coordinated), 2·83 Å; potassium *o*-nitrophenolate hemihydrate (Anderson & Anderson, 1975), 2·83 Å; potassium 5-ethylbarbiturate 5/3-hydrate (Gartland, Gatehouse & Craven, 1975) ($3K^+$ each seven-coordinated), 2·80 Å; and potassium violurate dihydrate (Gillier, 1965), 2·80 Å.

In the naphthalene rings there is no apparent alternation in length of the C—C bonds as was observed in the sodium (Brown & Corbridge, 1966) and calcium (Brown *et al.*, 1984) salts. The naphthalene rings are essentially regular and planar, the mean out-of-plane distances being 0·006 Å for the C(1)–(10) atoms and 0·002 Å for the C(11)–(20) atoms. The dihedral angle between the mean planes through the naphthalene rings is 24·46 (5)°.

The peculiar reversible flexibility shown by the crystals, *i.e.* they can readily be bent between the fingers if large enough, can be explained by referring to a model of the structure. The molecules lie in layers approximately parallel to (001) and there are no strong bonding forces across (100): hence *c* is the flex axis and (100) readily curves on bending.

Fig. 1 shows the atomic numbering used and the arrangement of the molecules in (001) projection.

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Bis(methyltriphenylphosphonium) Di-μ-bromo-dibromodicuprate(I)

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Abstract. $[P(CH_3)(C_6H_5)_3]_2[Cu_2Br_4]$, $M_r = 1001·4$, monoclinic, $C2/c$, $a = 22·937$ (9), $b = 9·288$ (4), $c = 19·280$ (12) Å, $\beta = 106·71$ (4)°, $V = 3934$ (3) Å^3, $Z = 4$, $D_x = 1·69$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 55·3$ cm^{-1}, $F(000) = 1968$, $T = 290$ K, $R = 0·047$ for 2580 unique observed reflections $[I \geq 3\sigma(I)]$ and 262 parameters. The $[Cu_2Br_4]^{2-}$ anion is a centrosymmetric dimer containing approximately trigonal-planar coordinated Cu^I. The Cu—Br(terminal) distance is 2·337 (2) Å, the Cu—Br(bridging) distances are 2·426 (2) and 2·455 (1) Å and the Cu···Cu separation 2·697 (2) Å.

Introduction. In halocuprates(I) crystallizing with symmetrically substituted tetraalkylammonium and related unipositive cations there would appear to be a correlation between the coordination number of Cu^I and the concentration of halide ligand in the crystalline phase, suggesting that the degree of dilution imposed on the ligands by the cations determines the Cu^I coordination in the resulting anion (Andersson & Jagner, 1986*a*). In order to examine the effect of cation size further, as well as lack of symmetry with respect to exposure of the positive charge, attempts are being made to prepare crystalline halocuprates(I) containing unsymmetrically substituted quaternary alkylammonium and related unipositive cations. Butyltriphenylphosphonium has been found to crystallize with a linear $[CuBr_2]^-$ monomer and with a $[Cu_4Br_6]^{2-}$ aggregate containing three-coordinated Cu^I (Andersson & Jagner, 1986*b*), whereas propyltriphenylphosphonium (Andersson & Jagner, 1985*c*) and ethyltriphenylphosphonium (Andersson & Jagner, 1985*b*) both crystallize with digonal, monomeric dibromocuprate(I) anions.

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Three bromocuprates(I) crystallizing with the methyltriphenylphosphonium cation have been prepared and investigated by means of far infrared and nuclear quadrupole resonance spectroscopy and have been shown to be $[P(CH_3)(C_6H_5)_3][CuBr_2]$, $[P(CH_3)(C_6H_5)_3]_2[CuBr_3]$ and $[P(CH_3)(C_6H_5)_3]_2[CuBr_2]Br$, respectively, it being demonstrated that $[P(CH_3)(C_6H_5)_3][CuBr_2]$ did not contain a discrete monomeric $[CuBr_2]^-$ anion (Bowmaker, Clark, Rogers, Camus & Marsich, 1984). In order to determine the configuration of the anion and thus the coordination of Cu^{II} in this compound, a crystal structure determination has been undertaken.

Experimental. The compound was prepared according to the method of Bowmaker *et al.* (1984), colourless needles, m.p. 380–381 K being obtained. Cleaved fragment (0·35 × 0·31 × 0·18 mm) used to collect intensity data on a Syntex $P2_1$ diffractometer; graphite-monochromated radiation; 15 reflections used to determine unit-cell parameters; $2\theta \geq 50°$: $0 \geq h \geq 27$, $0 \geq k \geq 11$, $-22 \geq l \geq 22$; ω–2θ scan mode, variable 2θ scan rate: 3·0–29·3° min^{-1}; 96-step profiles; Lehmann & Larsen (1974) profile-analysis method used to calculate the intensities (Lindqvist & Ljungström, 1979); variation in intensity of two standard reflections, measured every 48 reflections, <3%; 3803 reflections measured, of which 3488 unique and 2580 with $I \geq 3\sigma(I)$; empirical correction for absorption *DIFABS* (Walker & Stuart, 1983), transmission factors 0·789–1·148. Structure solved by direct methods: *MITHRIL* (Gilmore, 1984), *DIRDIF* (Beurskens, Bosman, Doesburg, Gould, van den Hark, Prick, Noordik, Beurskens & Parthasarathi, 1981). H atoms located from difference map; isotropic thermal parameters for H set equal to B_{eq} value of the carrying C atom and not refined. Full-matrix least-squares refinement based on F gave final $R = 0{\cdot}047$ (2580 reflections; 262 parameters), $wR = 0{\cdot}054$, $w = [\sigma^2(F_o) + 0{\cdot}0003F_o^2]^{-1}$. $(\Delta/\sigma)_{\max} = 0{\cdot}27$ for non-H atoms; final difference electron density: max. 0·53, min. −0·50 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs described by Lindgren (1977) and Andersen (1985). Atomic coordinates are listed in Table 1.*

Discussion. The anion in bis(methyltriphenylphosphonium) di-μ-bromo-dibromodicuprate(I) is a centrosymmetric $[Cu_2Br_4]^{2-}$ dimer containing approximately trigonal-planar coordinated Cu^I (Fig. 1; Table 2), the Cu^I atom lying 0·012 (1) Å from the plane defined by the three bromide ligands. Comparison with the other discrete $[Cu_2Br_4]^{2-}$ ions determined hitherto (Table 3) shows that there is considerable variation in the geometry of the four-membered $(Cu{-}Br)_2$ ring within these anions, in particular with respect to the magnitude of

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *for non-*H *atoms in* $[P(CH_3)(C_6H_5)_3]_2[Cu_2Br_4]$, *with e.s.d.'s in parentheses*

$$B_{eq} = \frac{8\pi^2}{3} \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	B_{eq}
Cu	0·22194 (4)	0·18271 (10)	0·43731 (5)	4·56 (3)
Br(1)	0·17346 (3)	0·07272 (8)	0·32672 (3)	4·25 (2)
Br(2)	0·20810 (3)	0·11334 (7)	0·55285 (4)	4·28 (2)
P	0·62500 (7)	0·1528 (2)	0·60020 (8)	3·13 (4)
C(11)	0·5596 (3)	0·2666 (6)	0·5884 (3)	3·2 (2)
C(12)	0·5166 (3)	0·2776 (7)	0·5215 (4)	3·6 (2)
C(13)	0·4623 (3)	0·3527 (7)	0·5138 (4)	3·8 (2)
C(14)	0·4512 (3)	0·4148 (7)	0·5737 (4)	4·3 (2)
C(15)	0·4940 (3)	0·4041 (8)	0·6407 (4)	4·9 (2)
C(16)	0·5485 (3)	0·3322 (9)	0·6491 (4)	5·0 (2)
C(21)	0·6335 (3)	0·1130 (6)	0·5131 (3)	3·4 (2)
C(22)	0·6171 (3)	−0·0230 (6)	0·4822 (3)	3·4 (2)
C(23)	0·6195 (3)	−0·0497 (8)	0·4106 (4)	4·3 (2)
C(24)	0·6389 (4)	0·0590 (9)	0·3725 (4)	5·1 (3)
C(25)	0·6544 (3)	0·1923 (9)	0·4029 (4)	4·9 (2)
C(26)	0·6532 (3)	0·2208 (8)	0·4738 (4)	4·3 (2)
C(31)	0·6110 (2)	−0·0115 (7)	0·6421 (3)	3·3 (2)
C(32)	0·5523 (3)	−0·0438 (8)	0·6462 (3)	4·0 (2)
C(33)	0·5419 (4)	0·1739 (8)	0·6768 (4)	4·9 (2)
C(34)	0·5880 (4)	−0·2704 (8)	0·7036 (4)	4·7 (2)
C(35)	0·6453 (4)	−0·2394 (8)	0·6991 (4)	4·4 (2)
C(36)	0·6580 (3)	−0·1101 (7)	0·6693 (4)	4·0 (2)
C(4)	0·6927 (3)	0·2399 (9)	0·6548 (4)	4·4 (2)

Table 2. *Interatomic distances* (Å) *and angles* (°) *within the di-μ-bromo-dibromodicuprate*(I) *anion*

Cu—Br(1)	2·337 (2)	Cu—Br(2^i)	2·455 (1)
Cu—Br(2)	2·426 (2)	Cu···Cu^i	2·697 (2)
Br(1)—Cu—Br(2)	124·60 (6)	Br(2)—Cu—Br(2^i)	112·91 (5)
Br(1)—Cu—Br(2^i)	122·47 (5)	Cu—Br(2)—Cu^i	67·09 (5)

Symmetry code: (i) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $1-z$.

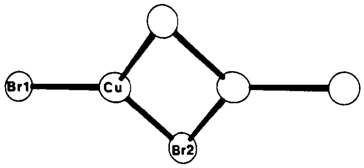

Fig. 1. The di-μ-bromo-dibromodicuprate(I) anion showing the atomic numbering. The thermal ellipsoids enclose 50% probability (*ORTEP*; Johnson, 1965).

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* Lists of structure factors, H-atom coordinates, anisotropic thermal parameters and bond distances and angles within the methyltriphenylphosphonium cation have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43624 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Comparison of discrete* $[Cu_2Br_4]^{2-}$ *anions*

Distances are in Å and angles in °. A terminal halogen ligand is denoted X_t and a bridging ligand X_b; d is the distance of Cu from the plane through X_t, X_b and X_b'.

Compound	Cu—X_t	Cu—X_b	Cu···Cu	Cu—X_b—Cu	X_b—Cu—X_b	X_b—Cu—X_t	d	$X_b\cdots X_b$	Ref.
$[N(C_2H_5)_4]_2[Cu_2Br_4]$	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)	(*a*)
$[N(C_6H_5)(CH_3)_3]_2[Cu_2Br_4]$	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)	(*b*)
$[P(CH_3)(C_6H_5)_3]_2[Cu_2Br_4]$	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)	This work
$(TTT)_2[Cu_2Br_4]$*	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)†	(*c*)

References: (*a*) Asplund & Jagner (1984*a*); (*b*) Andersson & Jagner (1985*a*); (*c*) Shibaeva & Kaminskii (1981).

* TTT = tetrathiotetracene, two additional Cu—S, 2·684 and 3·062 Å, to the tetrathiotetracene cation radicals.
† Estimated.

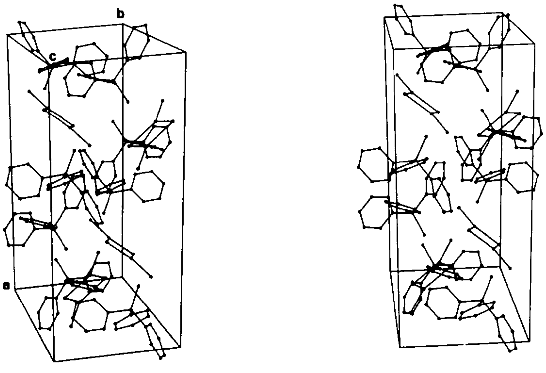

Fig. 2. Stereoscopic view of the unit cell (*ORTEP*; Johnson, 1965).

the Cu···Cu separation. Similar variations have been observed for the centrosymmetric $[Cu_2I_4]^{2-}$ anion (Asplund, Jagner & Nilsson, 1982; Asplund & Jagner, 1984*c*; Hartl, Brüdgam & Mahdjour-Hassan-Abadi, 1985), the Cu···Cu separation varying from 2·698 (2) Å in $[N(C_3H_7)_4]_2[Cu_2I_4]$ (Asplund & Jagner, 1984*c*) to 2·957 (1) Å in $[P(C_6H_5)_4]_2[Cu_2I_4]$ (Hartl, Brüdgam & Mahdjour-Hassan-Abadi, 1985). Moreover, non-planar $[Cu_2I_4]^{2-}$ ions have been found in $[As(C_6H_5)_4]_2[Cu_2I_4]$ (Asplund & Jagner, 1984*b*) and in a second modification of $[P(C_6H_5)_4]_2[Cu_2I_4]$ (Hartl, Brüdgam & Mahdjour-Hassan-Abadi, 1985), these anions being folded 146·61 (4)° and 146·34 °, respectively, about the bridging I···I contact. The $[Cu_2X_4]^{2-}$ ion would thus appear capable of considerable flexibility with respect to its geometry under different steric and electrostatic constraints in the solid state.

A stereoview of the structure is shown in Fig. 2. There is one short packing distance between anion and cation, *viz.* $Cu\cdots C(23^{ii}) = 3{\cdot}357\ (7)$ Å [symmetry code: (ii) $x - \frac{1}{2}, \frac{1}{2} + y, z$]. All other such distances are >3·7 Å. The P—C distances within the cation lie in the range 1·784 (7)–1·798 (8) Å, in good agreement with those determined for *e.g.* $[P(CH_3)(C_6H_5)_3]_2[CuI_3]$ (Bowmaker *et al.*, 1984). As in the latter compound, P—C(phenyl) and P—C(methyl) do not differ.

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