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(1-Methylimidazole)(*N*-salicylidene-*rac*-glutamato)copper(II)

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Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.003 Å
R factor = 0.041
wR factor = 0.144
Data-to-parameter ratio = 24.4

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

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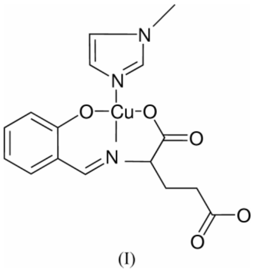
The title racemic compound, $[Cu(C_{12}H_{11}NO_5)(C_4H_6N_2)]$, adopts a square-planar copper(II) coordination mode with the tridentate *N*-salicylidenglutamato Schiff base dianion and the 1-methylimidazole ligand. Dimers of centrosymmetrically related molecules are formed. The theoretical investigation of the electronic structure of the title compound by the B3LYP method is presented.

Comment

In recent years, a group of copper(II) complexes containing Schiff base ligands, derived from salicylaldehyde and various amino acids, have received attention because of their proven antimicrobial and antiradical activities. From this group of substances, we have already described aqua(*N*-salicylidene methyl ester L-glutamato)copper(II) monohydrate (Langer *et al.*, 2004). The title compound, (I), was synthesized (Kohútová *et al.*, 2000) and its crystal structure and a theoretical investigation of the electronic structure are presented here.



(I)

The title compound, (I), consists of molecular units of Cu(*N*-sal-rac-glu)(1-methylimidazole) and its molecular structure is shown in Fig. 1. The chelate is stabilized by the Cu^{II} atom, which has a square-planar coordination. The atoms occupying the corners of the square are phenolic atom O1,

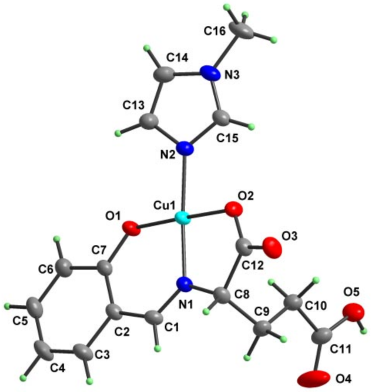


Figure 1
The molecular structure and atomic numbering scheme of (I). Displacement ellipsoids are drawn at the 50% probability level.

carboxylic atom O2, azometine atom N1 of the Schiff base *N*-salicylidenglutamate dianion, and atom N2 of the 1-methylimidazole ligand. The dimensions of the square (selected geometrical parameters are presented in Table 1) are comparable to the corresponding bond lengths found in (imidazole)(*N*-salicylideneglycinato)copper(II) (Warda, 1997) and dimeric (imidazole-N^3)(*N*-salicylidene-*rac*-alaninato-*O*,*N*,*O*′)copper(II) (Warda, 1998).

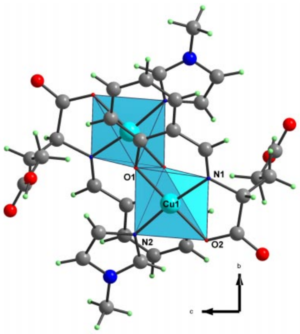


Figure 2
The dimer of the centrosymmetrically related molecules, showing the square-pyramidal arrangement.

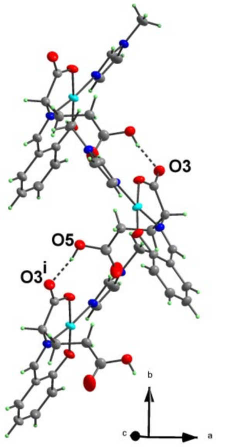


Figure 3
A chain of molecules in the *b* direction, formed by O—H$\cdots$O hydrogen bonds.

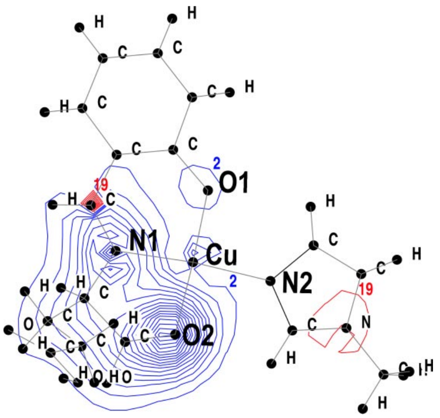


Figure 4
A section through the calculated molecular orbitals. Occupied molecular orbitals have maximum interactions of the Cu d_{zx} orbital with the p_y orbital of the N1 atom.

Dimers of centrosymmetrically related molecules with a Cu$\cdots$Cu^i distance of 4.0429 (5) Å are formed [symmetry code: (i) 2 $-x$, $-y$, $-z$]. The distance of phenolic atom O1 from the Cu^i atom within the dimer is 3.2206 (16) Å, and a weak interaction is formed. The coordination polyhedron can thus be regarded as a square pyramid (Fig. 2). The dimers are associated *via* hydrogen bonding (Table 2), thus forming a three-dimensional network. In addition to strong intermolecular O—H$\cdots$O hydrogen bonds, forming a chain of molecules along the *b* axis (Fig. 3), there are also weaker intramolecular and intermolecular C—H$\cdots$O hydrogen bonds (see Table 2).

It is apparent that the L-glutamic acid used for the synthesis gave a racemic Schiff base complex. This result is in agreement with previous results for the complex *N*-salicylideneglutamato-pyridinecopper(II) (Krätsmár-Šmogrovič *et al.*, 1985).

Mulliken charges and bond-overlap populations of important bonds of Cu to neighbouring atoms are presented in Table 3. The similar values of Mulliken charges (approximately -0.3 |e| for the N atoms and -0.4 |e| for the O atoms) indicate a symmetrical electron-density distribution. Calculations of bond-overlap populations show the equivalence of the Cu—N (0.18 |e|) and Cu—O bonds (0.19 |e|); such small values clearly indicate ionic character of the Cu—O and Cu—N bonds. Analysis of the contributions of atomic *d* orbitals of the Cu atom to individual molecular orbitals shows that the largest contribution to the Cu—O and Cu—N bonds is from the d_{zx} orbital of the Cu atom. Together with the p_y orbital of atom O2, the Cu d_{zx} orbital contributes to the Cu—O2 bond and also overlaps with the p_x orbital of atom N1 in the Cu—N1 bond. A section through the calculated molecular orbitals shows the region where the d_{zx} orbital of the Cu atom dominates (Fig. 4). The similar case is the interaction of the d_{xy} orbital of Cu with the p_y orbital of atom N1 and the p_z orbital of atom N2. The $d_{x^2-y^2}$ orbital of the Cu atom overlaps with the p_x orbital of atom O1 to form the Cu—O1 bond. This orbital also interacts weakly with the p_x orbital of atom N2. Finally, the d_{z^2} and d_{yz} orbitals participate in practically no interactions with any orbitals of the neighbouring atoms.

Experimental

The relevant data for the synthetic and analytical methods, as well as a description of the instruments and materials used for the preparation and characterization of the title compound, have been reported by Kohútová *et al.* (2000).

Crystal data

$[Cu(C_{12}H_{11}NO_5)(C_4H_6N_2)]$
M_r = 394.87
Monoclinic, $P2_1/n$
a = 7.92940 (10) Å
b = 11.33050 (10) Å
c = 18.53870 (10) Å
β = 98.7070 (10)°
V = 1646.40 (3) Å^3
Z = 4

D_x = 1.593 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7529 reflections
θ = 2.2–32.9°
μ = 1.36 mm^{-1}
T = 183 (2) K
Prism, blue
0.20 × 0.20 × 0.06 mm

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Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{\min} = 0.773$, $T_{\max} = 0.923$
28 068 measured reflections
5922 independent reflections
4602 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 32.9°$
$h = -12 \rightarrow 12$
$k = -16 \rightarrow 17$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.144$
$S = 1.02$
5922 reflections
243 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.92$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9142 (15)	Cu1—N2	1.9559 (16)
Cu1—N1	1.9199 (16)	Cu1—O2	1.9752 (14)
O1—Cu1—N1	94.58 (6)	O1—Cu1—O2	176.80 (6)
O1—Cu1—N2	91.96 (7)	N1—Cu1—O2	83.23 (6)
N1—Cu1—N2	173.09 (7)	N2—Cu1—O2	90.15 (6)
O1—Cu1—O2—C12	44.0 (12)	C9—C10—C11—O4	16.4 (4)
N2—Cu1—N1—C8	−20.6 (6)	C9—C10—C11—O5	−170.42 (19)
C1—N1—C8—C9	74.5 (2)	C9—C8—C12—O3	−67.0 (2)
C8—C9—C10—C11	−161.46 (18)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5$\cdots$O3$^{\rm ii}$	0.84	1.75	2.580 (2)	168.3
C1—H1$\cdots$O3$^{\rm iii}$	0.95	2.51	3.443 (2)	165.6
C15—H15$\cdots$O2	0.95	2.58	2.965 (2)	104.5
C16—H16$A\cdots$O2$^{\rm iv}$	0.98	2.53	3.369 (3)	143.8

Symmetry codes: (ii) $\frac{5}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $2 - x, 1 - y, -z$.

Table 3
Bond distances (Cu—X, Å) and Mulliken population analysis (|e|) for Cu and neighbouring atoms (X).

Atom X	Cu1—X	Mulliken charges	Overlap population
Cu1		0.481	
N1	1.9202	−0.293	0.183
N2	1.9559	−0.312	0.185
O1	1.9139	−0.380	0.185
O2	1.9757	−0.381	0.189

H atoms were refined isotropically but were constrained to an ideal geometry using an appropriate riding model [C—H = 0.95 Å for aromatic atoms, O—H = 0.84 Å and C—O—H = 109.5° for the OH group, and C—H = 0.98 Å and C—C—H = 109.5° for the methyl group]. In the OH and methyl groups, the torsion angles were allowed to refine with the starting position based on the circular Fourier synthesis, threefold averaged one in case of the methyl group. The quantum chemical calculations of the electronic structure of the title compound were performed using *GAUSSIAN*98 (Frisch *et al.*, 1998); the B3LYP/SVP method and basis set (SVP denotes split valence + polarization) (Becke, 1993) were applied. The geometry derived from the X-ray structural analysis was used for these calculations.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 2002); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXTL*.

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