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# (*N*-Salicylidene-D,L-glutamato)(2-methylimidazole)copper(II)

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**Key indicators**

Single-crystal X-ray study
*T* = 183 K
Mean σ(C–C) = 0.009 Å
*R* factor = 0.046
*wR* factor = 0.108
Data-to-parameter ratio = 12.4

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



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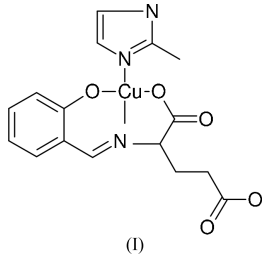
The title racemic compound, $[Cu(C_{12}H_{11}NO_5)(C_4H_6N_2)]$, adopts a square-pyramidal $Cu^{II}$ coordination with the tridentate *N*-salicylideneglutamate Schiff base dianion and the 2-methylimidazole ligand in the basal plane. The apex of the pyramid is occupied by a carboxylic acid O atom from the neighbouring chelate at a distance of 2.479 (4) Å, leading to infinite one-dimensional chains along the crystallographic *a* axis. Strong N—H···O and O—H···O hydrogen bonds form a helix parallel to the *c* axis. The electronic structure of the title compound has also been investigated by the *B3LYP* method.

## Comment

A group of copper(II) complexes containing Schiff bases, derived from salicylaldehyde and various amino acids, has attracted attention on account of their proven antimicrobial and antiradical activities. A series of copper(II) complexes containing the Schiff base derived from salicylaldehyde and L-glutamic acid was synthesized and studied. As neutral ligands, water, imidazole and its derivatives were used (Kohútová *et al.*, 2000). From this group of substances, we have already described (1-methylimidazole)(*N*-salicylidene-*rac*-glutamato)copper(II) (Langer *et al.*, 2003) and aqua-(*N*-salicylidene-methyl-ester-L-glutamato)copper(II) monohydrate (Langer *et al.*, 2004). The crystal structure and theoretical investigation of the electronic structure of the title compound, (I), are presented here.




(I)

The title compound, (I), consists of Cu(*N*-salicylidene-*rac*-glutamato)(2-methylimidazole) units (Fig. 1). Each copper ion displays a slightly distorted square-pyramidal coordination geometry. The base of the pyramid is formed by the phenolic atom O1, carboxylic acid atom O2 and azomethine atom N1 of the Schiff base *N*-salicylideneglutamate dianion, and atom N2 of the 2-methylimidazole ligand. The apex of the pyramid consists of the weakly bonded $O3^{iv}$ atom [symmetry code: (iv) $1 + x, y, z$] of the carboxylic acid group of an adjacent molecule, at a distance of 2.479 (4) Å. The Cu atom is 0.146 (2) Å above the mean plane defined by the base atoms O1, O2, N1 and N2 (r.m.s. deviation is 0.020 Å), in the direction of the apex. The dimensions of the square base (selected geometrical

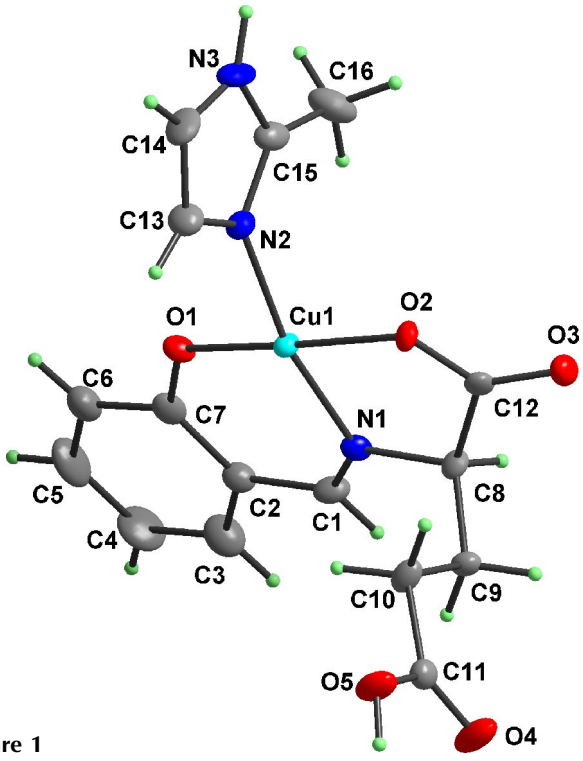



**Figure 1**
The asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level.

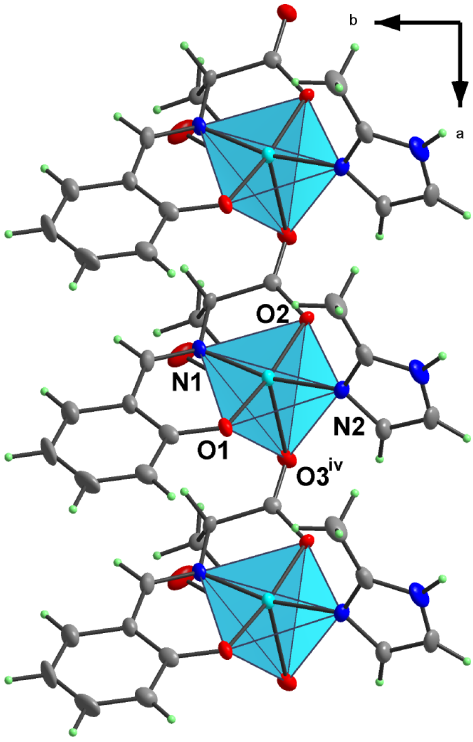



**Figure 2**
A chain of molecules in the *a*-axis direction, showing the square-pyramidal coordination of $Cu^{II}$ atoms. For symmetry code, see Table 2.

parameters are presented in Table 1) and the apical bond length are comparable with the corresponding values found in other compounds of this structural type, *e.g.* aqua(*N*-salicylideneglycinato)copper(II) hemihydrate (Ueki *et al.*, 1967; Bkouche-Waksman *et al.*, 1988) and polymeric (3,5-dimethylpyridine-*N*)(*N*-salicylideneglycinato-*O,N,O′:O″*)copper(II) (Warda, 1997). A polymeric chain is formed by the O3—C12—O2—Cu1···$O3^{iv}$ sequence along the crystallographic *a* axis. Polymeric structures are generally achieved when the apical position is occupied by a carboxylic O atom from an adjacent molecule, forming infinite zigzag chains (Warda, 1997; Langer *et al.*, 2004). The chain of molecules with the square-pyramidal coordination of $Cu^{II}$ atoms is depicted in Fig. 2.

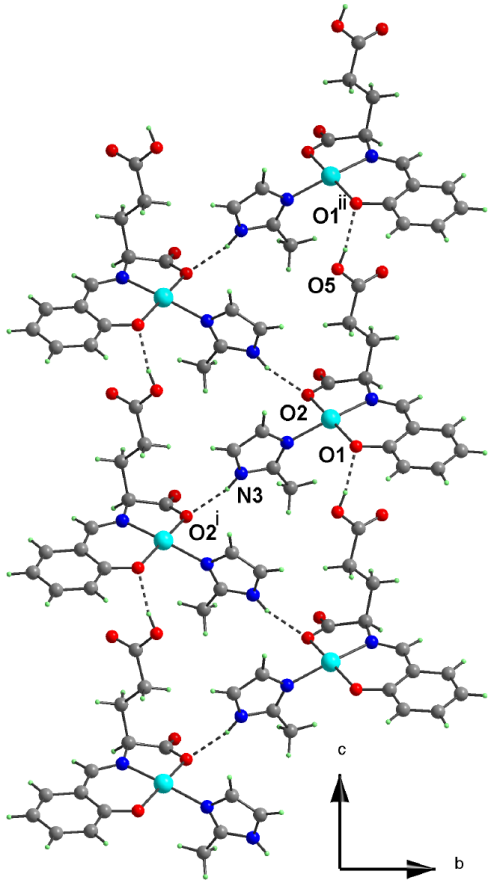



**Figure 3**
A helical arrangement of molecules *via* hydrogen bonds parallel to the *c* axis. For symmetry codes, see Table 2.

The chains are associated through hydrogen bonding (Table 2). There are strong intermolecular N—H···O and O—H···O hydrogen bonds, forming a helix parallel to the *c* axis (Fig. 3.). Weaker hydrogen bonds of the C—H···O type stabilize the three-dimensional network.

The synthesis of the title compound gave a racemic mixture of [Cu(*N*-salicylidene-D,L-glutamato)(2-methylimidazole)], even though an optically active parent complex [Cu(*N*-salicylidene-L-glutamato)$(H_2O)_2$] was used in the reaction with imidazole (Kohútová *et al.*, 2000); a similar result was found by Sivý *et al.* (1994) for [Cu(salicylidene-D,L-glutamato)(pyridine)].

The values of the calculated Mulliken charges and bond overlap populations indicate a symmetrically distributed electron density around the Cu atom (approximately −0.3 |e| for the N atoms and −0.4 |e| for the O atoms) (Table 3). Such

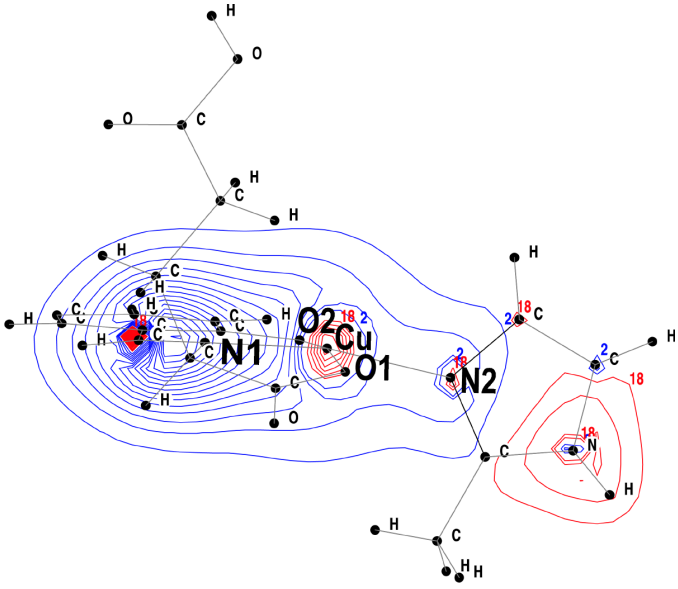



**Figure 4**
A section through the calculated molecular orbitals. Occupied molecular orbitals have maximum interactions of the Cu $d_{xy}$ orbital with the $p_y$ orbitals of the atoms N2, O1 and O2.

small values of bond overlap populations for Cu—O and Cu—N bonds clearly indicate their ionic character. The presence of the methyl group bonded to atom C15 next to N2 causes only negligible changes of bond overlap populations of Cu—O (approximately +0.02 |e|) and Cu—N1 bonds (approximately −0.02 |e|) in comparison with our previous study (Langer *et al.*, 2003). Analysis of the contributions of atomic *d* orbitals of the Cu atom to individual molecular orbitals shows that the $d_{xy}$ orbital of Cu makes a dominant contribution to the Cu—N2 bond, together with the $p_y$ orbital of atom N2. This orbital also overlaps with $p_y$ orbitals of O1 and O2 bonded to Cu. A section through the calculated molecular orbitals shows the region where the $d_{xy}$ orbital of the Cu atom dominates (Fig. 4). Rather weaker is the interaction of the $d_{z^2}$ orbital of the Cu atom with the $p_x$ orbital of N1 and the $p_z$ orbital of O1. The $d_{yz}$ orbital of the Cu atom interacts with the $p_z$ orbital of O2. Finally, the $d_{x^2-y^2}$ and $d_{zx}$ orbitals of the Cu atom participate in practically no interactions with any orbitals of the neighbouring atoms.

## Experimental

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 presented by Kohútová *et al.* (2000).

*Crystal data*

$[Cu(C_{12}H_{11}NO_5)(C_4H_6N_2)]$
$M_r$ = 394.87
Monoclinic, *Pc*
*a* = 5.2319 (1) Å
*b* = 16.2576 (3) Å
*c* = 9.6044 (1) Å
β = 96.530 (1)°
*V* = 811.63 (2) Å$^3$
*Z* = 2
$D_x$ = 1.616 Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 5004 reflections
θ = 2.5–25.0°
μ = 1.38 mm$^{-1}$
*T* = 183 (2) K
Needle, blue
0.15 × 0.02 × 0.01 mm

*Data collection*

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{min}$ = 0.820, $T_{max}$ = 0.980
7539 measured reflections
2849 independent reflections
2512 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.055
$\theta_{max}$ = 25.0°
*h* = −6 → 6
*k* = −19 → 19
*l* = −11 → 11

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.108
*S* = 1.04
2849 reflections
229 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0623P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.41 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.42 e Å$^{-3}$
Absolute structure: Flack (1983), 1181 Friedel pairs
Flack parameter = 0.02 (2)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cu1—N1 | 1.946 (5) | Cu1—O2 | 1.982 (4) |
| Cu1—O1 | 1.948 (4) | Cu1—O3$^{iv}$ | 2.479 (4) |
| Cu1—N2 | 1.979 (5) | | |
| N1—Cu1—O1 | 93.2 (2) | N1—Cu1—O2 | 83.31 (17) |
| N1—Cu1—N2 | 167.84 (19) | O1—Cu1—O2 | 172.15 (17) |
| O1—Cu1—N2 | 93.41 (18) | N2—Cu1—O2 | 88.86 (17) |
| N1—Cu1—O2—C12 | 11.6 (4) | Cu1—O2—C12—O3 | 162.2 (4) |
| N1—C8—C9—C10 | −65.4 (6) | Cu1—N2—C15—N3 | −169.7 (4) |
| C9—C10—C11—O4 | −2.2 (8) | Cu1—N2—C15—C16 | 12.4 (9) |
| C9—C10—C11—O5 | 177.5 (5) | | |

Symmetry code: (iv) 1 + *x*, *y*, *z*.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3···O2$^{i}$ | 0.88 | 2.08 | 2.940 (6) | 166 |
| O5—H5···O1$^{ii}$ | 0.84 | 1.87 | 2.682 (6) | 162 |
| C6—H6···O4$^{iii}$ | 0.95 | 2.52 | 3.362 (8) | 147 |
| C10—H10*B*···O3$^{iv}$ | 0.99 | 2.56 | 3.391 (7) | 142 |
| C14—H14···O3$^{v}$ | 0.95 | 2.50 | 3.157 (7) | 126 |

Symmetry codes: (i) *x*, −*y*, *z* − ½; (ii) *x*, *y*, 1 + *z*; (iii) 1 + *x*, *y*, *z* − 1; (iv) 1 + *x*, *y*, *z*; (v) 1 + *x*, −*y*, *z* − ½.

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

| Atom *X* | *d*(Cu—*X*) | Mulliken charges | Overlap population |
|---|---|---|---|
| Cu1 | | 0.821 | |
| N1 | 1.946 (5) | −0.323 | 0.164 |
| N2 | 1.947 (4) | −0.333 | 0.178 |
| O1 | 1.950 (4) | −0.378 | 0.204 |
| O2 | 1.984 (4) | −0.394 | 0.205 |

H atoms 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], with $U_{iso}$(H) values equal to 1.2$U_{eq}$ of the parent atom. In the OH group, the torsion angle was allowed to refine, with the starting position based on a

circular Fourier synthesis, while for the methyl group, the starting position was based on a threefold averaged circular Fourier synthesis. The quantum chemical calculations of the electronic structure of the title compound were performed using *GAUSSIAN*98 (Frisch *et al.*, 1998); the *B*3*LYP/SVP* method and basis set (*SVP* denotes split valence + polarization) (Becke, 1993) were used. The geometry derived from the X-ray structural analysis was used. The calculations were performed for a doublet as the most stable multiplet state; the title compound is an open-shell system, so the unrestricted formalism was used.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; 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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## References

Becke, A. D. (1993). *Chem. Phys.* **98**, 5648–5652.
Bkouche-Waksman, I., Barbe, J. M. & Kvick, Å. (1988). *Acta Cryst.* B**44**, 595–601.
Brandenburg, K. (2000). *DIAMOND*. Version 2.1d. Crystal Impact GbR, Bonn, Germany.
Bruker (2001). *SHELXTL*. Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Zakrzewski, V. G., Montgomery, J. A. Jr, Stratmann, R. E., Burant, J. C., Dapprich, S., Millam, J. M., Daniels, A. D., Kudin, K. N., Strain, M. C. *et al.* (1998). *GAUSSIAN*98. Revision A. Gaussian Inc., Pittsburgh, PA, USA.
Kohútová, M., Valent, A., Mišíková, E. & Mlynarčík, D. (2000). *Chem. Pap.* **54**, 87–90.
Langer, V., Gyepesová, D., Scholtzová, E., Mach, P., Kohútová, M., Valent, A., & Smrčok, Ľ. (2004). *Z. Kristallogr.* In the press.
Langer, V., Scholtzová E., Gyepesová, D., Kohútová, M. & Valent, A. (2003). *Acta Cryst.* E**59**, m1181–m1183.
Sheldrick, G. M. (2002). *SADABS*. Version 2.03. University of Göttingen, Germany.
Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sivý, J., Kettman, V., Krätsmár-Šmogrovič, J. & Breza, M. (1994). *Z. Naturforsch. Teil C*, **49**, 571–578.
Ueki, T., Ashida, T., Sasada, Y. & Kakudo, M. (1967). *Acta Cryst.* **22**, 870–878.
Warda, S. A. (1997). *Acta Cryst.* C**53**, 1010–1011.