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Short Communications

Crystal Structure of Ethyltriphenylphosphonium Dibromocuprate(I), $[P(C_2H_5)(C_6H_5)_3][CuBr_2]$

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Tetraalkylammonium bromocuprates(I) have hitherto been found to crystallize with discrete anions containing two-[1] or three-coordinated[2–4] copper(I). In $(NH_4)_2[CuBr_3]$, however, the anion is a chain of Cu(I)-Br tetrahedra linked through vertices.[5] Tetraphenylphosphonium, like tetrabutylammonium,[1] crystallizes with a discrete $[CuBr_2]^-$ anion.[6] There would seem to be a tendency towards increased coordination number of copper(I) from two,[1,6] through three,[2–4] to four[5] with decreasing size of the cation in this series. In order to examine this effect further, and also factors promoting $-Br-Cu-Br-$ catenation in the solid state, attempts are being made to prepare bromocuprates(I) of unsymmetrical quaternary alkyl- or arylphosphonium and ammonium cations. Whereas tetramethylammonium crystallizes with a discrete $[Cu_2Br_5]^{3-}$ anion containing trigonal-planar coordinated copper(I) and a single $Cu-Br-Cu$ bridge,[4] phenyltrimethylammonium dibromocuprate(I) contains a discrete centrosymmetric doubly bridged $[Cu_2Br_4]^{2-}$ dimer,[7] similar to that obtained with tetraethylammonium.[3] In order to investigate the effect on the anionic configuration of replacing a phenyl group in tetraphenylphosphonium by an ethyl group, ethyltriphenylphosphonium dibromocuprate(I) has been prepared and the crystal structure of the compound determined.

Ethyltriphenylphosphonium dibromocuprate(I) was prepared by dissolving ethyltriphenylphosphonium bromide and copper(I) bromide (molar ratio 1:1) in ethanol. Colourless prisms, m.p. 117–118 °C, were deposited from the concentrated solution after a few days. Crystals of $[P(C_2H_5)(C_6H_5)_3][CuBr_2]$, M_r=514.7, are monoclinic, space group $P2_1$, with a=9.758(2), b=12.220(4), c=9.767(4) Å, β=118.70(3)°, Z=2, D_c=1.67 g cm^{-3} and μ(Mo$K\alpha$)=5.33 mm^{-1}. The Laue symmetry was established from Weissenberg photographs taken with **b** as rotation axis.

Diffracted intensities from a crystal, 0.22×0.18×0.20 mm, were measured at approximately 290 K for $2\theta < 50°$ with a Syntex $P2_1$ diffractometer, using graphite-monochromated Mo$K\alpha$ radiation and the $\omega-2\theta$ scan mode with a variable 2θ scan rate of 2.5–15° min^{-1}. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method[8] was used to calculate the intensities.[9] Of the 1913 independent reflections measured, excluding those systematically absent, 1342 had $I > 3.0\,\sigma(I)$ and were considered observed. Correction was made for Lorentz and polarisation effects; an empirical correction[10] for the effects of absorption was made after solution of the structure. The unit-cell dimensions were determined from diffractometer setting angles for 15 reflections.

The positions of the copper and bromine atoms were determined by direct methods (MULTAN 80),[11] intensity statistics clearly indicating acentricity. The remaining non-hydrogen atoms were located from subsequent electron-density maps.[12] Full-matrix least-squares refinement[12] of positional and isotropic thermal parameters gave R=0.091; after an empirical correction[10] for the effects of absorption R=0.072. Inclusion of anisotropic thermal parameters gave R=0.044 for 216 parameters and 1342 reflections. Comparable refinement based on the data uncorrected for absorption yielded R=0.047.

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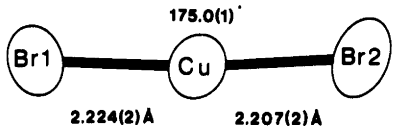

Fig. 1. The dibromocuprate(I) ion in $[P(C_2H_5)(C_6H_5)_3][CuBr_2]$. Estimated standard deviations in the distances and angle are given in parentheses. The thermal ellipsoids enclose 50 % probability.[14]

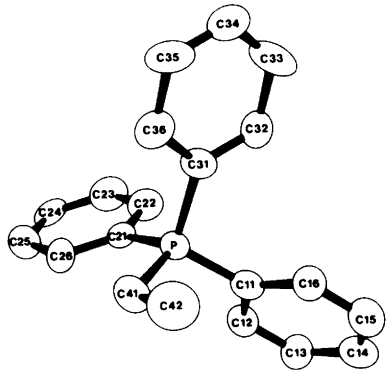

Fig. 2. The ethyltriphenylphosphonium ion showing the atomic numbering. The thermal ellipsoids enclose 50 % probability.[14] Hydrogen atoms have been omitted.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters ($Å^2$) for the non-hydrogen atoms in $[P(C_2H_5)(C_6H_5)_3][CuBr_2]$. 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}
Br(1)	0.2030(1)	0.3680	0.4164(1)	5.73(5)
Cu	0.4046(2)	0.3134(2)	0.3868(2)	5.00(5)
Br(2)	0.6143(2)	0.2731(2)	0.3661(2)	6.57(6)
P	0.8307(3)	0.1947(2)	0.9199(3)	3.08(8)
C(11)	0.9049(11)	0.1248(8)	1.1010(11)	3.6(3)
C(12)	1.0489(13)	0.0669(9)	1.1608(12)	4.1(4)
C(13)	1.1050(13)	0.0106(10)	1.3008(13)	4.8(4)
C(14)	1.0199(14)	0.0066(10)	1.3801(12)	4.9(5)
C(15)	0.8747(14)	0.0615(10)	1.3197(12)	4.8(4)
C(16)	0.8219(12)	0.1193(9)	1.1828(12)	4.1(4)
C(21)	0.9876(10)	0.2247(7)	0.8767(10)	3.0(3)
C(22)	1.1145(10)	0.2849(9)	0.9848(11)	4.0(3)
C(23)	1.2312(12)	0.3158(10)	0.9516(13)	5.1(4)
C(24)	1.2247(11)	0.2870(9)	0.8135(13)	4.1(4)
C(25)	1.0963(12)	0.2270(10)	0.7035(12)	4.4(4)
C(26)	0.9771(11)	0.1954(9)	0.7358(10)	4.0(3)
C(31)	0.7442(10)	0.3174(8)	0.9335(10)	3.2(3)
C(32)	0.7911(11)	0.3723(10)	1.0736(11)	3.9(3)
C(33)	0.7238(14)	0.4760(9)	1.0734(16)	5.3(5)
C(34)	0.6151(12)	0.5208(9)	0.9392(14)	4.5(4)
C(35)	0.5629(12)	0.4688(9)	0.8000(15)	4.5(4)
C(36)	0.6250(10)	0.3665(10)	0.7951(11)	4.0(3)
C(41)	0.6866(11)	0.1118(9)	0.7651(12)	4.2(4)
C(42)	0.5427(13)	0.0858(11)	0.7826(16)	5.9(5)

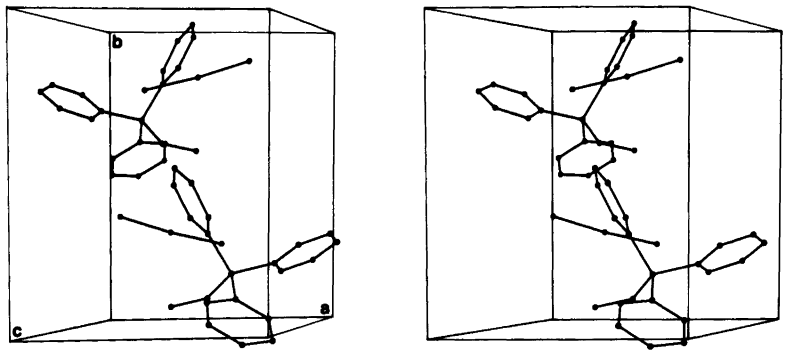

Fig. 3. Stereoscopic view[14] of the unit cell. All atoms are represented as spheres of radius 0.05 Å. Hydrogen atoms have been omitted.

Finally, the hydrogen atoms associated with the phenyl rings and the α-carbon of the ethyl group were included as a fixed contribution [C–H=1.0 Å and $B=B_{eq}$ of the carrying carbon atom], an R value of 0.039 being obtained (216 parameters; 1342 reflections). Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*,[13] the F_o values were weighted according to $w=[\sigma^2(F_o)+0.0009\,F_o^2]^{-1}$ and the origin was specified by holding the y coordinate of Br(1) invariant. A final difference map showed a maximum residual electron density of 0.48 eÅ^{-3}. It was not possible to locate the hydrogen atoms bonded to C(42). Atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table 1. Structure factors, anisotropic thermal parameters, hydrogen-atom coordinates and angles within the cation may be obtained from the authors.

Discussion. The anion in ethyltriphenylphosphonium dibromocuprate(I) is a nearly linear monomer (Fig. 1) similar to that in tetraphenylphosphonium dibromocuprate(I) in which Cu–Br=2.216(2) and 2.211(2) Å and Br–Cu–Br=173.62(7)°.[6] The geometry of the monomeric dibromocuprate(I) ion has also been determined in tetrabutylammonium dibromocuprate(I): Cu–Br=2.226(1) Å, Br–Cu–Br=180°;[1] in [{[$CH_3C(CH_2P(C_6H_5)_2)_3$]-IrP_3}$_3Cu_5Br_4$] [$CuBr_2$]: Cu–Br=2.221(10) Å, Br–Cu–Br=178.4(3)°[15] and in the cation radical salt of tetraselenotetracene, TSeT, with dibromocuprate(I), $C_{18}H_8Se_4CuBr_2$: Cu–Br=2.267(2) and 2.282(3) Å, Br–Cu–Br=153.8(1)°.[16] In the last compound there is an additional Cu···Br contact of 2.829(2) Å to an adjacent anion.[16]

Table 2. Interatomic distances (Å) within the ethyltriphenylphosphonium cation. Estimated standard deviations are given in parentheses.

P–C(11)	1.776(10)	C(23)–C(24)	1.36(2)
P–C(21)	1.810(9)	C(24)–C(25)	1.40(2)
P–C(31)	1.756(10)	C(25)–C(26)	1.40(1)
P–C(41)	1.803(11)	C(26)–C(21)	1.38(1)
C(11)–C(12)	1.42(2)	C(31)–C(32)	1.39(1)
C(12)–C(13)	1.39(2)	C(32)–C(33)	1.43(2)
C(13)–C(14)	1.38(2)	C(33)–C(34)	1.34(2)
C(14)–C(15)	1.42(2)	C(34)–C(35)	1.36(2)
C(15)–C(16)	1.38(2)	C(35)–C(36)	1.40(2)
C(16)–C(11)	1.39(1)	C(36)–C(31)	1.42(1)
C(21)–C(22)	1.39(1)	C(41)–C(42)	1.53(2)
C(22)–C(23)	1.38(1)		

The ethyltriphenylphosphonium cation is depicted in Fig. 2 and bond distances within the cation are given in Table 2. Phosphorus-carbon distances are similar to those determined for $[P(C_6H_5)_4][CuBr_2]$, *viz.* 1.768(7)–1.794(7) Å.[6] The crystal structure of the compound is illustrated in Fig. 3. The shortest Br···C contact involving the ethyl group, $Br(1)\cdots C(41^{i})=3.88(1)$ Å, is of the same magnitude, or slightly longer than, the shortest such contacts to the phenyl groups, *i.e.* $Br\cdots C(32^{ii})=3.80(1)$, $Br(1)\cdots C(15^{iii})=3.83(1)$, $Br(1)\cdots C(25^{iv})=3.84(1)$, $Br(2)\cdots C(26)=3.77(1)$, $Br(2)\cdots C(16^{v})=3.78(1)$ and $Br(2)\cdots C(15^{v})=3.80(1)$ Å. Cu···C(ethyl) distances are, however, considerably longer than the shortest Cu···C(phenyl) contacts: $Cu\cdots C(41^{i})=3.88(1)$, $Cu\cdots C(42^{i})=3.86(1)$, Cu···C(36)=3.56(1) and $Cu\cdots C(22^{ii})=3.59(1)$ Å [symmetry code: (*i*): $1-x,\frac{1}{2}+y,1-z$; (*ii*): $x-1,y,z-1$; (*iii*): $1-x,\frac{1}{2}+y,2-z$; (*iv*): $x-1,y,z$; (*v*): $x,y,z-1$]. In tetraphenylphosphonium dibromocuprate(I)[6] there is one very short Cu···C contact, 3.387(8) Å, and four other Cu···C distances less than 3.6 Å. The shortest Br···C distances in $[P(C_6H_5)_4][CuBr_2]$, 3.668(10)–3.681(8) Å,[6] are also slightly shorter than those in the present compound.

Like tetraphenylphosphonium,[6] ethyltriphenylphosphonium crystallizes with a monomeric dibromocuprate(I) anion. Replacement of a single phenyl group by the appreciably smaller ethyl group would thus not appear to affect the configuration of the anion in the solid state.

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