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ESR Studies of a New $3d_{z^2}$-Type Copper(II)-Crown Ether Complex with Pentagonal Bipyramidal Geometry

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In the presence of the optimum amount of water, the copper(II) ion and 15-crown-5 (15C5) derivatives gave the dihydrated complex in boron trifluoride-diethyl ether (BF_3-ether). Based on optical and ESR spectrometric titrations, we found that the crown ether captures the copper(II) ion in the equivalent metal/ligand molar ratio. The d-d band absorptions of the complexes were detected in the near-infrared region. The complexes revealed the characteristic ESR *g*-anisotropies ($g_z<g_x$, g_y) which are typical of the copper(II) complexes with a $3d_{z^2}$ ground-state doublet. The superhyperfine splittings due to the ^{17}O isotope was successfully detected, and the fact of the axial ligation of the water molecule was demonstrated. The ESR parameters were determined by means of the computer simulation of the line shape, while the copper-ligand bonding parameters were estimated from the ESR parameters by means of Bleaney's calculation.

The crown ether showed a pronounced ability to bind various cations and anions, with marked conformational changes in the polyether-ring moiety upon the metal chelations. Their hydrophobic exterior allows them to solubilize ionic substances in nonaqueous solvents.1) These novel properties of crown ethers have resulted in their use as ligands in the molecular design of a metal complex with an unusual metal coordination and a distinctive electronic structure.

For example, the first successful preparation of a Cu(II) complex with a $3d_{z^2}$ ground state has been reported for the systems composed of $CuCl_2$ and crown ethers containing five oxygen atoms. In this case, the ESR measurement clearly demonstrated that the unpaired electron occupies the $3d_{z^2}$ metal orbital, as judged from the typical *g*-anisotropies, $g_z<g_x$, g_y.2) The positive detection of a superhyperfine splitting ascribed to the axially ligated two chlorine atoms ($I=3/2$) suggested that the coordination geometry of the complex is a pentagonal bipyramid.3,4) The subsequent X-ray analysis of the Benzo-15-crown-5(B15C5)-$CuCl_2$ complex visualized the detailed molecular structure, in which the complex takes the pentagonal bipyramidal geometry with the five ethereal oxygen atoms in the equatorial positions and with the two chlorine atoms at the apical positions.5)

One of the distinct characteristics of the bonding scheme of the complex is the shorter Cu-Cl distances (2.254 and 2.242 Å) seen in the axial bond length, in comparison with the equatorial bond length (2.240—2.337 Å) between the metal and the ethereal oxygen atoms. In contrast to the case of the 5-*O*-membered crown ether, the Cu(II) complexes of 4-*O*- and 6-*O*-membered crown ethers reveal the ESR anisotropies assigned to those of the $3d_{x^2-y^2}$ or $3d_{xy}$-type ground state. In this case, the copper atom binds with the two chlorine atoms at the equatorial positions, thus forming a distorted octahedral geometry, in which the apical Cu-O distances (2.343 and 2.403 Å) are much longer than the equatorial bond length (Cu-Cl=2.214 Å, Cu-O=2.218 and 2.113 Å).6)

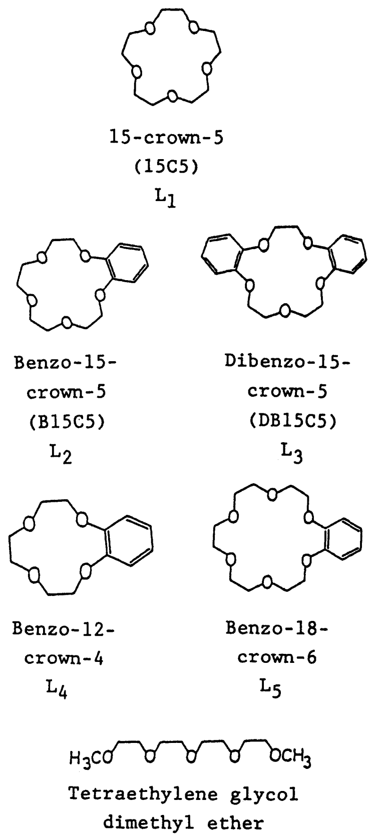

Fig. 1. Chemical structures of polyethers.

In order to elucidate in more detail the coordination chemistry with regard to the Cu(II) complex of 5-*O*-membered crown ether, we continued our efforts to obtain a similar Cu(II) complex generated in a BF_3-ether solution containing a small amount of water. Based on the spectrophotometric titration, we confirmed that the complex is a monomeric copper(II) complex, in which the Cu(II) ion is incorporated into the crown ether in the equivalent metal/ligand molar ratio. In the present paper, we wish to report the

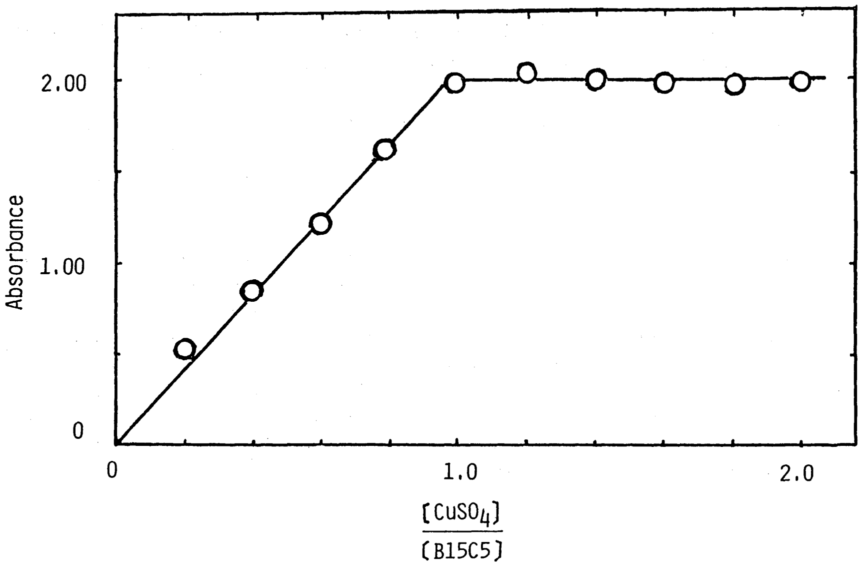

Fig. 2. Plot of the absorbance vs. the molar ratio of Cu(II) ion added to B15C5 solution.

spectroscopic properties of a new Cu(II)-5-*O*-membered crown ether complex in which two water molecules coordinate to the axial positions. The *g*-anisotropies measured, $g_z<g_x$, g_y, were indeed typical of Cu(II) complexes with the $3d_{z^2}$ ground state. The positive evidence for the axial ligation of the water molecule was successfully demonstrated by observing the ^{17}O-superhyperfine splitting, which is overlapped with each copper nuclear hyperfine splitting occurring at the g_z-component. By the aid of the MO scheme, the copper-ligand bonding nature was discussed in terms of the ^{17}O spin density.

Under the same reaction conditions, the complex formation was investigated between the Cu(II) ion and a crown ether with an even oxygen number, such as Benzo-12-crown-4(**L**$_4$) and Benzo-18-crown-6(**L**$_5$); the same experiment was also carried out for the 5-*O*-membered polyether with an open-chain structure(**L**$_6$, Fig. 1). In these cases, however, no experimental evidence to support the existence of a $3d_{z^2}$-type complex was obtained anywhere. It was thus confirmed that only 5-*O*-membered crown ethers gave the $3d_{z^2}$-type copper(II) complex in solution.

Experimental

The crown ethers used in this experiment were synthesized and purified according to Pedersen's procedure.[7] The tetraethylene glycol dimethyl ether and copper(II) salts were purchased at Wako Chemicals, Ltd., and they were used without further purification. A commercial grade of 47% BF_3-ether was used after dehydration and distillation.[8]

The electronic spectra were recorded with a JASCO UVIDEC-1 spectrometer and a JASCO UVIDEC-590 NIR spectrometer at room temperature. The ESR measurements were carried out at 77 K by using a JEOL-FE-2XG X-band spectrometer operating with a 100-KHz magnetic-field modulation. The *g*-values were determined by taking Li-TCNQ (g=2.0025) as a standard. The magnetic fields were calibrated based on the hyperfine splitting of Mn(II) in MgO (8.69 mT). All the measurements were performed at the Advanced Instrumental Center for Chemical Analysis, Ehime University.

Results and Discussion

Electronic Spectra. A 1.04×10^{-2} mol dm^{-3} solution (2.5 ml) of B15C5 dissolved in BF_3-ether was titrated with a 0.13 M $CuSO_4$ aqueous solution. By a step-by-step addition (0.04 ml) of the $CuSO_4$ solution, the growth in the absorption intensity was observed in the visible region of the electronic spectrum. An excellent linear increase in the visible absorption (λ_{max}=430 nm, ε=202 mol^{-1} dm^3 cm^{-1}) can be seen with an increase in the amount of $CuSO_4$ added, until the molar ratio of $CuSO_4$ to B15C5, [$CuSO_4$]/[B15C5], reaches unity (Fig. 2). When the total molar concentration of $CuSO_4$ exceeds that of B15C5, a sharp turning occurred on the linear plot, and no important changes in the absorption intensities were detected with a further increase in the [$CuSO_4$]/[B15C5] ratio. Based on the titration behavior between the B15C5 and the $CuSO_4$ solution, the Cu(II) complex formed in the present system is identified as a mononuclear copper(II) complex composed of the Cu(II) ion and the crown ether in an equivalent molar ratio. A similar titration behavior is obtained for the Dibenzo-15-crown-5(DB15C5)-Cu(II) complex by monitoring the characteristic absorption at λ_{max}=448 nm (ε=258 mol^{-1} dm^3 cm^{-1}).

The visible absorption bands thus characterized for DB15C5- and B15C5-Cu(II) complexes are probably to be attributed to the charge transfer between the benzene molecular orbital and the copper 3d atomic orbital, because no important absorption band can be detected for the 15C5-Cu(II) complex in the visible

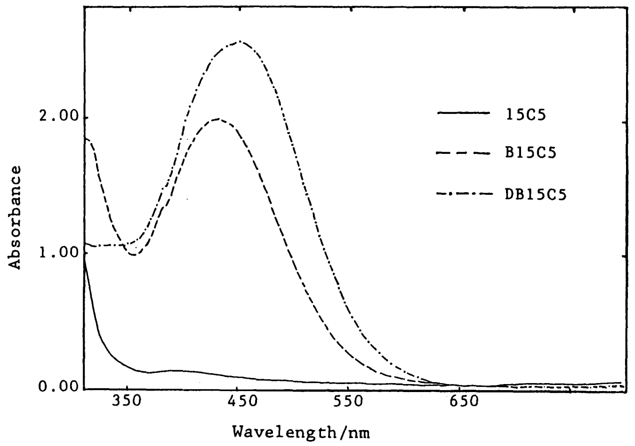

Fig. 3. Visible absorption spectra observed at room temperature for Cu(II)-complexes of L_1, L_2, and L_3.

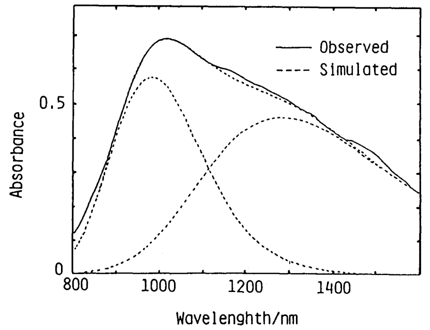

Fig. 4. Near infrared electronic absorption spectra observed at room temperature.

region of the electronic-absorption spectrum (Fig. 3). On the other hand, at the near-infrared band, broad, weak bands were found in the range from 850 to 1600 nm for all the Cu(II) complexes. The computer simulations show that the observed bands are resolved into two characteristic absorptions, occurring at 980 and 1300 nm, respectively (Fig. 4). The molar-extinction coefficients of the bands determined are of the order of 10; we thus assigned these bands to the copper d-d transition absorptions. Based on the ESR parameters (Table 2), the d-d transition energies, ΔE_{zx} and ΔE_{yz}, can be theoretically estimated as follows:

$$\Delta g_x = \frac{6\lambda'}{\Delta E_{zx}}, \quad \Delta g_y = \frac{6\lambda'}{\Delta E_{yz}}, \quad \lambda' = \alpha^2\lambda_0 \qquad (1)$$

where λ_0 ($-828\ \mathrm{cm}^{-1}$) is the spin-orbital interaction parameter of a copper(II)-free ion. The calculated wavelengths of the corresponding d-d absorptions (800 and 1000 nm) thus support the fact that the observed optical spectrum of each complex occurs at the near-infrared region, as is shown in Table 1.

ESR Spectra. In the same manner, the Cu(II) complexes were prepared by mixing the crown ethers (**L_1**, **L_2**, **L_3**) with $CuSO_4$ in BF_3-ether in the equivalent molar ratio. The ESR spectra were recorded at 77 K, as is shown in Fig. 5. The observed spectra together exhibit the rhombic *g*-anisotropies as are featured in the Cu(II) complexes with the $3d_{z^2}$ ground-state doublet. The computer simulation of the line shape (broken line) showed an excellent agreement with those of the observed spectra based on the ESR parameters summarized in Table 2. Based on the ESR intensity measured at 77 K, the complex formation between 15C5 and the Cu(II) ion was also investigated. A linear growth of the apparent ESR intensity was confirmed within the range in which the total concentration of Cu(II) ions added is less than the equivalent molar concentration of the crown ether (Fig. 6). When an excess amount of the Cu(II) ion is present in the reaction mixture, the ESR of another Cu(II) complex, which reveals the *g*-anisotropies typical of the $3d_{x^2-y^2}$ or

Table 1. Absorption Spectral Data of the Crown Ether-Cu(II) Complexes

Ligand	λ_{max} a)	ε a)	λ_{max}	ε	λ_{max}	ε
L_1	—	—	980	8.8	1325	8.7
L_2	430	202	980	6.8	1285	6.3
L_3	448	258	995	9.4	1330	6.8

a) λ_{max} in nm and ε in $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$.

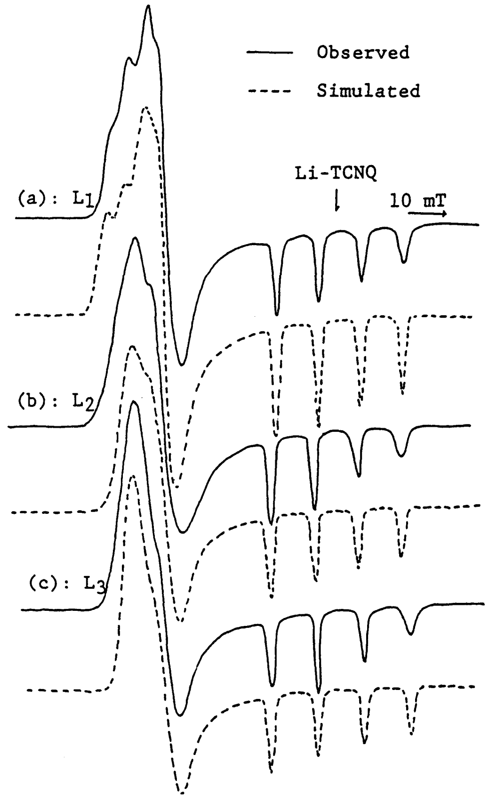

Fig. 5. ESR spectra observed at 77 K and simulated for the crown ether-copper(II) complexes in BF_3-ether. The simulations were carried out by taking the line width as follows: (a): σ_x=1.9 mT, σ_y=3.1 mT, σ_z=0.7 mT; (b): σ_x=2.8 mT, σ_y=2.7 mT, σ_z=0.7 mT; and (c): σ_x=2.2 mT, σ_y=2.8 mT, σ_z= 0.7 mT.

Table 2. ESR Parameters of the Crown Ether-Cu(II) Complexes

Ligand		g_x	g_y	g_z	A_x[a)]	A_y	A_z	A_z^o
L_1	Obsd.	2.400	2.334	1.993	56.0	10.0	107.3	24.3
	Calcd.	—	—	—	40.5	14.8	—	—
L_2	Obsd.	2.387	2.310	1.992	15.0	5.0	112.0	23.5
	Calcd.	—	—	—	42.1	16.0	—	—
L_3	Obsd.	2.387	2.313	1.989	10.0	1.0	117.6	22.9
	Calcd.	—	—	—	47.1	22.4	—	—

a) A in $10^{-4}\,\text{cm}^{-1}$.

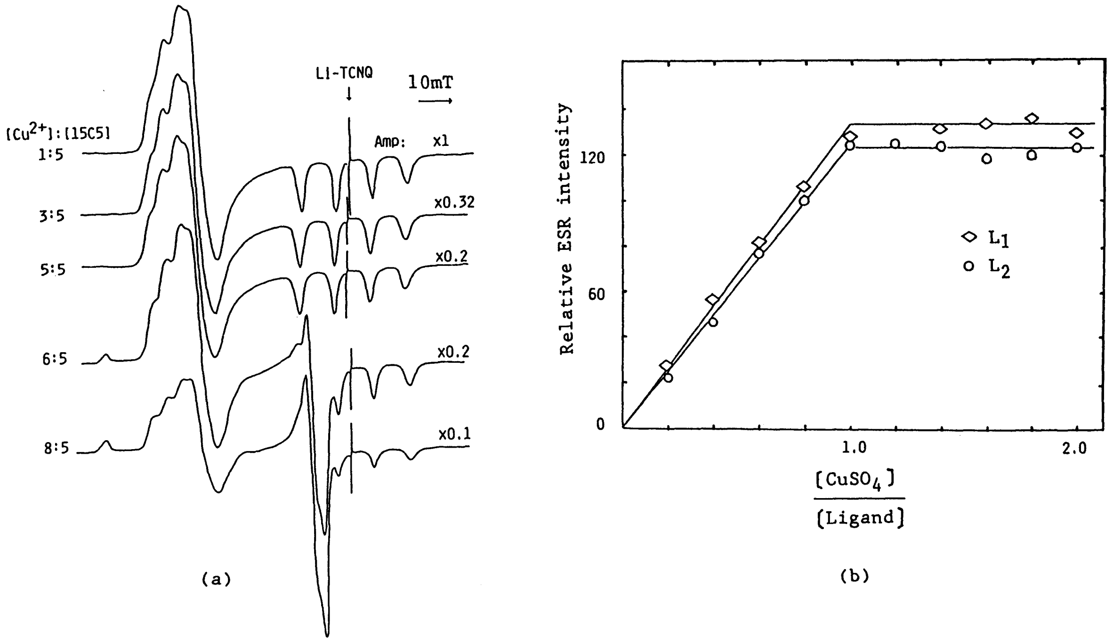

Fig. 6. ESR titration behavior observed for 15C5–Cu(II) systems. (a) ESR spectra observed at 77 K for 15C5–Cu(II) complex generated in the different copper(II) ion/ligand ratio. (b) Relation between the observed ESR intensities of 15C5–Cu(II) complex and the metal/ligand ratio during a titration.

$3d_{xy}$-type ground state, began to overlap with the ESR hyperfine structure of the 15C5-Cu(II) complex, as may be seen in Fig. 6(a). Further, we confirmed that the ESR hyperfine structure ascribed to the $3d_{z^2}$ ground state and that their intensities were not affected by the addition of another ether, 4-*O*-, 6-*O*-membered crown ether (**L$_4$** and **L$_5$**) or 5-*O*-membered open-chain ether (**L$_6$**), in a large excess. The ESR spectra of the **L$_4$**, **L$_5$**, and **L$_6$**-Cu(II) complexes revealed the *g*-anisotropies, $g_z > g_x$, g_y, appreciate to the $3d_{x^2-y^2}$ or $3d_{xy}$ ground state. One can now conclude that the complexation between the polyether and the Cu(II) ion to give the $3d_{z^2}$ ground-state doublet is strictly limited to the case of the 5-*O*-membered crown ether.

In order to confirm the fact that the water molecules are coordinated to the Cu(II) ion at the apical positions, the **L$_1$**, **L$_2$**, and **L$_3$**-Cu(II) complexes have been obtained by using a $CuSO_4$ aqueous solution containing $H_2{}^{17}O$ (^{17}O atom%=10). The second derivative ESR spectra of the g_z-component measured are shown in Fig. 7, where the ligand superhyperfine splitting due to the ^{17}O isotope (I=5/2) may clearly be seen; the positive evidence of the water ligation is thus successfully demonstrated. Because of the lower concentration of the ^{17}O isotope contained in the H_2O used here, the possibility of the observation of superhyperfine interactions ascribed to the two ^{17}O atoms can be safely disregarded. The superhyperfine coupling constants, A_z^o, are listed in Table 2.

With reference to the X-ray analysis of the molecular structure of the **L$_2$**-$CuCl_2$ complex,[5] one can now assume that the present complex has two water molecules axially coordinated above and below the pentagonal crown ring.

Calculation of Bonding Parameters. The appropriate molecular orbital occupied by an unpaired electron, which involves the metal $3d_{z^2}$ orbital and also the ligand orbital, can be expressed as follows, provided that the complexes take the pentagonal bipyramidal geometry, D_{5h}:

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

Table 3. Bonding Parameters of the Crown Ether-Cu(II) Complexes

Ligand	Dihydrated				Dichlorinated			
	α^2	P[a)]	κ	β^2	α^2	P	κ	β^2
L_1	0.763	275	0.1003	0.0806	0.914	329	0.1561	0.0875
L_2	0.771	277	0.0904	0.0859	0.914	329	0.1235	0.0995
L_3	0.777	280	0.0700	0.0950	0.916	330	0.0995	0.1085

a) P in $10^{-4}\,\mathrm{cm}^{-1}$.

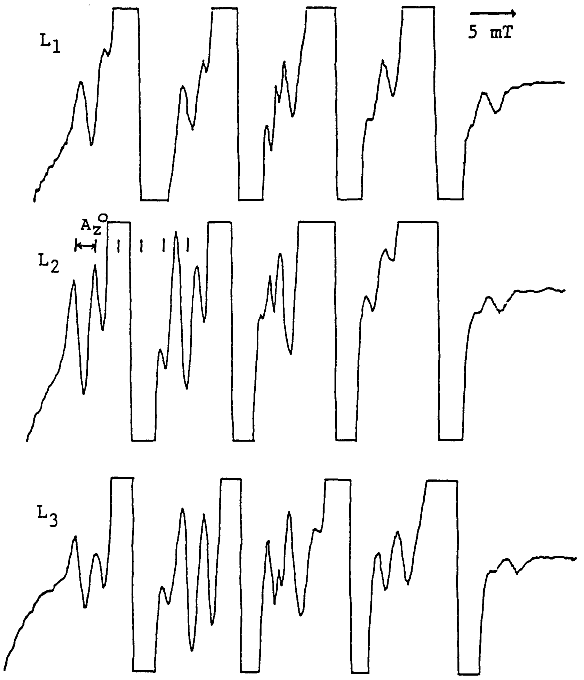

Fig. 7. Enlarged second derivative ESR spectra observed at 77 K for the g_z-components. The six-line superhyperfine structure is attributed to the ^{17}O atom of $H_2{}^{17}O$ which is axially coordinated to the Cu(II) complex.

where Z_1 and Z_2 denote the atomic orbitals in the axial ligands, where Z_3—Z_7 are those in the equatorial ligands, and where the atomic orbitals of the oxygen atoms axially coordinated are described in terms of the sp^3 hybridization, expressed as:

$$Z_i = np \pm \sqrt{1-n^2}\,s \quad (n^2 = 3/4) \tag{3}$$

The spin density on the apical ligand ^{17}O, ρ_0, was thus calculated by means of the following equation:

$$A_z^{\circ} = \rho_o(1\text{-}n^2)(A_f+2A_p) \tag{4}$$

where A_f ($-1544\times10^{-4}\,\mathrm{cm}^{-1}$) and A_p ($-48\times10^{-4}\,\mathrm{cm}^{-1}$) are the isotropic and anisotropic hyperfine constants respectively for the unit spin density on a ^{17}O atom.[9)] The total ligand spin densities thus obtained are 0.223—0.237 for the complexes, The magnitude of the spin density on the $3d_{z^2}$ copper atomic orbital, α^2, was estimated by neglecting the overlap integral between the copper and ligand orbitals. Based on the α^2 value thus determined, the Fermi contact term, κ, was calculated from the A_z value using Bleaney's equation,[10)] expressed as:

$$A_x = P_0(-\kappa\alpha^2 + \Delta g_x + \frac{1}{14}\Delta g_y - \frac{2}{7}\alpha^2) \tag{5}$$

$$A_y = P_0(-\kappa\alpha^2 + \Delta g_y + \frac{1}{14}\Delta g_x - \frac{2}{7}\alpha^2) \tag{6}$$

$$A_z = P_0(-\kappa\alpha^2 + \Delta g_z - \frac{1}{14}(\Delta g_x + \Delta g_y) + \frac{4}{7}\alpha^2) \tag{7}$$

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

where P_0 (360×10^{-4} cm^{-1}) is the dipolar-term of a Cu(II)-free ion. The calculated bonding parameters of the Cu(II) complexes are summarized in Table 3. The magnitude of the calculated A_x and A_y values show an excellent accordance with the experimental tendency, $A_x > A_y$, which was determined by a computer simulation of the observed line shapes, (cf. Table 2). The anomalously small κ values estimated here may be attributed to the mixing of the 4s orbital into the $3d_{z^2}$ atomic orbital, in the correct symmetry, A_{1g}. The isotropic-interaction term measures the sum of the spin polarization attributable to the $3d_{z^2}$ and 4s electrons, written as:

$$-P_0\kappa = A_{3d}\alpha^2 + A_{4s}\beta^2 \tag{8}$$

where $A_{3d}=-142\times10^{-4}\,\mathrm{cm}^{-1}$ and $A_{4s}=896\times10^{-4}\,\mathrm{cm}^{-1}$.[11)]

In Table 3, the bonding parameters of the dihydrated crown ether-Cu(II) complexes are compared with those of the dichlorinated crown ether-Cu(II) complexes previously reported.[3)] It was again confirmed that the contribution of about 8—9.5% from 4s reduces the κ values to a large extent. In both cases, one may see a common tendency for the Δg_z values, a measure of the admixture of $3d_{x^2-y^2}$ into the ground state, to approach that of the pure $3d_{z^2}$ ground state, $\Delta g_z = -0.021$,[10)] with an increase in the number of fused benzene rings. A concomitant increase in the A_z value can be noted with the increase in the Δg_z and β^2 values. These findings imply that the planar-fused benzene restricts a conformational change in the crown ring upon the optimum metal coordination at the equatorial positions.

For the spin densities on the copper $3d_{z^2}$ orbital, however, one may note a large discrepancy between the values of the dichlorinated crown ether-Cu(II) complexes and those of the dihydrated crown ether-Cu(II) complexes. The considerable reduction in α^2 values noted for the dihydrated Cu(II) complexes means that the covalent bonding nature between the copper and the axial ligand is more dominant in the present complexes than in the dichlorinated-Cu(II) complexes.

Finally, we would like to consider the reason why the formation of the Cu(II) complex with the $3d_{z^2}$ ground state is limited to cyclic 5-*O*-membered crown ether, not including either the cyclic 4-*O*-, 6-*O*-membered crown ethers or the open-chain 5-*O*-membered polyether. One of the ways to solve the puzzle is by a comparison of the metal-ion radii, which would give the best fit in the cavity of the 15C5. Of interest is the fact that the molecular structure of the dichlorinated B15C5-Cu(II) complex is very much like that of the B15C5-$Mg(NCS)_2$ complex, taking a pentagonal bipyramidal structure.[5,12] The effective radius reported for the Cu(II) ion (0.87 Å) is, indeed, close to that of the Mg(II) ion (0.86 Å).[13] On the other hand, the unpaired copper $3d_{z^2}$ orbital, A_{1g}, would be effectively stabilized in the pentagonal bipyramidal ligand field (D_{5h}), which has the proper symmetry with a metal atomic orbital in terms of the Jahn-Teller distortion.

It has been believed that a strict annihilation of all aerial moisture from the reaction mixture is necessary for the preparation of the crown ether-Cu(II) complex revealing the $3d_{z^2}$ ground state in solution.[3,4] In the present paper, however, the existence of a new dihydrated crown ether-Cu(II) complex with the $3d_{z^2}$ ground state has successfully been demonstrated. Thereafter, we could confirm that the ground-state electronic configuration of the crown ether-Cu(II) complex is greatly dependent on the number of ethereal oxygen donors of the crown ether, and that the $3d_{z^2}$ ground state is exactly limited to the case of the Cu(II) complex of 5-*O*-membered crown ether. In order to put our proposal on a more rigorous experimental base, ESR studies of the Cu(II) complexes with 3-*O*- and 7-*O*-membered crown ethers are now under way.

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