

Dimeric (isoquinoline)(*N*-salicylidene-*D,L*-glutamato)copper(II) ethanol solvate

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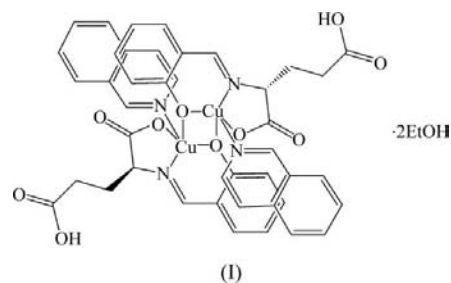
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The title racemic complex, bis[μ -*N*-(2-oxidobenzylidene)-*D,L*-glutamato(2-)]bis[(isoquinoline)copper(II)] ethanol disolvate, [Cu₂(C₁₂H₁₁NO₅)₂(C₉H₇N)₂].2C₂H₆O, adopts a square-pyramidal Cu^{II} coordination mode with a tridentate *N*-salicylidene-glutamato Schiff base dianion and an isoquinoline ligand bound in the basal plane. The apex of the pyramid is occupied by a phenolic O atom from the adjacent chelate molecule at an apical distance of 2.487 (3) Å, building a dimer located on the crystallographic inversion center. The Cu...Cu spacing within the dimers is 3.3264 (12) Å. The ethanol solvent molecules are hydrogen bonded to the dimeric complex molecules, forming infinite chains in the *a* direction. The biological activity of the title complex has been studied.

Comment

Copper(II) complexes containing a Schiff base derived from salicylaldehyde and various amino acids have received considerable attention in view of their impact in many fields of bioinorganic chemistry. A series of copper(II) complexes containing the Schiff base derived from salicylaldehyde and *L*-glutamic acid were synthesized (Andrezálová *et al.*, 1998; Kohútová *et al.*, 2000) and studied on account of their antimicrobial and antiradical activities, especially for their observed capability to imitate the role of the natural superoxide dismutase enzyme. Several structures of these complexes containing molecular ligands such as water, pyridine, pyrazole, and imidazole and its derivatives have already been described, namely (1-methylimidazole)(*N*-salicylidene-*rac*-glutamato)copper(II) (Langer *et al.*, 2003), (*N*-salicylidene-*DL*-glutamato)(2-methylimidazole)copper(II) (Langer, Scholtzová *et al.*, 2004) and aqua(*N*-salicylidene-methylester-*L*-glutamato)copper(II) monohydrate (Langer, Gyepesová *et al.*, 2004). The title compound, (I), showed antimicrobial

activity tested against gram-negative bacteria *Escherichia coli* (IC₅₀ = 0.60 mmol dm⁻³), yeast *Candida parapsilosis* (IC₅₀ = 0.63 mmol dm⁻³), and filamentous fungi *Microsporium gypseum* and *Botrytis cinerea* (IC₅₀ = 0.45 and 0.44 mmol dm⁻³, respectively) (Valent *et al.*, 2004). Its crystal and molecular structures are presented here.



The crystal structure of (I) consists of centrosymmetric dimers of (isoquinoline)(*N*-salicylidene-*rac*-glutamato)copper(II) and ethanol solvent molecules (for the numbering of the asymmetric part of the structure, see Fig. 1). Each copper ion in the title complex displays a slightly distorted square-pyramidal coordination geometry. The base of the pyramid is formed by the phenolic O3, carboxylate O4 and azomethine N1 atoms of the Schiff base *N*-salicylidene-glutamato dianion and by atom N1Q of the isoquinoline ligand. The apex of the pyramid consists of the weakly bonded phenolic O3 atom of an adjacent molecule at an apical distance of 2.487 (3) Å (Table 1 and Fig. 2). The size of the pyramidal base and the apical bond length are comparable to the corresponding bond lengths found in other compounds of this structure type, *e.g.* dimeric (imidazole-*N*³)(*N*-salicylidene-*rac*-alaninato-*O,N,O'*)-

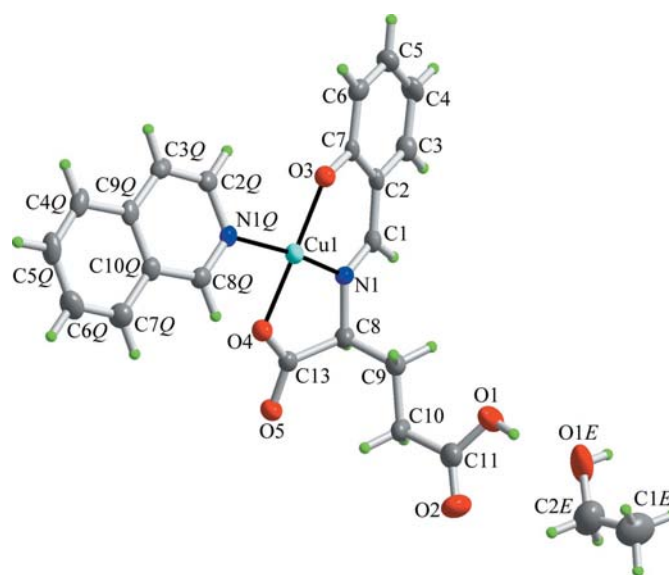


Figure 1
A perspective drawing of the symmetry-independent part of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

copper(II) (Warda, 1998), dimeric (pyrazole- N^2)(N -salicylidene-2,2-dimethylglycinato- O,N,O')copper(II) pyrazole solvate (Hill & Warda, 1999) and (imidazole)(N -salicylidene- β -alaninato)copper(II) (Plesch *et al.* 1998). In (I), the Cu1—O3 distance of 1.922 (3) Å is considerably shorter than the Cu1—O4 distance of 1.952 (3) Å, as is the case in the above-mentioned related compounds, indicating that more negative charge is localized on the phenolic O3 atom than on the carboxy O4 atom; the C1=N1 bond formed by the condensation reaction of length 1.284 (5) Å is in the normal double-bond range of 1.28–1.30 Å. In the structures of copper(II) complexes containing various N -salicylidene-amino acid Schiff bases and different neutral ligands, the local environment in the plane where the chelate and neutral ligands are bound undergoes only slight changes. A rich variety of axial distortions ranging from square-planar to square-pyramidal has been found. Such structural adaptability may be one of the reasons for the diversity of interactions of these complexes with biological systems (Plesch *et al.*, 1998). As an example, (1-methylimidazole)(N -salicylidene-*rac*-glutamato)copper(II) (Langer *et al.*, 2003) adopts a square-planar copper(II) coordination mode with the tridentate N -salicylidene-glutamato

Schiff base dianion and the 1-methylimidazole ligand. Dimers of centrosymmetrically related molecules are formed [the Cu \cdots Cu distance within dimers is 4.0429 (5) Å]; the distance of the phenolic O atom from the Cu atom within the dimer is 3.2206 (16) Å and a weak interaction was formed. The Cu \cdots Cuⁱ distance in (I) within the dimers is 3.3264 (12) Å [symmetry code: (i) $-x, -y, -z + 1$]. The dimers are linked into infinite chains running parallel to the a axis *via* medium-strong hydrogen bonds (Table 2), with the hydroxy group of the ethanol solvent molecule acting as both H-atom donor and acceptor (Fig. 3). In addition, there is a strong π – π interaction between the isoquinoline ring systems of neighbouring dimers, with a perpendicular distance of 3.236 (2) Å between the parallel planes.

Experimental

The title complex, (I), was synthesized by the reaction of diaqua (N -salicylidene-*L*-glutamato)copper(II) monohydrate, prepared according to the method of Nakao *et al.* (1967), and isoquinoline in a 1:1 molar ratio with a 10% excess of isoquinoline (molecular ligand) in ethanol at ambient temperature. The precipitated green product was isolated, washed with ethanol and dried in air. The synthesis of the title compound resulted in a racemic mixture of bis[(μ - N -salicylidene-*D,L*-glutamato)bis(isoquinoline)dication] ethanol disolvate even though an optically active parent complex diaqua(N -salicylidene-*L*-glutamato)copper(II) was used in the reaction with isoquinoline. The racemization of the Schiff base ligand readily occurs under mild conditions even in neutral or weak acidic aqueous or alcohol solutions (Sivý *et al.*, 1994).

Crystal data

[Cu ₂ (C ₁₂ H ₁₁ NO ₅) ₂ (C ₉ H ₇ N) ₂] \cdot 2C ₂ H ₆ O	$\beta = 69.288 (3)^\circ$
$M_r = 975.98$	$\gamma = 69.139 (3)^\circ$
Triclinic, $P\bar{1}$	$V = 1076.1 (4) \text{ \AA}^3$
$a = 9.4211 (16) \text{ \AA}$	$Z = 1$
$b = 10.949 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 12.565 (3) \text{ \AA}$	$\mu = 1.06 \text{ mm}^{-1}$
$\alpha = 66.477 (5)^\circ$	$T = 153 \text{ K}$
	$0.21 \times 0.19 \times 0.12 \text{ mm}$

Data collection

Siemens SMART CCD area-detector diffractometer	8414 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	3744 independent reflections
$T_{\min} = 0.808, T_{\max} = 0.884$	2710 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.064$

Table 1

Selected bond lengths (Å).

Cu1—O3	1.922 (3)	Cu1—N1 <i>Q</i>	2.006 (3)
Cu1—N1	1.933 (3)	Cu1—O3 ⁱ	2.487 (3)
Cu1—O4	1.952 (3)		

Symmetry code: (i) $-x, -y, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O1E	0.84	1.79	2.576 (5)	154
O1E—H1E \cdots O5 ⁱⁱ	0.84	1.92	2.750 (5)	169

Symmetry code: (ii) $x + 1, y, z$.

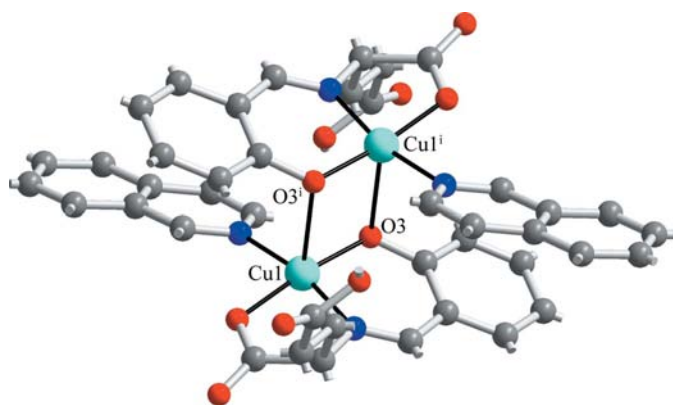


Figure 2

The dimer of the centrosymmetrically related molecules, showing the square-pyramidal arrangement. H atoms have been omitted for clarity. [Symmetry code: (i) $-x, -y, -z + 1$.]

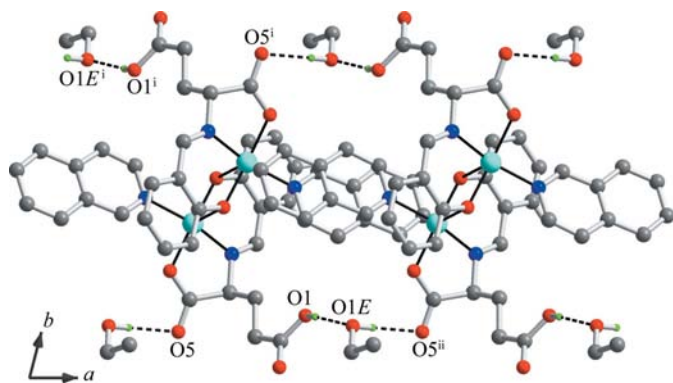


Figure 3

A projection of the structure of (I) along the c axis. Hydrogen bonds are shown as broken lines. H atoms not involved in the hydrogen-bonding pattern have been omitted for clarity. [Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $x + 1, y, z$.]

Refinement

$$R[F^2 > 2\sigma(F^2)] = 0.048$$

$$wR(F^2) = 0.124$$

$$S = 1.00$$

3744 reflections

292 parameters

18 restraints

H-atom parameters constrained

$$\Delta\rho_{\max} = 0.84 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.52 \text{ e } \text{\AA}^{-3}$$

H atoms were refined isotropically and their positions were constrained to an ideal geometry using an appropriate riding model, with C—H distances in the range 0.95–1.00 Å. For the methyl group, the O—C—H angles (109.5°) were kept fixed, while the torsion angle was allowed to refine with the starting positions based on the circular Fourier synthesis averaged using the local threefold axis. For the hydroxy groups, the O—H distances (0.84 Å) and C—O—H angles (109.5°) were kept fixed, while the torsion angles were allowed to refine with the starting positions based on the circular Fourier synthesis. The ethanol solvent molecule is slightly disordered (the maximum residual density peak is in this region) and the U_{ij} components for the non-H atoms were restrained with an effective standard deviation of 0.01 Å² to approximate isotropic behaviour.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE* and *SADABS* (Sheldrick, 2003); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3299). Services for accessing these data are described at the back of the journal.

References

- Andrežalová, L., Ďuračková, Z., Valent, A. & Devínsky, F. (1998). *Pharmazie*, **53**, 338–342.
- Brandenburg, K. (2008). *DIAMOND*. Version 3.1f. Crystal Impact GbR, Bonn, Germany.
- Bruker (2003). *SMART* (Version 5.63) and *SAINTE* (Version 6.45). Bruker AXS Inc., Madison, Wisconsin, USA.
- Hill, E. & Warda, S. A. (1999). *Acta Cryst.* **C55**, 1431–1434.
- Kohútová, M., Valent, A., Mišíková, E. & Mlynářčík, D. (2000). *Chem. Pap.* **54**, 87–90.
- Langer, V., Gyepesová, D., Scholtzová, E., Mach, P., Kohútová, M., Valent, A. & Smrček, Ľ. (2004). *Z. Kristallogr.* **219**, 112–116.
- Langer, V., Scholtzová, E., Gyepesová, D., Kohútová, M. & Valent, A. (2003). *Acta Cryst.* **E59**, m1181–m1183.
- Langer, V., Scholtzová, E., Gyepesová, D., Kohútová, M. & Valent, A. (2004). *Acta Cryst.* **E60**, m129–m132.
- Nakao, Y., Sakurai, K. & Nakahara, A. (1967). *Bull. Chem. Soc. Jpn.*, **40**, 1536–1538.
- Plesch, G., Kettmann, V., Sivý, J., Švajlenová, O. & Friebe, C. (1998). *Polyhedron*, **17**, 539–545.
- Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sivý, J., Kettmann, V., Krätzmár-Šmogrovič, J. & Breza, M. (1994). *Z. Naturforsch. Teil C*, **49**, 571–578.
- Valent, A., Kohútová, M., Švajlenová, O., Hudecová, D., Olejníková, P. & Melnik, M. (2004). *J. Coord. Chem.* **57**, 1279–1285.
- Warda, S. A. (1998). *Acta Cryst.* **C54**, 304–306.