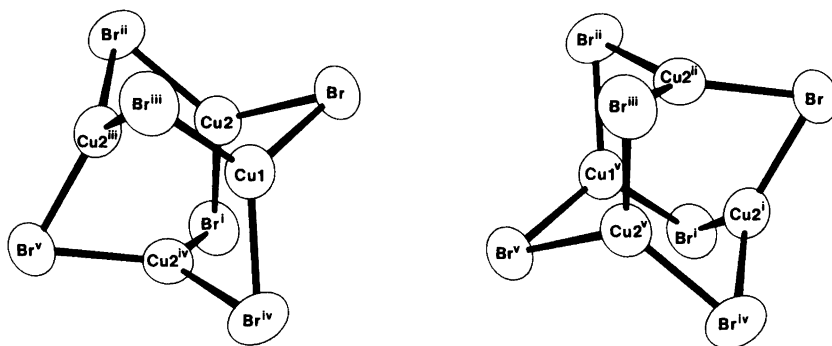


Fig. 2. The  $[\text{Cu}_4\text{Br}_6]^{2-}$  ion in  $[\text{P}(\text{C}_4\text{H}_9)(\text{C}_6\text{H}_5)_3]_2[\text{Cu}_4\text{Br}_6]$  showing the two orientations of the copper(I) tetrahedron. Symmetry code: i:  $\bar{z}, \bar{x}, \bar{y}$ ; ii:  $\bar{y}, \bar{z}, \bar{x}$ ; iii:  $z, x, y$ ; iv:  $\bar{y}, \bar{z}, \bar{x}$ ; v:  $\bar{x}, \bar{y}, \bar{z}$ . The thermal ellipsoids enclose 50% probability.<sup>17</sup>

occurrence of anions with the orientation of Fig. 2a and that of Fig. 2b. Preferential orientation of the anions was not investigated.

The  $[\text{Cu}_4\text{Br}_6]^{2-}$  ion is essentially similar to that in the tetrapropylammonium compound<sup>3</sup> and to the  $[\text{Cu}_4\text{I}_6]^{2-}$  ion in  $[\text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_3]_2[\text{Cu}_4\text{I}_6]$ ,<sup>18</sup> both of which also show similar disorder with respect to the copper(I) tetrahedron. Cu(1) lies on a threefold axis 0.030(3) Å from the plane through the three bromide ligands (Br, Br<sup>iii</sup> and Br<sup>iv</sup>). Cu(2) is also trigonal-planar coordinated by Br, Br<sup>i</sup> and Br<sup>ii</sup> (for symmetry code see Table 4 and Fig. 2) and lies 0.023(3) Å from the plane through these ligands. Distances and angles within the anion agree well with those determined for  $[\text{Cu}_4\text{Br}_6]^{2-}$  in bis(tetrapropylammonium) hexa- $\mu$ -bromotetrahydro-tetracuprate(I).<sup>3</sup>

The ligand concentration in the compound  $[\text{P}(\text{C}_4\text{H}_9)(\text{C}_6\text{H}_5)_3]_2[\text{Cu}_4\text{Br}_6]$  is 7.79 mol dm<sup>-3</sup>; that in  $[\text{N}(\text{C}_3\text{H}_7)_4]_2[\text{Cu}_4\text{Br}_6]$  is 10.3 mol dm<sup>-3</sup>.<sup>3,6</sup> It

would thus seem likely that the ligand dilution in the solid state required for the attainment of a discrete bromocuprate(I) species containing two-coordinated copper(I) lies between 6.50 and 7.79 mol dm<sup>-3</sup>.

That the butyltriphenylphosphonium cation crystallizes both with a  $[\text{CuBr}_2]^-$  anion and with a  $[\text{Cu}_4\text{Br}_6]^{2-}$  anion, suggests, as discussed previously,<sup>6</sup> that a given cation may be associated with a fairly broad ligand concentration range within which the formation of more than one anionic species is favourable. Iodocuprate(I) anions of various stoichiometries have been obtained with *e.g.* the tetrapropylammonium cation, *viz.*  $[\text{Cu}_2\text{I}_4]^{2-}$ ,<sup>19</sup>  $[\text{Cu}_5\text{I}_7]^{2-}$ ,<sup>20</sup> and  $[\text{Cu}_3\text{I}_4]^-$ .<sup>21</sup> The ligand concentrations in the crystalline compounds are 7.21, 10.1 and 11.8 mol dm<sup>-3</sup>, respectively.<sup>6</sup>

The butyltriphenylphosphonium cation in  $[\text{P}(\text{C}_4\text{H}_9)(\text{C}_6\text{H}_5)_3][\text{CuBr}_2]$  is depicted in Fig. 3 and distances within the cations in both structures are

Table 4. Interatomic distances (Å) and angles (°) within the  $[\text{Cu}_4\text{Br}_6]^{2-}$  ion, the orientation being as in Fig. 2a. Symmetry code: (i):  $\bar{z}, \bar{x}, \bar{y}$ ; (ii):  $\bar{y}, \bar{z}, \bar{x}$ ; (iii):  $z, x, y$ .

Cu(1)–Br	2.410(3)	Cu(1)⋯Cu(2)	2.755(6)
Cu(2)–Br	2.443(4)	Cu(2)⋯Cu(2 <sup>ii</sup> )	2.719(6)
Cu(2)–Br <sup>i</sup>	2.413(4)		
Cu(2)–Br <sup>ii</sup>	2.358(4)		
Br–Cu(1)–Br <sup>iii</sup>	120.0(1)	Cu(1)–Br–Cu(2)	69.2(2)
Br–Cu(2)–Br <sup>i</sup>	117.9(1)	Cu(2)–Br–Cu(2 <sup>ii</sup> )	69.5(2)
Br–Cu(2)–Br <sup>ii</sup>	120.0(1)	Cu(2)⋯Cu(1)⋯Cu(2 <sup>ii</sup> )	59.1(1)
Br <sup>i</sup> –Cu(2)–Br <sup>ii</sup>	122.0(2)	Cu(1)⋯Cu(2)⋯Cu(2 <sup>ii</sup> )	60.4(1)

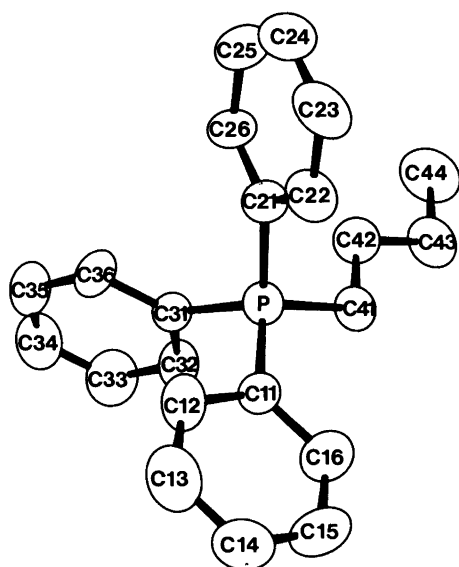


Fig. 3. The butyltriphenylphosphonium ion in  $[P(C_4H_9)(C_6H_5)_3][CuBr_2]$  showing the atomic numbering. The thermal ellipsoids enclose 50 % probability.<sup>17</sup> Hydrogen atoms have been omitted.

given in Table 5. The structures of the compounds are illustrated in Figs. 4 and 5.

As in ethyltriphenylphosphonium dibromocuprate(I),<sup>8</sup> and in propyltriphenylphosphonium dibromocuprate(I),<sup>9</sup> the shortest anion – cation distances in butyltriphenylphosphonium dibromocuprate(I) involve the phenyl groups:  $Cu \cdots C(24^i) = 3.63(1)$ ,  $Br(1) \cdots C(14^{ii}) = 3.832(8)$ ,  $Br(1) \cdots C(34^{iii}) = 3.842(9)$  and  $Br(2) \cdots C(26^{iv}) = 3.701(7)$  Å [symmetry code: (i):  $1+x, y, 1+z$ ; (ii):  $1+x, y, z$ ; (iii):  $2-x, \bar{y}, 1-z$ ; (iv):  $x, y, 1+z$ ].

Whereas the shortest  $Cu \cdots C$  contact in  $[P(CH_3)(C_6H_5)_3]_2[Cu_4I_6]$ , 3.46(2) Å, is to the

Table 5. Interatomic distances (Å) within the butyltriphenylphosphonium cations in  $[P(C_4H_9)(C_6H_5)_3][CuBr_2]$  and  $[P(C_4H_9)(C_6H_5)_3]_2[Cu_4Br_6]$ . Estimated standard deviations are given in parentheses.

Butyltriphenylphosphonium dibromocuprate(I)

P–C(11)	1.800(6)	C(24)–C(25)	1.40(2)
P–C(21)	1.793(7)	C(25)–C(26)	1.39(1)
P–C(31)	1.797(6)	C(26)–C(21)	1.37(1)
P–C(41)	1.785(7)	C(31)–C(32)	1.40(1)
C(11)–C(12)	1.40(1)	C(32)–C(33)	1.38(1)
C(12)–C(13)	1.40(1)	C(33)–C(34)	1.38(1)
C(13)–C(14)	1.38(1)	C(34)–C(35)	1.38(1)
C(14)–C(15)	1.38(1)	C(35)–C(36)	1.38(1)
C(15)–C(16)	1.40(1)	C(36)–C(31)	1.40(1)
C(16)–C(11)	1.39(1)	C(41)–C(42)	1.54(1)
C(21)–C(22)	1.40(1)	C(42)–C(43)	1.53(1)
C(22)–C(23)	1.41(1)	C(43)–C(44)	1.54(1)
C(23)–C(24)	1.35(1)		

Bis(butyltriphenylphosphonium) hexa- $\mu$ -bromo-tetrahydro-tetracuprate(I)

P–C(1)	1.76(1)	C(5)–C(6)	1.40(3)
P–C(7)	2.01(5)	C(6)–C(1)	1.40(2)
C(1)–C(2)	1.41(2)	C(7)–C(8)	1.55(6)
C(2)–C(3)	1.37(2)	C(8)–C(9)	1.58(6)
C(3)–C(4)	1.39(2)	C(9)–C(10)	1.16(6)
C(4)–C(5)	1.39(4)		

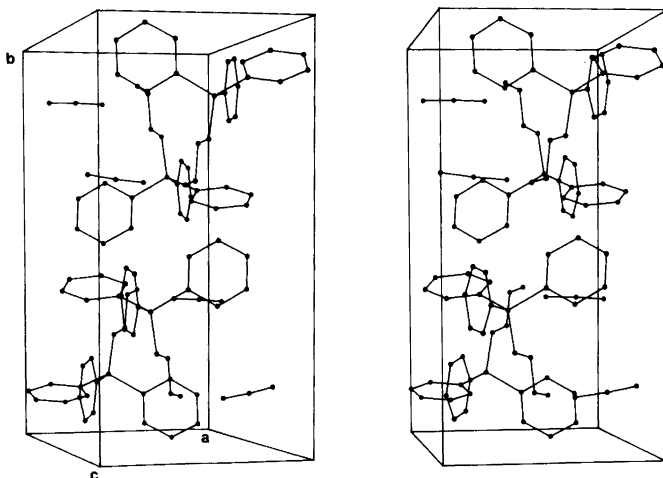
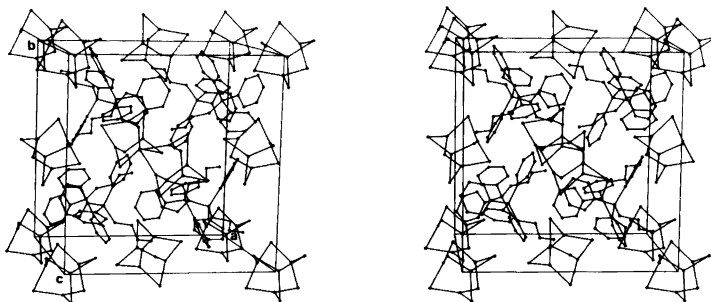


Fig. 4. Stereoscopic view<sup>17</sup> of the unit cell of  $[P(C_4H_9)(C_6H_5)_3][CuBr_2]$ . All atoms are represented as spheres of radius 0.05 Å. Hydrogen atoms have been omitted.

Fig. 5. Stereoscopic view<sup>17</sup> of the structure of  $[P(C_4H_9)(C_6H_5)_3]_2[Cu_4Br_6]$ . For clarity all atoms are represented as spheres of radius 0.05 Å and the anion and the butyl group of the cation are each drawn in only one of the possible orientations. Hydrogen atoms have been omitted.



methyl group,<sup>18</sup> there are no copper(I)⋯carbon contacts less than 4 Å to the butyl group in  $[P(C_4H_9)(C_6H_5)_3]_2[Cu_4Br_6]$ . The only Cu⋯C contacts < 4 Å are Cu(2)⋯C(5') = 3.43(2) and Cu(2)⋯C(6') = 3.87(2) Å. The closest Br⋯C distance is also to the phenyl group: Br⋯C(2<sup>ii</sup>) = 3.75(2) Å, the closest contacts to the butyl group being Br⋯C(8<sup>iii</sup>) = 3.80(5) and Br⋯C(10<sup>iii</sup>) = 3.79(6) Å [symmetry code: (i):  $\frac{1}{2}-y, \bar{z}, x-\frac{1}{2}$ ; (ii):  $y, z, x$ ; (iii):  $z, \frac{1}{2}-x, y-\frac{1}{2}$ ]. Similar but less severe orientational disorder is exhibited by one of the cations in  $[N(C_3H_7)_4]_2[Cu_4Br_6]$ ,<sup>3</sup> the disorder being attributable to equally favourable long-range interactions associated with the two orientations of the propyl groups. That the butyl group of the cation in  $[P(C_4H_9)(C_6H_5)_3]_2[Cu_4Br_6]$  exhibits orientational disorder is perhaps surprising in that the closest anion – cation contacts involve a single orientation of this group.

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