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Key indicators

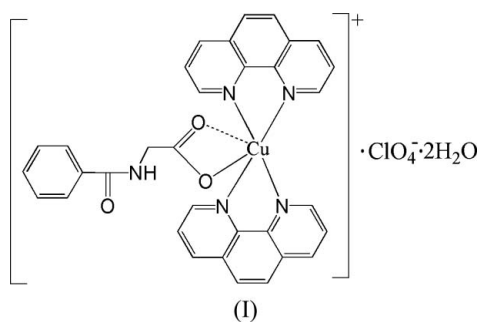
Single-crystal X-ray study
T = 298 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.038
wR factor = 0.090
Data-to-parameter ratio = 16.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**(Hippurato- $\kappa^2\text{O},\text{O}'$)bis(1,10-phenanthroline- $\kappa^2\text{N},\text{N}'$)copper(II) perchlorate dihydrate**

In the title complex, $[\text{Cu}(\text{C}_9\text{H}_7\text{NO}_3)(\text{C}_{12}\text{H}_{10}\text{N}_2)_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$, the Cu atom exhibits a significantly distorted octahedral geometry as a result of the Jahn–Teller effect and the chelating influence of the ligands. In the crystal structure, the molecules are linked by hydrogen bonds into one-dimensional double chains, which are further linked into two-dimensional layers by π – π stacking interactions between neighbouring aromatic ligands.

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Comment

Many copper(II) complexes with carboxylate ligands have been studied due to their magneto–structural correlations (Kato & Muto, 1988) and copper(II) is prominent in the active sites of many metallobiomolecules (Kain & Schwederski, 1994). Hippuric acid, an *N*-protected amino acid, has previously been found to act as an oxygen-donor anionic ligand in the construction of coordination compounds (Morelock *et al.*, 1979, 1982; Grewe *et al.*, 1982; Brown & Trefonas, 1973; Huber *et al.* 1988; Jones & Schelbach, 1988; Darensbourg *et al.*, 1994; Battistuzzi *et al.*, 1996; Severin *et al.*, 1996). However, there are few reported crystal structures of mixed-ligand complexes of hippuric acid and heteroaromatic ligands, such as 1,10-phenanthroline, 2,2-bipyridine and 4,4-bipyridine (Antolini *et al.*, 1982; Capllonch *et al.* 2001). We present here the crystal structure of the title compound, (I).



The title compound contains (hippurato)bis(1,10-phenanthroline)copper(II) complex cations in which the Cu atom is six-coordinated by two O atoms of the hippurate group and four N atoms of two 1,10-phenanthroline ligands, forming a distorted octahedral geometry with the axial positions occupied by pyridyl N atoms (N2 and N4) from two 1,10-phenanthroline ligands (Fig. 1). The Cu1–O2 distance (Table 1) is longer than other Cu–O and Cu–N bond distances, and the Cu1–N5 bond distance *trans* to it is also elongated. Two *trans* angles at Cu1 deviate considerably from the linear values of a perfect octahedron (Table 1). As a result,

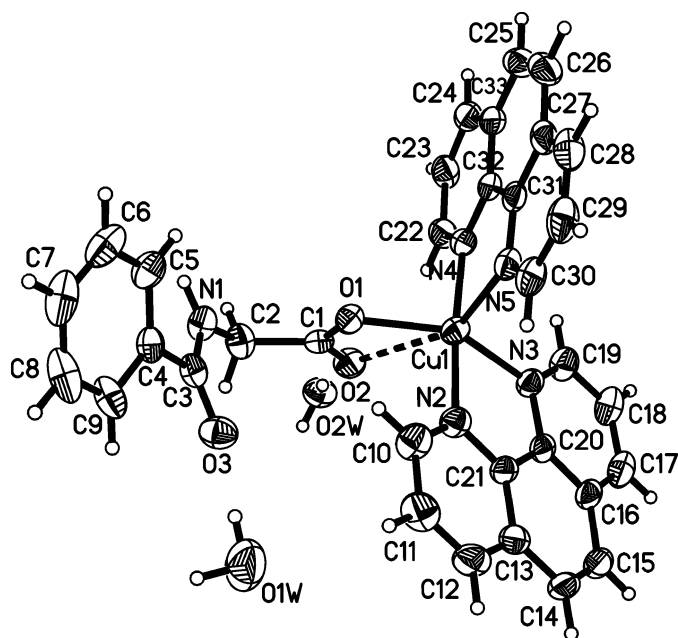


Figure 1
The cation and water molecules of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level.

CuN_4O_2 exhibits a significantly distorted octahedral geometry, which can be thought of as resulting from the Jahn–Teller elongation effect and the ligand's chelating influence (Simmons *et al.*, 1987; Hathaway & Tomlinson, 1970).

In the crystal structure, the acyl radical O atom (O3) and the carboxylate O atom (O2) serve as intramolecular hydrogen-bonding acceptors, receiving H atoms from water molecules, and atoms O3 and O2W accept H atoms from water molecules, generating intermolecular hydrogen bonds (Table 2). The title complex cations and water molecules are linked by intra- and intermolecular hydrogen-bonding interactions into one-dimensional double chains along the [010] direction, with the aromatic ligands on the outside. These chains are further held together by π – π stacking interactions between the 1,10-phenanthroline groups of neighbouring cations [mean interplanar distances: 3.431 (3) and 3.394 (5) Å] into two-dimensional layers parallel to (201) (Fig. 2).

Experimental

An aqueous solution (5 ml) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.365 g, 1.0 mmol) was slowly added to a stirred solution of 1,10-phenanthroline monohydrate (0.396 g, 2.0 mmol) and hippuric acid (0.179 g, 1.0 mmol) in 20 ml ethanol. The mixture was further stirred for ca 30 min at room temperature, and the pH was adjusted to the range 6–7 with 1 M NaOH solution. The mixture was further stirred for another 2 h and filtered, and the resulting filtrate was allowed to stand at room temperature. Blue prism-shaped crystals were obtained by slow evaporation after one week in a yield of 85% based on the initial $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ quantity. Analysis calculated for $\text{C}_{33}\text{H}_{28}\text{ClCuN}_5\text{O}_9$: C 53.69, H 3.80, N 9.49%; found: C 53.60, H 3.86, N 9.43%.

Crystal data

$[\text{Cu}(\text{C}_9\text{H}_7\text{NO}_3)(\text{C}_{12}\text{H}_{10}\text{N}_2)_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$
 $M_r = 737.59$
 Monoclinic, $P2_1/c$
 $a = 16.8105$ (13) Å
 $b = 10.1481$ (8) Å
 $c = 19.6316$ (14) Å
 $\beta = 106.370$ (4)°

$V = 3213.3$ (4) Å³
 $Z = 4$
 $D_x = 1.525$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.83$ mm⁻¹
 $T = 298$ (2) K
 Prism, blue
 0.34 × 0.28 × 0.26 mm

Data collection

Bruker SMART CCD APEX-II diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.752$, $T_{\max} = 0.811$

33934 measured reflections
 8015 independent reflections
 4850 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$
 $\theta_{\max} = 28.4^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.090$
 $S = 1.00$
 8015 reflections
 493 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.7P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.029$
 $\Delta\rho_{\max} = 0.35$ e Å⁻³
 $\Delta\rho_{\min} = -0.37$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1–N4	1.9908 (19)	Cu1–N3	2.061 (2)
Cu1–N2	1.991 (2)	Cu1–N5	2.1685 (19)
Cu1–O1	2.0195 (16)	Cu1–O2	2.7782 (17)
N4–Cu1–N2	175.32 (8)	O1–Cu1–N5	106.02 (7)
N4–Cu1–O1	93.38 (7)	N3–Cu1–N5	108.88 (7)
N2–Cu1–O1	90.98 (8)	O2–Cu1–N5	153.69 (6)
N4–Cu1–N3	95.88 (8)	O2–Cu1–N4	86.38 (6)
N2–Cu1–N3	81.46 (9)	O2–Cu1–N3	94.95 (6)
O1–Cu1–N3	144.91 (7)	O2–Cu1–N2	97.67 (7)
N4–Cu1–N5	80.37 (8)	O2–Cu1–O1	51.95 (6)
N2–Cu1–N5	96.79 (8)		

Table 2

Hydrogen-bond geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O1W–H1WA ⁱ ⋯O2W ⁱ	0.92 (6)	1.89 (6)	2.803 (4)	172 (5)
O1W–H1WB ⁱ ⋯O3	0.90 (5)	2.19 (5)	2.990 (4)	148 (5)
O2W–H2WA ⁱⁱ ⋯O3 ⁱⁱ	0.78 (3)	2.10 (3)	2.876 (3)	172 (3)
O2W–H2WB ⁱ ⋯O2	0.77 (3)	2.02 (3)	2.774 (3)	169 (3)

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

All H atoms attached to C atoms and N atoms were positioned geometrically and treated as riding, with C–H = 0.93–0.97 Å, N–H = 0.86 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. The H atoms of water molecules were found in difference Fourier syntheses and the O–H distances (Table 2) were refined. The O atoms of the perchlorate anion are disordered and were modelled with split positions of occupancies 0.526 (8) and 0.474 (8). The Cl–O distances involving the disordered atoms were restrained to be equal.

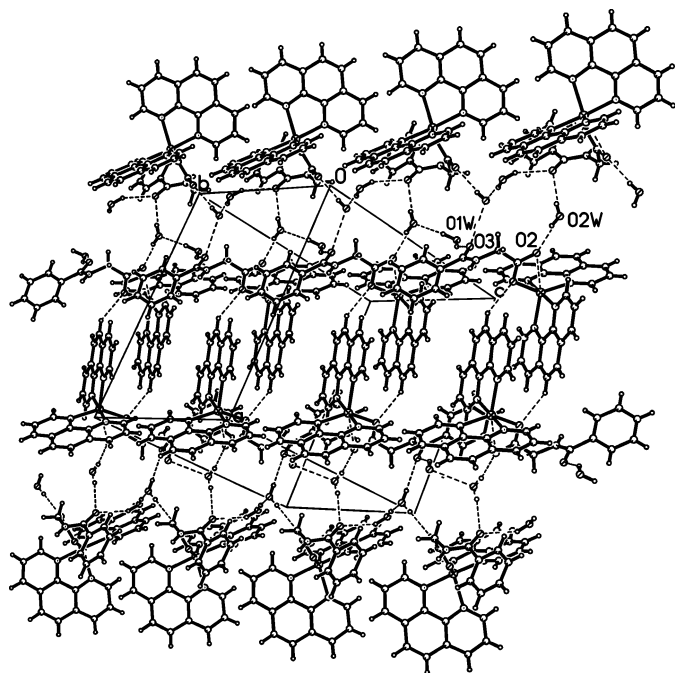


Figure 2

The two-dimensional layer parallel to $(\bar{2}01)$ generated by hydrogen-bonding interactions and π - π stacking interactions. Dashed lines indicate hydrogen bonds.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2003); software used to prepare material for publication: *SHELXTL*.

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