Poly[[aquacopper(I)-μ-bromo]-μ-(5-methylpyrazine-2-carboxylato)-κ^3N^4:O,N^1-[diaquacopper(II)]-μ-(5-methylpyrazine-2-carboxylato)-κ^3O,N^1:N^4-[aquacopper(I)-μ-bromo]]

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In the structure of the title compound, [Cu$_3$Br$_2$(C$_6$H$_5$-N$_2$O$_2$)$_2$(H$_2$O)$_4$], both copper(I) and copper(II) cations are present. The copper(II) cations are located on centres of inversion and are coordinated by two N atoms and two carboxylate O atoms from two symmetry-related 5-methyl-pyrazine-2-carboxylate anions, with two water molecules completing a distorted octahedron. The copper(I) cations are coordinated by the second N atom of the 5-methyl-pyrazine-2-carboxylate anion, one water molecule and two bromide anions within a distorted tetrahedron. Each of the bromide anions connects two symmetry-equivalent copper(I) cations to form zigzag-like CuBr chains. These chains are connected by the [diaquabis(5-methylpyrazine-2-carboxylato)]copper(II) complexes, forming corrugated sheets parallel to (100). The CuBr chains and the sheets are connected *via* O—H···O and O—H···Br hydrogen bonding.

Comment

Recently, we have been interested in the synthesis, structures and properties of new coordination polymers based on copper(I) halides and aromatic amine ligands (Näther *et al.*, 2001; Näther & Greve, 2001; Näther & Jeß, 2001). Depending on the copper(I) halide and the nature of the amine ligand, interesting CuX (X = Cl, Br or I) substructures, such as rings, tetramers, and single or double chains, are found (Blake *et al.*, 1999; Graham *et al.*, 2000; Roßenbeck & Sheldrick, 2000; Persky *et al.*, 2001). In contrast to the most common octahedral coordination of copper(II) cations, the copper(I) cations in such compounds are four-coordinate within distorted tetrahedra. During our investigations, we isolated red crystals of the title compound, (I), which contain both copper(I) and copper(II) cations in their typical coordination polyhedra.

The copper(II) cations of (I) are coordinated by one N atom and one carboxylate O atom from each of the two symmetry-equivalent 5-methylpyrazine-2-carboxylate anions, which are

related by a centre of inversion located at the copper(II) cation (Fig. 1). The coordination sphere of the copper(II) cations is completed by two long contacts of 2.552 (3) Å to

(I)
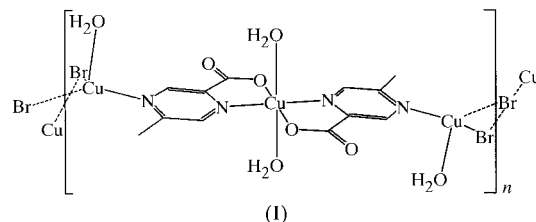
the O atoms of two symmetry-related water molecules, forming a [diaquabis(5-methylpyrazine-2-carboxylato)]copper(II) complex. The copper(II) coordination in this complex shows a typical Jahn–Teller distortion and the coordination polyhedron can be described as a strongly distorted octahedron, with the water molecules in axial positions and the carboxylate O atoms and the N atoms in the basal plane of the octahedron.

The bond lengths and angles about Cu1 of the copper(II) cation are comparable with those in *catena*-[bis(μ_2-2-methyl-pyrazine-5-carboxylato-N,N',O)diaquacopper(II)silver(I) tetrafluoroborate] and *catena*-[bis(μ_2-2-methylpyrazine-5-carboxylato-N,N',O)diaquacopper(II)silver(I) nitrate] (Dong *et al.*, 2000). In the related compound, aquabis(2-methyl-pyrazine-5-carboxylato-N,O)copper(II) trihydrate (Dong *et al.*, 2000), the copper(II) cation is only five-coordinate, *i.e.* by the N atom and the carboxylate O atom of two pyrazine ligands and by just one water molecule. In this structure, the Cu—N and Cu—O bond lengths are comparable to those in the title compound, but the Cu—O distance to the water molecule is shorter by about 0.2 Å.

The copper(II) and copper(I) cations are connected *via* μ-N:N coordination by the N atoms of the anions. The geometry of this interaction, *e.g.* the relative orientation of the copper cations and the pyrazine unit, shows that the copper cations are oriented in the direction of the nitrogen lone-pair (Table 1).

The copper(I) cations are coordinated by the second N atom of the 5-methylpyrazine-2-carboxylate anions involved in copper(II) coordination, one water molecule and two symmetry-related bromide anions within a distorted tetra-hedron. Each of the bromide anions connects two symmetry-equivalent copper(I) cations, forming zigzag-like CuBr chains in the direction of the crystallographic *c* axis (Fig. 2). Such
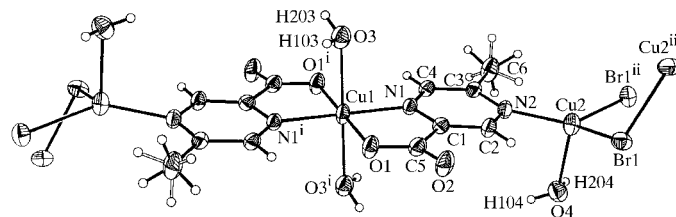

Figure 1
The crystal structure of the title compound showing the copper coordination, with labelling and displacement ellipsoids drawn at the 50% probability level (the disorder of the methyl H atoms is shown using full and open bonds).

zigzag chains are frequently observed in the crystal structures of Cu^IX (X = Cl, Br or I) coordination polymers (Blake *et al.*, 1999). These CuBr chains are connected *via* the N atoms of the [diaquabis(5-methylpyrazine-2-carboxylato)]copper(II) complexes, forming corrugated sheets parallel to (100), which are stacked in the direction of the crystallographic a axis. The water molecules are connected *via* O—H···O hydrogen bonding to other water molecules and to the carboxylate O atoms which are not involved in copper(II) coordination (Table 2). There are additional short intermolecular contacts between the water molecules and the bromide anions. The geometry of this interaction indicates O—H···Br hydrogen bonding. The corrugated sheets are further connected by O—H···O hydrogen bonding between the water molecules, forming a three-dimensional network.
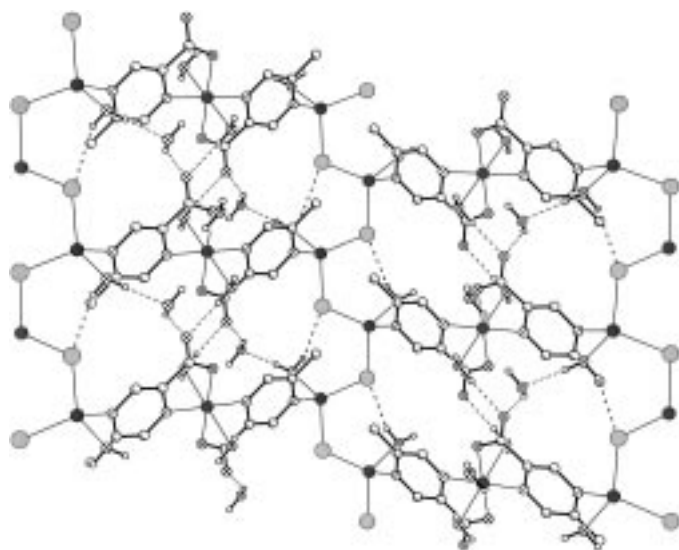

Figure 2
View of the structure on (100). The non-water H atoms have been omitted for clarity [symmetry codes: (i) $-x + 2$, $-y + 1$, $-z + 1$; (ii) x, $-y + \frac{1}{2}$, $z - \frac{1}{2}$; (iii) x, $-y + \frac{1}{2}$, $z + \frac{1}{2}$].

There are several structures known in which formal copper(I) and copper(II) cations are both present, such as in tetraisothiocyanatocopper(I)-bis(μ_2-{2-[(3-aminopropyl)-amino]ethanolate}-N,N,μ-O)dicopper(II)-μ-thiocyanato (Nieminen, 1981), but in most of them, the cations are embedded in macrocyclic ligands. To the best of our knowledge, no structure has been reported in which the typical Cu^IX (X = Cl, Br or I) substructures known from Cu^IX coordination polymers are interconnected *via* typical distorted octahedral copper(II) complexes.

Experimental

The title compound was prepared by the reaction of 5-methyl-pyrazine-2-carboxylic acid (34.6 mg, 0.25 mmol; ACROS) and CuBr [71.7 mg, 0.5 mmol; freshly prepared according to the method given in Gmelin (1958)] in water (3 ml) at room temperature in a glass container. After 2 d, dark-red crystals of the title compound had formed and could be isolated manually. The reaction mixture additionally contained a small amount of a green microcrystalline phase which could not be identified.

Crystal data

$[Cu_3Br_2(C_6H_5N_2O_2)_2(H_2O)_4]$	$D_x = 2.307$ Mg m^{-3}
$M_r = 696.74$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 114
$a = 7.1796$ (18) Å	reflections
$b = 23.238$ (3) Å	$\theta = 10$–$19°$
$c = 6.5358$ (16) Å	$\mu = 7.18$ mm^{-1}
$\beta = 113.069$ (18)°	$T = 293$ (2) K
$V = 1003.2$ (4) Å^3	Block, red
$Z = 2$	$0.10 \times 0.08 \times 0.05$ mm

Data collection

Philips PW1100 four-circle	$R_{int} = 0.018$
diffractometer	$\theta_{max} = 28.0°$
ω–θ scans	$h = -9 \rightarrow 8$
Absorption correction: numerical	$k = -1 \rightarrow 30$
(*X-SHAPE*; Stoe & Cie, 1998)	$l = 0 \rightarrow 8$
$T_{min} = 0.341$, $T_{max} = 0.390$	4 standard reflections
2741 measured reflections	frequency: 120 min
2420 independent reflections	intensity decay: none
1866 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0279P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$+ 0.5653P]$
$wR(F^2) = 0.064$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
2420 reflections	$\Delta\rho_{max} = 0.54$ e Å^{-3}
134 parameters	$\Delta\rho_{min} = -0.47$ e Å^{-3}
H atoms treated by a mixture of	
independent and constrained	
refinement	

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9517 (19)	Cu2—O4	2.281 (2)
Cu1—N1	1.983 (2)	Cu2—Br1^i	2.4030 (6)
Cu2—N2	2.018 (2)	Cu2—Br1	2.5000 (7)
O1—Cu1—N1^{ii}	96.56 (9)	O4—Cu2—Br1	107.89 (6)
O1—Cu1—N1	83.44 (9)	Br1^i—Cu2—Br1	103.079 (19)
O1^{ii}—Cu1—N1	96.56 (9)	Cu2^{iii}—Br1—Cu2	106.195 (19)
N2—Cu2—O4	98.92 (9)	C3—N2—Cu2	124.3 (2)
N2—Cu2—Br1^i	139.52 (7)	C2—N2—Cu2	117.20 (18)
O4—Cu2—Br1^i	97.44 (6)	C5—O1—Cu1	114.79 (19)
N2—Cu2—Br1	106.61 (7)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1O3···O2^i	0.82	2.00	2.818 (3)	174
O3—H2O3···O2^{ii}	0.82	2.05	2.791 (3)	150
O4—H1O4···O3^{iii}	0.82	1.96	2.771 (3)	172
O4—H2O4···Br1^{iv}	0.82	2.65	3.390 (2)	150

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

The positions of all the H atoms were initially located from a difference map. The aromatic H atoms were then positioned with idealized geometry and refined using a riding model. The methyl H atoms were disordered and were refined as idealized disordered methyl groups with two positions rotated from each other by 60° and site-occupation factors of 0.69 and 0.31. The H atoms of the water

molecules were identified from difference syntheses but were refined as rigid groups with idealized O—H bond lengths of 0.82 Å. All H atoms were assigned fixed isotropic displacement parameters defined as $U_{iso}(H) = xU_{eq}(C,O)$, where $x = 1.5$ for methyl C and water O atoms, and $x = 1.2$ for aromatic C atoms.

Data collection: *DIF*4 (Stoe & Cie, 1992); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1122). Services for accessing these data are described at the back of the journal.

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