Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Thermal disorder in the anion of bis(triphenylphosphoranylidene)iminium di-μ-bromido-bis[bromidocuprate(I)]

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.033
wR factor = 0.074
Data-to-parameter ratio = 20.1

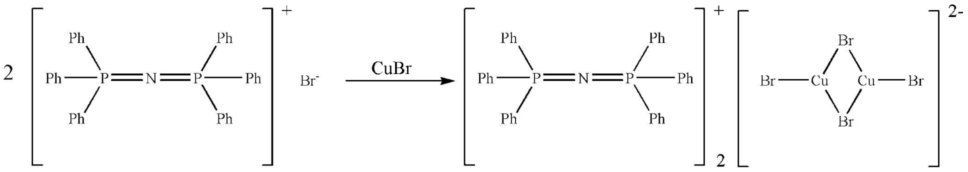
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 2 March 2007
Accepted 21 March 2007

The low-temperature study of the title compound, $(C_{36}H_{30}NP_2)_2[Cu_2Br_4]$, revealed the nature of rotational disorder which has been observed at room temperature for the $[Cu_2Br_4]^{2-}$ anion. The centrosymmetric anion has a planar structure with slightly distorted trigonal coordination of the Cu atoms.

Comment

A number of compounds containing dimeric halogenocuprate(I) anions $[Cu_2X_4]^{2-}$ (X = Cl, Br or I) have been reported in the literature. Thus, $[Cu_2X_4]^{2-}$ units are known to crystallize with large cations such as $[NR_4]^+$ (Asplund *et al.*, 1982; Asplund & Jagner, 1984*a*,*b*), $[PR_4]^+$ (Andersson & Jagner, 1987*a*,*b*; Andersson *et al.*, 1993; Håkansson & Jagner, 1991; Pfitzner & Schmitz, 1997) or $[AsR_4]^+$ (Asplund & Jagner, 1984*c*) (R = alkyl or phenyl), tetrathiotetracene (Shibaeva *et al.*, 1980; Shibaeva & Kaminskii, 1981), bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) (Ito *et al.*, 2005) *etc.* These compounds have potential applications as low-dimensional semiconductor systems (Ito *et al.*, 2005; Papavassiliou *et al.*, 1999). Recently, it has been reported that the inorganic semiconductor [BEDT-TTF][Cu_2Br_4] exhibits rather high conductivity (Ito *et al.*, 2005). In the present paper, the room-temperature (RT) [deposited with Cambridge Structural Database (Allen, 2002) No. 638764] and low-temperature (LT, 100 K) X-ray crystal structure determinations of $[PPN^+]_2$-$[Cu_2Br_4]^{2-}$, (I) (PPN = [$Ph_3P{=}N{=}PPh_3$]), are described.



(I)

The RT investigation showed disorder in the anion of (I) (Fig. 1). It was found that the bridging Br1 and Br1*A* atoms are disordered over three positions, with site occupancies of 0.55, 0.33 and 0.12, respectively. To understand the nature of this disorder, the structure has been reinvestigated at LT (Fig. 2 and Table 1). Under low-temperature conditions, the disorder was 'frozen', an observation that indicates that the disorder found in the RT structure reflected rotational motion of the anion around the Br—Cu···Cu—Br axis. The configuration of Br atoms around the Cu atoms in the centrosymmetric anion is approximately trigonal planar, the deviation of the Cu1 atom being 0.0246 (4) Å from the plane of the three Br atoms. The bond lengths and angles are in the ranges reported for

$[Cu_2Br_4]^{2-}$ anions (Asplund & Jagner, 1984*a*, 1987*a*; Shibaeva *et al.*, 1980; Shibaeva & Kaminskii, 1981). The P—N [1.582 (2)–1.83 (2) Å] and P—C [1.800 (3)–1.810 (3) Å] distances are in a good agreement with those previously determined, *e.g.* bis[bis(triphenylphosphine)iminium] bis-(μ-chlochlorido)tetrachloridodicuprate(II) (Dance *et al.*, 2002).

Experimental

The title complex (I) was prepared as described in the literature (Nilsson, 1982) except that, instead of tetrabutylammonium bromide, bis(triphenylphosphoranylidene)imminium bromide was used. Crystals suitable for X-ray diffraction analysis were obtained by recrystallization from an ethanol solution of (I).

Crystal data

$(C_{36}H_{30}NP_2)_2[Cu_2Br_4]$
M_r = 1523.82
Orthorhombic, *Pbca*
a = 19.718 (5) Å
b = 15.994 (4) Å
c = 20.097 (5) Å
V = 6338 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.34 mm^{-1}
T = 100 (2) K
0.60 × 0.50 × 0.30 mm

Data collection

Bruker SMART APEX II CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.139, T_{max} = 0.377
81872 measured reflections
7625 independent reflections
5652 reflections with $I > 2\sigma(I)$
R_{int} = 0.082

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.074
S = 1.00
7625 reflections
379 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.60 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—Br1	2.4201 (7)	Cu1—Br1^i	2.4558 (6)
Cu1—Br2	2.3369 (6)	Cu1—Cu1^i	2.8278 (8)
Br1—Cu1—Br2	129.51 (2)	Br2—Cu1—Br1^i	121.35 (2)
Br1—Cu1—Br1^i	109.110 (18)	Cu1—Br1—Cu1^i	70.890 (18)

Symmetry code: (i) $-x+2, -y, -z+1$.

During the refinement of the room-temperature structure, the bridging Br1 atom was found to have displacement parameters enlongated in the direction perpendicular to the plane of the four-membered ring, which was attributed to rotational disorder of the anion over three major positions. This was modeled successfully. Refinement included similarity restraints on the Cu1—Br1, Cu1—Br1′ and Cu1—Br1″ distances and displacement parameters, as well as rigid bond restraints for anisotropic displacement parameters. The relative occupancies for the disordered components were refined freely to yield relative occupancies of 0.550 (5), 0.331 (5) and 0.124 (5), respectively, for Br1, Br1^i and Br1^{ii}. The low-temperature structure does not demonstrate significant disorder. However, the displacement ellipsoids of the bridging Br atoms are in the same direction as in the room-temperature structure. All H atoms were geometrically placed (C—H = 0.95 Å at 100 K and C—H = 0.93 Å at room-temperature) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$.

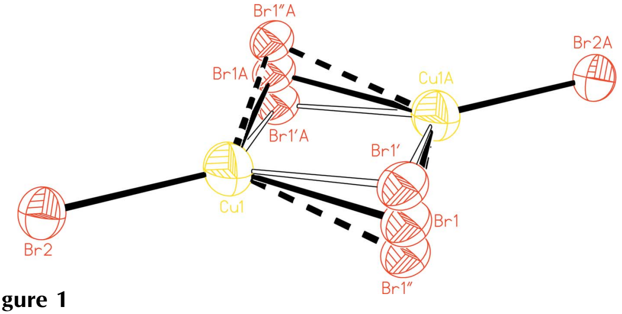


Figure 1
The structure of the anion in (I) determined at room temperature, showing 30% displacement ellipsoids. Atoms Br1 and Br1A are disordered over three positions with occupancies 0.55, 0.33 and 0.12, respectively. [Symmetry code (A): $1 - x, -y, 1 - z$.]

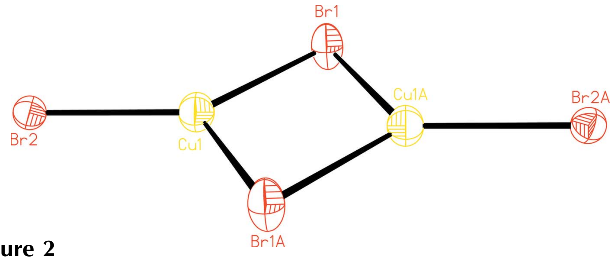


Figure 2
The molecular structure of the anion in (I), determined at 100 K, showing 50% displacement ellipsoids. [Symmetry code (A): $2 - x, -y, 1 - z$.]

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors are grateful for NSF support *via* the NM EPSCoR program and DMR/NSF grant No. 0420863.

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