

***trans*-Bis(dimethyl sulfoxide- κ O)-
bis(3-oxo-3,4-dihydroquinoxaline-
2-carboxylato- κ^2 N¹,O²)copper(II)**Zora Popović,^{a*} Gordana Pavlović^b and Boris-Marko
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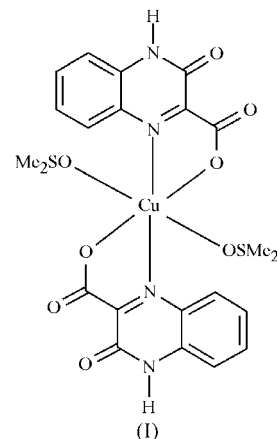
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The title compound, [Cu(C₉H₅N₂O₃)₂(C₂H₆OS)₂], consists of octahedrally coordinated Cu^{II} ions, with the 3-oxo-3,4-dihydroquinoxaline-2-carboxylate ligands acting in a bidentate manner [Cu—O = 1.9116 (14) Å and Cu—N = 2.1191 (16) Å] and a dimethyl sulfoxide (DMSO) molecule coordinated axially *via* the O atom [Cu—O = 2.336 (5) and 2.418 (7) Å for the major and minor disorder components, respectively]. The whole DMSO molecule exhibits positional disorder [0.62 (1):0.38 (1)]. The octahedron around the Cu^{II} atom, which lies on an inversion centre, is elongated in the axial direction, exhibiting a Jahn–Teller effect. The ligand exhibits tautomerization by H-atom transfer from the hydroxyl group at position 3 to the N atom at position 4 of the quinoxaline ring of the ligand. The complex molecules are linked through an intermolecular N—H...O hydrogen bond [N...O = 2.838 (2) Å] formed between the quinoxaline NH group and a carboxylate O atom, and by a weak intermolecular C—H...O hydrogen bond [3.392 (11) Å] formed between a carboxylate O atom and a methyl C atom of the DMSO ligand. There is a weak intramolecular C—H...O hydrogen bond [3.065 (3) Å] formed between a benzene CH group and a carboxylate O atom.

Comment

Kynurenic acid (4-hydroxyquinoline-2-carboxylic acid), a well known tryptophane metabolite, has neuroactivity to inhibit excitatory amino acid (EAA) receptor-mediated neurodegeneration (Jauch *et al.*, 1993; Stone, 1993). 3-Hydroxyquinoxaline-2-carboxylic acid (HQC), a substance which is structurally related to kynurenic acid, shows similar effects on EAA receptors. However, the above-mentioned properties of HQC exhibit some ambiguities and side effects. Therefore, it is of interest to obtain a deeper insight into the structure–function relationship, not only of the acid alone, but of its metal

complexes, particularly those with metals of pharmacological importance, such as copper (Krogsgaard-Larsen *et al.*, 2002). To the best of our knowledge, the only metal complex of HQC known so far is a nickel(II) complex of formula NiCl₂(HQC) (Turvey & Allan, 1996), characterized by spectroscopic, magnetic and conductivity measurements and by thermal methods. In this study, the structure of the title copper complex, (I), with HQC has been determined.



Compound (I) contains a Cu^{II} ion on a crystallographic inversion centre. The Cu^{II} ion is octahedrally coordinated by two 3-oxo-3,4-dihydroquinoxaline-2-carboxylate ligands in the equatorial plane [Cu1—O1 = 1.9116 (14) Å and Cu1—N1 = 2.1191 (16) Å] and by two disordered dimethyl sulfoxide (DMSO) molecules in the apical positions [Cu1—O4A = 2.336 (5) Å and Cu1—O4B = 2.418 (7) Å] (Table 1 and Fig. 1). The bond angles around atom Cu1 lie within the range 80–100°, with the largest angle being O1ⁱ—Cu1—N1 of 99.26 (6)° [symmetry code: (i) $-x, -y, -z$]. The Cu1—O1 bond is shorter than other chemically similar Cu—O bond distances (1.94–1.98 Å; Segl'a *et al.*, 1998; Klein *et al.*, 1982; Ptasiwicz-Bąk *et al.*, 1995), *e.g.* in the mixed-valence Cu^I/Cu^{II} complex with pyrazine-2-carboxylic acid [1.941 (3) Å; Liu *et al.*, 2003]. On the other hand, Cu1—N1 is longer than analogous Cu—N bonds (1.98–2.00 Å) found in the copper(II) complex with picolinic acid (Segl'a *et al.*, 1998) and in the two copper(II) complexes with pyrazine-2-carboxylic acid (Klein *et al.*, 1982; Ptasiwicz-Bąk *et al.*, 1995). It is even slightly longer than the analogous bond of 2.061 (3) Å in the coordination polymer of copper(II) with pyrazine-2,3-dicarboxylic acid (Konar *et al.*, 2004), which is the longest found to date in the literature for copper(II) complexes containing carboxylic acid with pyrazine and/or a pyridine ring.

The chelate ring defined by atoms Cu1/O1/C9/C1/N1 is approximately planar, with a maximum out-of-plane deviation of 0.11 Å for Cu1. This plane makes a significantly large angle of 20.84 (7)° with the planar quinoxaline ring (atoms N1/C1/C2/N2/C3–C8). The geometry of the quinoxaline ring corresponds to tautomeric protonation at N2 [O3=C2 = 1.220 (3) Å and C2—N2 = 1.360 (3) Å] (Allen, 2002).

The O1—C9 bond distance of the carboxylate group [1.280 (2) Å] is longer than O2—C9 [1.217 (2) Å], due to the coordination of atom O1 to Cu^{II}. This deviation of the carb-

oxylate group geometry is well known, with the longer C—O bond being in the range 1.28–1.30 Å and the shorter one in the range 1.22–1.24 Å (Segl'a *et al.*, 1998; Klein *et al.*, 1982; Ptasiwicz-Bak *et al.*, 1995; Konar *et al.*, 2004).

The Cu1—O4A and Cu1—O4B bond distances (from DMSO) (Table 1) in (I) fall within the range 2.34–2.46 Å (Cu1—O4A is slightly shorter) found for octahedral copper(II) complexes containing DMSO in axial positions (Benali-Cherif *et al.*, 1995; Bieller *et al.*, 2005; Djedouani *et al.*, 2006; Chan *et al.*, 1996). The longest Cu—O(DMSO) bond in the previously reported complexes is 2.463 Å in bis[3-acetyl-6-methyl-2H-pyran-2,4(3H)-dionato]bis(dimethyl sulfoxide)-

copper(II) (Djedouani *et al.*, 2006), reflecting Jahn–Teller distortion. The Cu1—O4A bond (from the major DMSO component) in (I) differs slightly from the corresponding bond in hexakis(dimethyl sulfoxide)copper(II) bis(hydrogensulfate) [2.34 (1) Å; Bieller *et al.*, 2005] and from that observed in bis[2,4-diamino-6-(4-pyridyl)-1,3,5-triazine]bis(dimethyl sulfoxide)copper(II) perchlorate [2.353 (9) Å; Chan *et al.*, 1996]. In the latter compound, the S atom shows positional disorder in both DMSO ligands.

The complexes are linked by an intermolecular N—H···O hydrogen bond [2.838 (2) Å], formed between the quinoxaline NH group and a carboxylate O atom, and by a weak intermolecular C—H···O hydrogen bond [3.392 (11) Å], which is formed between carboxylate O and methyl C atoms of a DMSO molecule. There is a weak intramolecular C—H···O hydrogen bond [3.065 (3) Å] formed between a benzene CH group and the ligated carboxylate O-donor atom (Table 2 and Fig. 2).

Experimental

A suspension of copper(II) hydroxide (0.03 g, 0.31 mmol) and 3-hydroxyquinoxaline-2-carboxylic acid (0.12 g, 0.63 mmol) in dimethyl sulfoxide (20 ml) (molar ratio 1:2) was refluxed for 4 h to give a dark-red solution. Slow evaporation of this solution at room temperature yielded brown crystals of the title compound suitable for X-ray analysis.

Crystal data

[Cu(C ₉ H ₅ N ₂ O ₃) ₂ (C ₂ H ₆ OS) ₂]	V = 1213.09 (3) Å ³
M _r = 598.13	Z = 2
Monoclinic, P2 ₁ /n	Mo Kα radiation
a = 9.4426 (1) Å	μ = 1.13 mm ⁻¹
b = 8.3584 (1) Å	T = 296 (2) K
c = 15.7881 (3) Å	0.43 × 0.43 × 0.10 mm
β = 103.213 (2)°	

Data collection

Oxford Xcalibur2 diffractometer with a Sapphire-3 CCD area-detector	T _{min} = 0.810, T _{max} = 1.000 (expected range = 0.723–0.893)
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2006)	15817 measured reflections
	2625 independent reflections
	2280 reflections with I > 2σ(I)
	R _{int} = 0.021

Refinement

R[F ² > 2σ(F ²)] = 0.035	H atoms treated by a mixture of independent and constrained refinement
wR(F ²) = 0.087	Δρ _{max} = 0.39 e Å ⁻³
S = 1.11	Δρ _{min} = -0.31 e Å ⁻³
2624 reflections	
214 parameters	

The DMSO molecule exhibits positional disorder, which was easily resolved as 0.62 (1):0.38 (1) beginning with the electron density found in difference Fourier maps and refined using SHELXL97 instructions FVAR and PART (Sheldrick, 1997). The S—C bond distances were restrained using the SHELXL97 DFIX instruction to average values of 1.782 (2) and 1.786 (2) Å for the S—C11 and S—C10 bonds, respectively (Table 1). Atoms C10A and C10B were refined anisotropically in order to model as faithfully as possible the electron density in the disordered region, but these displacement parameters should not be taken as faithful representations of atomic displacement for these atoms. The H atom belonging to the quinoxaline N atom was found in a difference Fourier map at the final stages of

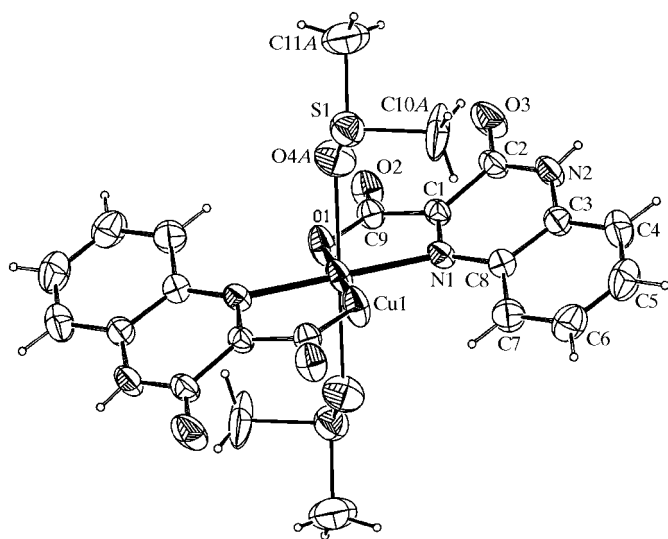


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Only the major component of the disordered DMSO molecule is shown. Unlabelled atoms are related to labelled atoms by the symmetry operator (-x, -y, -z).

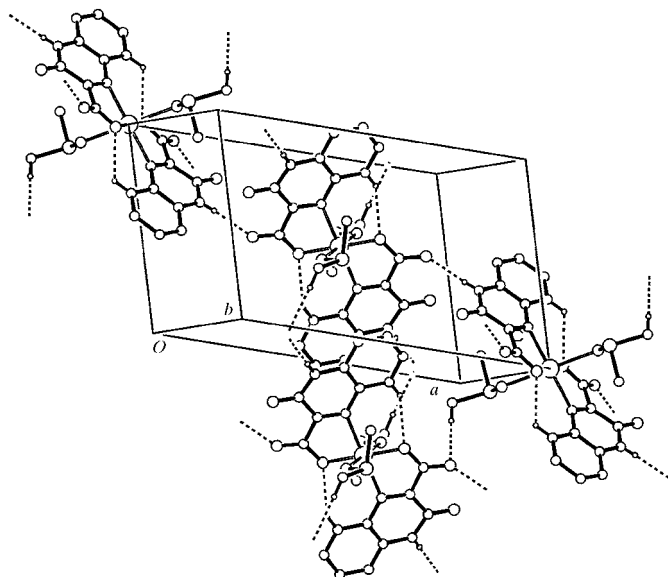


Figure 2
A packing view of (I). Hydrogen bonds are represented by dashed lines.

Table 1

Selected geometric parameters (Å, °).

Cu1—O1	1.9116 (14)	N2—C3	1.372 (3)
Cu1—N1	2.1191 (16)	S1—O4A	1.514 (4)
Cu1—O4A	2.336 (5)	S1—C11A	1.782 (2)
Cu1—O4B	2.418 (7)	S1—C10A	1.786 (2)
O1—C9	1.280 (2)	S2—O4B	1.494 (7)
O2—C9	1.217 (2)	S2—C11B	1.782 (2)
O3—C2	1.220 (3)	S2—C10B	1.786 (2)
C2—N2	1.360 (3)		
O1—Cu1—N1	80.74 (6)	O1—Cu1—O4B	95.9 (2)
O1—Cu1—O4A	81.46 (11)	N1—Cu1—O4B	93.82 (17)
N1—Cu1—O4A	83.58 (12)		

Symmetry code: (i) $-x, -y, -z$.**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H1N2\cdots O2^{ii}$	0.76 (3)	2.08 (3)	2.838 (2)	176 (3)
$C7-H7\cdots O1^i$	0.93	2.43	3.065 (3)	125
$C11A-H11C\cdots O2^{iii}$	0.96	2.43	3.392 (11)	177

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

refinement as a small electron density (approximately $0.5 \text{ e } \text{Å}^{-3}$) and refined freely (Table 2). H atoms bonded to C atoms were introduced in calculated positions and refined using a riding model, with $C-H = 0.93 \text{ Å}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms, and $C-H = 0.96 \text{ Å}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms. Due to the absorption coefficient and crystal dimensions, the absorption effect was minimized using the multi-scan technique.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON98* (Spek, 1998); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3073). Services for accessing these data are described at the back of the journal.

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