

Crystal Structure of Bis(phenyltrimethylammonium) Di- μ -bromo-dibromodicuprate(I)

STAFFAN ANDERSSON and SUSAN JAGNER

Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden

The crystal structure of the title compound has been determined from single-crystal X-ray diffraction data. $[\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_3]_2[\text{Cu}_2\text{Br}_4]$ crystallizes in space group $P\bar{1}$ with $a=9.127(4)$, $b=9.266(3)$, $c=7.914(2)$ Å, $\alpha=96.96(3)$, $\beta=92.10(3)$, $\gamma=67.36(3)^\circ$ and $Z=1$. Full-matrix least-squares refinement of 160 structural parameters gave $R=0.035$ for 1588 observed [$I > 3.0\sigma(I)$] reflections.

The $[\text{Cu}_2\text{Br}_4]^{2-}$ anion is a discrete centrosymmetric dimer containing approximately trigonal-planar coordinated copper(I). The Cu–Br_{terminal} distance is 2.310(1) Å; the Cu–Br_{bridging} distances are 2.417(1) and 2.421(1) Å and the Cu···Cu separation 2.738(2) Å.

Crystalline tetraalkylammonium bromocuprates(I) investigated hitherto have been found to contain discrete anions.^{1–4} $(\text{NH}_4)_2[\text{CuBr}_3]$, on the other hand, contains chains of Cu(I)–Br tetrahedra linked through vertices.⁵ In tetrabutylammonium dibromocuprate(I) the anion is a linear monomer;¹ in the compounds obtained with tetrapropylammonium, tetraethylammonium and tetramethylammonium as cations, *viz.* $[\text{N}(\text{C}_3\text{H}_7)_4]_2[\text{Cu}_4\text{Br}_6]$,² $[\text{N}(\text{C}_2\text{H}_5)_4]_2[\text{Cu}_2\text{Br}_4]$,³ and $[\text{N}(\text{CH}_3)_4]_3[\text{Cu}_2\text{Br}_5]$,⁴ copper(I) is, however, approximately trigonal-planar coordinated. Tetraphenylphosphonium, which is similar in shape to, but slightly smaller than, tetrabutylammonium, and which might be expected to have a somewhat less well-screened positive charge, crystallizes with an almost linear monomeric $[\text{CuBr}_2]^-$ ion.⁶ There would thus seem to be a tendency towards increased coordination number of copper(I) with decreasing size of, and less well-screened positive charge on, the cation. In order to examine this tendency further, as well as factors promoting –Br–Cu–Br– catenation, attempts are being made presently to prepare bromocuprates(I) with unsymmetrical quaternary alkyl- and arylammonium and phosphonium cations. Crystals of phenyltrimethylammonium dibromocuprate(I) have thus been obtained and the structure of the compound investigated.

EXPERIMENTAL

Bis(phenyltrimethylammonium) di- μ -bromo-dibromodicuprate(I) was prepared by dissolving phenyltrimethylammonium bromide and copper(I) bromide (molar ratio 1:1) in ethanol. Colourless prisms of $[\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_3]_2[\text{Cu}_2\text{Br}_4]$ were deposited from the concentrated solution after a few days.

0302-4377/85 \$2.50

© 1985 Acta Chemica Scandinavica

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (\AA^2) for the non-hydrogen atoms in $[\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_3]_2[\text{Cu}_2\text{Br}_4]$. 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 | <i>x</i> | <i>y</i> | <i>z</i> | B_{eq} |
|-------|-------------|-------------|------------|-----------------|
| Cu | -0.13244(8) | 0.08684(8) | 0.09766(9) | 4.14(2) |
| Br(1) | -0.36441(7) | 0.22924(6) | 0.25048(8) | 4.06(2) |
| Br(2) | 0.03483(7) | -0.18482(7) | 0.12475(8) | 4.43(2) |
| N | 0.3877(5) | 0.2867(4) | 0.7661(5) | 3.1(1) |
| C(1) | 0.4290(9) | 0.1319(8) | 0.8360(9) | 5.0(2) |
| C(2) | 0.2875(8) | 0.4139(8) | 0.8979(8) | 4.3(2) |
| C(3) | 0.5381(7) | 0.3111(8) | 0.7414(9) | 4.5(2) |
| C(4) | 0.2977(6) | 0.2936(6) | 0.6041(6) | 2.9(2) |
| C(5) | 0.2547(8) | 0.1739(7) | 0.5371(8) | 4.1(2) |
| C(6) | 0.1693(8) | 0.1857(9) | 0.3876(9) | 5.1(2) |
| C(7) | 0.1334(8) | 0.3154(10) | 0.3051(9) | 5.3(3) |
| C(8) | 0.1757(8) | 0.4369(8) | 0.3723(8) | 4.7(2) |
| C(9) | 0.2591(7) | 0.4284(7) | 0.5218(7) | 3.7(2) |

Crystals of $[\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_3]_2[\text{Cu}_2\text{Br}_4]$, $M_r=719.1$, are triclinic, space group $P\bar{1}$, with $a=9.127(4)$, $b=9.266(3)$, $c=7.914(2)$ \AA , $\alpha=96.96(3)$, $\beta=92.10(3)$, $\gamma=67.36(3)^\circ$, $Z=1$, $D_c=1.95$ g cm^{-3} and $\mu(\text{MoK}\alpha)=8.70$ mm^{-1} . Diffracted intensities from a crystal, $0.19 \times 0.18 \times 0.16$ mm, were measured at approximately 290 K for $2\theta \leq 50^\circ$, on a Syntex $P2_1$ diffractometer, using graphite-monochromated $\text{MoK}\alpha$ radiation and the $\omega-2\theta$ scan mode with a variable 2θ scan rate of $2.5-15^\circ \text{ min}^{-1}$. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method⁷ was used to calculate the intensities.⁸ Of the 2168 independent reflections thus measured, 1588 had $I > 3.0\sigma(I)$ and were regarded as being observed. Intensities were corrected for Lorentz and polarisation effects; and empirical correction⁹ was made for the effects of absorption after solution of the structure. The unit-cell parameters were determined from diffractometer setting angles for 15 reflections.

STRUCTURE DETERMINATION AND REFINEMENT

The atomic coordinates of the anion and subsequently those of the cation were determined by direct methods (RANTAN 81,¹⁰ DIRDIF¹¹). Full-matrix least-squares refinement¹² of positional and isotropic thermal parameters gave $R=0.129$; after an empirical correction⁹

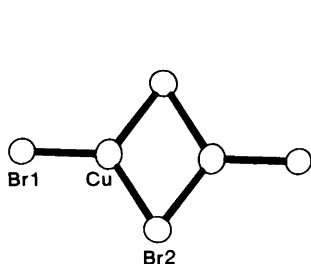


Fig. 1. The di- μ -bromo-dibromodicuprate(1) ion in $[(\text{C}_6\text{H}_5)(\text{CH}_3)_3]_2[\text{Cu}_2\text{Br}_4]$ showing the atomic numbering. The thermal ellipsoids enclose 50% probability.¹⁴

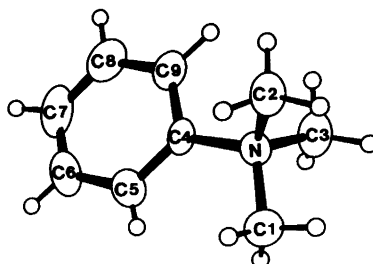


Fig. 2. The phenyltrimethylammonium ion showing the atomic numbering. The thermal ellipsoids enclose 50% probability¹⁴ and hydrogen atoms are represented as spheres of radius 0.1 \AA .

Table 2. Interatomic distances (Å) and angles (°) within the $[Cu_2Br_4]^{2-}$ ion. Estimated standard deviations are given in parentheses. The superscript (*i*) denotes an atom in \bar{x} , \bar{y} , \bar{z} .

| | | | |
|------------------------|----------|------------------------------|-----------|
| Cu—Br(1) | 2.310(1) | Br(1)—Cu—Br(2) | 124.70(4) |
| Cu—Br(2) | 2.421(1) | Br(1)—Cu—Br(2 ⁱ) | 124.12(4) |
| Cu—Br(2 ⁱ) | 2.417(1) | Br(2)—Cu—Br(2 ⁱ) | 111.05(4) |
| Cu...Cu ⁱ | 2.738(2) | Cu—Br(2)—Cu ⁱ | 68.95(4) |

for the effects of absorption $R=0.076$. Inclusion of anisotropic thermal parameters and of positional parameters for the hydrogen atoms (located from a difference map), the isotropic thermal parameters of the latter being set equal to the equivalent isotropic values of the carrying carbon atoms (see Table 1), gave a final R of 0.035 (160 parameters; 1588 reflections). Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*¹³ and the F_o values were weighted according to $w = [\sigma^2(F_o) + 0.0012 F_o^2]^{-1}$. A final difference map showed a maximum electron density of $0.46 \text{ e } \text{Å}^{-3}$. 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 carbon-hydrogen distances may be obtained from the authors.

DISCUSSION

In bis(phenyltrimethylammonium) di- μ -bromo-dibromodicuprate(I) the anion is a discrete centrosymmetric $[Cu_2Br_4]^{2-}$ dimer containing approximately trigonal-planar coordinated copper(I) (Fig. 1; Table 2). The copper(I) atom lies $0.049(1) \text{ Å}$ from the plane defined by the three bromide ligands [Br(1), Br(2) and Br(2ⁱ)]. Comparison with discrete $[Cu_2Br_4]^{2-}$ anions determined previously (Table 3) shows that, whereas Cu—Br_{terminal} distances barely differ, there is considerable variation in the geometry of the four-membered (Cu—Br)₂ ring. Perhaps the most marked difference between the three dimers lies in the magnitude of the Cu...Cu separation. In the cation radical salt of tetrathiotetracene (TTT) with dibromocuprate(I) there are additional Cu—S contacts to the tetrathiotetracene cation radicals such that the configuration of ligands about copper(I) is approximately trigonal bipyramidal.¹⁵ The steric requirements of these interactions might thus be instrumental in the attainment of a

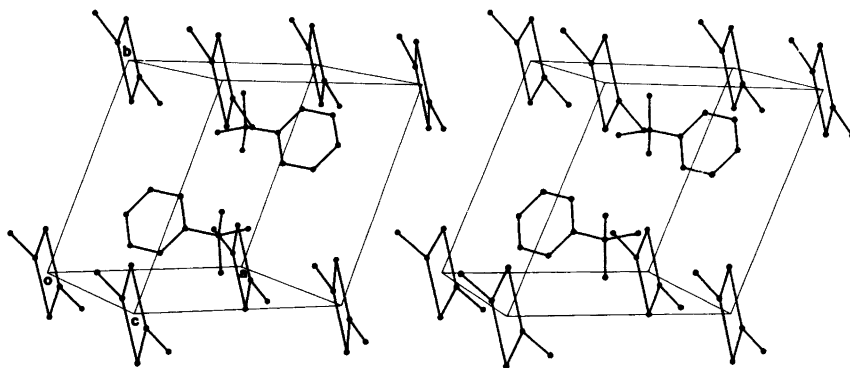


Fig. 3. Stereoscopic view¹⁴ of the unit cell. All atoms are represented as spheres of radius 0.05 Å . Hydrogen atoms have been omitted.

Table 3. Copper(I) coordination geometry in discrete $[\text{Cu}_2\text{Br}_4]^{2-}$, $[\text{Cu}_2\text{Br}_5]^{3-}$ and $[\text{Cu}_2\text{I}_4]^{2-}$ anions. Distances are in Å and angles in °. A terminal halogen ligand is denoted X_t and a bridging X_b .

| Compound | Cu-X _t | Cu-X _b | Cu...Cu | Cu-X _b -Cu | X _b -Cu-X _b | X _b ...X _b | Ref. |
|---|-------------------|-------------------|----------|-----------------------|-----------------------------------|----------------------------------|-----------------|
| $[\text{N}(\text{C}_2\text{H}_5)_4]_2[\text{Cu}_2\text{Br}_4]$ | 2.319(2) | 2.441(2) | 2.937(3) | 73.7(1) | 106.3(1) | 3.916(3) | 3 |
| | | 2.454(2) | | | | | |
| $(\text{TTT})_2[\text{Cu}_2\text{Br}_4]^a$ | 2.328(3) | 2.472(3) | 2.660(3) | 64.7(1) | 115.4(1) | 4.188(4) ^b | 15 |
| | | 2.490(2) | | | | | |
| $[\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_3]_2[\text{Cu}_2\text{Br}_4]$ | 2.310(1) | 2.417(1) | 2.738(2) | 68.95(4) | 111.05(4) | 3.988(2) | present work |
| | | 2.421(1) | | | | | |
| $[\text{N}(\text{CH}_3)_4]_3[\text{Cu}_2\text{Br}_5]$ | 2.381(3) | 2.392(3) | 2.837(4) | 72.8(1) | - | - | 4 |
| | 2.397(2) | | | | | | |
| $[\text{N}(\text{C}_4\text{H}_9)_4]_2[\text{Cu}_2\text{I}_4]$ | 2.514(2) | 2.566(2) | 2.726(4) | 63.8(1) | 116.2(1) | 4.380(3) | 16 |
| | | 2.592(2) | | | | | |
| $[\text{N}(\text{C}_3\text{H}_7)_4]_2[\text{Cu}_2\text{I}_4]$ | 2.499(1) | 2.571(1) | 2.698(2) | 63.14(3) | 116.86(3) | 4.390(1) | 17 |
| | | 2.582(1) | | | | | |
| $[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Cu}_2\text{I}_4]$ | 2.490(3) | 2.578(3) | 2.663(4) | 61.4(1) | 114.2(1) | 4.360(3) | 18 |
| | 2.491(3) | 2.584(3) | | 62.1(1) | 114.4(1) | | |
| | | 2.609(3) | | | | | |
| | | 2.610(3) | | | | | |

^a TTT=tetrathiotetracene, two additional Cu-S contacts, 2.684 and 3.062 Å, to the tetrathiotetracene cation radicals. ^b estimated.

Table 4. Interatomic distances (Å) and angles (°) within the phenyltrimethylammonium cation. Estimated standard deviations are given in parentheses.

| | | | |
|-------------|----------|----------------|-----------|
| N—C(1) | 1.506(8) | C(5)—C(6) | 1.385(9) |
| N—C(2) | 1.502(8) | C(6)—C(7) | 1.359(11) |
| N—C(3) | 1.498(8) | C(7)—C(8) | 1.369(10) |
| N—C(4) | 1.491(6) | C(8)—C(9) | 1.377(9) |
| C(4)—C(5) | 1.357(8) | C(9)—C(4) | 1.396(7) |
| C(1)—N—C(2) | 107.4(4) | N—C(4)—C(9) | 117.5(4) |
| C(1)—N—C(3) | 108.4(5) | C(9)—C(4)—C(5) | 120.6(5) |
| C(1)—N—C(4) | 112.0(4) | C(4)—C(5)—C(6) | 120.1(6) |
| C(2)—N—C(3) | 108.4(4) | C(5)—C(6)—C(7) | 119.7(6) |
| C(2)—N—C(4) | 109.4(4) | C(6)—C(7)—C(8) | 120.4(6) |
| C(3)—N—C(4) | 111.1(4) | C(7)—C(8)—C(9) | 120.8(6) |
| N—C(4)—C(5) | 121.9(4) | C(8)—C(9)—C(4) | 118.3(5) |

shorter Cu...Cu separation and a more regular trigonal-planar coordination geometry of copper(I) in this compound than in the isolated $[\text{Cu}_2\text{Br}_4]^{2-}$ dimers in $[\text{N}(\text{C}_2\text{H}_5)_4]_2[\text{Cu}_2\text{Br}_4]^{3-}$ and $[\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_3]_2[\text{Cu}_2\text{Br}_4]$. In the anions in the latter compounds, the Cu...Cu separation differs, however, by 0.2 Å (Table 3), the larger Cu...Cu in $[\text{N}(\text{C}_2\text{H}_5)_4]_2[\text{Cu}_2\text{Br}_4]$ being accompanied by a smaller $\text{Br}_b\text{—Cu—Br}_b$ angle, a larger Cu— $\text{Br}_b\text{—Cu}$ angle and a shorter non-bonded $\text{Br}\cdots\text{Br}$ contact over the four-membered ring than in the anion in $[\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_3]_2[\text{Cu}_2\text{Br}_4]$.

There is less variation in the geometry of the centrosymmetric $[\text{Cu}_2\text{I}_4]^{2-}$ dimers determined in $[\text{N}(\text{C}_4\text{H}_9)_4]_2[\text{Cu}_2\text{I}_4]^{16}$ and $[\text{N}(\text{C}_3\text{H}_7)_4]_2[\text{Cu}_2\text{I}_4]^{17}$. In $[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Cu}_2\text{I}_4]$ the anion is not, however, planar but is folded about the bridging I...I contact such that the planes through the two ligand triangles are inclined at an angle of 147°.¹⁸ With tetraphenylphosphonium as cation both planar and bent $[\text{Cu}_2\text{I}_4]^{2-}$ dimers have been isolated.¹⁹ The $[\text{Cu}_2\text{X}_4]^{2-}$ entity would thus appear capable of considerable flexibility with respect to its geometry under different steric and electrostatic constraints in the solid state. Despite lack of the restrictions imposed by the bridging bromide ligands in $[\text{Cu}_2\text{Br}_4]^{2-}$, the $[\text{Cu}_2\text{Br}_5]^{3-}$ ion in $[\text{N}(\text{CH}_3)_4]_3[\text{Cu}_2\text{Br}_5]$ has a Cu— $\text{Br}_b\text{—Cu}$ angle of comparable magnitude to those in the $[\text{Cu}_2\text{Br}_4]^{2-}$ anions and a Cu...Cu separation intermediate between that in $[\text{N}(\text{C}_2\text{H}_5)_4]_2[\text{Cu}_2\text{Br}_4]$ and that in $[\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_3]_2[\text{Cu}_2\text{Br}_4]$.

The phenyltrimethylammonium cation is depicted in Fig. 2 and bond distances and angles within the cation are given in Table 4. In bis(tetraethylammonium) di- μ -bromodibromodicuprate(I) the closest approach distance between anion and cation, 3.56(1) Å, is between copper(I) and one of the carbon atoms bonded to nitrogen.³ In the present compound it is the terminal bromide ligand which lies closest to the cation, viz. $\text{Br}(1)\cdots\text{C}(1^i)=3.598(7)$ Å, ($\text{Br}_{\text{terminal}}\cdots\text{C}=3.84(1)$ Å in $[\text{N}(\text{C}_2\text{H}_5)_4]_2[\text{Cu}_2\text{Br}_4]^{3-}$ but 3.56(2) Å in $[\text{N}(\text{CH}_3)_4]_3[\text{Cu}_2\text{Br}_5]^{4-}$). The closest contact between copper(I) and carbon in $[\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_3]_2[\text{Cu}_2\text{Br}_4]$ is $\text{Cu}\cdots\text{C}(6)=3.829(7)$ Å, whereas the bridging bromide ligand has three contacts to carbon, viz. $\text{Br}(2)\cdots\text{C}(2^{ii})=3.802(7)$, $\text{Br}(2)\cdots\text{C}(3^{iii})=3.764(7)$ and $\text{Br}(2)\cdots\text{C}(5^i)=3.795(6)$ Å, of similar magnitude to the closest $\text{Br}_{\text{bridging}}\cdots\text{C}$ in $[\text{N}(\text{C}_2\text{H}_5)_4]_2[\text{Cu}_2\text{Br}_4]$, 3.80(1) Å.³ [Symmetry code: (i): $\bar{x}, \bar{y}, 1-z$; (ii): $x, y-1, z-1$; (iii): $1-x, \bar{y}, 1-z$].

With tetramethylammonium as cation a $[\text{Cu}_2\text{Br}_5]^{3-}$ anion containing three-coordinated copper(I) has been obtained.⁴ The phenyl group in $[\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_3]^+$ can be considered to

exhibit a slightly smaller radius, in that direction, than tetraphenylphosphonium which crystallizes with an almost linear $[\text{CuBr}_2]^-$ monomer.⁶ The group provides, however, a slightly larger radius than tetrapropylammonium with which cation a $[\text{Cu}_4\text{Br}_6]^{2-}$ aggregate containing trigonal-planar coordinated copper(I) was obtained.² It would appear that the net effect of the unsymmetrical phenyltrimethylammonium cation is the stabilization of a three-coordinated copper(I) species in the solid state. The di- μ -bromo-dibromodicuprate(I) anion thus obtained is similar to that obtained with tetraethylammonium as cation³ but there are significant differences in the geometries of these $[\text{Cu}_2\text{Br}_4]^{2-}$ entities.

Acknowledgement. Financial support from the Swedish Natural Science Research Council (NFR) is gratefully acknowledged.

REFERENCES

1. Asplund, M., Jagner, S. and Nilsson, M. *Acta Chem. Scand. A* 37 (1983) 57.
2. Asplund, M. and Jagner, S. *Acta Chem. Scand. A* 38 (1984) 725.
3. Asplund, M. and Jagner, S. *Acta Chem. Scand. A* 38 (1984) 135.
4. Asplund, M. and Jagner, S. *Acta Chem. Scand. A* 39 (1985) 47.
5. Brink, C. and van Arkel, A.E. *Acta Crystallogr.* 5 (1952) 506.
6. Andersson, S. and Jagner, S. *Acta Chem. Scand. A* 39 (1985) 297.
7. Lehmann, M.S. and Larsen, F.K. *Acta Crystallogr. A* 30 (1974) 580.
8. Lindqvist, O. and Ljungström, E. *J. Appl. Crystallogr.* 12 (1979) 134.
9. Walker, N. and Stuart, D. *Acta Crystallogr. A* 39 (1983) 158.
10. Jia-Xing, Y. *RANTAN 81*: University of York, York, United Kingdom 1981.
11. Beurskens, P.T., Bosman, W.P., Doesburg, H.M., Gould, R.O., van den Hark, T.E.M., Prick, P.A.J., Noordik, J.H., Beurskens, G. and Parthasarathi, V. *DIRDIF: Direct Methods for Difference Structures*, Technical Report 1981/2, Crystallography Laboratory, Toernooiveld, Nijmegen, Netherlands 1981.
12. Lindgren, O. *An Integrated Set of Crystallographic Programs*. In *On the Oxygen Coordination of Cerium in Some Sulfates and Chromates*, Thesis, Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, Göteborg 1977.
13. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. 4, p. 72.
14. Johnson, C.K. *ORTEP*: Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge 1965.
15. Shibaeva, R.P. and Kaminskii, V.F. *Kristallografiya* 26 (1981) 332.
16. Asplund, M., Jagner, S. and Nilsson, M. *Acta Chem. Scand. A* 36 (1982) 751.
17. Asplund, M. and Jagner, S. *Acta Chem. Scand. A* 38 (1984) 411.
18. Asplund, M. and Jagner, S. *Acta Chem. Scand. A* 38 (1984) 297.
19. Mahdjour-Hassan-Abadi, F. and Hartl, H. *In preparation*.

Received December 14, 1984.