Crystal Structure and Properties of a New Copper(II) Complex of Dioxocyclam Appended with 8-Methylquinoline (Dioxocyclam = 1,4,8,11-tetraazacyclotetradecane-5,7-dione)

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Abstract. A new macrocyclic dioxotetraamine ligand 1-(quinolin-8-ylmethyl)-1,4,8,11-tetraaza-cyclotetradecane-5,7-dione (H_2L) has been synthesized. The resulting dioxocyclam readily forms a 1:1 Cu(II) complex (CuL) with concomitant double deprotonation of the ligand. CuL has been isolated as single crystals and the structure was determined by X-ray diffraction analysis. CuL·$5H_2O$ (**1**·$5H_2O$) crystallizes in monoclinic crystal system, $P2_1/n$ space group with $a = 12.979(2)$, $b = 13.638(6)$, $c = 13.634(4)$ Å, $\beta = 103.02(2)°$, $V = 2351(2)$ Å^3, $M_r = 521.07$, $Z = 4$, $D_{calc} = 1.472$ g/cm^3, $\mu = 9.78$ cm^{-1}, $F(000) = 1100$, room temperature, and $R = 0.039$, $R_w = 0.042$ for 2137 observed reflections with $I > 3\sigma(I)$. In complex **1**, the Cu atom is five coordinate to form a distorted square pyramid in which N(5) of the quinoline pendant is at the apical site. The Cu—N(5) bond distance (2.262(4) Å) is longer than the basal average Cu—N bond lengths (1.994(4) Å). The behavior of CuL in solution has been studied further with ESR, UV-Vis and cyclic voltammetry.

Key words: Crystal structure, properties, new copper(II) complex, dioxocyclam, 8-methylquinoline.

1. Introduction

The chemistry of macrocyclic dioxotetraamines has received a great deal of attention and has been extensively studied in recent years [1–5]. Macrocyclic diox-otetraamines, which Kimura's group originally studied, bear the dual structural features of macrocyclic tetraamines and oligopeptides and have many interesting

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H₂L₀   **H₂L**
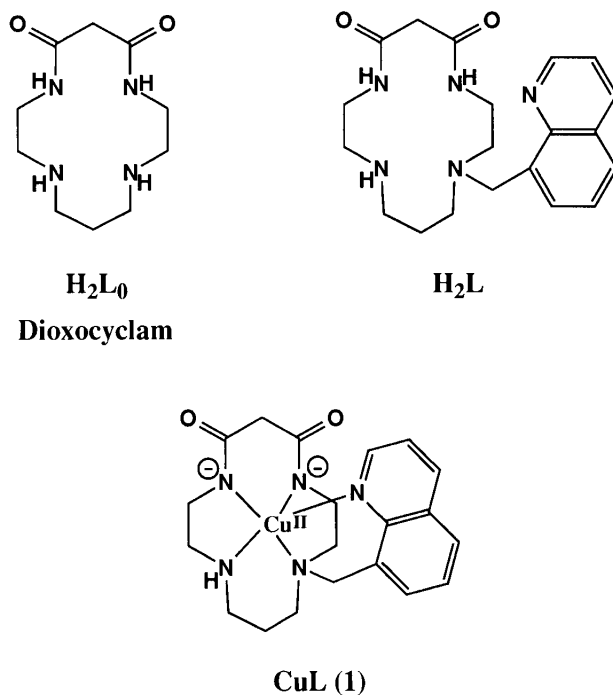
Dioxocyclam

CuL (1)

Chart I.

properties and important functions. They can stabilize the higher oxidation states of some transition metals [1, 2a, 6]. These properties have been developed to give effective oxidants and biomimetic redox catalysts [7]. Furthermore, some of these compounds function as powerful chelating agents [8].

To date, great efforts have been made to incorporate functionalized pendant groups into a saturated macrocyclic tetraamine structure (e.g., cyclam), in order to modify the structural and functional properties of the metal complex [9]. However, so far, only a few examples of macrocyclic dioxotetraamines bearing functionalized pendant groups have been reported [2i–j, 10–14].

Here we report the synthesis and characterization of a novel macrocyclic ligand dioxocyclam (dioxocyclam = 1,4,8,11-tetraazacyclotetradecane-5,7-dione) bearing 8-methyl quinoline as an additional coordinating donor pendant (Chart 1), its complexation with Cu(II), and the crystal structure of the Cu(II) complex.

2. Experimental

2.1. GENERAL INFORMATION

Most of the starting materials and solvents for syntheses were obtained commercially and purified prior to use. Dioxocyclam (H_2L_0, 1,4,8,11-tetraazacyclotetradecane-5,7-dione) was prepared according to a modified literature method [13]. N-Bromosuccinimide (NBS) was recrystallized from distilled water. 8-Methyl quinoline was purchased from BDH (UK) and used without further purification. 8-Bromomethyl quinoline was prepared as described previously [12a]. All the other reagents for syntheses and analyses were of analytical grade. FT-IR spectra were obtained with a 170SX (Nicolet) spectrometer. EI-MS was performed using a VG ZAB-HS instrument. Elemental analysis was done on a P-E 240C analyzer. ^{1}H-NMR measurements were made with a Bruker AC-P 200 spectrometer (200 MHz, 25 °C, in CDCl$_3$, tetramethylsilane internal reference). UV-Vis spectra were obtained with a Shimadzu UV-240 spectrophotometer.

2.2. SYNTHESIS OF 1-(QUINOLIN-8-YLMETHYL)-1,4,8,11-TETRAAZACYCLOTETRADECANE-5,7-DIONE (H_2L)

A solution of 8-bromomethylquinoline [12a] (650 mg, 2.93 mmol) in 20 mL of deoxygenated dimethyl formamide (DMF) was added dropwise to a solution of H_2L_0 (2.7 g, 11.7 mmol) in 80 mL of deoxygenated DMF in the presence of excess fine, dried K_2CO_3 at ca. 80 °C. The resulting reaction mixture was heated at 80 °C for about 10 h under argon. After filtration of the reaction mixture, the filtrate was evaporated to dryness, dissolved in H_2O, and then extracted with CHCl$_3$. The combined CHCl$_3$ extracts were dried and evaporated, and the residue was purified by column chromatography on silica gel by eluting with CH_2Cl_2/MeOH/NH$_3$ (aq) (100 : 5 : 1). The product was finally recrystallized from CH_2Cl_2–acetonitrile as prisms (1.7 g, 40%). ^{1}H-NMR (CDCl$_3$): $\delta \sim$ 1.65 (2H, m), 2.44–2.67 (8H, m), 3.26 (2H, s), 3.32 (2H, quintet), 3.55 (2H, quintet), 4.17 (2H, s), 7.42–7.79 (4H, m), 8.15–8.19 (1H, m), 8.92–8.95 (1H, m). IR (KBr pellet): 3272 (N—H), 2872, 2795, 1646 (C=O), 1530, 1354, 1169, 797 cm^{-1}. EI-MS: m/z = 369 (M_r = 369.47). *Found*: C, 65.38; H, 7.66; N, 18.92%. *Calcd.* for $C_{20}N_5H_{27}O_2$: C, 65.02; H, 7.37; N, 18.96%. H_2L has also been characterized by X-ray structural analysis [14].

2.3. PREPARATION OF CuL·5H$_2$O (1·5H$_2$O)

For complex **1**, single crystals suitable for X-ray analysis were obtained by mixing a 1 : 1 molar ratio of Cu(CH$_3$COO)$_2$·H$_2$O and H_2L in deoxygenated MeOH under reflux for about 15 min. The blue reaction mixture was filtered and evaporated under argon. The residue was then treated with CH$_3$CN. A crystal suitable for X-ray analysis was obtained from mixed CH$_3$CN—MeOH solvent. *Found*: C, 45.83;

H, 7.01; N, 13.12%. *Calcd.* for $C_{20}H_{35}CuN_5O_7$: C, 46.10; H, 6.77; N, 13.44%.
IR(KBr pellet): 3400 (br), 3194, 2941, 2856, 1579 (C=O), 1372, 1032, 793 cm^{-1}.

2.4. ESR STUDIES

ESR spectra were measured on a Bruker ER-200-D-SRC10 spectrophotometer.
MeOH solutions of Cu(II) complexes were prepared by mixing equimolar amounts
of ligand and $Cu(NO_3)_2$ in MeOH and adjusting the pH to $\sim$9 (NaOH/MeOH).
These solutions were then placed in ESR tubes and the measurements were per-
formed at 298 K and 112 K.

2.5. ELECTROCHEMICAL STUDIES

Cyclic voltammetric measurement was performed with a PARC Model 273 electro-
chemical apparatus in aqueous solution at 25 °C with 0.50 M Na_2SO_4 as supporting
electrolyte. Pure argon gas was passed through the solution. The concentrations of
the CuL_0 and CuL complexes were kept at 2×10^{-3} M. The pH was adjusted with
concentrated NaOH or H_2SO_4 solution. The cyclic voltammograms (scan rate =
100 mV s^{-1}) were evaluated graphically. A three-electrode system was employed:
glassy carbon as working electrode, a saturated calomel electrode (SCE) as refer-
ence, and Pt as a counterelectrode.

2.6. CRYSTALLOGRAPHIC STUDIES

A crystal (approximately 0.2 × 0.2 × 0.35 mm) of complex **1** was mounted on
an Enraf-Nonius CAD-4 diffractometer equipped with a graphite crystal mono-
chromator situated in the incident beam for data collection. The determination
of the unit cell and the data collection were performed with MoK_α radiation (λ
= 0.710 73 Å). Unit cell dimensions were obtained by least-squares refinements
using 25 reflections in the range of $7.89° < \theta < 11.79°$. The intensities of reflec-
tions were measured using the $\omega/2\theta$ scan mode in the range of $2° < \theta < 23°$ at
room temperature. A total of 2932 independent reflections were collected, in which
2137 reflections with $I > 3\sigma(I)$ were considered to be observed and were used in
the subsequent refinement. The structure was solved using the Patterson method.
The Cu atom was located from an E map. The other non-hydrogen atoms were
determined with successive differential Fourier syntheses. The final refinement by
the full matrix least-squares method using anisotropic thermal parameters for the
non-hydrogen atoms converged with unweighted and weighted (unit weights for all
observed reflections) agreement factors (R and R_w) 0.039 and 0.042, respectively.
The highest peak on the final difference Fourier map had a height of 0.58 e/Å^3.

All the calculations were performed on a PDP11/44 computer, using SDP-PLUS,
SHELXS-86 and SHELXL-93 [15] programs.

Table I. Crystal data and data collection summary for complex **1**.

	1·5H$_2$O
Formula	C$_{20}$H$_{27}$N$_5$O$_2$Cu·5H$_2$O
F_w	521.07
Crystal colour	Deep blue
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	12.979(2)
b, Å	13.638(6)
c, Å	13.634(4)
β, deg	103.02(2)
V, Å^3	2351(2)
Z	4
D_c, g cm^{-3}	1.472
D_c, g cm^{-3}	1.46
μ(MoK_α), cm^{-1}	9.78
$F(000)$	1100
Crystal dimens., mm	0.2 × 0.2 × 0.35
λ, Å	0.71073
T, K	298
Max. $2\theta(^\circ)$	46
Index range	−14–14; 0–15; 0–15
No. of indep. reflcns.	2932
No. of obsd. reflcns.	
$(I > 3\sigma(I))$	2137
Absorption correction	Empirical absorption correction [16]
Refinement method	Full-matrix least-squares
Quantity minimized	$\Sigma w(|F_0| - |F_c|)^2$
R	0.039
R_w	0.042
Weighting scheme	$w = 1/\sigma^2(F)$
GOF	0.84
Max. residual peak (eÅ^{-3})	0.58

3. Results and Discussion

3.1. CRYSTAL STRUCTURE

The crystallographic data and data collection for complex **1** are summarized in Table I. The molecular structure of **1** is shown in Figure 1. The atomic positional parameters, important bond lengths, and angles are listed in Tables II and III, respectively.

From Figure 1, it is obvious that the Cu atom in complex **1**, is five-coordinate with [N(1), N(2), N(3), N(4) and N(5)] and forms a distorted square-pyrimidal
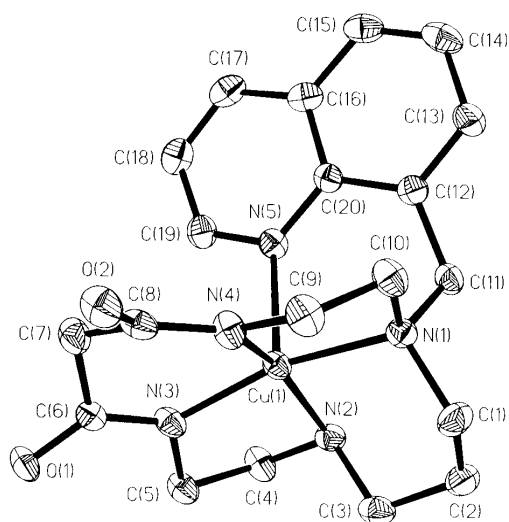
Figure 1. ORTEP drawing of complex **1** with 35% probability thermal ellipsoids.

configuration. The two deprotonated amide nitrogens [N(3), N(4)] have stronger coordination bonds (Cu—N^- bonds 1.93–1.95 Å) than those for the secondary amine [N(2)] (2.061 Å) and the tertiary amine [N(1)] (2.034 Å). The four equatorial basal nitrogens [N(1), N(2), N(3), and N(4)] deviate from their least-squares plane by ca. ±0.057 Å and are nearly coplanar.

The Cu(II) ion deviates from the least-squares plane of the four basal nitrogens towards the pendant nitrogen N(5) by ca. 0.3 Å to accept apical coordination. Unlike the 13-membered macrocycle ring [12a], the macrocycle cavity of dioxocyclam should be large enough to allow the Cu(II) ion to fill it completely. In reality, however, the Cu(II) ion in CuL resides above the mean plane of the macrocycle N_4 to accept the coordination from the quinoline pendant. This indicates that the quinoline pendant has a strong tendency to coordinate with Cu(II) and the macrocycle is more rigid and crowded than the unsubstituted dioxocyclam.

The Cu—N distances of the four basal nitrogens, in the range of 1.93–2.06 Å, are normal Cu—N coordination bonds [11, 17]. The Cu—N(5) distance of 2.262(4) Å is longer than those of the basal Cu—N distances, indicating weak coordination of the pendant nitrogen, due either to steric constraints or the Jahn–Teller effect. The distances of C(6)—N(3) (1.308(7) Å) and C(8)—N(4) (1.309(7) Å) are obviously shorter than the normal C—N distance (1.47 Å) and show a partial double bond character which arises from the conjugation between O(1)—C(6)—N(3) and O(2)—C(8)—N(4). The conjugation was also confirmed by the IR spectrum (the C=O vibrational peak of the IR spectrum for CuL is 67 cm^{-1} lower than that of H_2L). The dihedral angle between the quinoline plane and the basal least-squares plane of the macrocycle is 70.8°, which means that the quinoline

Table II. Atomic coordinates ($\times 10^4$) and thermal parameters ($\text{Å}^2 \times 10^3$) for complex **1** (estimated standard deviations in parentheses).

Atom	x	y	z	U_{eq}
Cu(1)	2353(1)	1299(1)	2881(1)	28(1)
O(1)	781(3)	2456(3)	4904(2)	39(1)
O(2)	371(3)	3613(3)	1850(3)	44(1)
N(1)	3189(3)	1251(3)	1787(3)	30(1)
N(2)	3522(3)	545(3)	3868(3)	33(1)
N(3)	1822(3)	1578(3)	4067(3)	33(1)
N(4)	1606(3)	2393(3)	2117(3)	34(1)
N(5)	1422(3)	−48(3)	2242(3)	32(1)
C(1)	4252(4)	1697(4)	2180(4)	42(3)
C(2)	4919(4)	1209(4)	3110(4)	42(2)
C(3)	4455(4)	1187(4)	4032(4)	41(2)
C(4)	3119(4)	377(4)	4794(4)	40(2)
C(5)	2502(4)	1266(4)	5018(3)	38(2)
C(6)	1026(4)	2154(3)	4107(3)	32(2)
C(7)	291(4)	2407(4)	3100(4)	41(2)
C(8)	788(4)	2860(4)	2297(3)	34(2)
C(9)	2107(4)	2745(4)	1333(4)	41(2)
C(10)	2602(4)	1873(4)	940(4)	38(2)
C(11)	3295(4)	235(4)	1431(4)	33(2)
C(12)	2301(4)	−261(3)	881(4)	32(2)
C(13)	2269(4)	−631(4)	−59(4)	41(2)
C(14)	1392(5)	−1172(4)	−589(4)	47(2)
C(15)	571(4)	1357(4)	−180(4)	44(2)
C(16)	555(4)	−996(3)	794(4)	36(2)
C(17)	−277(4)	−1172(4)	1272(4)	41(2)
C(18)	−246(4)	−811(4)	2198(4)	43(2)
C(19)	633(4)	−243(4)	2655(4)	38(2)
C(20)	1423(4)	−426(3)	1322(3)	30(2)
O(11)	6536(3)	−865(3)	2517(3)	52(1)
O(12)	5469(3)	−866(3)	434(3)	60(2)
O(13)	8033(3)	−2474(3)	2991(3)	63(2)
O(14)	7254(4)	5832(4)	1894(4)	89(2)
O(15)	4332(4)	4176(4)	−108(4)	91(2)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

pendant does not coordinate to Cu(II) from a perpendicular position, and thus that the coordination is weak.

Table III. Selected bond lengths (Å) and bond angles (°) for complex **1** (estimated standard deviations in parentheses).

Bond lengths (Å)			
Cu(1)—N(1)	2.034(4)	N(1)—C(11)	1.485(7)
Cu(1)—N(2)	2.061(4)	N(2)—C(3)	1.471(7)
Cu(1)—N(3)	1.934(4)	N(2)—C(4)	1.489(7)
Cu(1)—N(4)	1.947(4)	N(3)—C(5)	1.458(6)
Cu(1)—N(5)	2.262(4)	N(3)—C(6)	1.308(7)
O(1)—C(6)	1.267(6)	N(4)—C(8)	1.309(7)
O(2)—C(8)	1.253(6)	N(4)—C(9)	1.453(8)
N(1)—C(1)	1.492(4)	C(11)—C(12)	1.500(6)
N(1)—C(10)	1.496(6)		
Bond angles (deg)			
N(1)—Cu(1)—N(2)	91.5(2)	Cu(1)—N(1)—C(11)	112.0(3)
N(1)—Cu(1)—N(3)	165.8(2)	C(1)—N(1)—C(11)	110.6(4)
N(2)—Cu(1)—N(3)	84.3(2)	C(10)—N(1)—C(11)	110.2(3)
N(1)—Cu(1)—N(4)	85.2(2)	Cu(1)—N(2)—C(3)	105.2(3)
N(2)—Cu(1)—N(4)	159.3(2)	Cu(1)—N(2)—C(4)	106.4(3)
N(3)—Cu(1)—N(4)	93.9(2)	C(3)—N(2)—C(4)	113.4(4)
N(1)—Cu(1)—N(5)	91.1(2)	Cu(1)—(3)—C(5)	115.3(3)
N(2)—Cu(1)—N(5)	95.6(1)	Cu(1)—(3)—C(6)	125.9(3)
N(3)—Cu(1)—N(5)	102.8(2)	C(5)—N(3)—C(6)	117.7(4)
N(4)—Cu(1)—N(5)	104.9(2)	Cu(1)—N(4)—C(8)	126.9(4)
Cu(1)—N(1)—C(1)	109.1(3)	Cu(1)—N(4)—C(9)	113.3(3)
Cu(1)—N(1)—C(10)	108.3(4)	C(8)—N(4)—C(9)	119.5(4)

The molecular stacking of complex **1** in the unit cell is shown in Figure 2. It is obvious that the different molecules in the complex are linked to each other by water through hydrogen bonds, which may thus stabilize the structure.

3.2. ELECTROCHEMICAL STUDIES

The cyclic voltammograms of the Cu(II) complexes of L_0 and L examined in aqueous solution (0.5 M Na_2SO_4, at 25 °C) are shown in Figure 3, and the electrochemical data are summarized in Table IV. Each of the cyclic voltammograms of CuL_0 and CuL display one quasi-reversible oxidation wave. The $Cu^{II/III}$ potential for CuL, +0.78 V vs. SCE, is 0.14 V more positive than that of the CuL_0 complex under similar conditions ($E_{1/2}$ = 0.64 V) [1a], implying that the ligand L appended with 8-methylquinoline destabilized the Cu(III) state compared with the unsubstituted L_0.

This fact can be interpreted as follows: the change from Cu(II) (d^9) to Cu(III) state (d^8, low spin) involves a drastic reduction of the metal ion radius and a change of electronic configuration (Scheme I) [3b]. In complex **1**, as shown in Figure 1,
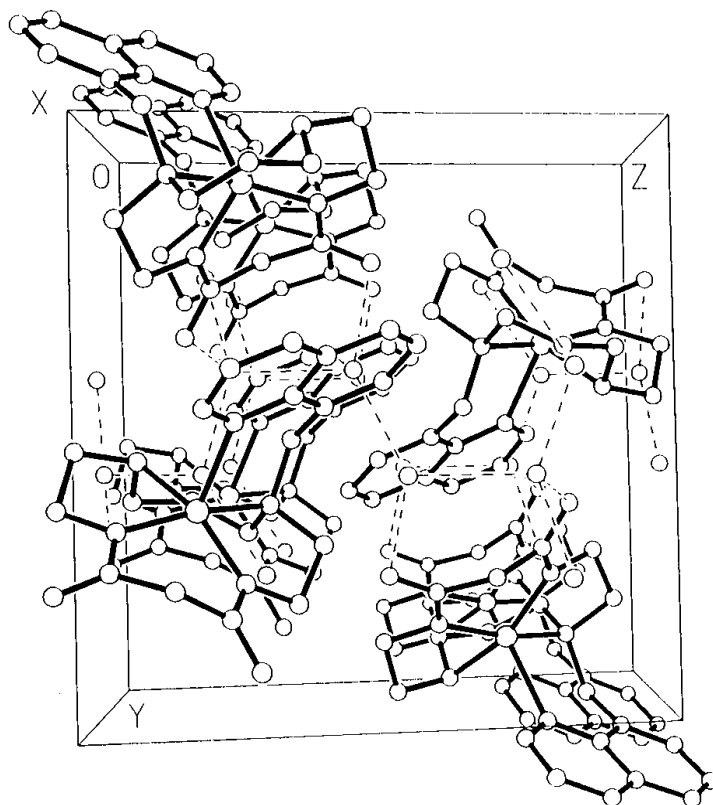
Figure 2. Perspective drawing of molecular stacking in the unit cell of complex **1**.

Table IV. Physical properties of complexes CuL_0 and **1**.

Complex		CuL_0	**1**
$CV^{a,b}$	pH	~5	~6
	E_{pa}, V	0.58	0.73
	E_{pc}, V	0.71	0.83
	ΔE_p, mV	130	90
	$E_{1/2}$, V	0.64	0.78
UV-Vis^c	λ_{max}, nm (ε)	516 (100)	559 (120)

^{a} In H_2O at 25 $^\circ$C and scan rate at 100 mV s^{-1}, V vs. SCE.
^{b} [CuL_0] and [**1**] were kept at 2×10^{-3} M.
^{c} At 25 $^\circ$C in MeOH.

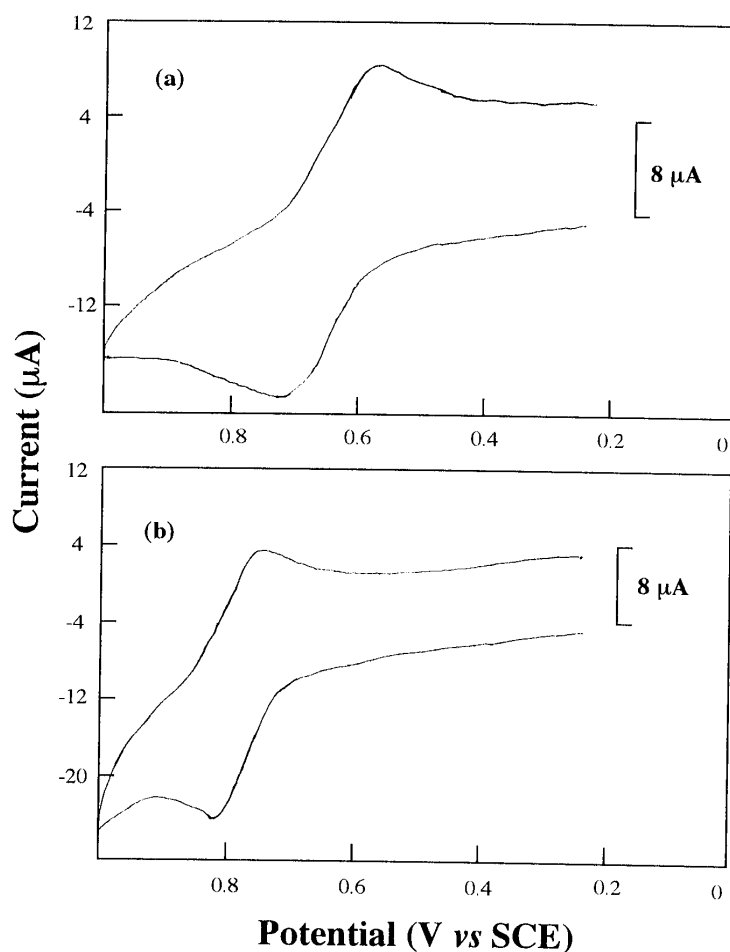*Figure 3.* Cyclic voltammograms for (a) CuL_0 and (b) CuL in aqueous solution at a glassy-carbon electrode vs. SCE. The concentration was kept at 2×10^{-3} M in 0.5 M Na_2SO_4 and at a scan rate of 100 mV s^{-1}.

the quinoline pendant coordinates to Cu(II) from the apical site, and the Cu(II) ion resides above the mean plane of the four basal nitrogens. The coordination of the quinoline pendant to Cu(II) stabilizes the Cu(II) ion. But when Cu(II) is oxidized to Cu(III), like Ni(II) (d^8, low spin), Cu(III) tends to adopt a square-planar coordination rather than a five-coordinate one, which means the quinoline pendant will not coordinate to Cu(III). Since the N-substitution by the quinoline pendant increases the steric constraint of the macrocycle ring and lowers the coordinative ability of the macrocycle, the Cu(III) ion in L is not stabilized to the same extent as in the unsubstituted L_0.
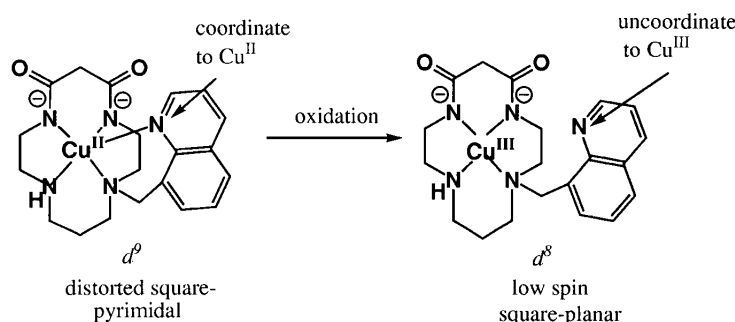
Scheme I.

Table V. ESR parameters of complexes CuL_0 and **1** in MeOH solution at 298 K and 112 K.[a]

Complex	298 K		112 K			
	g_{iso}	A_{iso}, G (cm^{-1})	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$, G (cm^{-1})	$A_{\perp}$, G (cm^{-1})
CuL_0	2.087	97(9.45 × 10^{-3})	2.176	2.043	206(2.093 × 10^{-2})	43(4.102 × 10^{-3})
1	2.094	86(8.41 × 10^{-3})	2.186	2.048	191(1.949 × 10^{-2})	34 (3.251 × 10^{-3})

[a] $A_{\perp}$ was calculated according to formula $3A_{iso} = A_{\parallel} + 2A_{\perp}$ and $g_{\perp}$ according to $3g_{iso} = g_{\parallel} + 2g_{\perp}$.

3.3. SPECTROSCOPIC STUDIES

The absorption maxima data of CuL and CuL_0 in MeOH solution are listed in Table IV. The d–d transition band of the CuL complex (559 nm) shifts to significantly higher wavelengths compared with that of CuL_0 (518 nm). Since the d–d absorption band gives an empirical measure of the in-plane Cu^{II}—N interactions [18], the remarkable red-shift observed for **1** indicates weakened in-plane bonding due to the N-substitution.

3.4. ESR STUDIES

Figure 4 presents the ESR spectra of CuL in MeOH solution at room temperature and 112 K. It is obvious that the room-temperature spectrum of the complex is split into four equally spaced absorptions by the interaction with the Cu(II) nucleus (I = 3/2) (Figure 4a). The isotropic ESR parameters are g_{iso} = 2.094 and A_{iso} = 86 G (8.41 × 10^{-3} cm^{-1}) (Table V). When the solution is frozen at 112 K, an ESR spectrum characteristic of nearly axial symmetry is observed, which is very similar to that of CuL_0.

The approximate ESR parameters of complex **1** are graphically evaluated as $g_{\parallel}$ = 2.186, $g_{\perp}$ = 2.048, $A_{\parallel}$ = 191 G (1.949 × 10^{-2} cm^{-1}), and $A_{\perp}$ = 34 G (3.251 × 10^{-3} cm^{-1}), where $g_{\perp} = (3g_{iso} - g_{\parallel})/2$ and $A = (3A_{iso} - A_{\parallel})/2$ [19]. It is obvious that the observed $A_{\parallel}$ value decreases and the $g_{\parallel}$ value increases from CuL_0 to CuL. The tendencies for $A_{\parallel}$ to decrease and $g_{\parallel}$ to increase have been taken as parameters to

$A_{iso} = 86$ G

(a)

$g_{iso} = 2.094$

(b)

$g_{//} = 2.186$ $g_{\perp} = 2.048$
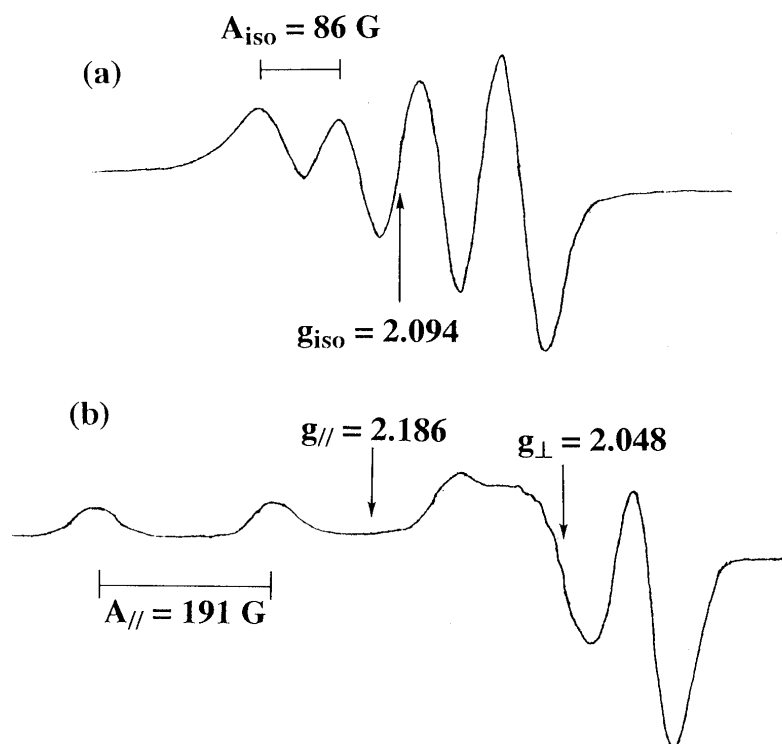
$A_{//} = 191$ G

Figure 4. X-Band ESR spectra of complex **1** in MeOH at (a) 298 K and (b) 112 K.

measure the lowering of the strength of in-plane ligand fields under the tetragonal basal square arrangement of copper(II) complexes [20]. Therefore, ESR spectra also support the weakened in-plane bonding in complex **1** due to N-substitution. This is consistent with the results of CV and UV-Vis measurements. The ESR parameters of **1** also indicate a $d^1_{x^2y^2}$ ground state of Cu(II) in this complex.

Acknowledgements

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