

Crystal Structures of Tetrabutylammonium Dichlorocuprate(I) and Tetrabutylammonium Dibromocuprate(I), $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuCl}_2]$ and $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuBr}_2]$

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The crystal structures of the title compounds have been determined from single-crystal X-ray diffractometer data collected at 168 K. $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuCl}_2]$ and $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuBr}_2]$ are isostructural and crystallize in space group $C2/c$, with $a = 13.055(1)$, $b = 9.844(1)$, $c = 15.776(2)$ Å, $\beta = 92.39(1)^\circ$, $Z = 4$ and $a = 13.059(8)$, $b = 10.060(5)$, $c = 15.920(7)$ Å, $\beta = 92.56(4)^\circ$, $Z = 4$, respectively. Full-matrix least-squares refinement of the 147 structural parameters gave $R = 0.038$ for tetrabutylammonium dichlorocuprate(I) [1094 observed independent reflections, $I > 3.0 \sigma(I)$] and $R = 0.033$ for tetrabutylammonium dibromocuprate(I) [1291 observed independent reflections, $I > 3.0 \sigma(I)$]. The $[\text{CuCl}_2]^-$ and $[\text{CuBr}_2]^-$ ions are linear with Cu at a centre of symmetry; Cu–Cl = 2.107(1) Å and Cu–Br = 2.226(1) Å.

Whereas the dichlorocuprate(I) ion has been found as a linear monomer in a number of crystal structures,^{1–6} there seems to be little evidence for the existence of discrete dibromocuprate(I) or diiodocuprate(I) ions in the solid state. Recently, tetrabutylammonium diiodocuprate(I) has been shown to contain discrete centrosymmetric $[\text{Cu}_2\text{I}_4]^{2-}$ dimers in which copper(I) has approximately trigonal planar coordination.⁷ The structure of the analogous $[\text{Cu}_2\text{Br}_4]^{2-}$ has been determined in the cation radical salt of tetrathiotetracene with dibromocuprate(I); there are, however, additional Cu–S contacts to the tetrathiotetracene cation radicals such that the configuration of ligands about copper(I) is approximately trigonal bipyramidal.⁸ There does not appear to be any crystallographic determination of a discrete linear $[\text{CuBr}_2]^-$ ion, though infrared and Raman spectra and nuclear

quadrupole resonance frequencies suggest that tetrabutylammonium dichlorocuprate(I) and tetrabutylammonium dibromocuprate(I) both contain linear centrosymmetric anions.⁹ In order to ascertain the nature of the copper(I) coordination in these compounds, their crystal structures have been investigated.

EXPERIMENTAL

Tetrabutylammonium dichlorocuprate(I) and tetrabutylammonium dibromocuprate(I) were prepared from the copper(I) halides as described previously.¹⁰ The compounds crystallize as rhombic plates showing pronounced polysynthetic twinning. Single-crystal fragments of the approximate size indicated in Table 1 were used for the measurement of intensities at 168 K with a Syntex $P2_1$ diffractometer and graphite-monochromated $\text{MoK}\alpha$ radiation. Crystal data and details concerning the data collection are given in Table 1.

Periodical measurement of the intensities of two reflections showed that the crystals were not subject to decay during the collection of data. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method¹¹ was used to calculate the intensities.¹² Data were corrected¹³ for Lorentz and polarization effects but not for absorption, owing to the irregular shapes of the crystals. The unit-cell parameters at 168 K were determined by least-squares from diffractometer setting angles for 14 reflections.

STRUCTURE DETERMINATION AND REFINEMENT

The structure of $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuBr}_2]$ was determined from Patterson and successive electron

Table 1. Crystal data for tetrabutylammonium dichlorocuprate(I) and tetrabutylammonium dibromocuprate(I).

	$[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuCl}_2]$	$[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuBr}_2]$
M_r	376.9	465.8
Unit-cell dimensions	$a = 13.055(1)$, $b = 9.844(1)$, $c = 15.776(2)$ Å $\beta = 92.39(1)^\circ$	$a = 13.059(8)$, $b = 10.060(5)$, $c = 15.920(7)$ Å $\beta = 92.56(4)^\circ$
Space group ^{15a}	$C2/c$ (No. 15)	$C2/c$ (No. 15)
Z	4	4
D_c	1.24 g cm^{-3}	1.48 g cm^{-3}
$\mu(\text{MoK}\alpha)$	13.8 cm^{-1}	51.3 cm^{-1}
Habit	Colourless rhombic plates	Colourless rhombic plates
Crystal size	$0.18 \times 0.26 \times 0.04 \text{ mm}$	$0.11 \times 0.20 \times 0.08 \text{ mm}$
Temperature	168 K	168 K
$2\theta_{\text{max}}$	50°	50°
Scan mode;	$\omega - 2\theta$; $2.5 - 12.0^\circ \text{ min}^{-1}$	$\omega - 2\theta$; $2.5 - 12.0^\circ \text{ min}^{-1}$
2θ scan rate		
No. of independent reflections measured	1771	1851
No. of observed independent reflections [$I > 3\sigma(I)$]	1094	1291
No. of parameters refined	147	147
Weighting scheme ¹⁶	$w = (30.0 + F_o + 0.010 F_o^2)^{-1}$	$w = (36.0 + F_o + 0.007 F_o^2)^{-1}$
Final R (observed reflections)	0.038	0.033
Final R (observed + unobserved reflections)	0.072	0.058

density maps¹³ and the atomic coordinates were used as the starting point also for the refinement of $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuCl}_2]$. Block-diagonal least-squares refinement¹³ of positional, isotropic and then anisotropic thermal parameters for the non-hydrogen atoms yielded $R = 0.064$ for $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuCl}_2]$ and $R = 0.049$ for $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuBr}_2]$. The hydrogen atoms were located from difference maps and included in the refinement with isotropic temperature factors set equal to the equivalent isotropic

values¹⁴ of the carrying carbon atoms. Full-matrix least-squares refinement of 147 parameters terminated in $R = 0.038$ for $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuCl}_2]$ (1094 reflections) and $R = 0.033$ for $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuBr}_2]$ (1291 reflections). Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*^{15b} and F_o values were weighted¹⁶ as indicated in Table 1. Final difference maps showed a maximum electron density of $0.26 \text{ e } \text{Å}^{-3}$ for $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuCl}_2]$ and $0.40 \text{ e } \text{Å}^{-3}$ for $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuBr}_2]$. Atomic coordinates and thermal parameters are listed in Tables 2 and 3. Structure factors are available from the authors on request.

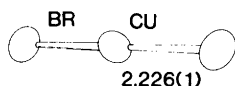
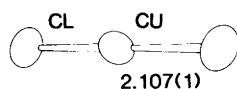


Fig. 1. The dichlorocuprate(I) and dibromocuprate(I) ions.¹⁸

DISCUSSION

In tetrabutylammonium dichlorocuprate(I) and tetrabutylammonium dibromocuprate(I) the anions are linear with copper(I) at a centre of symmetry. The Cu–Cl bond length (Fig. 1) appears to be

Table 2. Fractional coordinates and thermal parameters, $U_{ij} \times 10^3$ or B (\AA^2), for $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuCl}_2]$. For the non-hydrogen atoms the anisotropic temperature factor has the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \dots + U_{23}b^*c^*kl)]$. For the hydrogen atoms $B = B_{\text{eq}}$ of the carrying carbon atom where B_{eq} is defined as $B_{\text{eq}} = (8\pi^2/3)(U_{11}a^{*2}a^2 + \dots + U_{23}b^*c^*bc \cos \alpha)$. Estimated standard deviations are given in parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0.2500	0.2500	0.5000	46.5(4)	51.7(5)	37.4(4)	-18.5(9)	11.7(6)	-14.4(8)
Cl	0.2660(1)	0.0710(1)	0.5725(1)	75.8(9)	52.3(8)	51.0(7)	22.8(13)	8.3(12)	4.4(12)
N	0.0000	0.1524(4)	0.2500	27(2)	21(2)	29(2)	0	9(3)	0
C(1)	0.0930(3)	0.0592(4)	0.2653(3)	28(2)	29(2)	33(2)	6(3)	1(3)	-4(3)
C(2)	0.1959(3)	0.1318(4)	0.2702(2)	26(2)	35(2)	37(2)	6(3)	7(3)	-5(4)
C(3)	0.2792(3)	0.0386(5)	0.3071(3)	29(2)	39(3)	45(2)	6(4)	-9(4)	-4(4)
C(4)	0.3827(3)	0.1084(6)	0.3125(4)	31(2)	50(3)	65(3)	1(4)	0(4)	3(5)
C(5)	0.0139(3)	0.2451(4)	0.1738(2)	29(2)	23(2)	29(2)	0(4)	3(3)	5(4)
C(6)	0.0293(4)	0.1753(4)	0.0901(2)	38(2)	35(2)	33(2)	7(4)	4(3)	4(4)
C(7)	0.0637(4)	0.2802(5)	0.0255(3)	56(3)	43(3)	32(2)	-9(4)	22(4)	-1(4)
C(8)	0.0875(5)	0.2146(6)	-0.0590(3)	68(3)	64(4)	35(2)	19(6)	18(5)	7(4)

Atom	x	y	z	B	Atom	x	y	z	B
H(11)	0.084(4)	0.012(6)	0.320(3)	2.4	H(51)	-0.043(4)	0.309(5)	0.171(3)	2.1
H(12)	0.091(4)	-0.011(6)	0.223(3)	2.4	H(52)	0.071(4)	0.305(5)	0.191(3)	2.1
H(21)	0.220(4)	0.168(6)	0.210(3)	2.6	H(61)	0.077(4)	0.107(6)	0.097(3)	2.8
H(22)	0.196(4)	0.211(6)	0.305(3)	2.6	H(62)	-0.030(4)	0.133(6)	0.070(3)	2.8
H(31)	0.275(4)	-0.052(6)	0.279(3)	3.0	H(71)	0.013(4)	0.356(6)	0.013(3)	3.4
H(32)	0.267(4)	0.009(6)	0.368(4)	3.0	H(72)	0.123(5)	0.334(6)	0.051(3)	3.4
H(41)	0.380(5)	0.194(7)	0.336(4)	3.9	H(81)	0.031(5)	0.169(7)	-0.083(4)	4.4
H(42)	0.440(5)	0.045(6)	0.344(4)	3.9	H(82)	0.141(5)	0.144(7)	-0.051(4)	4.4
H(43)	0.391(5)	0.125(6)	0.254(4)	3.9	H(83)	0.109(5)	0.284(7)	-0.096(4)	4.4

Table 3. Fractional coordinates and thermal parameters, $U_{ij} \times 10^3$ or B (\AA^2), for $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuBr}_2]$. For the non-hydrogen atoms the anisotropic temperature factor has the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \dots + U_{23}b^*c^*kl)]$. For the hydrogen atoms $B = B_{\text{eq}}$ of the carrying carbon atom where B_{eq} is defined as $B_{\text{eq}} = \frac{8\pi^2}{3}(U_{11}a^{*2}a^2 + \dots + U_{23}b^*c^*bc \cos \alpha)$. Estimated standard deviations are given in parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0.2500	0.2500	0.5000	48.0(5)	50.9(5)	34.6(4)	-19.8(9)	6.2(7)	-8.5(8)
Br	0.27181(4)	0.06186(6)	0.57223(3)	66.5(4)	53.0(3)	46.5(3)	23.0(6)	4.4(5)	2.4(5)
N	0.0000	0.1477(5)	0.2500	26(2)	23(2)	27(2)	0	0(4)	0
C(1)	0.0923(3)	0.0586(4)	0.2653(3)	31(2)	29(2)	33(2)	2(4)	-6(4)	1(4)
C(2)	0.1956(3)	0.1271(5)	0.2722(3)	27(2)	43(3)	37(2)	7(4)	0(4)	-3(4)
C(3)	0.2778(4)	0.0347(5)	0.3095(3)	31(2)	44(3)	43(3)	5(4)	-6(4)	-11(4)
C(4)	0.3825(4)	0.1004(7)	0.3142(4)	29(2)	62(4)	75(4)	8(5)	-3(5)	-7(6)
C(5)	0.0147(3)	0.2400(4)	0.1750(2)	33(2)	25(2)	31(2)	0(4)	2(3)	8(3)
C(6)	0.0267(4)	0.1704(5)	0.0905(3)	41(3)	36(2)	31(2)	-9(4)	2(4)	6(4)
C(7)	0.0624(4)	0.2708(5)	0.0276(3)	53(3)	43(3)	36(3)	-6(5)	13(4)	7(4)
C(8)	0.0787(5)	0.2076(6)	-0.0571(3)	68(4)	55(3)	35(3)	13(6)	9(5)	7(5)

Atom	x	y	z	B	Atom	x	y	z	B
H11	0.081(4)	0.008(6)	0.313(4)	2.4	H(51)	-0.042(5)	0.302(6)	0.171(3)	2.3
H(12)	0.093(4)	-0.006(6)	0.218(4)	2.4	H(52)	0.072(5)	0.302(6)	0.189(3)	2.3
H(21)	0.218(5)	0.161(6)	0.215(4)	2.8	H(61)	0.070(5)	0.100(7)	0.099(4)	2.8
H(22)	0.189(5)	0.201(6)	0.307(4)	2.8	H(62)	-0.035(5)	0.124(6)	0.075(4)	2.8
H(31)	0.282(5)	-0.041(7)	0.282(4)	3.1	H(71)	0.023(5)	0.339(7)	0.020(4)	3.5
H(32)	0.263(5)	0.002(7)	0.362(4)	3.1	H(72)	0.115(5)	0.307(7)	0.047(4)	3.5
H(41)	0.380(6)	0.193(8)	0.340(5)	4.4	H(81)	0.020(6)	0.157(8)	-0.080(4)	4.2
H(42)	0.435(6)	0.036(7)	0.342(4)	4.4	H(82)	0.131(5)	0.135(8)	-0.048(4)	4.2
H(43)	0.391(6)	0.104(8)	0.266(5)	4.4	H(83)	0.099(5)	0.275(7)	-0.102(4)	4.2

Table 4. Bond lengths (Å) within the tetrabutylammonium ions in tetrabutylammonium dichlorocuprate(I) and tetrabutylammonium dibromocuprate(I). Estimated standard deviations in parentheses.

	$[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuCl}_2]$	$[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuBr}_2]$
N—C(1)	1.533(5)	1.514(5)
C(1)—C(2)	1.521(5)	1.514(6)
C(2)—C(3)	1.519(6)	1.521(7)
C(3)—C(4)	1.515(6)	1.517(7)
N—C(5)	1.526(4)	1.531(5)
C(5)—C(6)	1.510(5)	1.530(6)
C(6)—C(7)	1.531(6)	1.511(7)
C(7)—C(8)	1.526(7)	1.514(7)
C(1)—H(11)	0.99(5)	0.93(6)
C(1)—H(12)	0.96(5)	0.99(6)
C(2)—H(21)	1.08(5)	1.02(6)
C(2)—H(22)	0.95(6)	0.94(6)
C(3)—H(31)	1.00(6)	0.88(7)
C(3)—H(32)	1.03(6)	0.92(7)
C(4)—H(41)	0.92(7)	1.02(8)
C(4)—H(42)	1.08(6)	1.02(7)
C(4)—H(43)	0.96(6)	0.79(8)
C(5)—H(51)	0.98(5)	0.96(6)
C(5)—H(52)	0.98(5)	1.00(6)
C(6)—H(61)	0.92(6)	0.91(7)
C(6)—H(62)	0.92(6)	0.96(6)
C(7)—H(71)	1.02(6)	0.86(7)
C(7)—H(72)	1.01(6)	0.82(7)
C(8)—H(81)	0.93(7)	0.99(7)
C(8)—H(82)	0.99(7)	1.01(8)
C(8)—H(83)	0.95(7)	1.03(7)

slightly longer than values reported for $[\text{CuCl}_2]^-$ at room temperature¹⁻⁶ but is in close agreement with that in $[\text{N}_6\text{P}_6(\text{N}(\text{CH}_3)_2)_{12}\text{CuCl}][\text{CuCl}_2]$ after

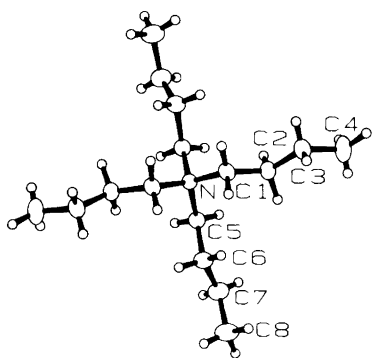


Fig. 2. The tetrabutylammonium ion in $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuBr}_2]$ showing the atomic numbering.¹⁸ The thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are represented as spheres of radius 0.1 Å.

correction for thermal libration, *i.e.* 2.11(1) Å.²

We believe that this is the first determination of Cu—Br in a discrete $[\text{CuBr}_2]^-$ ion. As expected, the distance, 2.226(1) Å, is shorter than both Cu—Br_{terminal} and Cu—Br_{bridging} in $[\text{Cu}_2\text{Br}_4]^{2-}$, *i.e.* 2.328(2), and 2.490(2) and 2.472(3) Å, respectively, in which copper(I) is essentially three-coordinated with two longer Cu—S contacts completing a trigonal bipyramid.⁸ In $[\text{Cu}(\text{NH}_3)_4][\text{CuBr}_2]_2$ in which the anions form infinite chains of edge-sharing Cu(I)—Br tetrahedra the Cu—Br distance is 2.503(4) Å.¹⁷

Which factors are decisive for the attainment of discrete linear $[\text{CuX}_2]^-$ ions *contra* a dimeric or polymeric configuration seem as yet to be uncertain. It has been suggested^{1b} that stabilization of monomeric $[\text{CuCl}_2]^-$ may be due to the presence of large bulky cations. The structures of the anions in the series $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuX}_2]$, X = Cl, Br, I, might thus suggest an increased tendency to polymerization from X = Cl to X = I counterbalanced by stabilization of a monomeric configuration by

Table 5. Interatomic angles ($^\circ$) within the tetrabutylammonium ions in tetrabutylammonium dichlorocuprate(I) and tetrabutylammonium dibromocuprate(I). Estimated standard deviations in parentheses. Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

	$[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuCl}_2]$	$[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuBr}_2]$
C(1)–N–C(1 ⁱ)	106.5(4)	107.3(4)
C(1)–N–C(5)	111.3(2)	111.0(2)
C(1)–N–C(5 ⁱ)	110.7(2)	111.1(2)
C(5)–N–C(5 ⁱ)	106.5(4)	105.4(4)
N–C(1)–C(2)	114.8(3)	116.2(4)
C(1)–C(2)–C(3)	110.6(3)	111.1(4)
C(2)–C(3)–C(4)	111.7(4)	111.8(4)
N–C(5)–C(6)	116.2(3)	115.4(4)
C(5)–C(6)–C(7)	109.2(4)	108.9(4)
C(6)–C(7)–C(8)	111.8(4)	111.6(4)

tetrabutylammonium ions. The far infrared spectrum of tetraethylammonium dibromocuprate(I) has been interpreted in terms of a polymeric structure for the anion,⁹ which would also support the hypothesis that a cation the size of $[\text{N}(\text{C}_4\text{H}_9)_4]^+$ is a prerequisite for suppression of polymerization.

Bond distances and angles within the tetrabutylammonium ion in the two compounds are given in Tables 4 and 5, the atomic numbering being in accordance with Fig. 2. A stereoscopic view¹⁸ of the unit cell is shown in Fig. 3. The cation has the

usual staggered conformation and there are no abnormal bond distances or angles. Nor do any of the carbon atoms have large thermal parameters as was the case in bis(tetrabutylammonium)di- μ -iodo-diiododicuprate(I).⁷ The closest non-bonded approach distances between carbon and copper(I) are C(3) \cdots Cu = 3.720(4) Å in $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuCl}_2]$ and C(3) \cdots Cu = 3.757(5) Å in $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuBr}_2]$. The shortest distances between carbon and halogen are C(2) \cdots Cl = 3.846(4) Å and C(2) \cdots Br = 3.876(5) Å.

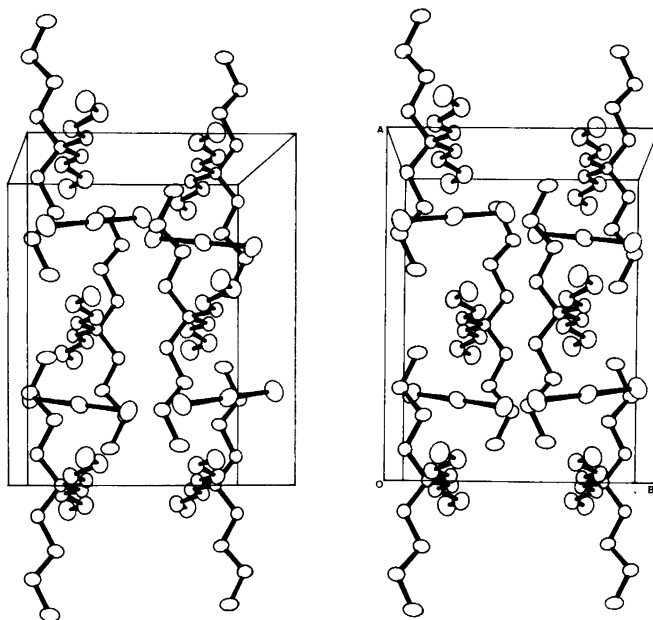


Fig. 3. Stereoscopic view of the unit cell of $[\text{N}(\text{C}_4\text{H}_9)_4][\text{CuBr}_2]$.

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