Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Bis(3-methylbenzoato-κ^2O,O')(phenanthroline-κ^2N,N')copper(II)

Tu-Gen Xu‡ and Duan-Jun Xu*

Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China

‡ Current address: Department of Chemistry, Hangzhou Teachers' College, People's Republic of China.

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

Received 7 October 2004
Accepted 12 October 2004
Online 16 October 2004

Key indicators

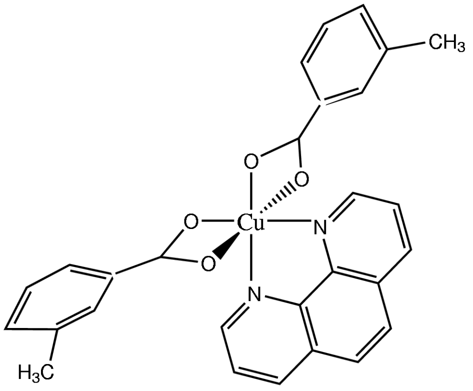
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.037
wR factor = 0.091
Data-to-parameter ratio = 16.7

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

In the title complex, $[Cu(C_8H_7O_2)_2(C_{12}H_8N_2)]$, the Cu^{II} atom is located on a twofold axis and assumes a distorted octahedral coordination geometry, formed by a phenanthroline molecule and two methylbenzoate anions, all in chelating mode. The carboxylate group chelates to the Cu^{II} atom with greatly differing Cu—O distances, *viz*. 2.5923 (19) Å in the axial direction and 1.9435 (14) Å in the equatorial plane.

Comment

The Jahn–Teller distortion of copper(II) complexes is well known. Most copper(II) complexes display an elongated distortion, and the coordinate bonds in the axial direction are usually longer than those in the equatorial coordination plane by 0.2–0.6 Å. In the title copper(II) complex, (I), a pair of long Cu—O bonds is observed.



(I)

The molecular structure of (I) is shown in Fig. 1. The Cu^{II} atom is located on a twofold axis and is surrounded by a phenanthroline (phen) molecule and two methylbenzoate anions in a distorted octahedral coordination geometry. Two O atoms from carboxyl groups and two phen N atoms form a tetrahedrally distorted equatorial coordination plane, with a dihedral angle of 9.7 (2)° between the Cu/O1/O1^{i} and Cu/N1/N1^{i} planes [symmetry code: (i) $1-x$, y, $\frac{1}{2}-z$]. The bond lengths in the equatorial plane are normal (Table 1). In the axial direction, the Cu—O2 distance is longer than the Cu—O1 distance in the equatorial plane by 0.649 (2) Å.

The Cu—O1—C7 angle of 104.54 (13)° is similar to values found in copper(II) complexes with a chelating benzoate ligand, for example, 104.93 (16)° (Bakalbassis & Terzis, 1994), 106.1 (4)° (Cano *et al.*, 1997) and 100.50 (17)° (Parkanyi & Speier, 1995), but is much smaller than those in copper(II) complexes with a monodentate benzoate ligand, for example,

doi: 10.1107/S1600536804025759

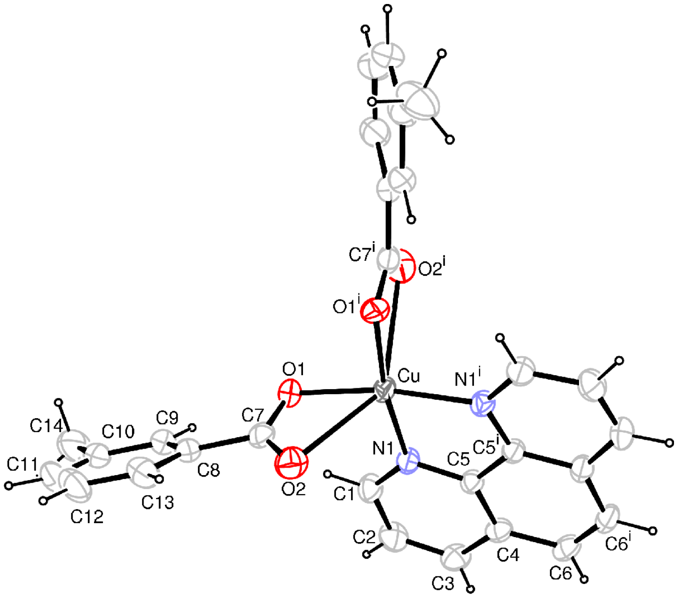


Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids. [Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.]

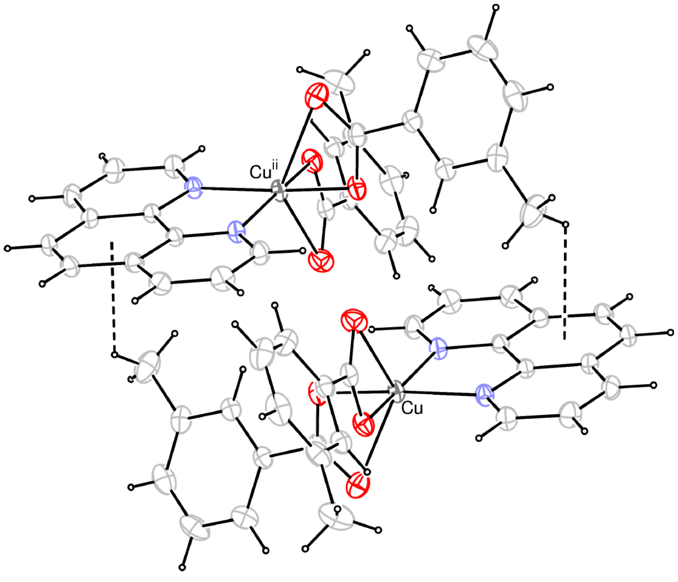


Figure 2
The C—H$\cdots\pi$ interaction between neighbouring complex molecules [symmetry code: (ii) $1 - x, 1 - y, 1 - z$.]

127.3 (3)° (Hoang *et al.*, 1992) and 131.80 (10)° (Rodrigues *et al.*, 1999). This suggests the existence of a bonding interaction between atoms Cu and O2 in (I).

Besides the elongated Jahn–Teller distortion, the smaller O2—Cu—O2^i angle of 137.53 (8)° is also the possible reason for the larger difference in Cu—O bond distances within the same carboxylate group.

A C—H$\cdots\pi$ interaction occurs between the methyl group and the ring containing atom C6 (*Cg* denotes the centroid of this ring) of a phen ligand of a neighbouring molecule (Fig. 2), with an H$\cdots$*Cg* distance of 3.01 Å and a C—H$\cdots$*Cg* angle of 126°. The π–π stacking between phen ligands which is usually observed in metal complexes is not observed in (I).

Experimental

An acetonitrile–water solution (20 ml) containing $CuSO_4{\cdot}5H_2O$ (0.25 g, 1 mmol), 3-methylbenzoic acid (1.36 g, 10 mmol) and NaOH (0.40 g, 10 mmol) was refluxed for 1 h, yielding a blue precipitate. After adding phen (0.2 g, 1.1 mmol), this blue precipitate gradually dissolved. The resulting dark-blue solution was refluxed for a further 3 h and then filtered. Blue single crystals of (I) were obtained from the filtrate after one week.

Crystal data

$[Cu(C_8H_7O_2)_2(C_{12}H_8N_2)]$
$M_r = 514.02$
Monoclinic, $C2/c$
$a = 21.1482$ (13) Å
$b = 9.9476$ (12) Å
$c = 11.9730$ (8) Å
$\beta = 112.690$ (2)°
$V = 2323.9$ (4) Å^3
$Z = 4$
$D_x = 1.469$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9404 reflections
$\theta = 2.5$–26.0°
$\mu = 0.98$ mm^{-1}
$T = 295$ (2) K
Platelet, blue
0.31 × 0.27 × 0.08 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.740$, $T_{max} = 0.920$
10 454 measured reflections
2666 independent reflections
2238 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 27.5$°
$h = -27 \rightarrow 27$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.091$
$S = 1.04$
2666 reflections
160 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 1.5001P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—O1	1.9435 (14)	Cu—N1	2.0113 (16)
Cu—O2	2.5923 (19)		
O2—Cu—N1	95.30 (6)	O2—Cu—O1^i	94.13 (6)
O2—Cu—N1^i	117.09 (6)	O2—Cu—O2^i	137.53 (8)
O2—Cu—O1	56.13 (6)	C7—O1—Cu	104.54 (13)

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

H atoms on aromatic rings were placed in calculated positions, with C—H = 0.93 Å, and were included in the final cycles of refinement in the riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$. Methyl H atoms were placed in calculated positions, with C—H = 0.96 Å, and refined in the riding model, with $U_{iso}(H) = 1.5U_{eq}(C)$.

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: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This project was supported by the National Natural Science Foundation of China (grant No. 29973036).

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Bakalbassis, E. G. & Terzis, A. (1994). *Inorg. Chim. Acta*, **218**, 167–172.

Cano, J., De Munno, G., Sanz, J. L., Ruiz, R., Faus, J., Lloret, F., Julve, M. & Caneschi, A. (1997). *J. Chem. Soc. Dalton Trans.* pp. 1915–1920.

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.

Hoang, N. N., Valach, F., Macaskova, L. & Melnik, M. (1992). *Acta Cryst.* C**48**, 1933–1936.

Parkanyi, L. & Speier, G. (1995). *Z. Kristallogr.* **210**, 307–309.

Rigaku (1998). *PROCESS-AUTO*. Version 1.06. Rigaku Corporation, Tokyo, Japan.

Rigaku/MSC (2002). *CrystalStructure.* Version 3.00. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.

Rodrigues, B. L., Costa, M. D. D. & Fernandes, N. G. (1999). *Acta Cryst.* C**55**, 1997–2000.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.