metal-organic compounds

Bis(2,3-dimethylquinoxalinium) tribromocuprate(I)

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The title compound, $(C_{10}H_{11}N_2)_2[CuBr_3]$, contains layers of planar monoprotonated cations. Isolated trigonal–planar $[CuBr_3]^{2-}$ anions are hydrogen bonded to cations in adjacent layers, providing three-dimensional stability to the crystal structure.

Comment

The triclinic structure of the title compound, (I), contains trigonal planar $[CuBr_3]^{2-}$ anions and planar monoprotonated 2,3-dimethylquinoxaline cations (henceforth dmqH$^+$). Hydrogen bonding between the two crystallographically independent cations and the $[CuBr_3]^{2-}$ anions defines the basic structural unit in the crystal, as illustrated in Fig. 1. Each protonated N atom is involved in a short hydrogen bond to one of the bromide ions (Table 1). Interactions between these units build up an interesting layered structure.

(I)
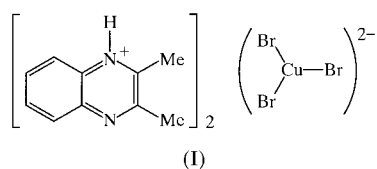
The cations aggregate in sheets that lie approximately normal to the [111] direction, with a separation of 3.39 (2) Å between adjacent sheets. As seen in Fig. 2, the dmqH$^+$ cations within each layer are spaced apart by the inorganic anions. The two independent quinoxalinium cations are essentially coplanar, with only 3.5 (1)° between the normals of the two planes, and the two different cations are oriented roughly perpendicular to each other.

As illustrated in Fig. 3, the $[CuBr_3]^{2-}$ anions span adjacent layers, with the Br atoms lying in the planes formed by the cations. Each bridging anion is hydrogen bonded by one cation in each of the two layers spanned. These interactions, coupled with π–π interactions between the cations in adjacent layers, provide three-dimensional stability to the lattice. The planes of the $[CuBr_3]^{2-}$ anions make angles of approximately 68.69 (4) and 71.90 (4)° to the planes of the two cations.
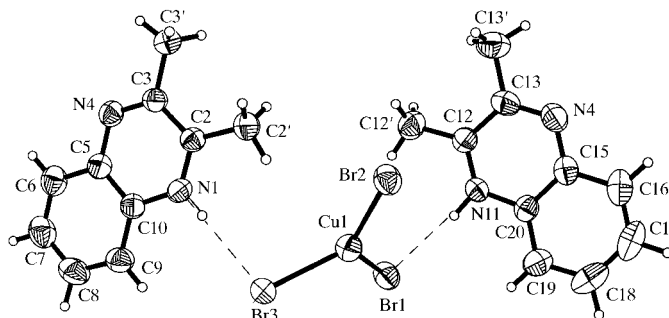
Figure 1
A view of the asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

The steric constraints imposed by the hydrogen-bonding interactions prevent the dmqH$^+$ cations in adjacent layers from maximizing their π–π interactions. Each of the two independent cations is located near a center of inversion in the structure. In this manner, π–π interactions lead to the formation of dimer species. These are illustrated in Fig. 4(a) for cation A (containing atoms N1–C3′) and in Fig. 4(b) for cation B (atoms N3–C13′). Significant interactions are limited to those between crystallographically equivalent pairs. The 90° rotation between the two independent cations and the presence of the $[CuBr_3]^{2-}$ anions appear to prevent aggregation of these dimers into more extensive stacks. The π–π interactions appear stronger in the cation A dimers than in the cation B dimers, as indicated by a greater overlap of the conjugated portion of the cations. Not surprisingly, with the cations in the dimers related by inversion symmetry, the distances between positive charges are maximized. Goddard *et al.* (1995) have discussed the types of π–π interactions observed in planar conjugated polycyclic systems. Two of the motifs are the so-called β and χ types where parallel stacks are formed with short distances between adjacent layers. The prototypical example for the β type is graphite, where the interplanar spacing is 3.35 Å (Wells, 1984). A measure of the strength of the π–π interactions proposed by Goddard was an offset parameter. This was defined as the horizontal displacement of the centroids of the overlapping rings. In graphite, this offset, 1.42 Å, is of the order of the length of the C—C
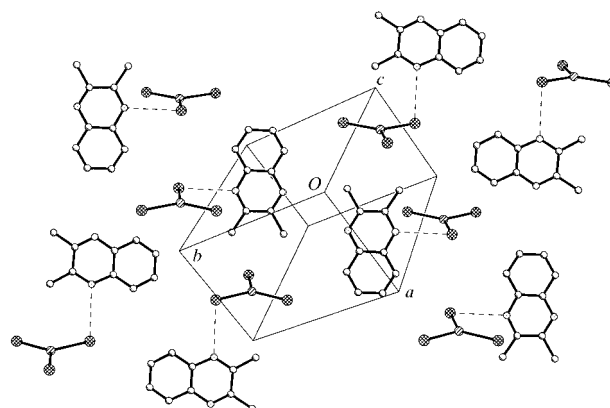
Figure 2
An illustration of an individual layer.

bond length. Short offsets of this nature are characteristic of the β type, while longer offsets are observed for the χ types. In the current study, the offset parameter for cation A is 1.491 (4) Å while it is substantially larger, 2.603 (4) Å, for cation B. This latter type has been labeled a type β^* by Kiralj *et al.* (1999).

This structure contains one of the few reported examples of isolated trigonal planar [CuBr₃]²⁻ anions. The Cu—Br bond distances range from 2.3349 (6) Å for Br2 to 2.4049 (6) Å for Br3. The Br—Cu—Br angles also show substantial deviation from ideal trigonal values, ranging from 114.93 (2) to 124.52 (2)°.

Previous examples of isolated [CuBr₃]²⁻ cations have been reported in several different compounds. A [CuBr₃]²⁻ anion with rigorous threefold symmetry is found in the Me₄P⁺ salt (Andersson & Jagner, 1987). Four other structures containing [CuBr₃]²⁻ anions have been reported (Bowmaker *et al.*, 1990;

Figure 3
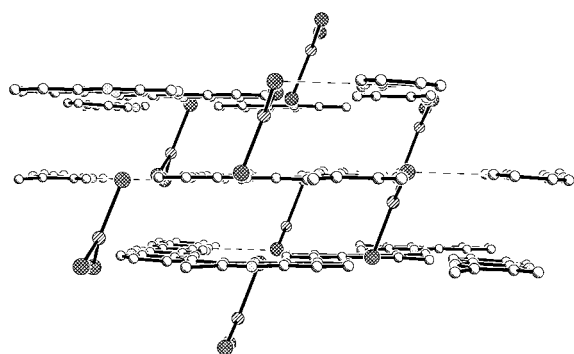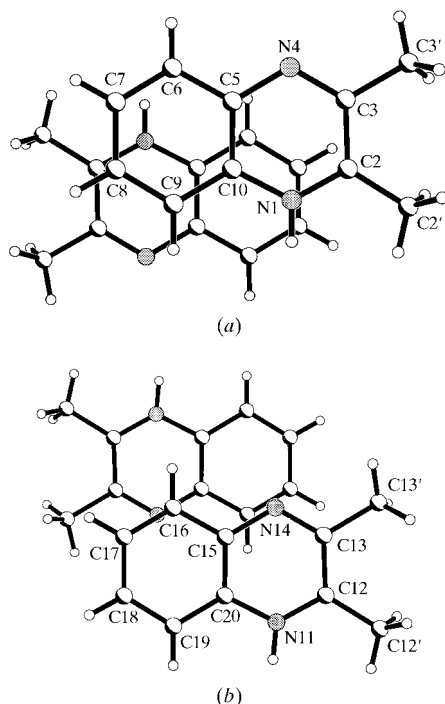A side view illustrating the bridging of the [CuBr₃]²⁻ anions between layers.

(a)

(b)

Figure 4
An illustration of the π–π interactions between dimers of (*a*) cation *A* and (*b*) cation *B*.

Sundberg *et al.*, 1992; Bencini & Mani, 1984; Haddad & Willett, 2001). All of the anions in these compounds show distortions of a magnitude similar to those in the structure reported here. Interestingly, the compound reported by Sundberg *et al.* (1992) is a mixed valence system containing both the [CuBr₃]²⁻ anion and the [CuBr₄]²⁻ anion. Two crystalline forms of the compound reported by Bowmaker *et al.* (1990) exist. One form contains the [CuBr₃]²⁻ anion, while the other contains a combination of [CuBr₂]²⁻ and Br⁻ anions. One example of an isolated [CuCl₃]²⁻ anion has also been reported (Andersson & Jagner, 1988), as well as two [CuI₃]²⁻ anions (Bhadur *et al.*, 1991; Hartl & Brudgam, 1989).

In addition to its existence as an isolated species, the [CuX₃]²⁻ (X = Cl, Br) anions act as bridging ligands in several (CuL_n)CuX₃ linear chain compounds, where the [CuL_n]²⁺ cations have a square-planar coordination (Clegg *et al.*, 1988; Chen *et al.*, 1996; Willett & Vij, 2001). Stacks of [CuCl₃]²⁻ anions can be found in Cu(N₂H₅)₂(CuCl₃)₂, with the stacks stabilized by hydrogen bonding from the hydrazinium cations and bridging to the Cu^{II} ion (Scott & Willett, 1991). The trigonal–planar coordination also occurs in numerous polymeric anionic copper(I) halide salts (Subramanian & Hoffmann, 1992).

Experimental

CuBr (approximately 0.0005 mol, 0.80 g) and 2,3-dimethyl-quinoxaline (0.0005 mol, 0.72 g) were added to HBr (approximately 50 ml of 0.10 M) in a sealed Erlenmeyer flask. The solution was heated to approximately 323 K and stirred for about 30 min. A portion of the supernatant liquid was placed on a microscope slide. Over a period of about 10 min, yellow crystals formed with a maximum dimension of approximately 0.5 mm. One such crystal was selected for X-ray analysis.

Crystal data

(C₁₀H₁₁N₂)₂[CuBr₃]	$Z = 2$
$M_r = 621.69$	$D_x = 1.858$ Mg m⁻³
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.2603$ (16) Å	Cell parameters from 951
$b = 10.777$ (2) Å	reflections
$c = 15.197$ (3) Å	$\theta = 3.0$–27.8°
$\alpha = 73.544$ (4)°	$\mu = 6.39$ mm⁻¹
$\beta = 77.338$ (4)°	$T = 295$ (2) K
$\gamma = 83.827$ (4)°	Needle, yellow
$V = 1111.3$ (4) Å³	0.27 × 0.14 × 0.05 mm

Data collection

Siemens SMART 1000 CCD area-detector diffractometer	5273 independent reflections
	3792 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.026$
Absorption correction: empirical	$\theta_{max} = 28.3°$
(*SADABS*; Sheldrick, 1999)	$h = -9 \rightarrow 9$
$T_{min} = 0.277$, $T_{max} = 0.741$	$k = -13 \rightarrow 14$
11 900 measured reflections	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R[F^2 > 2\sigma(F^2)] = 0.031$	independent and constrained
$wR(F^2) = 0.072$	refinement
$S = 0.99$	$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2]$
5273 reflections	where $P = (F_o^2 + 2F_c^2)/3$
265 parameters	$(\Delta/\sigma)_{max} = 0.001$
	$\Delta\rho_{max} = 0.78$ e Å⁻³
	$\Delta\rho_{min} = -0.43$ e Å⁻³

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Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Br3	0.86 (3)	2.44 (3)	3.302 (3)	177 (3)
N11—H11···Br1	0.89 (4)	2.39 (4)	3.272 (3)	173 (3)

C—H distances were constrained to 0.93 and 0.96 Å. H atoms bonded to N atoms were refined (see Table 1 for distances).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1998); program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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