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Notes

Double Hydrogen Bond- and $\pi-\pi$-Stacking-Assembled Two-Dimensional Copper(I) Complex of 2-Hydroxyquinoxaline

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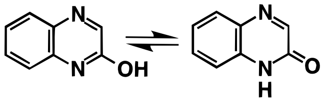
Introduction

Predictable self-organization of molecules into one-, two-, or three-dimensional supramolecular architecture is of current interest for a number of applications.[1] Among several notable systems, H bond-assembled molecular materials have received considerable interest, because H bonds are well suited for the design of solids for two reasons: they are directional and their formation is reversible at room temperature.[2] Many research groups have attempted to use H-bonding strategies to control molecular aggregation in organic chemistry, and some success has been achieved.[3] Mingos et al. recently demonstrated that the incorporation of a transition metal ion into H-bonded systems is important in the crystal engineering of nonlinear optical, conducting, and ferromagnetic materials.[4] Recently, we[5] and others[6] have reported a number of H bond-assembled coordination systems with supramolecular structures.

A few H bond-linked tautomeric systems were explored, such as those in azophenine (NH···N⇔N···HN) and in quinhydrone (OH···O⇔O···HO). Some of them showed cooperative interaction between charge transfer and proton transfer, and further, a phase transition occurred when either the temperature or the pressure was changed.[7] Introducing metal ions into such systems may offer new materials with interesting properties.

2-Hydroxyquinoxaline (Hhq) has been extensively used as an intermediate in organic synthesis;[8] however, little is known about its coordination chemistry. Until now, only one characterized complex, CuCl·Hhq, was reported in 1979, but there were no crystal structure data.[9] The ligand Hhq was herein selected to construct the copper(I) complex, since it possesses both a N-coordination site and a potential double H-bonding site (CN═COH or CNHC═O) that can undergo tautomerization.



Hhq

On the other hand, an organic electron donor−acceptor complex of Hhq with $\pi-\pi$ interactions has been found.[10] In the light of these features, we designed and synthesized a Cu(I) complex, $[Cu(Hhq)_2(C_2H_4)]ClO_4$ (**1**), possessing both H bond and $\pi-\pi$ interactions.

The use of ethylene as the other ligand was rationalized: ethylene is a good ligand for Cu(I) and its small volume, compared with other organic ligands, can reduce the packing volume, ensuring the effective stacking of the π system. It is also well known to be a plant hormone[11] and is extensively present in many biosystems.

Experimental Section

General Comments. The preparation was performed using Schlenk techniques. The reagent Hhq was obtained from Tokyo Kasei Co. and used without further purification. All the solvents were dried and distilled by a standard method before use. Infrared spectra were measured as KBr disks on a JASCO FT/IR 8000 spectrometer, and electronic spectra were recorded with a Hitachi 150-20 spectrophotometer. ^1H NMR spectra were obtained using a JEOL GX-270 NMR spectrometer. Electrical resistivity was measured by a conventional two-probe method at room temperature with a compressed pellet.

$[Cu(Hhq)_2(C_2H_4)]ClO_4$ (1). Copper(II) perchlorate hexahydrate (10.2 mg, 28 μmol) and copper plates were reacted in ethanol (7 mL) under an ethylene atmosphere for 0.5 h to give a colorless solution, to which was added 8.2 mg (56 μmol) of Hhq. The mixture was stirred and filtered, and the pale yellow filtrate was transferred to a 7 mm diameter glass tube. After the mixture was left to stand for 3 days at 25 °C, brick yellow crystals were isolated. ^1H NMR (250 MHz, acetone-d_6): $\delta = 5.22$ (s, 4H, C_2H_4), 7.37 (s, H7), 7.39 (s, H6), 7.59 (s, H8), 7.88 (s, H5), 8.25 (m, H3), 11.26 (broad, NH). Anal. Calcd for $C_{18}H_{16}N4CuClO_6$: C, 44.72; H, 3.33; N, 11.59. Found: C, 44.06; H, 3.17; N, 11.57.

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Table 1. Crystallographic Data for Complex **1**

chemical formula	$C_{18}H_{16}N_4CuClO_6$
formula weight	483.35
crystal system	monoclinic
space group	$P2_1/m$
a, Å	7.296(9)
b, Å	17.890(2)
c, Å	7.655(3)
β, deg	108.02(5)
V, Å^3	950(1)
Z	2
ρ (calc), g cm^{-3}	1.689
μ(Mo Kα), cm^{-1}	13.36
temp, °C	23
R^a	0.055
$R_w{}^b$	0.062

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$. $w = 4F_o{}^2/\sum\sigma^2(F_o{}^2)$.

Table 2. Atomic Coordinates of Non-H Atoms and Equivalent Isotropic Thermal Parameters[a]

atom	*x*	*y*	*z*	B_{eq}/Å^2
Cu(1)	0.8179(1)	1/4	0.9960(1)	2.90(4)
Cl(1)	0.3026(4)	1/4	0.6586(3)	5.4(1)
O(1)	0.8256(6)	0.0708(2)	0.4567(4)	4.1(2)
O(2)	0.124(1)	1/4	0.525(1)	8.2(4)
O(3)	0.441(2)	1/4	0.577(2)	15(1)
O(4)	0.325(1)	0.1897(7)	0.758(1)	25.2(8)
N(1)	0.9179(6)	0.1623(2)	0.8881(5)	2.9(2)
N(2)	1.0493(6)	0.0427(2)	0.7300(5)	2.8(2)
C(1)	0.8414(8)	0.1459(3)	0.7157(7)	3.2(2)
C(2)	0.9047(7)	0.0844(3)	0.6233(7)	3.0(2)
C(3)	1.1339(7)	0.0569(3)	0.9150(6)	2.6(2)
C(4)	1.2795(8)	0.0110(3)	1.0219(7)	3.2(2)
C(5)	1.3641(8)	0.0273(3)	1.2062(7)	3.7(2)
C(6)	1.3037(8)	0.0885(3)	1.2839(7)	3.7(2)
C(7)	1.1568(8)	0.1332(3)	1.1808(7)	3.5(2)
C(8)	1.0698(7)	0.1175(3)	0.9951(7)	2.8(2)
C(9)	0.664(1)	0.2132(3)	1.1618(8)	4.6(3)

[a] $B_{eq} = 8\pi^2/3(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

Iodine-doped **1** was synthesized in a manner similar to that of **1.** To pale yellow solution was added an iodine−ethanol solution; the color immediately turned brown. The filtrate was transferred to a 7 mm diameter glass tube and allowed to stand for 1 day at 25 °C, affording a black-brown precipitate.

X-ray Structure Determination. A single yellow plate crystal of dimensions 0.10 mm × 0.10 mm × 0.05 mm was used. Diffraction data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation. The data were collected using the $\omega - 2\theta$ scan technique within a 2θ range of 55.0°. A total of 2462 reflections (2265 unique) were collected. An empirical absorption correction, based on azimuthal scans of several reflections, was applied, which resulted in transmission factors ranging from 0.72 to 1.00. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods,[12] and the hydrogen atoms were found by D mapping. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$, was based on 1433 observed reflections [$I > 3.00\sigma(I)$] and 142 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.055$, $R_w = 0.062$. All crystallographic computations were performed on a VAX computer by using the TEXSAN program system.[13] The detailed crystal data for **1** are listed in Table 1, and the atomic coordinates of non-H atoms are given in Table 2. The average $\pi-\pi$-stacking distance was calculated from the distances of the atom in one Hhq plane to the least-squares plane of the stacked Hhq molecule.

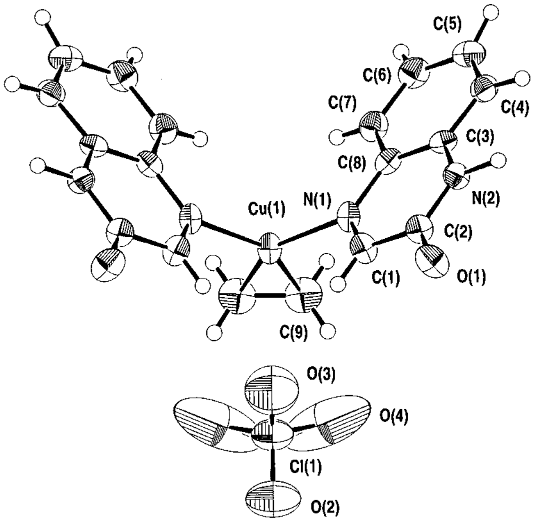

Figure 1. ORTEP view of complex **1,** showing 40% probability displacement ellipsoids and the atom labeling scheme.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of Complex **1**

Cu(1)−N(1)	2.013(4)	Cu(1)−C(9)	2.046(6)
O(1)−C(2)	1.250(6)	N(1)−C(1)	1.297(6)
N(1)−C(8)	1.407(6)		
N(1)−Cu(1)−N(1)	102.5(2)	N(1)−Cu(1)−C(9)	110.0(2)
N(1)−Cu(1)−C(9′)	147.5(2)	C(9)−Cu(1)−C(9)	37.5(3)
Cu(1)−N(1)−C(1)	119.8(4)	Cu(1)−N(1)−C(8)	121.7(3)

Results and Discussion

Description of the Structure of 1. Figure 1 illustrates the X-ray single-crystal-determined structure of $[Cu(Hhq)_2(C_2H_4)]ClO_4$ (**1**) with the atom numbering scheme. The Cu(I) ion is coordinated by two Hhq molecules, with the N(1)−Cu(1)−N(2) angle of 102.5°, and an ethylene molecule, with the C(9)−Cu(1)−C(9′) angle of 37.5°. The bond angles around the copper atom, N(1)−Cu(1)−N(1′), N(1′)−Cu(1)−C(9′), C(9′)−Cu(1)−C(9), and C(9)−Cu(1)−N(1), sum to 360° within experimental error, showing a planar trigonal coordinating geometry. The cation structure of $[Cu(Hhq)_2(C_2H_4)]^+$ resembles a butterfly, since two Hhq ligands coordinating to the Cu(I) atom through the N ligand are regarded as the two wings with a plane of symmetry through the Cu(1) atom. The perchlorate ion is not coordinated to the metal.

The Cu(1)−N(1) distances are 2.013(4) Å, within the expected Cu−N (N-aryl type) bond distances 1.93−2.16 Å, and the ethylene is coordinated to Cu(1), with the distance for Cu(1)−C(9) of 2.046(6) Å falling in the range 1.93−2.07 Å observed previously.[14] The C=C double bond distance of ethylene of 1.32(1) Å is essentially the same as that for free ethylene (1.337(2) Å). Thompson and Whitney have implied that the unusually short bond distance is due to the predominance of σ-bonding from ethylene to the metal ion.[15] The π-back-donation in the present complex is weaker than those of $[Cu(C_2H_4)(bipy)]^+$ and $[Cu(C_2H_4)(phen)]^+$,[14] since the π-back-donation from the metal's d orbital to the antibonding π orbital of the olefin is considered to cause lengthening of the C=C bond distance.

The crystal structure of the free ligand shows strong intermolecular NH···O H bonds in the keto form (distance of

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(12) MITHRIL90: an integrated direct methods computer program, University of Glasgow, Scotland, 1984.

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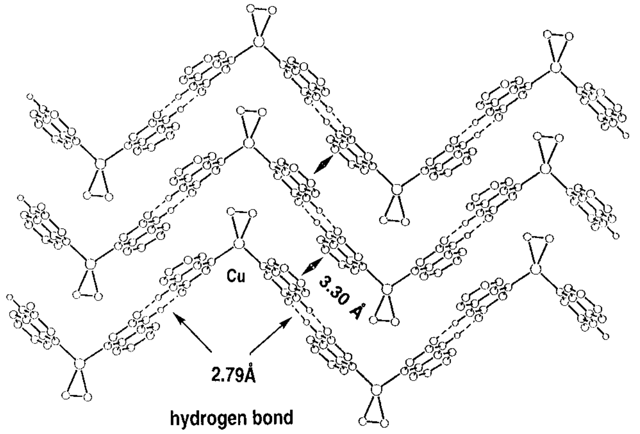

Figure 2. Side view of the packing of the coordination and H bond-linked chains in **1**.

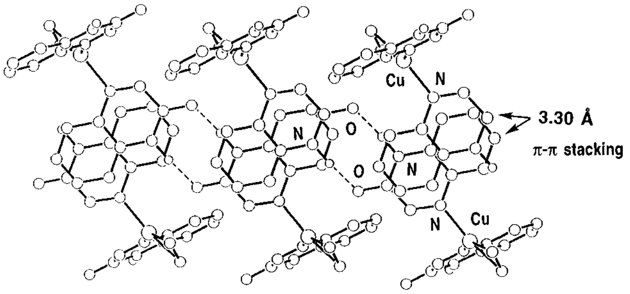

Figure 3. Top view of the H-bonding and $\pi-\pi$-stacking plans.

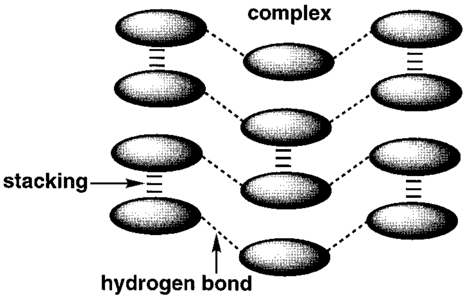

Figure 4. Two-dimensional interaction pattern of H bonding and $\pi-\pi$ stacking in **1**.

C=O, 1.239 Å), with the N···O distance of 2.78 Å.[16] The cations of **1** also maintained the fundamental feature of the free ligand and are linked to each other by head-to-tail double H bonds on each side of the two wings to form one-dimensional infinite zig-zag chains. Figure 2 shows the chains packing and the double H bond. In this AD:::DA type double H bond (A = H bond acceptor; D = H bond donor), the N(2′)−O(1) distance of 2.79(1) Å is essentially the same as that in the free ligand and shorter than the N···O single H bond distance, in the range of 3.1−2.8 Å.[17] The C(2)−O(1) distance of 1.250(6) Å in **1** shows that the keto form (C=O···HN) is predominant in these H bonds. However, it is possible that a proton transfer or a structural resonance of C=O···HN ⇔ COH···N occurred under certain conditions. The proposed H transfer strategy has been discussed in quinhydrone systems.[7a]

Linked by the double H bond, two adjacent Hhq molecules are approximately coplanar, with a mean deviation of 0.0136 Å. These H bond-assembled Hhq molecule planes are stacked next to each other, with the average distance of 3.30 Å (Figure 2). Figure 3 shows the top view of the $\pi-\pi$ stacking. Two Hhq molecules (half of each H bond-assembled plane) are stacked and connect to the neighbor pairs through H bonds. The interaction pattern of H bond and $\pi-\pi$ stacking is shown schematically in Figure 4. This gives a unique two-dimensional cooperating structure, which is a fundamental characteristic of proton−electron transition (PET) systems.[7,18]

Properties of the Complexes. The ^{1}H NMR chemical shifts of **1** were given in the Experimental Section. The ^{1}H resonances at 8.25 and 7.88 ppm for H(C1) and H(C7), respectively, clearly shift down-field compared to those in the free ligand (8.13 and 7.80 ppm, respectively), indicating the metal ion coordination. The ^{1}H (NH) resonance of 11.17 ppm of the ligand is also shifted to 11.26 ppm upon formation of the complex. The ^{1}H resonance of C_2H_4 in **1** (5.22 ppm) shifts slightly upfield compared with 5.40 ppm for free ethylene and other Cu(I)−ethylene complexes (4.7−5.3 ppm).[19] This is consistent with the complexation of the C=C bond distance discussed above, indicating the weak d(Cu) → π(ethylene) back-donation in this complex.

The IR spectra of **1** shows the ν(NH) stretching frequency in the 2950−3050 cm^{-1} region. Nakamoto et al. have indicated a correlation between NH···O distances and the corresponding ν(NH) stretching frequencies for the formation of strong H bonds.[17] The short NH···O distance and low ν(NH) stretching frequency found in **1** are completely in agreement with this correlation. Complex **1** shows a strong ν(C=O) stretching frequency at 1672 cm^{-1} and a ν(Cl-O) stretching frequency at about 1092 cm^{-1} indicative of the presence of C=O group (keto form) and perchlorate anion. A unique peak at about 850 nm, due to $\pi-\pi$ electron interactions, appeared in the solid state UV−vis spectra.[20]

Electrical resistivity of compacted pellets of **1** and iodine-doped **1** was measured by the conventional two-probe technique. Complex **1** is an insulator [$\sigma_{(25°C)} < 10^{-12}$ S cm^{-1}], while the doped **1** behaves as a semiconductor with conductivity of 10^{-6} S cm^{-1} at 25 °C. Unfortunately, attempted crystal growth of the doped complex failed. From the IR and elemental analysis data (found: C, 26.71; H, 1.63; N, 7.41), we proposed that, instead of the ethylene, I^- ion coordinates to Cu(I) ion and the Hhq molecules are partial oxidized (25%), giving the compound [$Cu(Hhq)I_{1.25}$] (calcd: C, 26.08; H,1.64; N, 7.60).

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Supporting Information Available: Tables of complete crystal data, atom (including hydrogen atom) coordinates, anistropic thermal parameters, bond distances, bond angles, tables of least-squares plane, and the $\pi-\pi$-stacking distances for complex **1** (14 pages). Ordering information is given on any current masthead page.

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