Data collection

Rigaku AFC-7R diffractometer	4710 reflections with $I > 0$
ω–2θ scans	$R_{int} = 0.016$
Absorption correction:	$\theta_{max} = 30°$
ψ scan (North *et al.*, 1968)	$h = 0 \rightarrow 13$
	$k = -16 \rightarrow 16$
$T_{min} = 0.529$, $T_{max} = 0.860$	$l = -10 \rightarrow 10$
5276 measured reflections	3 standard reflections
4999 independent reflections	every 150 reflections
	intensity decay: 2.1%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 1.52$ e Å^{-3}
$R(F) = 0.031$	$\Delta\rho_{min} = -1.33$ e Å^{-3}
$wR(F^2) = 0.089$	Extinction correction:
$S = 1.551$	Zachariasen (1967), type
4999 reflections	2, Gaussian isotropic
227 parameters	Extinction coefficient:
H atoms not refined	0.042 (3)
$w = 1/[\sigma^2(F_o^2)$	Scattering factors from
$+ 0.0025(F_o^2)^2]$	*International Tables for*
$(\Delta/\sigma)_{max} = 0.001$	*Crystallography* (Vol. C)

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

Sn1—O1	2.099 (2)	Sn1—N1	2.424 (2)
Sn1—O2	2.102 (2)	Sn1—N2	2.419 (2)
O1—Sn1—O2	97.43 (7)	O2—Sn1—N1	79.19 (6)
O1—Sn1—N1	73.13 (6)	O2—Sn1—N2	72.90 (7)
O1—Sn1—N2	79.13 (6)	N1—Sn1—N2	137.32 (6)

The diffractometer was equipped with a Rigaku low-temperature device. H atoms were placed in calculated positions and were not refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *PATTY* in *DIRDIF92* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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[CuCl(C$_{12}$H$_9$N$_2$O$_5$)(C$_{12}$H$_{10}$N$_2$O$_5$)(H$_2$O)]

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Abstract

In the title compound, aquachloro(1-ethyl-1,4-dihydro-4-oxo-1,3-dioxolo[4,5-*g*]cinnoline-3-carboxylato-O^3,O^4)-(1-ethyl-1,4-dihydro-4-oxo-1,3-dioxolo[4,5-*g*]cinnoline-3-carboxylic acid-O^3,O^4)copper(II), the Cu^{II} ion adopts a tetragonally distorted octahedral geometry. In the equatorial plane, the Cu^{II} ion is coordinated to two O atoms (O$_{keto}$ and O$_{carboxylate}$) of one cinoxacinate ligand, and to two O atoms (O$_{keto}$ and O$_{carboxylic}$) of one cinoxacin molecule. The apical positions are occupied by one O atom from the water molecule and one Cl$^-$ ion, resulting in a CuClO$_5$ chromophore.

Comment

Cinoxacin, HCx (1-ethyl-1,4-dihydro-4-oxo-1,3-dioxolo[4,5-*g*]cinnoline-3-carboxylic acid; Cx is the deprotonated form, 1-ethyl-1,4-dihydro-4-oxo-1,3-dioxolo[4,5-*g*]cinnoline-3-carboxylate), is a quinolone antimicrobial

agent which is active, both *in vitro* (Giamarellon & Jackson, 1975) and *in vivo* (Grenwood & O'Grady, 1978), against a large variety of gram-negative bacteria. In the last few years, we have studied the crystal structures of several complexes of cinoxacin with cobalt, nickel, zinc and cadmium ions (Chulvi *et al.*, 1991; Ruíz *et al.*, 1993, 1994, 1998). Likewise, the structural properties of two complexes of cinoxacin have been reported (Ruíz *et al.*, 1995, 1997) showing square-planar and distorted square-pyramidal environments. The present investigation was aimed at determining the crystal structure of a new copper–cinoxacin complex, [Cu(Cx)(HCx)(H$_2$O)Cl], (I), and comparing the results with data from known Cu^{II} complexes. This compound is the first reported in which the ligand is present in both its neutral and its anionic forms.

(I)
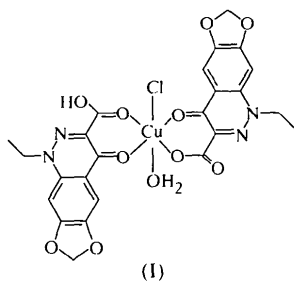
The structure consists of neutral monomeric [Cu(Cx)-(HCx)(H$_2$O)Cl] units linked by hydrogen-bond inter-

actions. The complex exhibits a six-coordinate motif with a tetragonally distorted octahedral environment around the metal centre. In the equatorial plane, the Cu^{II} atom is coordinated to two O atoms (O$_{keto}$ and O$_{carboxylate}$) of one cinoxacinate ligand, Cx, and to two O atoms (O$_{keto}$ and O$_{carboxylic}$) of one cinoxacin molecule, HCx. The apical positions are occupied by one O atom from the water molecule (O10) and the Cl$^-$ ion, resulting in a CuClO$_5$ chromophore. The Cu—Cl [2.6043 (10)] and Cu—O10 [2.588 (3) Å] distances are longer than the equatorial Cu—O distances, thus confirming the tetragonal distortion. The Cu—O$_{keto}$ distances [mean 1.9354 (17) Å] are similar and are slightly shorter than the Cu—O$_{carboxylic}$ [2.0081 (18)] and Cu—O$_{carboxylate}$ [1.9880 (18) Å] distances. The Cu^{II} ion deviates from the mean least-squares basal plane formed by these O atoms, by 0.174 (1) Å in the direction of the coordinated Cl$^-$ ion.

The Cu—O$_{keto}$ equatorial distances are similar to those observed in the square-pyramidal compound [Cu(Cx)$_2$(H$_2$O)]·H$_2$O reported recently; whereas the Cu—O$_{carboxylic}$ bond lengths are shorter in (I), the Cu—O10 axial bond length is longer than that observed for the square-pyramidal compound [Cu—O1W 2.226 (5) Å; Ruíz *et al.*, 1997]. Also, complex (I) presents equatorial bond lengths longer than those reported for the square-planar compound [Cu(Cx)$_2$]·2H$_2$O (Ruíz *et al.*, 1995). The O—Cu—O and Cl—Cu—O angles in (I) vary from 80.30 (8) to 100.53 (7)°; these values differ from those expected for a regular octahedron.
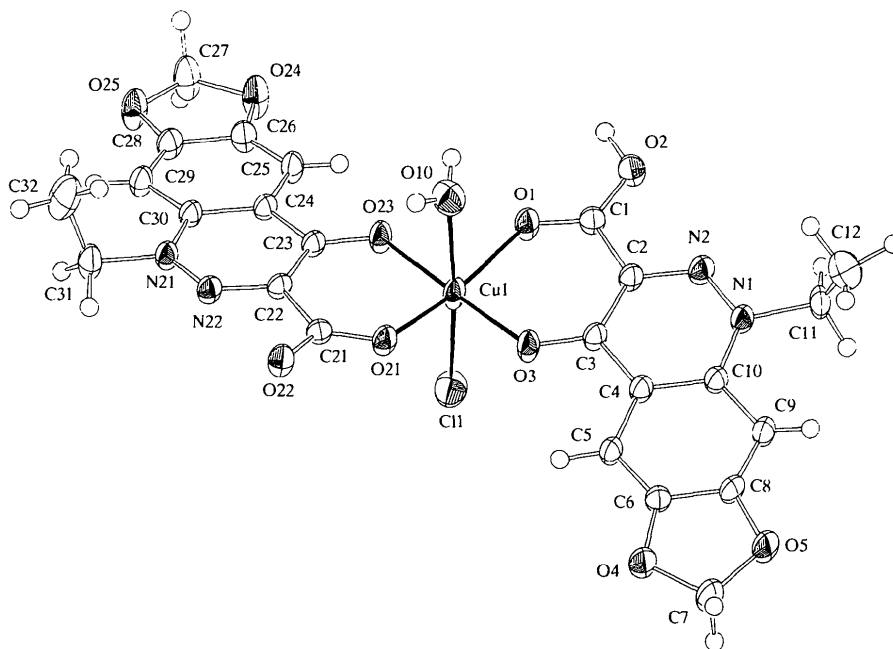

Fig. 1. The molecular structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

The geometry of the hydrogen bonds is given in Table 2. The hydrogen bonds involve atoms $O2_{carboxylic}$, $O22_{carboxylate}$, $O21_{carboxylate}$, $O10$ of the coordinated water molecule and $N22$ of the pyrimidine group. The H atom in the carboxylic acid group is hydrogen-bonded to the carboxylate O atoms.

Experimental

Crystals of (I) were prepared in warm methanol (333–343 K) by mixing solutions containing cinoxacin (0.5 mmol, 0.13 g) and $CuCl_2$ (1 mmol, 0.17 g); the final volume was 100 ml. A green–yellow microcrystalline compound was obtained after a few days, which was separated by filtration. Slow evaporation of the resulting solution at room temperature over the period of a year yielded yellow crystals suitable for single-crystal diffraction work.

Crystal data

[CuCl(C₁₂H₉N₂O₅)(C₁₂H₁₀-N₂O₅)(H₂O)]
$M_r = 640.44$
Triclinic
$P\bar{1}$
$a = 8.8712\,(18)$ Å
$b = 10.2642\,(12)$ Å
$c = 14.4412\,(9)$ Å
$\alpha = 98.780\,(5)°$
$\beta = 92.483\,(9)°$
$\gamma = 104.804\,(14)°$
$V = 1251.7\,(3)$ Å³
$Z = 2$
$D_x = 1.699$ Mg m⁻³
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 18.98–42.39°$
$\mu = 2.863$ mm⁻¹
$T = 293\,(2)$ K
Prism
$0.25 \times 0.25 \times 0.10$ mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction:
ψ scan (North et al., 1968)
$T_{min} = 0.619$, $T_{max} = 0.751$
5436 measured reflections
5089 independent reflections
4011 reflections with
$I > 2\sigma(I)$

$R_{int} = 0.027$
$\theta_{max} = 74.22°$
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.120$
$S = 1.080$
5089 reflections
455 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0682P)^2 + 0.4087P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.432$ e Å⁻³
$\Delta\rho_{min} = -0.571$ e Å⁻³
Extinction correction:
SHELXL97 (Sheldrick, 1997)
Extinction coefficient:
0.0025 (3)
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu1—O3	1.9323 (17)	Cu1—O1	2.0081 (18)
Cu1—O23	1.9384 (17)	Cu1—O10	2.588 (3)
Cu1—O21	1.9880 (18)	Cu1—Cl1	2.6043 (10)
O3—Cu1—O23	177.71 (9)	O21—Cu1—O10	80.30 (8)
O3—Cu1—O21	87.37 (7)	O1—Cu1—O10	82.04 (8)
O23—Cu1—O21	92.30 (7)	O3—Cu1—Cl1	90.98 (7)
O3—Cu1—O1	90.95 (7)	O23—Cu1—Cl1	91.31 (7)
O23—Cu1—O1	88.68 (7)	O21—Cu1—Cl1	97.23 (6)
O21—Cu1—O1	162.19 (9)	O1—Cu1—Cl1	100.53 (7)
O3—Cu1—O10	91.96 (9)	O10—Cu1—Cl1	176.06 (6)
O23—Cu1—O10	85.75 (8)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H20···O22ⁱ	1.11 (6)	1.33 (6)	2.445 (2)	174 (6)
O10—H101···O22ⁱⁱ	0.76 (4)	2.21 (4)	2.916 (3)	155 (4)
O10—H101···N22ⁱⁱ	0.76 (4)	2.67 (4)	3.308 (3)	142 (4)
O10—H102···O23ⁱⁱⁱ	0.81 (4)	2.32 (4)	3.087 (3)	158 (4)

Symmetry codes: (i) $x - 1, y, z$; (ii) $1 - x, -y, -z$; (iii) $-x, -y, -z$.

All H atoms were located from difference maps and refined isotropically (C—H = 0.76–1.11 Å and $U_{iso} = 0.032–0.14$ Å²).

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994). Cell refinement: CAD-4 EXPRESS. Data reduction: HELENA (Spek, 1997). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: ZORTEP (Zsolnai, 1997). Software used to prepare material for publication: SHELXL97.

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