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Key indicators

Single-crystal X-ray study

T = 295 K

Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

R factor = 0.039

wR factor = 0.103

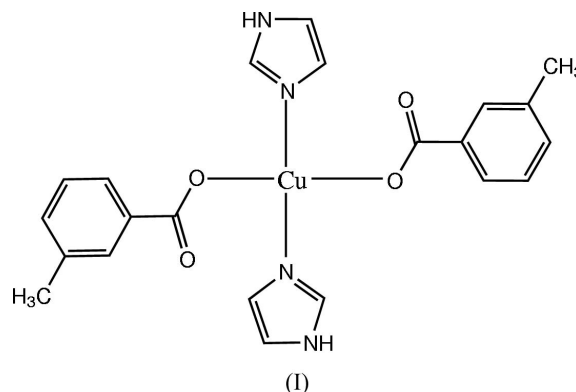
Data-to-parameter ratio = 13.3

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis(1*H*-imidazole- κN^3)bis(3-methylbenzoato- κO)-
copper(II)

In the title complex, $[\text{Cu}(\text{C}_8\text{H}_7\text{O}_2)_2(\text{C}_3\text{H}_4\text{N}_2)_2]$, the Cu^{II} atom, located on an inversion center, has a square-planar coordination geometry formed by imidazole molecules and 3-methylbenzoate anions. Hydrogen-bonding and $\text{C}-\text{H}\cdots\pi$ interactions occur between imidazole and methylbenzoate ligands of neighboring complex molecules.

Comment

$\pi-\pi$ stacking between aromatic rings is correlated with the electron-transfer process in some biological systems (Deisenhofer & Michel, 1989). Several metal complexes incorporating imidazole show $\pi-\pi$ stacking between imidazole rings (Lin *et al.*, 2005). The crystal structure of the title copper(II) complex, (I), shows no $\pi-\pi$ stacking between imidazole rings.



The molecular structure of (I) is shown in Fig. 1. The Cu^{II} atom is located on an inversion center and has a square-planar coordination geometry formed by 3-methylbenzoate anions and imidazole molecules (Table 1). The $\text{Cu}\cdots\text{O}2$ separation of 2.835 (2) Å is much longer than the $\text{Cu}-\text{O}1$ bond distance by 0.893 (3) Å . In most copper(II) complexes with an elongated octahedral coordination geometry, the $\text{Cu}-\text{O}$ bond distances in the axial direction are longer than those in the equatorial plane by 0.2–0.6 Å . The difference of 0.893 (3) Å found in (I), therefore, suggests no bonding interaction between Cu and $\text{O}2$ atoms. We proposed that the $M-\text{O}1-\text{C}1$ bond angle is an additional criterion of the coordination mode for the carboxyl group in metal complexes; for example, a $\text{Cu}-\text{O}1-\text{C}1$ angle close to 105° implies the existence of a bonding interaction between Cu and the other carboxyl O atom ($\text{O}2$) and suggests a chelate mode for the carboxyl group in Cu^{II} complexes (Li *et al.*, 2005). According to this criterion, the $\text{Cu}-\text{O}1-\text{C}1$ bond angle of $113.79(17)^\circ$ in (I), which is much larger than 105° , suggests no bonding interaction between the Cu and $\text{O}2$ atoms. Thus, the methylbenzoate anion acts as a monodentate

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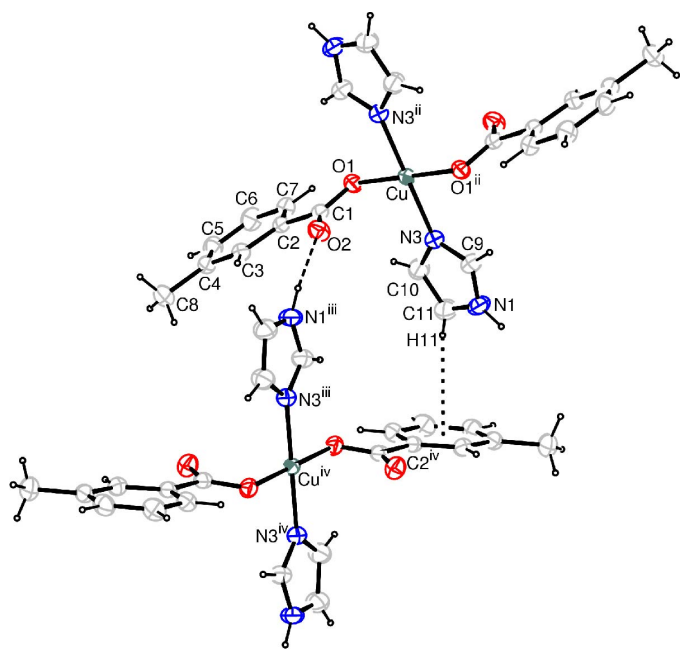


Figure 1

The molecular structure of (I) shown with 30% probability displacement ellipsoids. The dashed line indicates the hydrogen bonding and the dotted line indicates the C–H··· π interaction between imidazole and benzene rings. [Symmetry codes: (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$].

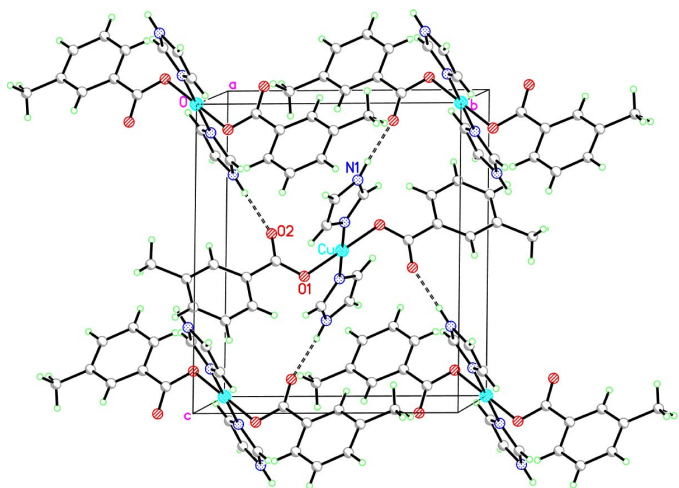


Figure 2

The packing, showing intermolecular hydrogen bonds as dashed lines.

rather than a chelate ligand in (I). Uncoordinated carboxyl atom O2 is hydrogen bonded to the imidazole ligand of a neighboring complex molecule, as shown in Figs. 1 and 2, and Table 2.

A PLATON analysis (Spek, 2003) shows that C–H··· π interactions occur between the imidazole and neighboring benzene rings (Fig. 1); C11–H11···Cg = 145° and H11···Cg = 2.825 Å, where Cg denotes the centroid of the C2^{iv}-benzene ring [symmetry code: (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$]. No π – π stacking occurs between aromatic rings in (I).

Experimental

An acetonitrile–water (1:1) solution (20 ml) containing 3-methylbenzoic acid (1.36 g, 10 mmol), NaOH (0.40 g, 10 mmol), imidazole (0.68 g, 10 mmol) and CuSO₄·5H₂O (0.25 g, 1 mmol) was refluxed for 4 h and filtered. Blue single crystals of (I) were obtained from the filtrate after 2 d.

Crystal data

[Cu(C₈H₇O₂)₂(C₃H₄N₂)₂]
M_r = 469.98
 Monoclinic, *P*2₁/*n*
a = 8.8630 (16) Å
b = 10.3923 (15) Å
c = 12.1022 (16) Å
 β = 100.466 (2)°
V = 1096.2 (3) Å³
Z = 2

D_x = 1.424 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 4226 reflections
 θ = 2.6–24.0°
 μ = 1.03 mm⁻¹
T = 295 (2) K
 Plate, blue
 0.45 × 0.43 × 0.13 mm

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
*T*_{min} = 0.630, *T*_{max} = 0.868
 5025 measured reflections

1900 independent reflections
 1560 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.033
 θ _{max} = 25.0°
h = –10 → 10
k = –12 → 11
l = –14 → 14

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.039
wR(*F*²) = 0.103
S = 1.08
 1900 reflections
 143 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2 + 0.5969P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.25 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.42 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu–O1	1.9417 (18)	Cu–N3	1.994 (2)
Cu–O2	2.835 (2)		
O1–Cu–O2	51.20 (7)	O2–Cu–N3	84.45 (8)
O1–Cu–N3	89.88 (9)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1···O2 ⁱ	0.86	1.91	2.754 (3)	167

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

Methyl H atoms were placed in calculated positions (C–H = 0.96 Å) and the torsion angle was refined from the electron density [*U*_{iso}(H) = 1.5*U*_{eq}(C)]. Aromatic H atoms were placed in calculated positions (C–H = 0.93 Å and N–H = 0.86 Å) and included in the final cycles of refinement as riding [*U*_{iso}(H) = 1.2*U*_{eq}(C,N)].

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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