Jian-Rong Su,[a] Jian-Ming Gu[b]
and Duan-Jun Xu[a]*

[a]Department of Chemistry, Zhejiang University,
People's Republic of China, and [b]The Central
Laboratory, Zhejiang University, People's
Republic of China

Correspondence e-mail: xudj@mail.hz.zj.cn

Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.039
wR factor = 0.109
Data-to-parameter ratio = 15.6

For details of how these key indicators were
automatically derived from the article, see
http://journals.iucr.org/e.

Bis(4-hydroxybenzoato-κ^2O,O')(1,10-phenanthroline-κ^2N,N')copper(II)

In the title complex, [Cu(C$_7$H$_5$O$_3$)$_2$(C$_{12}$H$_8$N$_2$)], the Cu^{II} atom is located on a twofold axis and assumes an elongated octahedral geometry formed by two 4-hydroxybenzoate anions and a 1,10-phenanthroline (phen) molecule. There is a C—H···π interaction between phen and the benzene ring of benzoate.

Comment

In some biological systems, π–π stacking between aromatic rings is correlated with the electron-transfer process (Deisenhofer & Michel, 1989). A series of metal complexes incorporating aromatic ligands has been prepared in our laboratory to study the regularity of π–π stacking. As part of our ongoing investigations, the title complex, (I), incorporating 1,10-phenathroline (phen), has been prepared.

(I)
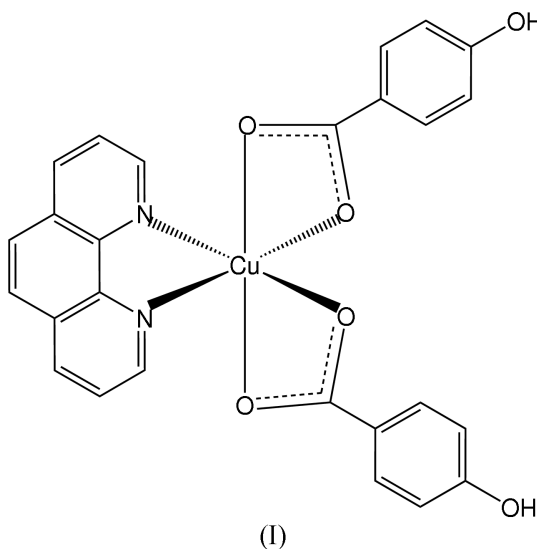
The molecular structure of (I) is illustrated in Fig. 1. The Cu^{II} atom is located on a twofold axis. The phen N atoms and two O atoms of 4-hydroxybenzoate anions form the equatorial plane of octahedral coordination, with normal bond distances (Table 1). Owing to the Jahn–Teller effect, the Cu—O bonds in the axial direction are longer than those in the equatorial plane by 0.2–0.6 Å, while the Cu—O2 bond in (I) is longer than Cu—O1 by 0.673 (2) Å. It is notable that the Cu—O1—C1 angle of 106.99 (14)° is much smaller than the value of 120° expected for a normal sp^2-hybridized O atom. This implies the existence of genuine coordination between atoms Cu and O2 (Li *et al.*, 2005; Su *et al.*, 2005). Thus, the coordination geometry around the Cu^{II} atom is described as elongated octahedral.
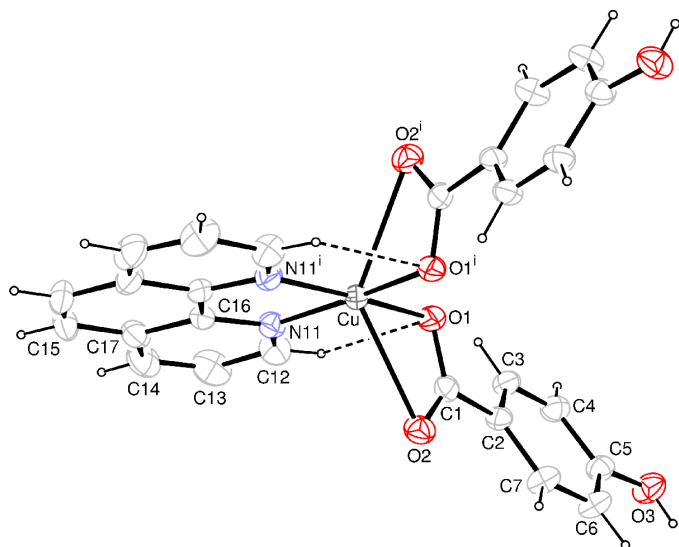
Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds. [Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.]
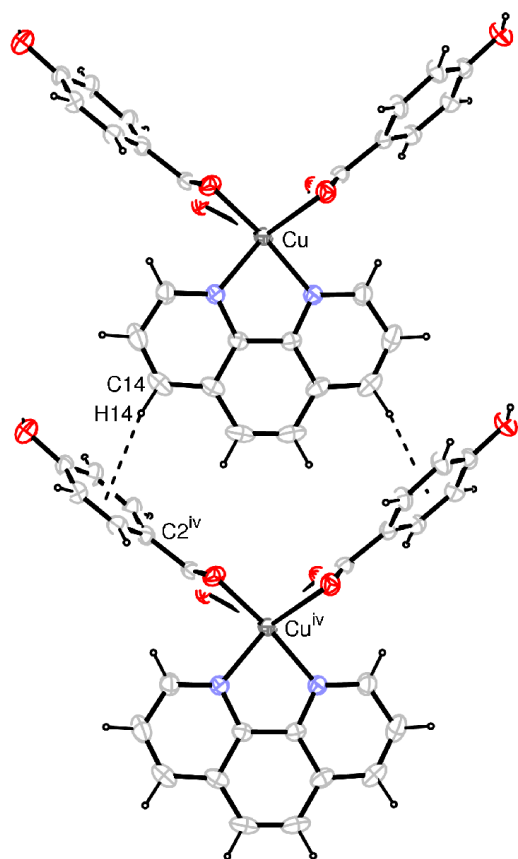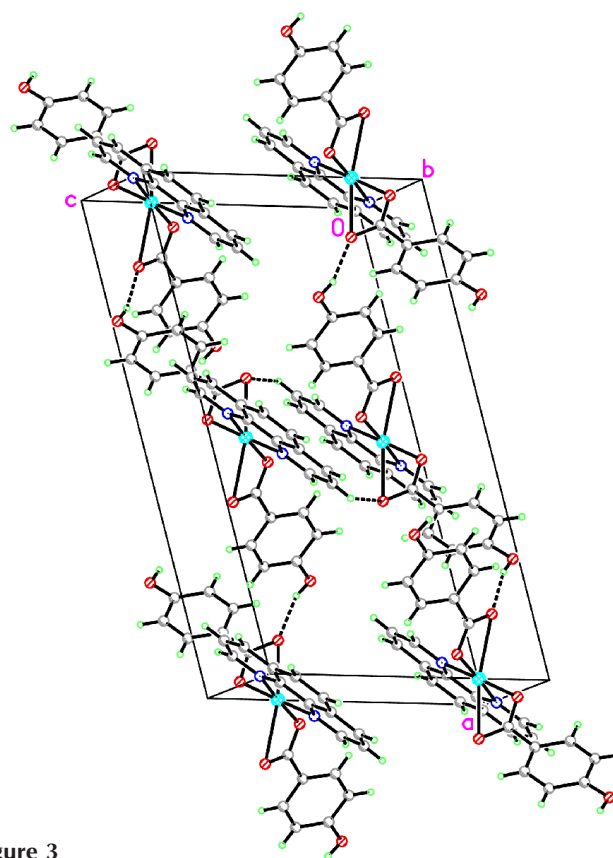

Figure 3
The crystal packing, showing the intermolecular hydrogen bonding (dashed lines).

hydrogen bond and a weak C13—H13···O2^{iii} hydrogen bond [symmetry codes: (ii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x, 1 - y, -\frac{1}{2} + z$], to form a supramolecular structure (Table 2 and Fig. 3).

Experimental

Each reagent was commercially available and of analytical grade. $CuCl_2 \cdot 2H_2O$ (0.17 g, 1 mmol), 4-hydroxybenzoic acid (0.14 g, 1 mmol), phen (0.20 g, 1 mmol) and Na_2CO_3 (0.05 g, 1 mmol) were dissolved in a water/ethanol (1:1, 20 ml) mixture. The solution was refluxed for 5 h, then cooled to room temperature and filtered. Blue single crystals of (I) were obtained from the filtrate after two weeks.

Crystal data

$[Cu(C_7H_5O_3)_2(C_{12}H_8N_2)]$	$D_x = 1.578$ Mg m^{-3}
$M_r = 517.96$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 6854
$a = 19.9073 (15)$ Å	reflections
$b = 10.2232 (5)$ Å	$\theta = 3.1–25.3°$
$c = 11.0723 (7)$ Å	$\mu = 1.05$ mm^{-1}
$\beta = 104.705 (2)°$	$T = 295 (3)$ K
$V = 2179.6 (2)$ Å^3	Block, blue
$Z = 4$	$0.41 \times 0.34 \times 0.16$ mm

Data collection

Rigaku R-AXIS RAPID	2477 independent reflections
diffractometer	2119 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.037$
Absorption correction: multi-scan	$\theta_{max} = 27.4°$
(*ABSCOR*; Higashi, 1995)	$h = -25 \rightarrow 25$
$T_{min} = 0.651$, $T_{max} = 0.855$	$k = -13 \rightarrow 13$
9663 measured reflections	$l = -13 \rightarrow 14$

Figure 2
The C—H···π interaction (dashed lines) between neighboring Cu^{II} complexes. [Symmetry code: (iv) $x, -1 + y, z$.]

The C—H···π interaction occurs in (I), as shown in Fig. 2. The H14···C_g separation (C_g is the centroid of the C2^{iv}-benzene ring) and C14—H14···C_g angle are 2.76 Å and 143°, respectively [symmetry code: (iv) $x, -1 + y, z$]. Neighboring complexes are linked to each other *via* an O3—H3a···O2^{ii}

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0758P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$+ 0.6964P]$
$wR(F^2) = 0.109$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 0.99$	$(\Delta/\sigma)_{max} < 0.001$
2477 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
159 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu—O1	1.9535 (16)	Cu—N11	2.0143 (18)
Cu—O2	2.6262 (16)		
O1—Cu—O1^i	94.64 (10)	O2—Cu—N11	90.16 (6)
O1—Cu—O2	55.00 (6)	O2—Cu—N11^i	125.37 (6)
O1^i—Cu—O2	92.99 (6)	O2—Cu—O2^i	134.78 (7)
O1—Cu—N11	91.82 (7)	N11—Cu—N11^i	81.73 (10)
O1—Cu—N11^i	173.51 (7)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3a···O2^{ii}	0.86	1.80	2.652 (3)	170
C12—H12···O1	0.93	2.58	3.067 (3)	113
C13—H13···O2^{iii}	0.93	2.55	3.174 (4)	124

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

Aromatic H atoms were placed in calculated positions, with C—H = 0.93 Å, and were included in the final cycles of refinement in riding mode, with $U_{iso}(H) = 1.2U_{eq}(C)$. The hydroxy H atoms was located in a difference Fourier map and refined riding in its as-found position, with a fixed isotropic displacement parameter of 0.05 Å^2.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/ MSC, 2002); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL9*7 (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Deisenhofer, J. & Michel, H. (1989). *EMBO J.* **8**, 2149–2170.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Higashi, T. (1995). *ABSCOR.* Rigaku Corporation, Tokyo, Japan.
Li, H., Yin, K.-L. & Xu, D.-J. (2005). *Acta Cryst.* C**61**, m19–m21.
Rigaku (1998). *PROCESS-AUTO.* Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure.* Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
Sheldrick, G. M. (1997). *SHELXL97.* University of Göttingen, Germany.
Siemens (1994). *XP.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Su, J.-R., Gu, J.-M. & Xu, D.-J. (2005). *Acta Cryst.* E**61**, m244–m246.