

# Poly[tetramethylammonium [ $\mu_4$ -bromido-di- $\mu_2$ -bromido-dicuprate(I)]]

Xi Liu

College of Chemistry, Chongqing Normal University, Chongqing 400047, People's Republic of China

Correspondence e-mail: xliu@cqnu.edu.cn

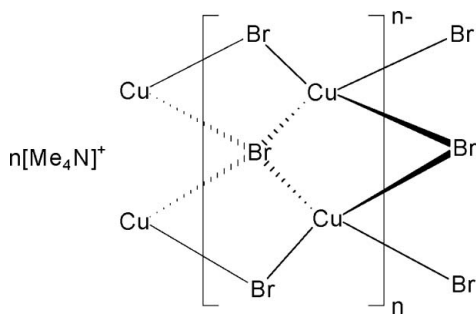
Received 16 September 2007; accepted 29 September 2007

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{N}-\text{C}) = 0.006$  Å;  $R$  factor = 0.036;  $wR$  factor = 0.097; data-to-parameter ratio = 18.9.

The title compound,  $\{(\text{C}_4\text{H}_{12}\text{N})[\text{Cu}_2\text{Br}_3]\}_n$ , consists of  $\text{Cu}^{\text{I}}$ -bromide complex anions and tetramethylammonium cations. The bromide ions bridge  $\text{Cu}^{\text{I}}$  ions to form one-dimensional polymeric chains. Both the cation and the anion have mirror symmetries; in the cation, the N atom and two C atoms are located on a mirror plane, while in the complex anion, the three bromide ions are located on two different mirror planes. No hydrogen bonding occurs in the crystal structure.

## Related literature

For general background, see: Subramanian & Hoffmann (1992); Ford *et al.* (1999); Place *et al.* (1998); Cariati *et al.* (2000). For related structures, see: Andersson & Jagner (1986, 1989); Liu *et al.* (2005).



## Experimental

### Crystal data

$(\text{C}_4\text{H}_{12}\text{N})[\text{Cu}_2\text{Br}_3]$   
 $M_r = 440.96$

Orthorhombic,  $Pnma$   
 $a = 17.018$  (2) Å

$b = 6.5466$  (7) Å  
 $c = 9.6698$  (13) Å  
 $V = 1077.3$  (2) Å<sup>3</sup>  
 $Z = 4$

Mo  $K\alpha$  radiation  
 $\mu = 15.01$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 $0.20 \times 0.10 \times 0.08$  mm

### Data collection

Rigaku Mercury CCD  
 diffractometer  
 Absorption correction: multi-scan  
 (*CrystalClear*; Rigaku, 2002)  
 $T_{\text{min}} = 0.080$ ,  $T_{\text{max}} = 0.300$

6754 measured reflections  
 1039 independent reflections  
 878 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.052$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.097$   
 $S = 1.00$   
 1039 reflections

55 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.68$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.86$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Cu1—Br1	2.5946 (6)	Cu1—Br2	2.4396 (6)
Cu1—Br1 <sup>i</sup>	2.6389 (6)	Cu1—Br3	2.4068 (6)
Br3—Cu1—Br2	122.07 (3)	Br2—Cu1—Br1	99.257 (19)
Br3—Cu1—Br1	111.94 (2)	Br3—Cu1—Br1 <sup>i</sup>	98.228 (19)

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

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We gratefully acknowledge financial support by the Scientific Research Foundation for Doctors of Chongqing Normal University, China (grant No. 06XLB016), the Scientific Project of Chongqing Municipal Education Commission (grant No. KJ070812) and the Natural Science Foundation Project of CQ, China (grant No. CSTC2007BB4234).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2327).

## References

- Andersson, S. & Jagner, S. (1986). *Acta Chem. Scand. Ser. A*, **40**, 177–181.  
 Andersson, S. & Jagner, S. (1989). *Acta Chem. Scand. Ser. A*, **43**, 39–43.  
 Cariati, E., Bu, X. & Ford, P. C. (2000). *Chem. Mater.* **12**, 3385–3391.  
 Ford, P. C., Cariati, E. & Bourassa, J. L. (1999). *Chem. Rev.* **99**, 3625–3648.  
 Liu, X., Guo, G.-C., Wu, A.-Q., Cai, L.-Z. & Huang, J.-S. (2005). *Inorg. Chem.* **44**, 4282–4286.  
 Place, H., Scott, B., Long, G. S. & Willett, R. D. (1998). *Inorg. Chim. Acta*, **279**, 1–6.  
 Rigaku (2002). *CrystalClear*. Version 1.35. Rigaku Corporation, Tokyo, Japan.  
 Siemens (1994). *SHELXTL*. Version 5. Siemens Energy and Automation Inc., Madison, Wisconsin, USA.  
 Subramanian, L. & Hoffmann, R. (1992). *Inorg. Chem.* **31**, 1021–1029.

**supplementary materials**

*Acta Cryst.* (2007). E63, m2651 [ doi:10.1107/S1600536807047885 ]

## Poly[tetramethylammonium [ $\mu_4$ -bromido-di- $\mu_2$ -bromido-dicuprate(I)]]

X. Liu

### Comment

Great interest is presently being focused on the controllable preparation of copper(I)-halide-based compounds due to their various structures (Subramanian & Hoffmann, 1992) and photophysical properties (Ford *et al.*, 1999). The various structural features may be ascribed to the diversity of the Cu(I) coordination geometry and the capability of the halide ions to bridge between the diamagnetic metal ions (Place *et al.*, 1998); while the photophysical properties may be associated with the  $d^{10}$  electronic configuration of the Cu(I) (Cariati *et al.*, 2000). In present paper, we report the synthesis and crystal structure of a CuBr-based complex,  $\{[\text{Me}_4\text{N}][\text{Cu}_2\text{Br}_3]\}_n$  (I).

The title compound is isomorphous with its chloride analogue (Andersson & Jagner, 1986). The crystal consists of one-dimensional  $[\text{Cu}_2\text{Br}_3]_n^{n-}$  anionic chain accompanying with isolated  $[\text{Me}_4\text{N}]^+$  cations (Figure 1). The  $\text{Cu}^{\text{I}}$  ion displays a slightly distorted tetrahedral geometry formed by two  $\mu$ -Br and two  $\mu_4$ -Br atoms. The Cu—Br bond distances rang from 2.4068 (6) to 2.6389 (6) Å, and the Br—Cu—Br bond angels vary between 98.23 (2) to 122.07 (3)° (Table 1), which are comparable to those in the  $[\text{Cu}_a\text{Br}_b]^{n-}$  clusters (Andersson & Jagner, 1989; Liu *et al.*, 2005). Two adjacent  $[\text{CuBr}_4]^{3-}$  tetrahedra along the a direction form a repeating unit of tetrahedra pair with inversion center through Br—Br edge-sharing. These tetrahedra pairs further connect each other through Br—Br edge-sharing to yield a one-dimensional  $[\text{Cu}_2\text{Br}_3]_n^{n-}$  anionic chain along the b direction. The  $[\text{Me}_4\text{N}]^+$  cations reside between these anionic chains without obvious C—H $\cdots$ Br hydrogen bonding interactions but electrostatic interactions and van der Waals force (Figure 2).

### Experimental

A mixture of CuCN (90 mg, 1.0 mmol) and  $\text{Me}_4\text{NBr}$  (231 mg, 1.5 mmol) in 10 ml of dry and distilled tetrahydrofuran was sealed into a 25 ml polytetrafluoroethylene-lined stainless steel containers under autogenous pressure and heated at 433 K for 4 d, followed by cooling at  $0.1 \text{ K}\cdot\text{min}^{-1}$  to room temperature. The resulted orange crystals were collected with *ca* 40% yield (based on CuCN). Calc. for  $\text{C}_4\text{H}_{12}\text{Br}_3\text{Cu}_2\text{N}$ : C, 10.90; H, 2.74; N, 3.18(%); Found: C, 10.83; H, 2.69; N, 3.25(%).

### Refinement

H atoms were added according to the theoretical models and torsion angles were refined with C—H = 0.96 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ .

## Figures



Fig. 1. The structure of the anionic chain with 30% probability of thermal ellipsoids [symmetry code A:  $-x, -y, -z$ ].

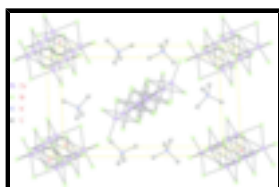


Fig. 2. A view of the unit cell structure.

## Poly[tetramethylammonium [ $\mu_4$ -bromido-di- $\mu_2$ -bromido-dicopper(I)]]

### Crystal data

(C<sub>4</sub>H<sub>12</sub>N)[Cu<sub>2</sub>Br<sub>3</sub>]

$M_r = 440.96$

Orthorhombic, *Pnma*

Hall symbol: -P 2ac 2n

$a = 17.018$  (2) Å

$b = 6.5466$  (7) Å

$c = 9.6698$  (13) Å

$V = 1077.3$  (2) Å<sup>3</sup>

$Z = 4$

$F_{000} = 824$

$D_x = 2.719$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 2070 reflections

$\theta = 3.1$ – $27.5^\circ$

$\mu = 15.01$  mm<sup>-1</sup>

$T = 293$  (2) K

Prism, orange

$0.20 \times 0.10 \times 0.08$  mm

### Data collection

Rigaku Mercury CCD  
diffractometer

Radiation source: rotating-anode generator

Monochromator: graphite

$T = 293$  (2) K

$\omega$  scans

Absorption correction: multi-scan  
(CrystalClear; Rigaku, 2002)

$T_{\min} = 0.080$ ,  $T_{\max} = 0.300$

6754 measured reflections

1039 independent reflections

878 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$

$\theta_{\max} = 25.0^\circ$

$\theta_{\min} = 3.2^\circ$

$h = -20 \rightarrow 20$

$k = -7 \rightarrow 7$

$l = -11 \rightarrow 8$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.097$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2]$

$S = 1.00$

1039 reflections

55 parameters

Primary atom site location: structure-invariant direct methods

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.68 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.86 \text{ e } \text{\AA}^{-3}$

Extinction correction: none

### Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu1	0.07375 (3)	0.50134 (6)	0.43157 (5)	0.06294 (15)	
Br1	0.04183 (2)	0.7500	0.63282 (4)	0.03593 (11)	
Br2	0.09825 (3)	0.7500	0.24868 (5)	0.05354 (14)	
Br3	0.16999 (2)	0.2500	0.49720 (5)	0.04730 (13)	
N1	0.15065 (18)	0.2500	-0.0327 (3)	0.0352 (9)	
C1	0.1572 (3)	0.4365 (5)	-0.1174 (4)	0.0848 (15)	
H1A	0.2077	0.4396	-0.1616	0.127*	
H1B	0.1516	0.5545	-0.0593	0.127*	
H1C	0.1167	0.4368	-0.1864	0.127*	
C2	0.2111 (3)	0.2500	0.0796 (5)	0.0642 (16)	
H2A	0.2626	0.2500	0.0392	0.096*	
H2B	0.2047	0.1303	0.1358	0.096*	0.50
H2C	0.2047	0.3697	0.1358	0.096*	0.50
C3	0.0709 (3)	0.2500	0.0330 (7)	0.079 (2)	
H3A	0.0313	0.2500	-0.0377	0.118*	
H3B	0.0651	0.3697	0.0895	0.118*	0.50
H3C	0.0651	0.1303	0.0895	0.118*	0.50

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0740 (3)	0.0491 (3)	0.0658 (3)	0.00909 (19)	0.0015 (3)	0.0110 (2)
Br1	0.0419 (2)	0.0317 (2)	0.0343 (2)	0.000	-0.00283 (17)	0.000
Br2	0.0905 (3)	0.0326 (2)	0.0376 (2)	0.000	0.0095 (2)	0.000
Br3	0.0437 (2)	0.0351 (2)	0.0631 (3)	0.000	-0.0052 (2)	0.000
N1	0.0446 (17)	0.0263 (16)	0.0346 (19)	0.000	-0.0041 (15)	0.000

## supplementary materials

C1	0.137 (4)	0.055 (2)	0.063 (2)	-0.019 (2)	-0.021 (2)	0.031 (2)
C2	0.066 (3)	0.069 (3)	0.058 (3)	0.000	-0.023 (3)	0.000
C3	0.052 (3)	0.079 (4)	0.104 (5)	0.000	0.018 (3)	0.000

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Cu1—Br1	2.5946 (6)	N1—C2	1.496 (6)
Cu1—Br1 <sup>i</sup>	2.6389 (6)	N1—C3	1.499 (5)
Cu1—Br2	2.4396 (6)	C1—H1A	0.9600
Cu1—Br3	2.4068 (6)	C1—H1B	0.9600
Cu1—Cu1 <sup>i</sup>	2.8377 (10)	C1—H1C	0.9600
Br1—Cu1 <sup>ii</sup>	2.5946 (6)	C2—H2A	0.9600
Br1—Cu1 <sup>i</sup>	2.6389 (6)	C2—H2B	0.9600
Br1—Cu1 <sup>iii</sup>	2.6389 (6)	C2—H2C	0.9600
Br2—Cu1 <sup>ii</sup>	2.4396 (6)	C3—H3A	0.9600
Br3—Cu1 <sup>iv</sup>	2.4068 (6)	C3—H3B	0.9600
N1—C1 <sup>iv</sup>	1.474 (4)	C3—H3C	0.9600
N1—C1	1.474 (4)		
Br3—Cu1—Br2	122.07 (3)	C1 <sup>iv</sup> —N1—C3	107.7 (2)
Br3—Cu1—Br1	111.94 (2)	C1—N1—C3	107.7 (2)
Br2—Cu1—Br1	99.257 (19)	C2—N1—C3	108.3 (4)
Br3—Cu1—Br1 <sup>i</sup>	98.228 (19)	N1—C1—H1A	109.5
Br2—Cu1—Br1 <sup>i</sup>	111.87 (2)	N1—C1—H1B	109.5
Br1—Cu1—Br1 <sup>i</sup>	114.337 (19)	H1A—C1—H1B	109.5
Br3—Cu1—Cu1 <sup>i</sup>	118.34 (3)	N1—C1—H1C	109.5
Br2—Cu1—Cu1 <sup>i</sup>	119.57 (3)	H1A—C1—H1C	109.5
Br1—Cu1—Cu1 <sup>i</sup>	57.919 (18)	H1B—C1—H1C	109.5
Br1 <sup>i</sup> —Cu1—Cu1 <sup>i</sup>	56.418 (18)	N1—C2—H2A	109.5
Cu1—Br1—Cu1 <sup>ii</sup>	77.72 (2)	N1—C2—H2B	109.5
Cu1—Br1—Cu1 <sup>i</sup>	65.663 (19)	H2A—C2—H2B	109.5
Cu1 <sup>ii</sup> —Br1—Cu1 <sup>i</sup>	111.735 (17)	N1—C2—H2C	109.5
Cu1—Br1—Cu1 <sup>iii</sup>	111.735 (17)	H2A—C2—H2C	109.5
Cu1 <sup>ii</sup> —Br1—Cu1 <sup>iii</sup>	65.663 (19)	H2B—C2—H2C	109.5
Cu1 <sup>i</sup> —Br1—Cu1 <sup>iii</sup>	77.15 (2)	N1—C3—H3A	109.5
Cu1 <sup>ii</sup> —Br2—Cu1	83.71 (3)	N1—C3—H3B	109.5
Cu1 <sup>iv</sup> —Br3—Cu1	86.26 (3)	H3A—C3—H3B	109.5
C1 <sup>iv</sup> —N1—C1	111.8 (4)	N1—C3—H3C	109.5
C1 <sup>iv</sup> —N1—C2	110.5 (2)	H3A—C3—H3C	109.5
C1—N1—C2	110.5 (2)	H3B—C3—H3C	109.5
Br3—Cu1—Br1—Cu1 <sup>ii</sup>	128.459 (17)	Cu1 <sup>i</sup> —Cu1—Br1—Cu1 <sup>iii</sup>	-63.70 (2)
Br2—Cu1—Br1—Cu1 <sup>ii</sup>	-1.76 (3)	Br3—Cu1—Br2—Cu1 <sup>ii</sup>	-121.45 (2)
Br1 <sup>i</sup> —Cu1—Br1—Cu1 <sup>ii</sup>	-120.959 (16)	Br1—Cu1—Br2—Cu1 <sup>ii</sup>	1.84 (3)
Cu1 <sup>i</sup> —Cu1—Br1—Cu1 <sup>ii</sup>	-120.959 (16)	Br1 <sup>i</sup> —Cu1—Br2—Cu1 <sup>ii</sup>	122.857 (18)

Br3—Cu1—Br1—Cu1 <sup>i</sup>	-110.58 (3)	Cu1 <sup>i</sup> —Cu1—Br2—Cu1 <sup>ii</sup>	60.09 (4)
Br2—Cu1—Br1—Cu1 <sup>i</sup>	119.20 (3)	Br2—Cu1—Br3—Cu1 <sup>iv</sup>	-119.47 (2)
Br1 <sup>i</sup> —Cu1—Br1—Cu1 <sup>i</sup>	0.0	Br1—Cu1—Br3—Cu1 <sup>iv</sup>	123.330 (17)
Br3—Cu1—Br1—Cu1 <sup>iii</sup>	-174.28 (2)	Br1 <sup>i</sup> —Cu1—Br3—Cu1 <sup>iv</sup>	2.85 (3)
Br2—Cu1—Br1—Cu1 <sup>iii</sup>	55.50 (2)	Cu1 <sup>i</sup> —Cu1—Br3—Cu1 <sup>iv</sup>	59.01 (4)
Br1 <sup>i</sup> —Cu1—Br1—Cu1 <sup>iii</sup>	-63.70 (2)		

Symmetry codes: (i)  $-x, -y+1, -z+1$ ; (ii)  $x, -y+3/2, z$ ; (iii)  $-x, y+1/2, -z+1$ ; (iv)  $x, -y+1/2, z$ .

Fig. 1

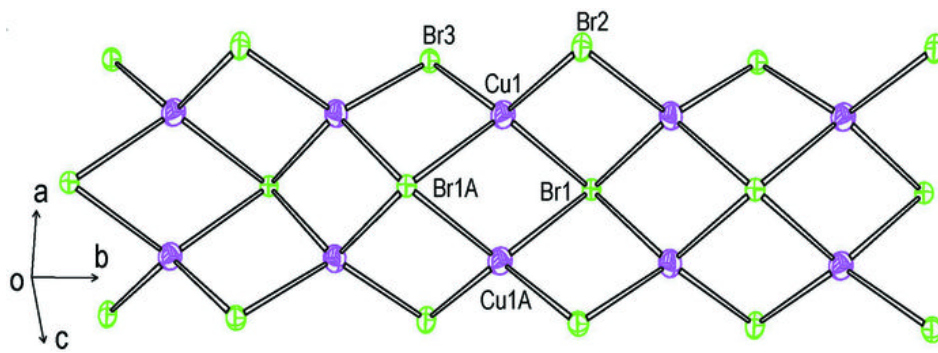




Fig. 2

