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Diaquabis(quinoxaline-2-carboxylato-κ^2N^1,*O*)copper(II)

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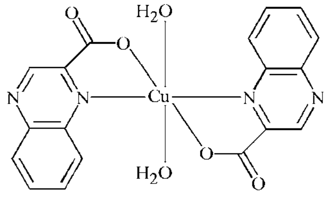
In the title compound, [Cu($C_9H_5N_2O_2$)$_2$(H_2O)$_2$], the Cu^{II} ion lies on an inversion centre and has an elongated centrosymmetric octahedral environment, equatorially *trans*-coordinated by two *N*,*O*-bidentate quinoxaline-2-carboxylate ligands and axially coordinated by two water O atoms. Symmetry-related molecules are linked by strong O—H···O hydrogen bonds, involving the uncoordinated carboxyl O atom of the carboxylate group and the coordinated water molecules, to form a two-dimensional network. Weak intermolecular C—H···N interactions also stabilize the crystal structure.

Comment

Copper complexes play an important role in catalysing enzymatic activity, and much interest has been shown in copper complexes of organic acids because of their special biocatalytic functions (Şengül & Büyükgüngör, 2005). It is well known that the incorporation of carboxylic acid groups into coordination compounds gives interesting supramolecular architectures (Puddephatt *et al.*, 2002). Quinoxaline-2-carboxylic acid (Hqlc) is a potential chelate with interesting possibilities, exhibiting *N*,*O*-chelation (through a quinoxaline N atom and the carboxylate group, forming a five-membered chelate ring). Several important solvothermal *in situ* metal/ligand reactions and their mechanisms, including oxidation of aldehydes into the corresponding carboxylates in the presence of Cu^{II} (Chen & Tong, 2007; Evans & Lin, 2002), have been reported. We found a similar phenomenon under mild conditions by conventional solution methods. In the reaction, Cu^{II} ions may act as an oxidative agent to oxidize quinoxaline-2-carbaldehyde into Hqlc in alkaline medium. To the best of our knowledge, no crystal structures of metal complexes with the Hqlc ligand have been reported to date, although there are several crystal structures of complexes with analogous ligands (Okabe *et al.*, 2004; Stachová *et al.*, 2006). As an extension of our work (Xie *et al.*, 2007), we report here our efforts to establish the preferred coordination mode of Hqlc to copper(II) in the structure of the title compound, (I).

X-ray analysis reveals that atom Cu1 (located on an inversion centre) has a Jahn–Teller-elongated octahedral coordination geometry completed by three pairs of symmetry-related atoms, equatorially by two carboxylate O atoms and two quinoxaline N atoms, and axially by two symmetry-equivalent water O atoms (Table 1). As shown in Fig. 1, the Cu1—O2 distance is slightly shorter than the Cu1—N2 distance. This effect is usually observed for the metal complexes of analogous compounds, such as (5-*n*-butylpyridine-2-carboxylato)copper(II) [Cu—O$_{eq}$ = 1.952 (2) Å and Cu—N = 1.977 (2) Å; Okabe *et al.*, 2002] and *trans*-bis(isoquinoline-3-carboxylato-κ^2N,*O*)bis(methanol-κO)copper(II) [Cu—O$_{eq}$ = 1.963 (2) Å and Cu—N = 1.979 (2) Å; Okabe *et al.*, 2004]. The coordination bond length in the axial direction is longer than the bond lengths in the equatorial plane. A similar behaviour is found for (5-*n*-butylpyridine-2-carboxylato)copper(II) [2.596 (3) and 1.952 (2) Å, respectively; Okabe *et al.*, 2002]. The coordination polyhedron displays a tetragonality factor *T* of 0.86, which indicates an additional elongation of the octahedron along the O1—Cu1—O1^{iv} axis [symmetry code: (iv) $-x+1, -y+1, -z+1$]. This distortion must be attributed to the Jahn–Teller effect and is consistent with a $d_{x^2-y^2}$ ground state of the Cu^{II} ion.



(I)

In the title compound, the carboxylic acid groups are deprotonated, which means that the ligand also serves as a counter-ion and the overall complex ion is neutral. In the molecule of (I), the angles around the Cu atom are slightly distorted from an ideal octahedral configuration [O2—Cu1—N2 = 81.54 (4)°]. Similar bond angles are observed in some related metal complexes, such as *trans*-bis(isoquinoline-3-carboxylato-κ^2N,*O*)bis(methanol-κO)copper(II) [O—Cu—N = 83.77 (7)°; Okabe *et al.*, 2004] and *trans*-diaquabis(3-

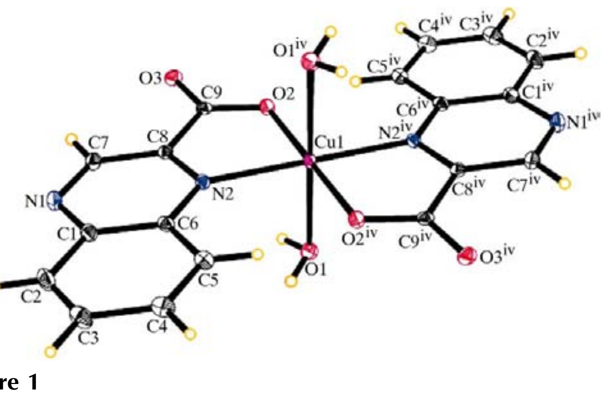


Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (iv) $-x+1, -y+1, -z+1$.]

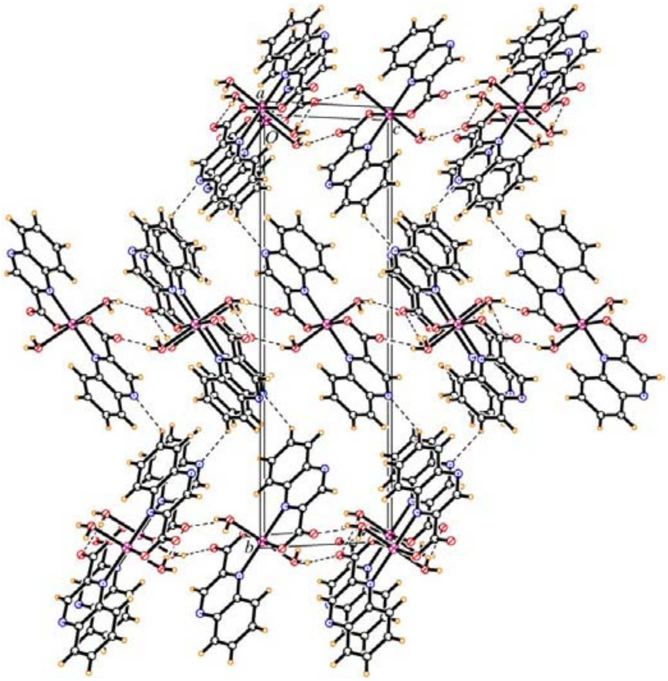


Figure 2
The packing of the title compound, viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

hydroxypicolinato)zinc(II) [O—Zn—N = 79.3 (1)°; Di Marco *et al.*, 2004]. The Cu^{II} ion chelates the Hqlc ligand *via* atoms N2 and O2 to form a five-membered ring. The N2/O2/Cu1/$N2^{iv}$/$O2^{iv}$ unit is strictly planar. Both Hqlc ligands are practically planar, the greatest deviations from the mean planes being 0.071 (2) Å (for atom O2) for the exocyclic atoms and 0.119 (1) Å (O3) for the endocyclic atoms. The ligand plane forms an angle of 4.93 (2)° with the five-membered chelate ring plane, which results in a copper out-of-plane distance from the Hqlc ligand of 0.221 Å.

In the crystal structure, there are three intermolecular hydrogen bonds, and no evidence was observed for the existence of intermolecular aromatic π–π interactions in the complex. The molecular units are linked by weak intermolecular C—H···N interactions (C3—H3*A*···N1; Table 2) to form infinite zigzig chains running along the *b* axis. Adjacent chains are further connected into a two-dimensional network by strong intermolecular hydrogen bonds between the coordinated water molecule and the uncoordinated O atom (O3) of the carboxylate group (Table 2), as shown in Fig. 2.

Experimental

To a 15 ml methanol solution of $Cu(ClO_4)_2\cdot 6H_2O$ (1 mmol, 371 mg) and quinoxaline-2-carbaldehyde (2 mmol, 316 mg) was added a 5 ml methanol solution of triethylenetetramine (1 mmol, 146.2 mg). The mixture was stirred for 3 h under reflux at 333 K. The precipitate was then filtered off, washed with methanol and dried in air. The deep-green filtrate was allowed to evaporate slowly, affording X-ray quality crystals of the title complex, (I) [m.p. > 573 K (decomposition)]. Analysis calculated for $C_{18}H_{14}CuN_4O_6$: C 48.49, H 3.16, N 12.57%; found: C 48.40, H 3.22, N 12.64%. IR (KBr pellet, cm^{-1}): 3590 (*b*), 3063 (*s*), 2942 (*s*), 2849 (*s*), 2010 (*m*), 1839 (*b*), 1707 (*sh*), 1611 (*s*, *b*), 1572 (*s*), 1530 (*s*), 1494 (*s*), 1465 (*s*), 1420 (*s*), 1368 (*s*), 1339 (*s*), 1214 (*s*), 1134 (*b*, *s*), 935 (*s*), 769 (*s*), 627 (*s*), 554 (*m*), 431 (*m*).

Crystal data

$[Cu(C_9H_5N_2O_2)_2(H_2O)_2]$
$M_r = 445.87$
Monoclinic, $P2_1/c$
$a = 5.9278\ (5)$ Å
$b = 22.256\ (2)$ Å
$c = 7.2456\ (6)$ Å
$\beta = 113.393\ (2)°$
$V = 877.34\ (12)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.29\ mm^{-1}$
$T = 153\ (2)$ K
0.40 × 0.38 × 0.35 mm

Data collection

Rigaku R-AXIS SPIDER diffractometer
Absorption correction: empirical (using intensity measurements) (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.594$, $T_{max} = 0.627$
8445 measured reflections
2019 independent reflections
1889 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.086$
$S = 1.08$
2019 reflections
142 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.70$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O2	1.9228 (12)	O2—C9	1.2628 (17)
Cu1—N2	2.1249 (11)	O3—C9	1.2328 (17)
Cu1—O1	2.3408 (11)		
O2—Cu1—N2	81.54 (4)	O3—C9—O2	124.79 (13)
O2—Cu1—O1	89.97 (5)	O3—C9—C8	119.38 (12)
N2—Cu1—O1	90.04 (4)	O2—C9—C8	115.82 (12)
O1—Cu1—N2—C8	95.24 (9)	N2—C8—C9—O3	−174.09 (11)
Cu1—N2—C8—C7	174.00 (10)	N2—C8—C9—O2	4.92 (17)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···$O3^{i}$	0.85 (2)	1.98 (2)	2.8076 (14)	162.5 (19)
O1—H1*B*···$O3^{ii}$	0.80 (2)	2.10 (2)	2.8839 (15)	166 (2)
C3—H3···$N1^{iii}$	0.95	2.58	3.345 (2)	137

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

H atoms on O atoms were located in a difference Fourier map and refined freely; the other H atoms were positioned geometrically and refined as riding on their attached C atoms, with C—H bond distances of 0.95 Å and with $U_{iso}(H)$ values of $1.2U_{eq}(C)$.

Data collection: *RAPID-AUTO* (Rigaku, 2004); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3062). Services for accessing these data are described at the back of the journal.

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