

Electron Spin Resonance Study of Cu(II)-Crown Ether Complexes with $3d_{z^2}$ Ground State Doublet in Solution

Kazuhiko ISHIZU,* Tokuhiro HARUTA, Yuji KOHNO, Kazuo MUKAI, Kiyonori MIYOSHI,† and Yukio SUGIURA††

Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790

†Department of Metallurgical Engineering, Niigata Technical College, Niigata 792

††Faculty of Pharmaceutical Science, Kyoto University, Sakyo-ku, Kyoto 606

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Copper(II) chloride and crown ethers (12-crown-4, 15-crown-5 and 18-crown-6) formed orange or orange-yellow complexes in dry chloroform. We found that the ESR g -anisotropy of the complexes was greatly dependent on the numbers of donor oxygens and the ring-numbers. The complexes obtained from 12-crown-4 and 18-crown-6 showed g -anisotropy ($g_{\parallel} > g_{\perp}$); these are well characterized by the $3d_{x^2-y^2}$ or $3d_{xy}$ ground state. On the other hand, the complexes of 15-crown-5 and its benzo derivatives exhibited the reverse g -anisotropy ($g_{\parallel} < g_{\perp}$); these are characterized by the $3d_z$ ground state with $S=1/2$. The electron nuclear dipolar term and the Fermi's isotropic term were estimated from the ESR parameters based on Bleaney's calculation. The chlorine superhyperfine splittings were observed in the g_{\parallel} -component. The MO bonding parameters were estimated by assuming the compressed octahedral, the trigonal bipyramidal, and pentagonal bipyramidal geometry at the paramagnetic site. The bonding nature was studied on the basis of the observed ligand spin densities.

Many synthetic macrocyclic polyethers, polyamines, and other related molecules have been known to possess very interesting and unusual binding properties. They show a pronounced ability to bind a wide variety of cations and anions with marked conformational changes during binding. In addition, their hydrophobic exterior allows them to solubilize ionic substances in nonaqueous solvents.¹⁾ These novel properties of crown ethers and polyamines resulted in their use as model ligands for ion transport systems, biological macrocycles, and the active chromophore of enzyme systems. It has been shown that the spectroscopic parameters of various model Cu(II)-polyamine or -macrocyclic complexes are useful in studying the paramagnetic active sites of Cu(II)-enzyme systems.

The ESR parameters of some cyclic polyamine-Cu(II) complexes have already been compared with those of the type (II)-Cu(II) protein.²⁾ Some model studies of the type (I)-Cu(II) protein have been performed using some thioether macrocyclic ligands.³⁾ Several investigators have also extensively studied the Cu(II)-proteins with model ligands such as nitrogen heterocyclics,⁴⁾ histidine and cysteine containing oligopeptide.^{5,6)} In fact, the ESR parameters as well as the optical absorption character of these model complexes showed the excellent agreement with those of the square planar ($3d_{x^2-y^2}$ ground state) and of the tetrahedral type ($3d_{xy}$ ground state) paramagnetic active sites in copper proteins, where the g -anisotropy has been shown to be $g_{\parallel} > g_{\perp}$ everywhere.

The possibility of the trigonal bipyramidal active site has also been proposed; the importance of the model studies with the $3d_{z^2}$ ground state in solution has been pointed out by Miskowski.⁷⁾ Several ESR studies of copper complexes with the $3d_{z^2}$ ground state have been reported for the compressed tetragonal, compressed trigonal bipyramidal, and *cis*-distorted octahedral site doped in solid matrices.⁸⁾ In solutions, however, formations of copper complexes with an axially compressed coordination require quite exceptional conditions, because the coordination geometries are usually

fixed by the strong equatorial coordination of the polar functional groups and of the solvent molecules. In order to reveal unusual coordinations, we have chosen the crown ethers as the ligand. ESR investigations have been made for several Cu(II)-crown ether ligands with 12, 15, and 18 ring members in dry chloroform solutions (shown in Fig. 1).

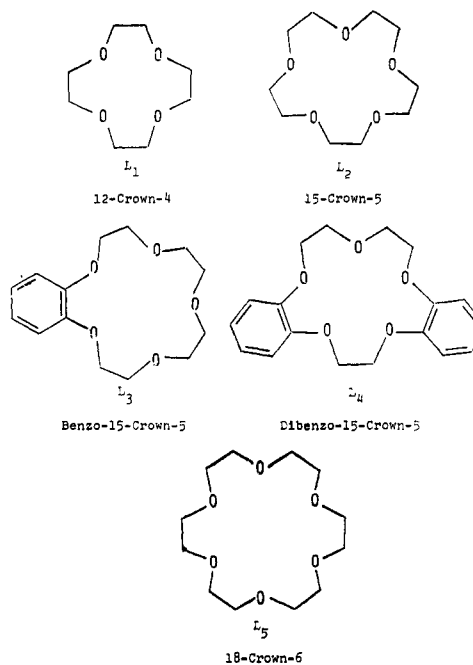


Fig. 1.

We found that the g -anisotropy of the crown ether Cu(II) complexes is strictly dependent on the numbers of ligand oxygen atoms. Cu(II) complexes with the L₂, L₃, and L₄ ligands reveal the inverted g -anisotropy ($g_{\parallel} < g_{\perp}$), while the L₁ and L₅ complexes show the usual g -anisotropy ($g_{\parallel} > g_{\perp}$). The bonding parameters in the copper-ligand bond of the L₂, L₃, and L₄ complexes were determined from the g and A tensors as well as

from the superhyperfine couplings of the chlorine atoms which are axially coordinated. The analysis of the ESR spectra confirmed that the L_2 , L_3 , and L_4 complexes are in the $3d_{z^2}$ ground state doublet. The electron nuclear dipolar term P and the Fermi isotropic term were determined based on Bleaney's calculation. The MO bonding parameters were estimated assuming the compressed octahedral, the trigonal, and the pentagonal bipyramidal geometry at the paramagnetic site. The bonding nature was characterized on the basis of the ligand spin densities.

Experimental

Benzo-15-crown-5 (L_3) and dibenzo-15-crown-5 (L_4) were synthesized according to Pedersen's procedure.⁹⁾ The pure materials were obtained by recrystallization in hexane; L_3 : mp 80–82 °C (uncorrected). Found: C, 62.48; H, 7.46%. Calcd for $C_{14}H_{20}O_5$: C, 62.69; H, 7.46%. L_4 : mp 114–115 °C (uncorrected). Found: C, 67.95; H, 6.33%. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37%. 12-Crown-4 (L_1), 15-crown-5 (L_2), and 18-crown-6 (L_6) purchased from Aldrich Chemicals were used without further purification.

Sample solutions were prepared as follows: commercial anhydrous cupric chloride, dried by heating the material at 110 °C for 6 h (0.04 mmol), and crown ether (0.4 mmol) were mixed with dry $CHCl_3$ (4 ml) under vacuum. The ESR spectra of the orange-to-yellow colored solutions were measured at 77 K. The details of the preparation and the ESR operating conditions were described in the previous paper.¹⁰⁾

Results and Discussion

ESR Spectra. ESR spectra (Fig. 2) measured at 77 K for the L_1 and L_5 complexes showed the usual g -anisotropy with axial symmetry ($g_{\parallel} > g_{\perp}$), whereas those of the L_2 and L_3 complexes¹⁰⁾ contained a typical line shape for nonoriented systems ($S=1/2$, $g_{\parallel} > g_{\perp}$) (Fig. 3). The ligand superhyperfine splittings due to the two equivalent chlorine atoms can be clearly detected in the g_z component of the ESR spectra of the L_2 , L_3 , and L_4 complexes. The ESR parameters

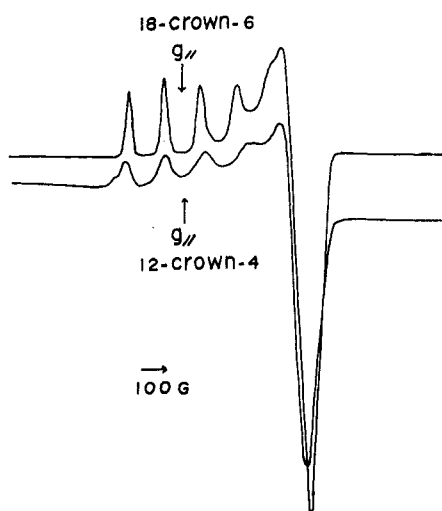


Fig. 2. ESR spectra of $CuCl_2$ -12-crown-4 and $CuCl_2$ -18-crown-6 measured at 77 K.

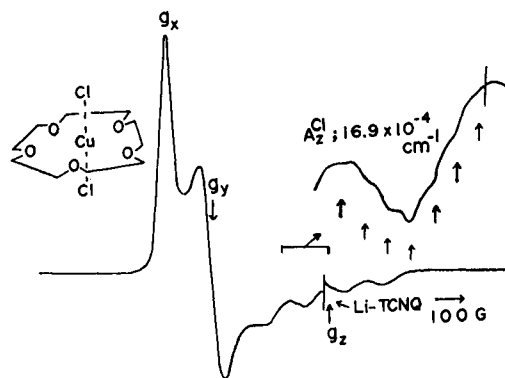


Fig. 3. ESR spectrum of $CuCl_2$ -15-crown-5 measured at 77 K.

TABLE 1. ESR PARAMETERS OF CROWN ETHER $CuCl_2$ COMPLEXES

Ligand	g_z	g_x	g_y	A_z	A_x	A_y	A_z^{Cl}
L_2 Obsd	2.000	2.372	2.265	121	—	—	16.9
L_2 Calcd	—	—	—	+126	-8	-39	—
L_3 Obsd	1.995	2.321	—	130	—	—	16.9
L_3 Calcd	—	—	—	+125	-23	—	—
L_4 Obsd	1.992	2.323	—	137	—	—	16.5
L_4 Calcd	—	—	—	+124	-22	—	—
L_1 Obsd	2.335	2.081	—	147	—	—	—
L_5 Obsd	2.345	2.077	—	126	—	—	—

A in 10^{-4} cm^{-1} . Calcd values are obtained using $P=319 \times 10^{-4} \text{ cm}^{-1}$ and $K=0.127$, based on Bleaney's method.

determined are summarized in Table 1. The X-ray analysis of the L_1 - $CuCl_2$ complex has already been performed. In this case, the copper atom binds with the two equatorial chlorine atoms and takes a distorted octahedral geometry, with the apical Cu-O (2.343 and 2.403 Å) distance much longer than the equatorial bond length (Cu-Cl=2.214, Cu-O=2.128 and 2.113 Å).¹¹⁾ The ESR parameters of the L_1 and L_5 complexes shown in Table 1 suggest that the unpaired electron occupies either $d_{x^2-y^2}$ or d_{xy} type orbitals in the axially elongated octahedral ligand field. In fact, this conclusion is consistent with the results of the X-ray analysis of the L_1 -complex. The structure of the L_5 -complex has not been determined yet, but an analogous coordination scheme can be assumed based on the similarity in the observed ESR parameters.¹²⁾ In both cases, one will see that the equatorial chlorine atoms play an important role in stabilizing the in-plane bonding ($d_{x^2-y^2}$ or d_{xy}) in the octahedral geometry. The inverted g -anisotropy observed for the L_2 , L_3 , and L_4 complexes indicates that the unpaired electrons mainly occupy the $3d_{z^2}$ orbital of the metal in the ground state, because their Δg_z -value ($g_z - g_e$) has a small negative value (see Table 2).¹³⁾ The ultimate value of Δg_z is -0.02 for the pure $3d_{z^2}$ ground state, according to the theory.¹⁴⁾ The L_3 and L_4 -complexes showed g -anisotropy with nearly axial symmetry. The L_2 -complex had rhombic symmetry, which is supposedly due to the distortion arising from some steric requirement

in coordinating the metal ions with crown ether.¹⁵⁾ The ligand hyperfine splitting due to the chlorine atoms associated with the g_z -component suggests an apical perturbation on the Cu ions due to the two chlorine atoms coordinated above and below the pentagonal crown ring (Fig. 4).

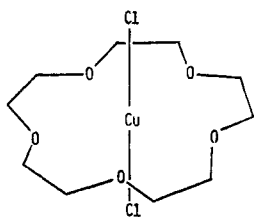


Fig. 4. The structure of CuCl₂-15-crown-5.

Characterization of the Bonding Parameters of L₂, L₃, and L₄ Complexes. The observed ESR spectra can be fitted by the spin Hamiltonian:

$$\hat{H} = \sum_{i=x,y,z} (g_i \beta H_i S_i + A_i \hat{S}_i \hat{I}_i) \quad (1)$$

if we neglect the copper nuclear Zeeman effect and the quadrupole interactions. A detailed discussion of the hyperfine tensor and its relation to the g -factors of the Cu(II) with the 3d_{z²} ground state has already been given in the work of Bleaney.¹⁴⁾ For rhombic symmetry of the paramagnetic site, the relations between the g and the hyperfine tensor elements are given as follows:

$$A_x = P[-K + \Delta g_x + \frac{1}{14} \Delta g_y - \frac{2}{7}] \quad (2)$$

$$A_y = P[-K + \Delta g_y + \frac{1}{14} \Delta g_x - \frac{2}{7}] \quad (3)$$

$$A_z = P[-K + \Delta g_z - \frac{1}{14} (\Delta g_x + \Delta g_y) + \frac{4}{7}] \quad (4)$$

$$\Delta g_z = g_z - g_e, \Delta g_x = g_x - g_e, \Delta g_y = g_y - g_e$$

where K is the Fermi isotropic term and P defines the dipolar interaction of the copper nucleus with the unpaired electron, which is proportional to the average value of the inverse cubic power of the metal-unpaired electron distance. In the previous paper, P and K values were evaluated for the L₃ complex based on Swalen's calculation:¹⁶⁾

$$P = 319 \times 10^{-4} \text{ cm}^{-1} \text{ and } K = 0.127.^{10)}$$

With the tentative use of these P and K values, the hyperfine tensor elements of the copper nucleus (A_x , A_y , and A_z) were calculated by using Bleaney's simple treatment; this gave satisfactory agreement between the observed and the calculated values for the L₂ and L₃ complexes, provided that $A_z > 0$ and $A_x, A_y < 0$ (see Table 1).

The considerable discrepancy between the observed and the calculated A_z values seen for the L₄ complex would be attributed to the overestimation of the K value; this will be revised in the following section. For nearly axially symmetry (L₃ and L₄) $\Delta g_{\perp}(g_{\perp} - g_e)$ can be expressed as a function of the ²A-²E, d-d transition energy $\Delta E_{xz, yz}$ and of the effective spin-orbital interaction parameter λ' , which gives a measure of the extent of the electron delocalization into the ligand; $\lambda' = \alpha^2 \lambda_0$, $\Delta g_{\perp} = 6\lambda' / \Delta E_{xz, yz}$, where α^2 is the spin density on the copper 3d_{z²} orbital. The effective value of spin-orbit interaction $\lambda'(-733.7 \text{ cm}^{-1})$ can be obtained based on the assumption that $\lambda' = (P/P_0)\lambda_0$,¹⁷⁾ where $P_0(360 \times 10^{-4} \text{ cm}^{-1})$ and $\lambda_0(-828 \text{ cm}^{-1})$ are the dipolar-term and the spin-orbit interaction parameter of a Cu(II) free ion, respectively.

The value of α^2 was ≈ 0.89 , and the corresponding d-d band transition energy $\Delta E_{xz, yz}$ was roughly 13800 cm⁻¹ for the L₃ and the L₄ complex. A more rigorous value of α^2 was estimated from the ligand superhyperfine structures.

MO Scheme of the Bonding Parameters. According to ligand field theory, the unpaired electron occupies the molecular orbital involving the metal ion 3d_{z²} and the ligand orbital.

The appropriate σ -unpaired orbital, ψ_{z^2} , can be expressed as follows:

$$\psi_{z^2} = \alpha d_{3z^2} - \frac{\alpha'}{2\sqrt{3}} (2Z_1 + 2Z_2 - Z_3 - Z_4 - Z_5 - Z_6) \quad (5)$$

$$\psi_{z^2} = \alpha d_{3z^2} - \frac{\alpha'}{2\sqrt{6}} (\sqrt{6}Z_1 + \sqrt{6}Z_2 - 2Z_3 - 2Z_4 - 2Z_5) \quad (6)$$

$$\psi_{z^2} = \alpha d_{3z^2} - \frac{\alpha'}{2\sqrt{10}} (\sqrt{10}Z_1 + \sqrt{10}Z_2 - 2Z_3 - 2Z_4 - 2Z_5 - 2Z_6 - 2Z_7) \quad (7)$$

for the octahedral (5), the trigonal bipyramidal (6), and the pentagonal bipyramidal (7) geometry, where Z_1 and Z_2 denote the AO's in the axial ligands, and Z_3 - Z_6 and Z_7 are those in the equatorial ligands.¹⁸⁾

The detailed structures of the L₂, L₃, and L₄ complexes are unknown. In order to obtain a qualitative view of the structure, however, some idealized calculations were carried out based on the chlorine hyperfine splitting. We used the assumption that the atomic orbitals of the two axially coordinated chlorine atoms can be described in term of the hybridization expressed as $Z_i = np \pm \sqrt{1-n^2} S$. For the maximum bonding of the ligand, the ideal sp hybridization may be assumed for

TABLE 2. BONDING PARAMETERS OF 15-CROWN-5 COPPER COMPLEXES

	Octahedral				Pentagonal bipyramidal Trigonal bipyramidal					A_z^{Cl}
	α^2	P	K	β^2	α^2	P	K	β^2	Δg_z	
L ₂	0.936	337	0.1648	0.0864	0.914	329	0.1561	0.0875	-0.0023	16.9
L ₃	0.936	337	0.1328	0.0984	0.914	329	0.1235	0.0995	-0.0073	16.9
L ₄	0.937	337	0.1082	0.1078	0.916	330	0.0995	0.1085	-0.0103	16.5

A_z^{Cl} and P in 10⁻⁴ cm⁻¹.

the chlorine atoms ($n^2=1/2$). The hyperfine tensor of the chlorine atoms ($A_{//}$) for unit spin density is thus given as follows:

$$A_{//} = (1 - n^2)[A_f + 2A_p], \quad n^2 = \frac{1}{2} \text{ for sp chlorine atoms}$$

$$A_f = g_N \beta_N g \beta \left[\frac{8}{9} \pi |\psi_{3s}(0)|^2 \right], \quad A_p = \frac{2}{5} g_N \beta_N g \beta \langle r^{-3} \rangle_{3p} \quad (8)$$

where A_f and A_p are isotropic and anisotropic hyperfine constants, respectively. The effective values of A_f ($1490 \times 10^{-4} \text{ cm}^{-1}$) and A_p ($44 \times 10^{-4} \text{ cm}^{-1}$) were obtained from the parameters of ^{35}Cl and ^{37}Cl based on their natural abundance ratio.¹⁹ The net spin densities ($\rho_{\text{Cl}}=0.011$) on the chlorine atoms are determined from the superhyperfine splittings due to the chlorine atoms listed in Table 1. The total ligand spin densities thus obtained are 0.066 for the octahedral ligand geometry and 0.088 for the trigonal and pentagonal bipyramidal geometry. The magnitudes of the spin density on the 3d orbital ($\alpha^2 \approx 0.912-0.934$) were estimated by neglecting the overlap integral between the copper and ligand orbitals. Based on the α^2 values thus determined, the electron-nuclear dipolar term P and the Fermi contact term K were calculated from the A_z values using Bleaney's equation (4). The calculated bonding parameters are given in Table 2. Both P and K values evaluated from the ligand spin densities are in excellent accord with the previous assumption; $P=319 \times 10^{-4} \text{ cm}^{-1}$ and $K=0.127$. Of interest is the anomalously small K value estimated for the Cu(II)-crown complexes in the $3d_z^2$ ground state, which is of the correct symmetry to mix with the 4s orbital.²⁰

The isotropic interaction term measures the sum of the spin polarization due to 3d and 4s electrons, as is expressed below; $-PK=A_{3d}\alpha^2+A_{4s}\beta^2$, where $A_{3d}=-142 \times 10^{-4} \text{ cm}^{-1}$ and $A_{4s}=+896 \times 10^{-4} \text{ cm}^{-1}$.²¹ The β^2 values thus obtained are cited in Table 2. One will see that contribution of about 10% from 4s reduces the K value to a large extent in the present complexes. From the inspection of the bonding parameters listed in Table 2, several important aspects of the bonding nature of the L_2 , L_3 , and L_4 complexes can be clarified. The α^2 -values assumed here are more or less qualitative, but at least it may be concluded that the natures of the copper-ligand bonds are rather ionic and that the unpaired electron weakly delocalizes into the ligand orbitals in these complexes. The Δg_z value, a measure of the admixture of $d_{x^2-y^2}$ into the ground state, decreases with increasing numbers of the fused benzene rings.

This means that the planar fused benzene restricts a conformational change in the crown ring during the optimum binding at the equatorial positions. The A_z value also shows a concomitant change with the Δg_z -value. The lower g_z value gives a larger A_z value, which is reflected in the K value. The smallest K -value can be calculated for the L_4 -complex, where the 4s admixture parameter increases with increasing z

character due to the octahedral Jahn-Teller distortion.

The ^1H , ^{14}N , and $^{63,64}\text{Cu}$ ENDOR spectra of steric lacyanin have been measured recently. The unusual copper hyperfine tensor was explained by assuming a flattened tetrahedral geometry.²² To our knowledge, the Cu(II)-chromophors or the complexes with the $3d_z^2$ ground state have not been clearly characterized in the biological systems. Nevertheless, the present work will present some fundamental knowledge for the ESR studies of Cu(II)-complexes with the $3d_z^2$ ground state as studied in solutions.

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