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Aquabis(*p*-chlorobenzoato)(1,10-phenanthroline)-copper(II)

The title compound, $[Cu(C_7H_4ClO_2)_2(C_{12}H_8N_2)(H_2O)]$, is a monomer in which the *p*-chlorobenzoate ligand is synthesized *in situ* from 4-carboxybenzeneboronic acid. The coordination around the Cu^{II} atom is square pyramidal. Two monodentate benzoate ligands are *cis*-arranged. Hydrogen bonds occur between coordinated water molecules and benzoate ligands, while π–π stacking interactions consolidate the crystal packing.
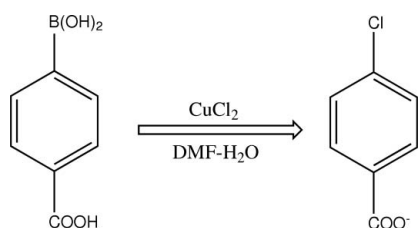
Comment

Four *p*-chlorobenzoate–copper(II) complexes (Zhang *et al.*, 2000; Uggla *et al.*, 1973; Turpeinen *et al.*, 1999, 2000) have been reported in the Cambridge Structural Database (CSD, May 2006 update; Allen, 2002) and these complexes were directly synthesized using *p*-chlorobenzoate. In exploring metal complexes with 4-carboxybenzeneboronic acid (Hcbba), Hcbba can be converted to benzoate under hydrothermal conditions (Zhu & Hu, 2006). Therefore, we used the typical method of mixing solutions at room temperature to obtain cbba complexes. Unexpectedly, Hcbba in the presence of $CuCl_2$ can be converted to the *p*-chlorobenzoate ligand (see reaction scheme). We present here the title complex, (I).

(I)

The title compound is a mononuclear complex in which the copper(II) atom is coordinated by two N-atom donors from
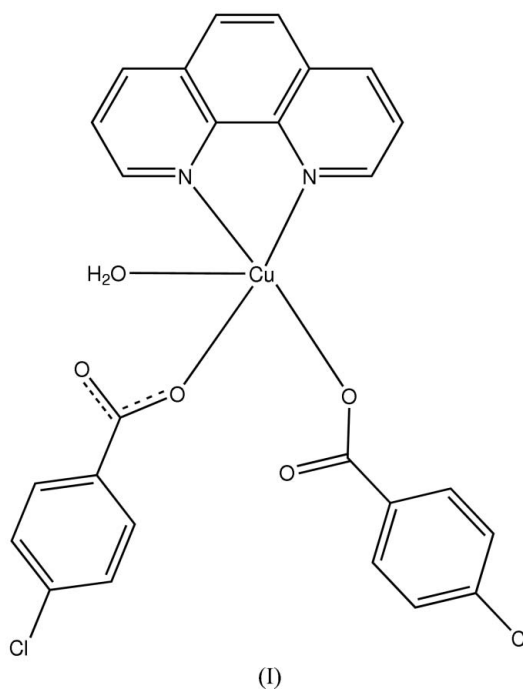
one 1,10-phenanthroline ligand, two O atoms from two *p*-chlorobenzoate ligands, and an aqua O atom (Fig. 1 and Table 1). The two *p*-chlorobenzoate ligands are coordinated to the metal atom in a monodentate manner. The coordinated water molecule acts as double donor to the carboxylate groups of two *p*-chlorobenzoate ligands, forming bifurcated hydrogen bonds (Table 2). There are strong π–π stacking interactions involving 1,10-phenanthroline and *p*-chlorobenzoate, assembling the complexes into a one-dimensional chain (Fig. 2). The centroid–centroid distances are 3.6140 (18), 3.5211 (19) and 3.5920 (19) Å for $Cg1\cdots Cg4^i$, $Cg2\cdots Cg4^{ii}$ and $Cg3\cdots Cg4^i$, respectively [where $Cg1$ is the centroid of atoms N1/C1–C4/C11, $Cg2$ of N2/C7–C10/C12, $Cg3$ of C4–C7/C11/C12 and $Cg4$ of C21–C26; symmetry codes: (i) $1 - x$, $1 - y$, $1 - z$; (ii) $-x$, $1 - y$, $1 - z$].
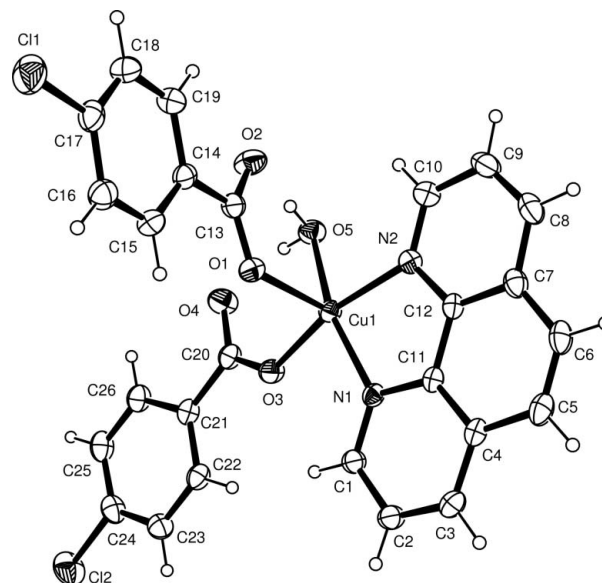

Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.
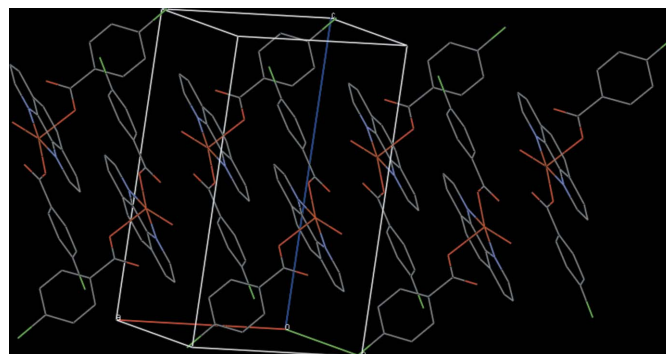

Figure 2
View of the one-dimensional π–π stacking chain. H atoms have been omitted.

Experimental

A mixed-solvent solution (30 ml of dimethylformamide and 20 ml of water) of $CuCl_2\cdot 2H_2O$ (0.092 g, 0.54 mmol), 1,10-phenanthroline monohydrate (0.102 g, 0.51 mmol) and 4-carboxybenzeneboronic acid (0.104 g, 0.63 mmol) was stirred for 1 h and filtered. The resulting solution was set aside and allowed to evaporate. After one month, dark-blue block-shaped crystals of (I) were obtained.

Crystal data

$[Cu(C_7H_4ClO_2)_2(C_{12}H_8N_2)(H_2O)]$	$V = 1161.90$ (17) Å³
$M_r = 572.86$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.637$ Mg m⁻³
$a = 7.9427$ (7) Å	Mo $K\alpha$ radiation
$b = 10.7301$ (9) Å	$\mu = 1.21$ mm⁻¹
$c = 14.8175$ (12) Å	$T = 295$ (2) K
$\alpha = 100.404$ (1)°	Block, dark blue
$\beta = 95.328$ (1)°	$0.25 \times 0.21 \times 0.16$ mm
$\gamma = 108.582$ (1)°	

Data collection

Bruker APEX area-detector diffractometer	6190 measured reflections
φ and ω scans	4081 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	3751 reflections with $I > 2\sigma(I)$
$T_{min} = 0.751$, $T_{max} = 0.830$	$R_{int} = 0.014$
	$\theta_{max} = 25.1°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 0.8244P]$
$wR(F^2) = 0.106$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
4081 reflections	$\Delta\rho_{max} = 0.37$ e Å⁻³
331 parameters	$\Delta\rho_{min} = -0.33$ e Å⁻³
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	2.297 (2)	Cu1—N1	2.014 (2)
Cu1—O3	1.948 (2)	Cu1—N2	2.023 (2)
Cu1—O5	1.980 (2)		
O3—Cu1—O5	94.73 (9)	N1—Cu1—N2	81.56 (9)
O3—Cu1—N1	89.28 (8)	O3—Cu1—O1	100.60 (8)
O5—Cu1—N1	164.96 (9)	O5—Cu1—O1	90.81 (8)
O3—Cu1—N2	167.24 (9)	N1—Cu1—O1	102.72 (8)
O5—Cu1—N2	91.99 (9)	N2—Cu1—O1	90.12 (8)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5A$\cdots$O1	0.86 (3)	2.61 (4)	3.053 (3)	113 (3)
O5—H5A$\cdots$O2	0.86 (3)	1.71 (3)	2.554 (3)	170 (4)
O5—H5B$\cdots$O3	0.85 (3)	2.56 (4)	2.890 (3)	104 (3)
O5—H5B$\cdots$O4	0.85 (3)	1.804 (17)	2.620 (3)	161 (4)

All C-bound H atoms were positioned geometrically and treated as riding, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The two water H atoms were found in a difference Fourier map and refined with a distance restraint of O—H = 0.85 (1) Å, with $U_{iso}(H) = 0.08$ Å^2.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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