Acta Cryst. (1994). **C50**, 1890–1892

Tetrakis(trimethylphenylammonium) Octa-μ-bromo-dibromohexacuprate(I)

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(*Received* 24 *November* 1993; *accepted* 18 *July* 1994)

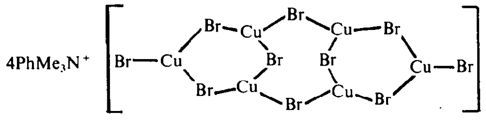
Abstract

The title complex, [N(CH$_3$)$_3$(C$_6$H$_5$)]$_4$[Cu$_6$Br$_{10}$], contains a centrosymmetric eight-membered ring of alternating Cu and Br atoms fused to two six-membered rings of alternating Cu and Br atoms. The average Cu—Br bond length is 2.377 (4) Å. A terminal Br atom is attached to one Cu atom of each of the six-membered rings [Cu—Br 2.290 (4) Å]. Two close Cu···Cu contacts [2.664 (4) and 2.706 (4) Å] exist in each six-membered ring.

Comment

Anionic copper(I) halide complexes exhibit a wide variety of stoichiometries and structural forms, which apparently depend upon the identity of the cation and the halide ion (Jagner & Helgesson, 1991). For example, (Et$_4$N)$_6$[Cu$_6$I$_{11}$]I contains a trigonal prism of six Cu atoms, each bound to a terminal I atom. The five faces of the geometric copper motif are each centered by an I atom. An uncoordinated I$^-$ ion is present in the unit cell (Mahdjour-Hassan-Abadi, Hartl & Fuchs, 1984). Changing the halide ion from iodide to chloride gives (Et$_4$N)$_3$[Cu$_7$Cl$_{10}$] (Asplund & Jagner, 1984), in which an eight-membered ring of alternating Cu and Cl atoms is fused to two six-membered rings of similar alternating atom identity. Adjacent Cu$_6$Cl$_9$ moieties are linked into a polymeric chain by linear Cl—Cu—Cl bridges between the six-membered rings. The Cu—Cl distances in the bridges [2.165 (2) Å] are shorter than the Cu—Cl distances for the three-coordinate Cu atoms in the ring system [2.206 (2)–2.346 (2) Å]. The Cu···Cu distances are all in excess of 2.890 (2) Å.

Similarly, the copper chloride formed using trimethylphenylammonium as a cation has a linear CuCl$_2^-$ structure (Andersson & Jagner, 1985*b*), whereas using the same cation but replacing Cl with Br leads to [N(C$_6$H$_5$)(CH$_3$)$_3$]$_2$Cu$_2$Br$_4$, in which a discrete dimer of Cu atoms is bridged by two Br atoms and each Cu atom is also bonded to a terminal Br atom [Cu—Br(terminal) 2.310 (1), Cu—Br(bridging) 2.417 (1) and 2.421 (1), Cu···Cu 2.738 (2) Å (Andersson & Jagner, 1985*a*)]. However, the fact that we have identified a second bromide containing N(CH$_3$)$_3$(C$_6$H$_5$)$^+$ as a cation serves as a warning that product mixtures may not be homogeneous and that further products of unanticipated stoichiometries may exist.



(I)

The ring system of the title structure, (I) (Fig. 1), resembles the polymeric structure of Cu$_7$Cl$_{10}$, but lacks the additional Cu atom that links the terminal halide atoms of adjacent Cu$_6$Cl$_{10}$ units. In the structure of Cu$_7$Cl$_{10}$ all the Cu···Cu distances exceed 2.890 (2) Å, whereas the title complex has two close Cu···Cu contacts [2.664 (4) and 2.706 (4) Å] in each six-membered ring. Furthermore, the Cu—Br1 distances [2.287 (4) and 2.279 (4) Å] are shorter than the average Cu—Br dis-

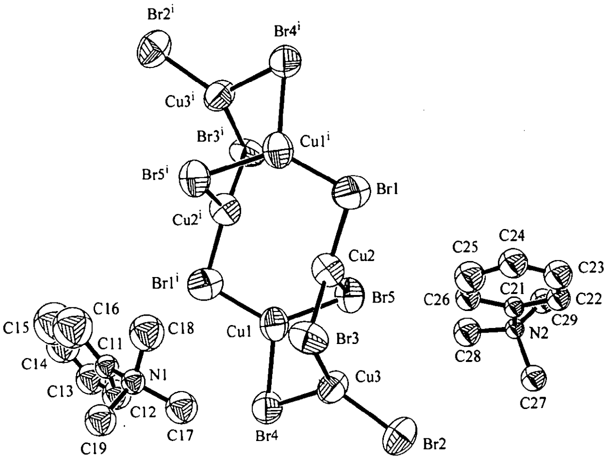


Fig. 1. A view of the title complex showing displacement ellipsoids at the 50% probability level. Symmetry code: (i) 1 $-x$, $-y$, 1 $-$ z.

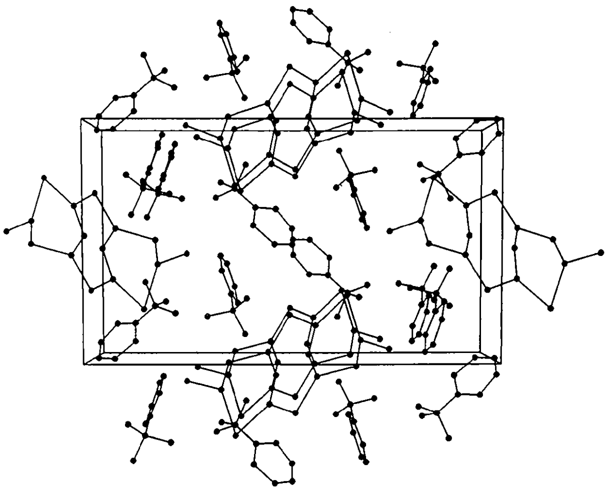


Fig. 2. The packing of the title complex in the unit cell.

tance of 2.377 (4) Å and the Cu2—Br1—Cu1 angle of 103.4 (2)° is larger than the average Cu—Br—Cu angle of 80.6 (1)°. The anomalous details of the bonding at Br1 undoubtedly stem from conformational changes within the six-membered rings as a result of Cu···Cu contacts which may be considered to be interactive (Mehrotra & Hoffmann, 1978).

The trimethylphenylammonium cations show no strong interactions with the copper bromide moieties (Fig. 2).

Experimental

[$N(CH_3)_3Ph$]Cl (0.347 g, 2 mmol) was dissolved in 20 ml of ethanol and the resulting colorless solution added to an ethanolic solution (20 ml) of CuBr (0.29 g, 2 mmol) and a small amount of ascorbic acid to retard oxidation. The combined solution was heated under reflux in an atmosphere of nitrogen for 6 h, cooled to room temperature, filtered and allowed to stand. Brown plate-like crystals were observed to form after four days.

Crystal data

$2(C_9H_{14}N)[Cu_3Br_5]$
$M_r = 862.59$
Monoclinic
$P2_1/n$
$a = 9.477\ (2)$ Å
$b = 21.712\ (4)$ Å
$c = 12.683\ (3)$ Å
$\beta = 94.43\ (3)°$
$V = 2601.9\ (10)$ Å^3
$Z = 4$
$D_x = 2.202$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 21 reflections
$\theta = 6.79–10.634°$
$\mu = 10.116$ mm^{-1}
$T = 293\ (2)$ K
Plate
$0.6 \times 0.4 \times 0.2$ mm
Brown

Data collection

Siemens *P*4 four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.352$, $T_{\max} = 0.794$
3157 measured reflections
2381 independent reflections
1019 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0563$
$\theta_{\max} = 19.99°$
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 25$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 97 reflections intensity variation: 0.009%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0582$
$wR(F^2) = 0.1335$
$S = 0.939$
2086 reflections
172 parameters
H-atom positions refined using a riding model
$w = 1/[\sigma^2(F_o^2) + (0.0947P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.665$ e Å^{-3}
$\Delta\rho_{\min} = -0.656$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1994)
Extinction coefficient: 0.0000 (9)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
Cu1	0.3462 (3)	0.0561 (2)	0.3444 (2)	0.0834 (10)
Cu2	0.4096 (3)	0.05981 (15)	0.5560 (2)	0.0799 (10)
Cu3	0.2784 (3)	0.16844 (15)	0.4082 (2)	0.0808 (10)
Br1	0.4779 (3)	0.0068 (2)	0.7065 (2)	0.1062 (11)
Br2	0.1242 (3)	0.24341 (14)	0.4536 (2)	0.0979 (10)
Br3	0.5071 (3)	0.15452 (13)	0.5079 (2)	0.0823 (9)
Br4	0.2753 (3)	0.13503 (14)	0.2213 (2)	0.0889 (10)
Br5	0.1779 (3)	0.03960 (13)	0.4738 (2)	0.0795 (9)
N1	0.7983 (15)	0.1430 (7)	0.2208 (11)	0.042 (4)
C11	0.7804 (20)	0.0921 (9)	0.1430 (14)	0.042 (5)
C12	0.6645 (23)	0.0967 (10)	0.0675 (15)	0.067 (7)
C13	0.6526 (26)	0.0450 (12)	−0.0096 (18)	0.081 (8)
C14	0.7362 (28)	0.0011 (14)	−0.0101 (20)	0.096 (9)
C15	0.8353 (36)	0.0015 (16)	0.0550 (24)	0.140 (12)
C16	0.8734 (33)	0.0427 (14)	0.1379 (23)	0.122 (10)
C17	0.6674 (20)	0.1753 (10)	0.2430 (16)	0.075 (7)
C18	0.8520 (23)	0.1164 (10)	0.3238 (14)	0.086 (8)
C19	0.8952 (20)	0.1919 (9)	0.1847 (15)	0.067 (7)
N2	−0.1139 (14)	0.1498 (6)	0.7120 (10)	0.032 (4)
C21	0.0216 (18)	0.1567 (8)	0.7798 (13)	0.032 (5)
C22	0.0137 (20)	0.1797 (9)	0.8789 (14)	0.044 (5)
C23	0.1444 (21)	0.1854 (9)	0.9412 (16)	0.059 (6)
C24	0.2732 (22)	0.1713 (10)	0.9065 (15)	0.060 (6)
C25	0.2690 (24)	0.1511 (10)	0.8058 (16)	0.070 (7)
C26	0.1496 (20)	0.1411 (9)	0.7377 (15)	0.048 (6)
C27†	−0.1682 (33)	0.2118 (10)	0.6889 (27)	0.054 (13)
C28†	−0.0918 (35)	0.1195 (15)	0.6089 (20)	0.067 (14)
C29†	−0.2168 (32)	0.1137 (15)	0.7651 (21)	0.051 (12)
C27′†	−0.1305 (59)	0.0875 (13)	0.6690 (42)	0.096 (26)
C28′†	−0.2433 (34)	0.1628 (23)	0.7698 (29)	0.045 (17)
C29′†	−0.1204 (47)	0.1945 (19)	0.6223 (29)	0.053 (19)

† Site occupancy = 0.5.

Table 2. *Selected geometric parameters* (Å, °)

Cu1—Br1$^{\rm i}$	2.287 (4)	C12—C13	1.49 (3)
Cu1—Br4	2.380 (4)	C13—C14	1.24 (3)
Cu1—Br5	2.402 (4)	C14—C15	1.20 (3)
Cu1—Cu3	2.664 (4)	C15—C16	1.40 (3)
Cu1—Cu2	2.706 (4)	N2—C29	1.46 (2)
Cu2—Br1	2.279 (4)	N2—C27′	1.46 (2)
Cu2—Br3	2.354 (4)	N2—C27	1.46 (2)
Cu2—Br5	2.397 (4)	N2—C29′	1.49 (2)
Cu3—Br2	2.290 (4)	N2—C28	1.49 (2)
Cu3—Br3	2.442 (4)	N2—C21	1.50 (2)
Cu3—Br4	2.477 (4)	N2—C28′	1.50 (2)
N1—C17	1.47 (2)	C21—C22	1.36 (2)
N1—C11	1.48 (2)	C21—C26	1.40 (2)
N1—C18	1.48 (2)	C22—C23	1.42 (2)
N1—C19	1.50 (2)	C23—C24	1.36 (2)
C11—C16	1.39 (3)	C24—C25	1.35 (2)
C11—C12	1.40 (2)	C25—C26	1.39 (2)
Br1$^{\rm i}$—Cu1—Br4	114.84 (15)	Br2—Cu3—Br4	119.2 (2)
Br1$^{\rm i}$—Cu1—Br5	129.9 (2)	Br3—Cu3—Br4	113.82 (14)
Br4—Cu1—Br5	112.8 (2)	Cu2—Br1—Cu1$^{\rm i}$	103.4 (2)
Br1—Cu2—Br3	124.5 (2)	Cu2—Br3—Cu3	83.79 (13)
Br1—Cu2—Br5	117.6 (2)	Cu1—Br4—Cu3	66.51 (12)
Br3—Cu2—Br5	114.3 (2)	Cu2—Br5—Cu1	68.64 (12)
Br2—Cu3—Br3	121.0 (2)		

Symmetry code: (i) $1 - x, -y, 1 - z$.

An extinction correction was calculated using *SHELXL*93 (Sheldrick, 1994), but proved to be negligible. The methyl groups are disordered such that the sites at C27, C28 and C29 are related to the sites at C27′, C28′ and C29′ by a 60° rotation, each site being only half occupied. Data collection, data reduction and cell refinement: *XSCANS* (Siemens, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990).

Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *XP*. Software used to prepare material for publication: *SHELXL*93.

The authors acknowledge NSF grant EHR-9108771

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: CR1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). **C50**, 1892–1894

$(BEDT\text{-}TTF)_3[CuBr_2Cl_2]$

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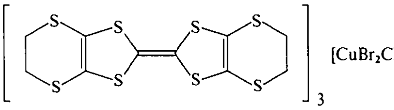
(*Received* 13 *September* 1993; *accepted* 19 *May* 1994)

Abstract

The structure of the title compound, tris[3,4,3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene] dibromodichlorocuprate(2−), $(C_{10}H_8S_8)_3[CuBr_2Cl_2]$, consists of alternate layers of BEDT-TTF molecules [BEDT-TTF = 3,4,3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene] and pseudo-square-planar $[CuBr_2Cl_2]^{2-}$ anions. Two crystallographically independent BEDT-TTF molecules (*A* and *B*) are observed with approximate charges of 0 and +1, respectively. The BEDT-TTF molecules are stacked in an *ABBABB* fashion with a dihedral angle of 67° between the stacks, as in the α phase; short S···S contacts result in two-dimensional conducting layers.

Comment

Considerable efforts are being devoted to the search for superconductors with higher transition temperatures (*Proceedings of the International Conference on Synthetic Metals*, 1993). Among the compounds studied are the salts of organic electron donors such as BEDT-TTF, which provides some of the highest T_c's among the organic chalcogenides. Several studies of the effect of the shape, size and charge of the counter anions have developed guidelines for the synthesis of conducting polytypes. Of particular interest, due to the interplay between superconductivity and magnetism, are the salts containing transition metal anions with a magnetic moment (Kurmoo *et al.*, 1993). We report here the crystal structure of one member of this family, which contains a d^9 ion, $(BEDT\text{-}TTF)_3[CuBr_2Cl_2]$, (I).



(I)

The title compound is isostructural with $(BEDT\text{-}TTF)_3[CuBr_4]$ (Guionneau *et al.*, 1994) and consists of BEDT-TTF layers separated by layers of $[CuBr_2Cl_2]^{2-}$ anions. Apart from the halogen atoms all of the atoms are ordered. The refined occupancies of the sites for the Cl and the Br atoms show statistical disorder such that each halide site is approximately 50% Cl and 50% Br. The mean Cu—Cl [2.311 (3) Å] and Cu—Br [2.391 (3) Å] dis-

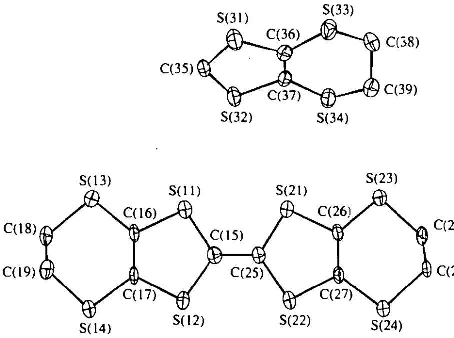


Fig. 1. A view of the two independent molecules of BEDT-TTF in the unit cell, showing displacement ellipsoids at the 50% probability level. The second half of the top molecule is generated by an inversion centre.