Crystal Structure of Bis(2-diethoxycarbonylethanyl-8-hydroxyquinolino-*N,O*)Cu(II)

Kuniaki ITOH, Jun-ichi TANAKA, Jun-ichiro SETSUNE, and Kazuo EDA[†]

Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657-8501, Japan

The crystal structure of bis(2-diethoxycarbonylethanyl-8-hydroxyquinolino-*N,O*) copper(II), Cu(C₁₇H₁₈NO₅)₂, was determined by X-ray diffraction analysis. The compound crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell. The cell parameters are $a = 6.0177(10)\text{\AA}$, $b = 14.307(2)\text{\AA}$, $c = 19.848(3)\text{\AA}$, $\alpha = 100.423(3)^\circ$, $\beta = 97.987(3)^\circ$, $\gamma = 93.783(3)^\circ$, $V = 1657.1(5)\text{\AA}^3$. The structure was refined to the final $R1 = 0.060$, and revealed that a 2:1 complex between the ligand and Cu(II) is formed. The geometry of Cu(II) is distorted square-planar.

(Received November 15, 2005; Accepted January 20, 2006; Published on web March 27, 2006)

It is well known that 8-hydroxyquinoline acts as a bidentate ligand, and forms stable chelates with various metal cations. Recently, such chelate complexes have been discovered to become light-emitting diodes,¹ electroluminescent devices,² and fungicides.³ They are thus the interest of applied science as well as materials science. Because of our interest in the geometrical control of metallic centers through functional groups introduced to hydroxyquinoline ligands, we have sought the synthesis of new complexes of 8-hydroxyquinoline. We recently reported the crystal structure resulting from the reaction of 8-hydroxyquinoline having a carboxyethyl group at the 2-position with Cu(II).⁴ The structure shows that the carboxyl oxygen atom of the substituent group takes part in the coordination to the Cu(II) center, resulting in the formation of a 1:1 complex between the ligand and Cu(II) with the distorted square-pyramidal geometry of the Cu(II) center coordinated to one nitrogen and four oxygen donors, two of which are from the hydration water molecules. In the present study, we attempted to react 2-diethoxycarbonylethanyl-8-hydroxyquinoline with Cu(II). We report here on the crystal structure of the resulting (title) compound.

The title compound was prepared by adding an aqueous solution of 1/2 eq. copper(II) perchlorate to a dioxane solution of 2-diethoxycarbonylethanyl-8-hydroxyquinoline. Yellow crystals were obtained from the resulting solution at room temperature by slow evaporation for one week. Diffraction data

were collected by a Bruker smart 1000 CCD diffractometer at 298 K with graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073\text{\AA}$). The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically by full-matrix least squares method. The positions of the hydrogen atoms were calculated geometrically. SHELX programs⁵ were used for these calculations.

The crystal and experimental data are given in Table 1. The chemical structure and the final atomic parameters of non-hydrogen atoms are shown in Fig. 1 and Table 2, respectively.

Table 1 Crystal and experimental data

Formula:	C ₃₄ H ₃₆ CuN ₂ O ₁₀
Formula weight	= 696.19
Temperature (K)	= 298(2)K
Wavelength (Å)	= 0.71073 Å
Crystal system:	triclinic
Crystal color, habit:	yellow, prism
Crystal size:	0.30 × 0.10 × 0.06 mm ³
Space group, Z:	$P\bar{1}$, 2
Unit cell dimensions:	
a	= 6.0177(10)Å
b	= 14.307(2)Å
c	= 19.848(3)Å
V	= 1657.1(5)Å ³
α	= 100.423(3)°
β	= 97.987(3)°
γ	= 93.783(3)°
Density _{calc.}	= 1.395 g/cm ³
No. of reflections used	= 6420
$\theta_{\max}$	= 27.22°
$R1$ [3039 refs. $I > 2\sigma(I)$]	= 0.060
$wR2$ (all data)	= 0.157
$(\Delta/\sigma)_{\max}$	= 0.000
$(\Delta\rho)_{\max}$	= 0.469 eÅ ⁻³
$(\Delta\rho)_{\min}$	= -0.526 eÅ ⁻³
Measurement:	Bruker smart 1000
Program system:	SHELX
Structure determination:	direct method
Refinements:	full-matrix least-squares on F^2

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free from charge, by quoting the publication citation and deposition number: CCDC289499.

Fig. 1 Chemical structure of the title compound.

[†] To whom correspondence should be addressed.
E-mail: eda@kobe-u.ac.jp

Table 2 Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$)

Atom	x	y	z	U_{eq}
(Molecule 1)				
Cu1	1.0	0.5	0.0	0.0434(2)
C1	0.6377(7)	0.6087(3)	0.0776(2)	0.0433(10)
C2	0.4648(7)	0.6052(4)	0.1181(2)	0.0565(12)
C3	0.4014(8)	0.5242(4)	0.1401(2)	0.0627(14)
C4	0.5146(7)	0.4427(3)	0.1240(2)	0.0495(12)
C5	0.4682(9)	0.3561(4)	0.1450(2)	0.0684(15)
C6	0.5944(9)	0.2826(4)	0.1289(2)	0.0674(14)
C7	0.7692(8)	0.2913(3)	0.0908(2)	0.0595(13)
C8	0.8200(7)	0.3731(3)	0.0668(2)	0.0438(10)
C9	0.6897(7)	0.4506(3)	0.0843(2)	0.0418(10)
C10	0.6989(7)	0.7000(3)	0.0549(2)	0.0507(12)
C11	0.9256(7)	0.7494(3)	0.0929(2)	0.0464(11)
C12	0.9891(9)	0.8353(4)	0.0629(3)	0.0623(14)
C13	1.2851(13)	0.9536(5)	0.0644(4)	0.157(4)
C14	1.4708(15)	0.9992(5)	0.1082(5)	0.158(4)
C15	0.9285(8)	0.7784(3)	0.1705(3)	0.0566(12)
C16	1.1206(11)	0.7720(5)	0.2811(3)	0.100(2)
C17	1.3171(12)	0.7323(5)	0.3107(3)	0.129(3)
N1	0.7483(5)	0.5322(2)	0.06097(16)	0.0407(8)
O1	0.9768(5)	0.3834(2)	0.02818(15)	0.0531(8)
O2	1.1947(7)	0.8708(3)	0.0896(2)	0.1094(15)
O3	0.8759(7)	0.8657(3)	0.0201(3)	0.1103(16)
O4	1.0935(6)	0.7448(3)	0.20626(17)	0.0732(10)
O5	0.7952(7)	0.8248(3)	0.1963(2)	0.1004(14)
(Molecule 2)				
Cu2	0.5	0.5	0.5	0.0489(3)
C18	0.1366(7)	0.6473(3)	0.5214(2)	0.0506(12)
C19	-0.0606(8)	0.6855(4)	0.4937(3)	0.0672(14)
C20	-0.1656(8)	0.6509(4)	0.4287(3)	0.0733(16)
C21	-0.0742(8)	0.5796(4)	0.3854(3)	0.0583(13)
C22	-0.1636(9)	0.5392(4)	0.3161(3)	0.0794(17)
C23	-0.0583(10)	0.4720(4)	0.2791(3)	0.0781(17)
C24	0.1411(8)	0.4398(3)	0.3082(2)	0.0627(13)
C25	0.2337(8)	0.4747(3)	0.3759(2)	0.0532(12)
C26	0.1252(7)	0.5453(3)	0.4152(2)	0.0463(11)
C27	0.2450(7)	0.6886(3)	0.5944(2)	0.0523(12)
C28	0.4630(8)	0.7506(3)	0.5980(2)	0.0569(13)
C29	0.5760(9)	0.7832(4)	0.6722(3)	0.0694(15)
C30	0.9393(14)	0.8394(7)	0.7487(5)	0.165(4)
C31	0.961(2)	0.9298(7)	0.7540(6)	0.244(7)
C32	0.4345(10)	0.8346(4)	0.5632(3)	0.0690(15)
C33	0.2903(17)	0.9844(5)	0.5685(5)	0.173(4)
C34	0.176(2)	1.0448(6)	0.6073(5)	0.251(7)
N2	0.2246(6)	0.5792(2)	0.48235(18)	0.0457(9)
O6	0.4165(5)	0.4456(2)	0.40694(15)	0.0624(9)
O7	0.7877(7)	0.8163(3)	0.6734(2)	0.1197(17)
O8	0.4909(7)	0.7815(4)	0.7219(2)	0.1097(16)
O9	0.3229(8)	0.8980(3)	0.5967(2)	0.1080(15)
O10	0.4984(9)	0.8417(3)	0.5098(2)	0.1210(17)

Anisotropic displacement parameters for atoms (C13,14,16,17,30,31,33,34 and O2,3,5,7-10) of the ethoxycarbonyl moieties are rather high compared with those for atoms of the other moieties. Moreover, some C-C bond distances (C13-C14 = 1.36 $\text{\AA}$, C30-C31 = 1.28 $\text{\AA}$, C33-C34 = 1.34 $\text{\AA}$) of the moieties are rather short compared with the ideal distance (1.54 $\text{\AA}$) of ordinary C-C single bonds. These displacement parameters and distances may result from the large thermal motion of the peripheral ethoxycarbonyl moieties. Although simple two-site disorder models were tried to refine the structure for the moieties, no reasonable structural solution was obtained. The selected bond distances and angles are given in Table 3. The crystal structure reveals that 2:1 complexes between the ligand and Cu(II) are formed (Fig. 2) and

Table 3 Selected bond distances and angles

Distances (Å)		Angles (°)	
(Molecule 1)			
Cu1-O1	1.856(3)	O1-Cu1-N1	83.84(13)
Cu1-N1	2.091(3)	O1-Cu1-N1 ⁽ⁱ⁾	96.16(13)
(Molecule 2)			
Cu2-O6	1.855(3)	O6-Cu2-N2	83.64(13)
Cu2-N2	2.093(3)	O6-Cu2-N2 ⁽ⁱⁱ⁾	96.36(13)

Symmetry operations: (i) $2 - x, 1 - y, -z$; (ii) $1 - x, 1 - y, 1 - z$.

Fig. 2 Perspective view of the molecular structure (Molecule 1) of the title compound. The thermal ellipsoids are drawn at the 50% probability level. The spheres represent the hydrogen atoms, and are drawn in an arbitrary scale. Cu1, C1-17, N1, and O1-5 correspond to Cu2, C18-34, N2, O6-10 in another molecule, respectively.

crystallize in the triclinic space group $P\bar{1}$ with two independent complexes, located on two different centers of symmetry, per unit cell. The Cu(II) atom is coordinated to two oxygen and two nitrogen atoms of the ligands. Its geometry is described as distorted square-planar (Cu-O = *ca.* 1.85 $\text{\AA}$, Cu-N = *ca.* 2.10 $\text{\AA}$, see Table 3). In this complex, the carbonyl oxygen atom of the substituent group at the 2-position does not take part in the coordination to the Cu(II) center, in contrast to our previous complex of 2-carbonylethanyl-8-hydroxyquinoline.⁴ The observed Cu-N bond distances (*ca.* 2.10 $\text{\AA}$) are slightly longer, while the observed Cu-O bond distances (*ca.* 1.85 $\text{\AA}$) are slightly shorter than those (1.93-2.00 $\text{\AA}$) reported in the bis(8-hydroxyquinoline)copper(II) complexes.^{3,6} These changes in the bond distances may be caused by an influence of the bulky diethoxycarbonylethanyl groups at the 2-position.

References

- G. Giro, M. Cocchi, P. Di Marco, E. Di Nicolò, V. Fattori, J. Kalinowski, and M. Ghedini, *Synth. Met.*, **1999**, *102*, 1018.
- Y. Hamada, *IEEE Trans. Electron Devices*, **1997**, *44*, 1208.
- M. Shoja, H. A. Gershon, D. Bray, and D. D. Clarke, *Monatsh. Chem.*, **1998**, *129*, 843.
- J. Tanaka, K. Itoh, and J. Setsune, *Z. Kristallogr. NCS*, **2003**, *218*, 333.
- G. M. Sheldrick, *Acta Cryst.*, **1990**, *A46*, 467.
- M. Shoja, H. Gershon, and D. D. Clarke, *Z. Kristallogr. NCS*, **2000**, *215*, 273.