

Poly[copper(I)- μ -bromo- μ -2,3-dimethylpyrazine- $N:N'$]

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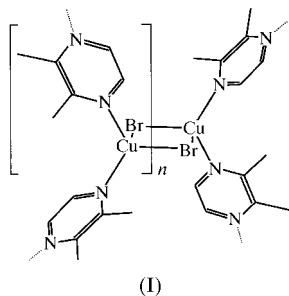
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In the structure of the title compound, $[\text{CuBr}(\text{C}_6\text{H}_8\text{N}_2)]_n$, each Cu^{2+} cation is surrounded by two 2,3-dimethylpyrazine ligands and two Br^- anions in a distorted tetrahedral arrangement. The Cu^{2+} cations and Br^- anions form $(\text{Cu}_2\text{Br}_2)_2$ rhomboid dimers located around a centre of inversion. The 2,3-dimethylpyrazine ligands connect the Cu^{2+} cations in the dimers into sheets parallel to (010).

Comment

The structure determination of the title compound, (I), was undertaken as part of a project on the synthesis and characterization of new coordination polymers based on copper(I) halides or pseudo-halides and having bridging N -donor ligands as organic spacers. Depending on the organic spacers, different types of oligomeric and polymeric $\text{Cu}X$ ($X = \text{Cl}, \text{Br}, \text{I}, \text{SCN}, \text{CN}$) substructures are observed.



In the crystal structure of (I), the Cu^{2+} cations are surrounded by two N atoms of two symmetry-equivalent 2,3-dimethylpyrazine ligands and two symmetry equivalent Br^- anions in a distorted tetrahedral arrangement (Fig. 1). Because of the neighbouring methyl group, the $\text{Cu}-\text{N}$ bond lengths are slightly elongated compared with those in poly[copper(I)- μ -bromo- μ -pyrazine] (Näther & Jeß, 2001). The Cu^{2+} cations and Br^- anions are connected to symmetry-equivalent Cu^{2+} cations and Br^- anions, forming $(\text{Cu}_2\text{Br}_2)_2$ rhomboid dimers located around a centre of inversion. Such copper(I) halide dimers are also found, for example, in the

structures of poly $[(\text{CuI})_2(\mu\text{-2-methylpyrazine})]\cdot 2\text{-methylpyrazine}$ (Roßenbeck & Sheldrick, 2000), poly $[(\text{Cu}^{\text{I}})_2(\mu\text{-2-cyanopyrazine})]$ (Roßenbeck & Sheldrick, 1999) and poly $[\text{CuBr}(\mu\text{-4,4'-bipyridine})]$ (Lu *et al.*, 1999; Batten *et al.*, 1999). In contrast to the 4,4'-bipyridine compounds, in which the

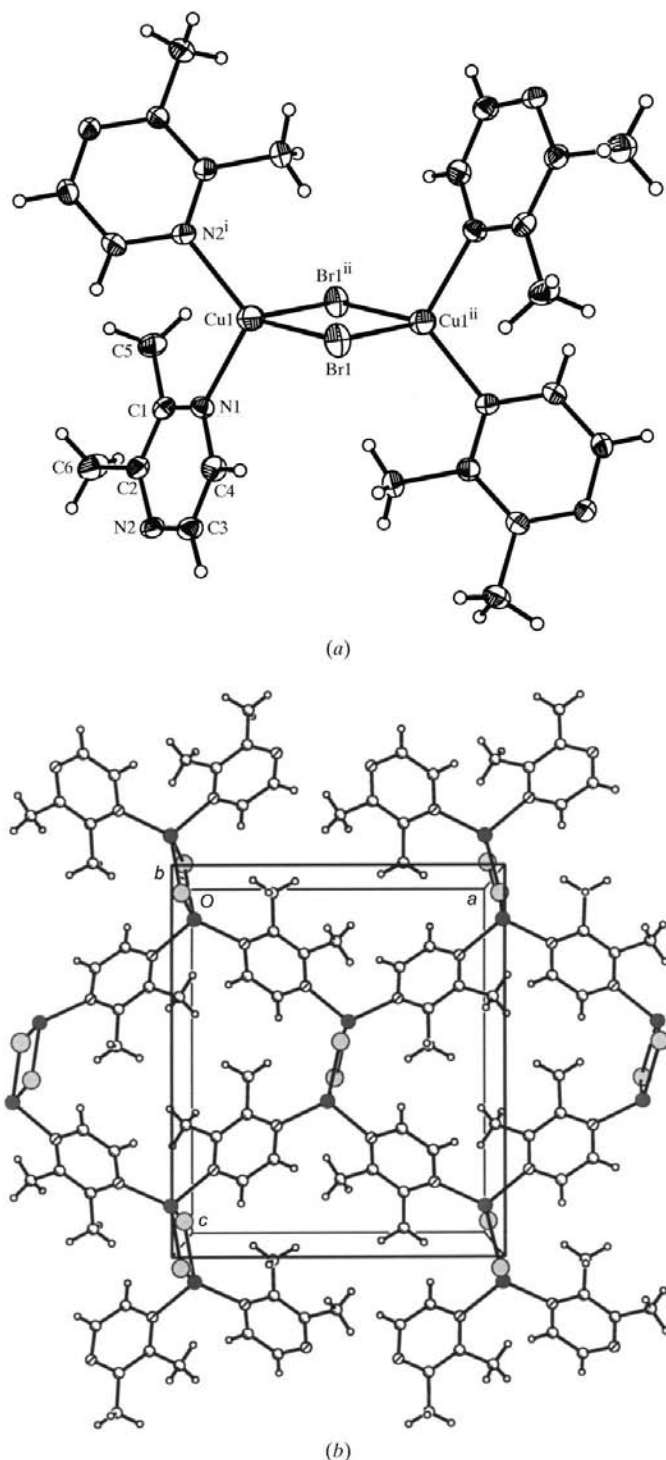


Figure 1
The crystal structure of (I) showing (a) a view of the copper coordination with labelling (the symmetry codes are as given in Table 1) and displacement ellipsoids drawn at the 50% probability level, and (b) a view of the structure along the b axis.

(CuBr)₂ dimers have a 'butterfly-like' structure, in (I), the rhomboid dimers are planar. The Cu...Cu distances within the dimers of 3.353 (1) Å are elongated compared with those in poly[CuBr(μ-4,4'-bipyridine)] of 2.804 (1) Å. The deviations of the Cu²⁺ cations from the N1/C1/C2/N2/C3/C4 six-membered ring are 0.214 (4) and 0.566 (4) Å for Cu1 and Cu1($\frac{1}{2} + x, y, \frac{3}{2} - z$), respectively, and the C—N—Cu angles deviate slightly from 120°, which shows that the cations are not exactly oriented in the direction of the nitrogen lone pair. This can be explained by the steric crowding caused by the neighbouring methyl group.

The 2,3-dimethylpyrazine ligands connect the (CuBr)₂ dimers, forming sheets parallel to (010). Altogether, each (CuBr)₂ dimer is connected to four 2,3-dimethylpyrazine ligands.

The structure of (I) shows clearly the influence of the organic spacers on the type of CuX substructure. In poly[copper(I)-μ-bromo-μ-pyrazine] (Näther & Jeß, 2001) and poly[copper(I)-μ-bromo-μ-2-methylpyrazine] (Roßenbeck & Sheldrick, 2000), infinite CuBr chains are found which are connected by non- and monosubstituted pyrazine ligands into sheets. If dimethyl-substituted pyrazine is used as the ligand, only (CuBr)₂ dimers are found.

Experimental

Freshly prepared Cu^IBr (35.85 mg, 0.25 mmol; Gmelin, 1958) in acetonitrile (0.75 ml) and 4,4'-bipyridine (0.298 ml, 0.275 mmol) were mixed. After 2 d, the residue was filtered off and washed with ethanol and diethyl ether. The precipitate was phase pure and consisted of a few orange crystals and an orange microcrystalline powder. The homogeneity of the product was checked by X-ray powder diffraction.

Crystal data

[CuBr(C ₆ H ₈ N ₂)]	Mo Kα radiation
<i>M_r</i> = 251.59	Cell parameters from 140 reflections
Orthorhombic, <i>Pbca</i>	$\theta = 12.0\text{--}18.5^\circ$
<i>a</i> = 11.459 (2) Å	$\mu = 8.17 \text{ mm}^{-1}$
<i>b</i> = 9.7078 (11) Å	<i>T</i> = 293 (2) K
<i>c</i> = 13.468 (4) Å	Irregular polyhedron, orange
<i>V</i> = 1498.2 (6) Å ³	0.12 × 0.10 × 0.08 mm
<i>Z</i> = 8	
<i>D_x</i> = 2.231 Mg m ⁻³	

Data collection

Phillips PW1100 four-circle diffractometer	<i>R</i> _{int} = 0.031
ω - θ scans	$\theta_{\text{max}} = 30.0^\circ$
Absorption correction: numerical (<i>X-SHAPE</i> ; Stoe & Cie, 1998)	<i>h</i> = -16 → 1
<i>T</i> _{min} = 0.386, <i>T</i> _{max} = 0.520	<i>k</i> = -13 → 1
2821 measured reflections	<i>l</i> = -1 → 18
2186 independent reflections	4 standard reflections
1681 reflections with <i>I</i> > 2σ(<i>I</i>)	frequency: 120 min
	intensity decay: none

Table 1

Selected geometric parameters (Å, °).

Cu1—N2 ⁱ	2.077 (2)	Cu1—Br1	2.4602 (7)
Cu1—N1	2.080 (2)	Cu1—Br1 ⁱⁱ	2.6358 (6)
N2 ⁱ —Cu1—N1	113.34 (10)	Br1—Cu1—Br1 ⁱⁱ	97.80 (2)
N2 ⁱ —Cu1—Br1	118.14 (7)	Cu1—Br1—Cu1 ⁱⁱ	82.20 (2)
N1—Cu1—Br1	111.79 (7)	C2—N2—Cu1 ⁱⁱⁱ	121.68 (19)
N2 ⁱ —Cu1—Br1 ⁱⁱ	112.15 (7)	C3—N2—Cu1 ⁱⁱⁱ	119.93 (19)
N1—Cu1—Br1 ⁱⁱ	101.21 (7)		

Symmetry codes: (i) $x - \frac{1}{2}, y, \frac{3}{2} - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $\frac{1}{2} + x, y, \frac{3}{2} - z$.

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2 + 0.6968P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.085$	$(\Delta/\sigma)_{\text{max}} = 0.001$
<i>S</i> = 1.05	$\Delta\rho_{\text{max}} = 0.72 \text{ e \AA}^{-3}$
2186 reflections	$\Delta\rho_{\text{min}} = -0.87 \text{ e \AA}^{-3}$
94 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0036 (4)

The H atoms were positioned with idealized geometry (C—H = 0.93 and 0.96 Å) and refined using a riding model.

Data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1990); software used to prepare material for publication: *CIFTAB* in *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1444). Services for accessing these data are described at the back of the journal.

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