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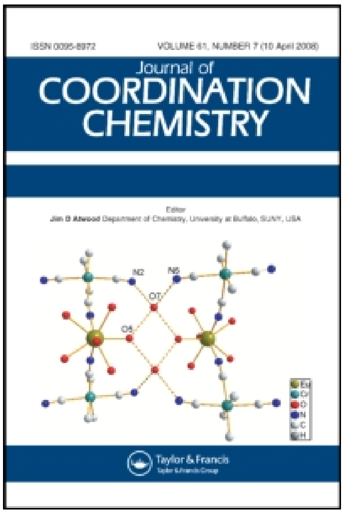

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ESR SPECTRA AND STRUCTURES OF $[Cu(B15C5)(H_2O)_2](ClO_4)_2$ IN $[Mg(B15C5)(H_2O)_2](ClO_4)_2$ CRYSTAL AND IN FROZEN 60% $HClO_4$; VIBRONIC INTERACTION THEORY

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ESR SPECTRA AND STRUCTURES OF $[Cu(B15C5)(H_2O)_2](ClO_4)_2$ IN $[Mg(B15C5)(H_2O)_2](ClO_4)_2$ CRYSTAL AND IN FROZEN 60% $HCLO_4$; VIBRONIC INTERACTION THEORY

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Obvious differences in $3d_{z^2}$ ground-state ESR spectra observed at 77K were detected between a powder sample of Cu(II) doped in $[Mg(B15C5)(H_2O)_2](ClO_4)_2$ single crystal and a Cu(B15C5) complex in 60% $HClO_4$. An X-ray diffraction analysis of $[Mg(B15C5)(H_2O)_2](ClO_4)_2$ demonstrated that the complex takes on a seven-coordinate pentagonal bipyramidal geometry and the axial ligands are also H_2O molecules, which is similar to $[Cu(B15C5)(H_2O)_2](ClO_4)_2$. Differences in ESR spectra are qualitatively explained as being due to changes in coordination bond distances and angles for both cases, based on vibronic interaction theory. The ground-state Kramers doublet wavefunctions were calculated and reveal an increase of admixture of $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals into a $3d_{z^2}$ ground-state for the Cu(II) ion doped in the crystal.

Keywords: benzo-15-crown-5; copper(II); ESR; X-ray structure; vibronic interaction theory

INTRODUCTION

Cu(II) complexes with 15-crown-5 (15C5) derivatives possess two characteristics. One is that the complexes take on a seven-coordinate pentagonal bipyramidal geometry; the other is that they show an unusual ESR g-anisotropy ($g_z < g_x, g_y$), which is due to a $3d_{z^2}$ ground-state doublet [1-5]. It is clear, based

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on previous X-ray analyses and ESR measurements [4], that for Cu(II) complexes of benzo-15-crown-5 (B15C5) prepared in 60% $HClO_4$ a Cu(II) ion is located in the centre of the crown ether ring and is axially coordinated by two water molecules. On the other hand, single crystal and powder ESR investigations were also carried out for the Cu(II) ion doped in a crystal of Mg(B15C5) complex in previous studies [6, 7]. Although the ESR parameters feature a $3d_{z^2}$ ground-state doublet, marked changes in the ESR spectra can be detected in frozen 60% $HClO_4$ solution. To explain this finding, an assumption was made that anions (ClO_4^-), rather than H_2O molecules may be the axial ligands [7]. In the present study, however, an X-ray analysis of $[Mg(B15C5)(H_2O)_2](ClO_4)_2$ (denoted as **A**) indicated that the axial ligands are water molecules, which perfectly contradicted the previous assumption. Thus, a new explanation is required for the differences in the ESR spectra between the Cu(II) complex in frozen 60% $HClO_4$ and doped in the **A** matrix. Here, the vibronic interaction theory is used for a qualitative explanation for changes in the bond distances and angles of the coordination sphere of the CuO_7 chromophore for Cu(B15C5) complexes in the dilute crystal and in the frozen solution, and which are considered to be able to produce the differences in the ESR spectra for both cases. Furthermore, the ground-state Kramers doublet wavefunctions were also calculated based on the ESR parameters and revealed an increase of admixtures of $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals into a $3d_{z^2}$ ground-state, which can cause a larger anisotropy in an ESR spectrum of the Cu(II) ion doped in the crystal.

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EXPERIMENTAL

Preparation and Crystallization of Complexes

B15C5 and $Mg(ClO_4)_2$ in a molar ratio of 1:1 were dissolved in 60% $HClO_4$. After two or three days, blocky colourless single crystals of **A** were obtained. Crystals of Cu(II) ion doped in the **A** matrix were obtained in the same method described above for **A**, except for adding less than 0.5% $Cu(ClO_4)_2 \cdot 6H_2O$ into the solution. The crystals were pulverized for ESR measurements. A solution of a Cu(B15C5) complex used for ESR measurements was prepared by dissolving B15C5 and $Cu(ClO_4)_2 \cdot 6H_2O$ in a molar ratio of 10:1 in 60% $HClO_4$ [4]. All the chemical reagents purchased from Wako Chemical Ltd. were guaranteed reagents and were used without further purification.

ESR Measurements

ESR measurements were carried out at 77K on a JEOL PX1050 ESR spectrometer. The g-values were determined by taking Li-TCNQ ($g = 2.0025$) as

TABLE I Crystal Data, Structure Determination and Refinement Data for **A**.

Formula	$C_{14}H_{24}O_{15}Cl_2Mg$	Scan method	ω-2θ
M.W.	527.55	2θ range/°	6.0-55.0
Crystal system	monoclinic	Scan speed/°min^{-1}	16.0
a/Å	10.385(2)	Scan width/°	0.84 + 0.30 tanθ
b/Å	16.589(3)	Standard reflcns	Three every 150 reflcns
c/Å	13.535(4)	No. of data measd	5353
β/°	107.30(2)	No. of unique data (R_{int})	5074 (0.065)
V/Å^3	2226.3(9)	No. of obsd data	2005 ($I > 1.5\sigma(I)$)
Space group	$P2_1/n$	No. of variables	322
Z	4	R; R_w	7.1; 5.5
Dc/gcm^{-3}	1.574	S, goodness of fit	1.47
μ/cm^{-1}	3.87	Range of (Δ/ρ)/e$^-$ Å^{-3}	−0.36 to 0.52
Radiation (λ/Å)	MoKα (0.71069)		

a standard, and magnetic fields were calibrated based on the hyperfine splitting of Mn(II) in MgO (8.69 mT). Computer simulation was performed using the program IER-PRIT-SIM-1 in the computer operating system of the ESR spectrometer.

X-ray Crystal and Molecular Structure Analyses

A blocky colourless single crystal of **A** having approximate dimensions of 0.4×0.4×0.15 mm sealed in a glass capillary was used for data collection on a Rigaku AFC5R diffractometer with a fine-focus 12kW rotating-anode generator. Cell constants were estimated from a least-squares refinement using 25 carefully centred reflections in the range $22.5° < 2\theta < 25.3°$. Crystal data and details concerning structure refinement are given in Table I. Intensity data were corrected for Lorentz, polarization and absorption effects. Empirical absorption corrections based on azimuthal scans of several reflections [8] were applied, which resulted in transmission factors ranging from 0.90 to 1.00. Corrections for secondary extinction also were applied (coefficient = 0.50809×10^{-6}).

The structure was solved by direct methods [9]. Coordinates and anisotropic temperature factors for the non-hydrogen atoms were refined by full-matrix least-squares procedures based on F^2 with weight $w = 1/\sigma^2(F^2)$. The positions of the hydrogen atoms were idealized (C-H 0.95 Å), assigned isotropic thermal parameters $B(\mathrm{H}) = 1.2B_{eq}(\mathrm{C})$ and allowed to ride on their parent carbon atoms. Anomalous dispersion effects were included in the F_c calculation. All calculations were carried out on a VAX station 3200 computer with the TEXSAN program [10], which used the atomic scattering factors taken from the *International Tables for X-ray Crystallography* [11]. Lists of H atom positions,

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anisotropic thermal parameters and observed and calculated structure factors are available from the authors on request.

RESULTS AND DISCUSSION

ESR Spectra

Figure 1 shows the ESR spectra of the Cu(II) ion doped in the **A** matrix and the Cu(B15C5) complex in frozen 60% $HClO_4$. Since the ESR spectrum in frozen

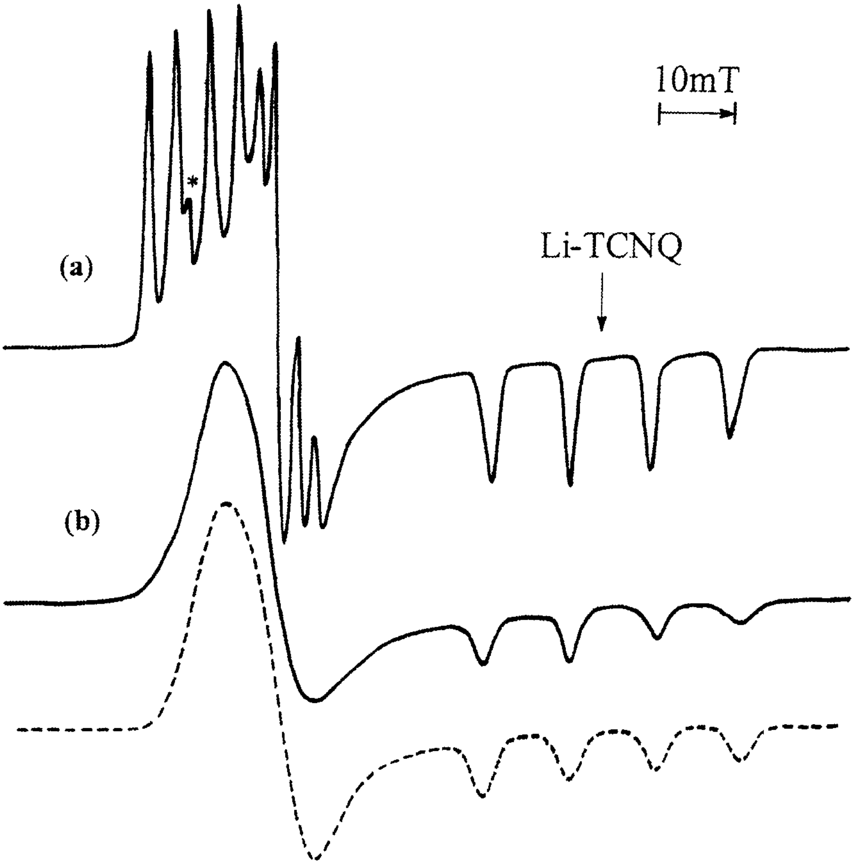

FIGURE 1 ESR spectra observed at 77K for (a) the Cu(II) ion doped in the Mg(B15C5) matrix (the signal marked by an asterisk is due to a forbidden transition [6, 7]), and (b) the Cu(B15C5) complex in frozen 60% $HClO_4$. The broken line shows the computer simulation of (b) calculated with line widths $\sigma_x = 6.0$ mT, $\sigma_y = 6.0$ mT, and $\sigma_z = 3.0$ mT.

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TABLE II ESR parameters for the present Cu(B15C5) complexes.

	Cu(II) ion doped in the Mg(B15C5) matrix	Cu(B15C5) complex in frozen 60% $HClO_4$
g_x	2.405	2.379
g_y	2.295	2.310
g_z	1.998	1.990
A_x[a]	5.17	1.50
A_y	3.05	1.30
A_z	10.52	11.60

[a] A values in mT.

solution shows no hyperfine structure in the perpendicular part, its ESR parameters were estimated based on computer simulation. ESR parameters of the Cu(II) ion doped in the **A** matrix listed in Table II are not perfectly the same, but are close to those obtained from the single crystal ESR measurements because of the effect of forbidden lines arising from a nuclear quadrupole interaction [6]. In the present study, the electronic configurations of both cases are assigned to a $3d_{z^2}$ ground-state doublet, as judged from the characteristic g-anisotropies ($g_z < g_x, g_y$). However, one can see that the shapes of the ESR spectra and the parameters, especially for the perpendicular components, are strikingly different for the two cases. The noticeably large anisotropy was observed for the Cu(II) ion doped in the **A** matrix. As mentioned above, although an attempt was made to explain the differences in terms of different axial ligands in a previous study [7], the present X-ray analysis denied the previous assumption as follows.

X-Ray Analysis of A

Figure 2 illustrates an ORTEP structure of **A** [12], together with the atom numbering scheme. The final atomic parameters and equivalent isotropic thermal parameters are given in Table III. Table IV lists pertinent bond lengths and bond angles.

The X-ray analysis clearly demonstrated that the metal ion in **A** takes on a seven-coordinate pentagonal bipyramidal geometry and H_2O molecules, but not the anions, are axial ligands. Furthermore, the coordination configuration of **A** is similar to that of $[Cu(B15C5)(H_2O)_2](ClO_4)_2$ (denoted as **B**) [4], of which crystals are also obtained from a 60% $HClO_4$ solution. For **A**, like **B**, the axial bond lengths (2.067(4) and 2.038(5)Å) are much shorter than those of the equatorial ones (Table IV). This fact is important because it implies that Cu(II) ions replacing Mg(II) ions will take a $3d_{z^2}$ ground-state doublet in terms of strong axial perturbation. That is to say, the Cu(II) ion doped in the Mg(B15C5) matrix

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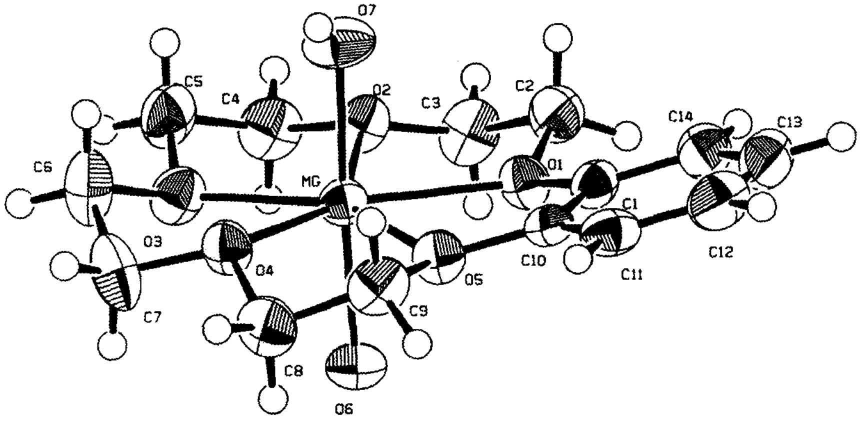

FIGURE 2 ORTEP drawing of $[Mg(B15C5)(H_2O)_2]^{2+}$ (**A**), together with the atom numbering scheme. Only one hydrogen atom of the axial water molecules was detected because of high thermal motion of the hydrogen atoms. The ClO_4^- anions, are not shown.

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also takes on a seven-coordinate pentagonal bipyramidal geometry with two axially coordinated water molecules as well as the Cu(B15C5) complex in 60% $HClO_4$.

As mentioned above, if the Cu(B15C5) complexes have similar coordination spheres in frozen solution and in the crystal, then there may be a question concerning the large change in the ESR spectrum for the Cu(II) ion doped in the Mg(B15C5) matrix. A possible reason is first considered to be the effect of different environments in solution and solid. However, a previous study showed that a powder sample of Cu(II) ion doped in a B15C5 matrix provided an ESR spectrum and parameters close to those of the Cu(B15C5) complex in the frozen solution but not to the Cu(II) ion doped in the Mg(B15C5) matrix [7]. Thus, it is necessary to find another reason from the complex molecules themselves. Here, a qualitative explanation based on vibronic interaction theory is proposed as follows.

Although studies of Cu(II) complexes with 15C5 and related O_5-crown ethers are almost focused on a strong perturbation due to axial ligands, which is the origin of the $3d_{z^2}$ ground-state doublet, the marked changes in the present ESR spectra seem to be mainly attributed to equatorial perturbation. As shown in Table IV, equatorial bond lengths of **B** show a unique trend. There are three longer bonds (Cu-O(1), Cu-O(3) and Cu-O(5)) and two shorter bonds (Cu-O(2) and Cu-O(4)) for **B**. On the other hand, the five equatorial bond lengths of **A** are not much different, and all of them are shorter than the corresponding ones in **B**. In addition, the axial bonds of **A** are clearly longer than those of **B** (1.922(6) and

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TABLE III Fractional Positional Parameters and Thermal Parameters for Non-Hydrogen Atoms with e.s.d. in Parentheses for **A**.

Atom	*x/a*	*y/b*	*z/c*	B_{eq}/Å^2
Mg	0.0755(2)	0.2106(1)	0.3288(1)	2.72(9)
Cl(1)	0.2787(2)	0.4545(1)	0.5090(1)	4.32(9)
Cl(2)	0.5756(2)	0.1402(1)	0.3588(1)	4.26(8)
O(1)	0.1078(4)	0.0966(2)	0.4196(3)	3.1(2)
O(2)	0.1782(4)	0.1284(2)	0.2571(3)	3.3(2)
O(3)	0.0819(4)	0.2664(3)	0.1842(3)	3.6(2)
O(4)	0.0106(4)	0.3329(2)	0.3338(3)	3.2(2)
O(5)	0.0063(4)	0.2243(2)	0.4663(3)	3.1(2)
O(6)	− 0.1187(4)	0.1729(2)	0.2535(3)	3.7(2)
O(7)	0.2650(5)	0.2460(3)	0.4111(4)	4.3(2)
O(8)[a]	0.301(1)	0.3728(6)	0.5478(7)	6.3(5)
O(8P)	0.168(2)	0.491(1)	0.453(1)	5.5(8)
O(9)	0.282(2)	0.4456(9)	0.4097(8)	11.8(9)
O(9P)	0.262(2)	0.398(2)	0.579(2)	11(1)
O(10)	0.3743(6)	0.5089(4)	0.5668(4)	7.4(3)
O(11)	0.151(1)	0.4731(8)	0.518(2)	15(1)
O(11P)	0.331(2)	0.420(2)	0.432(2)	10(1)
O(12)[b]	0.5058(5)	0.2109(3)	0.3704(5)	8.5(3)
O(13)	0.5430(6)	0.0768(4)	0.4135(5)	9.9(4)
O(14)	0.5428(8)	0.1209(4)	0.2547(5)	12.3(5)
O(15)	0.7134(5)	0.1556(4)	0.3932(5)	9.9(4)
C(1)	0.1037(6)	0.0995(4)	0.5210(4)	2.9(3)
C(2)	0.1961(7)	0.0379(4)	0.3953(5)	4.0(3)
C(3)	0.1747(7)	0.0441(4)	0.2802(5)	4.1(3)
C(4)	0.1733(6)	0.1443(4)	0.1511(5)	4.2(3)
C(5)	0.1824(7)	0.2338(5)	0.1431(5)	4.5(4)
C(6)	0.0849(7)	0.3524(4)	0.1874(5)	4.8(3)
C(7)	− 0.0210(8)	0.3761(4)	0.2375(5)	4.9(4)
C(8)	− 0.0868(6)	0.3461(4)	0.3890(5)	4.3(3)
C(9)	− 0.0361(6)	0.3031(4)	0.4900(5)	3.8(3)
C(10)	0.0481(6)	0.1693(4)	0.5471(5)	2.9(3)
C(11)	0.0372(6)	0.1796(4)	0.6452(5)	3.5(3)
C(12)	0.0799(7)	0.1193(5)	0.7161(5)	4.4(4)
C(13)	0.1358(7)	0.0501(5)	0.6924(5)	4.7(4)
C(14)	0.1481(6)	0.0391(4)	0.5932(5)	3.8(3)

[a] Oxygen atoms with numbers from (8) to (11) are connected to Cl(1) and are divided into two sets labelled with and without "P" (occupancies are 0.642 and 0.358, respectively) because of disordering. [b] Oxygen atoms from (12) to (15) are connected to Cl(2).

1.913(5)Å), in agreement with the general relationship between axial and equatorial bond distances; that is, the longer an axial bond, the shorter an equatorial bond [13]. Furthermore, compared with the equatorial bond angles of **A**, the corresponding ones of **B**, especially the angles ∠O(1)-Cu-O(5), ∠O(2)-Cu-O(3) and ∠O(3)-Cu-O(4), deviate markably from the standard angle (72°) in a regular pentagon (Table IV).

TABLE IV Equatorial Bond Lengths (Å) and Angles (°) for **A** and **B** (M = Mg or Cu).

	A	**B**
M-O(1)	2.226(4)	2.257(5)
M-O(2)	2.134(4)	2.186(5)
M-O(3)	2.184(5)	2.229(6)
M-O(4)	2.146(4)	2.150(6)
M-O(5)	2.197(4)	2.314(5)
O(1)-M-O(2)	72.2(2)	71.3(2)
O(2)-M-O(3)	73.2(2)	74.7(3)
O(3)-M-O(4)	73.8(2)	75.5(3)
O(4)-M-O(5)	71.9(2)	72.2(2)
O(5)-M-O(1)	69.8(2)	67.9(2)

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As is well known, Cu(II) complexes generally exhibit much stronger vibronic interactions, which play an important role in controlling molecular configuration, than other atoms [13,14]. The CuO_7 chromophore in **B** is approximately regarded as having D_{5h} symmetry. According to vibronic interaction theory, an e_2' vibration mode for D_{5h} symmetry causes a coupling of a molecular ground-state (A_1') and an excited state (E_2'). In the case of **B**, based on an EHMO calculation [4], the lowest E_2' excited state corresponds to an excitation of one electron from the highest fully occupied molecular orbital (e_2') containing $3d_{x^2-y^2}$ and $3d_{xy}$ atomic orbitals to singly occupied HOMO which is an a_1' molecular orbital containing $3d_{z^2}$ atomic orbital. Figure III qualitatively shows the possible changes in the equatorial coordination bond distances and angles caused by e_2' vibration modes [15]. Because the benzene ring restricts the two catechol oxygen atoms close to the Cu(II) ion to avoid large tensions of ∠Cu-O(1)-C(1) and ∠Cu-O(5)-C(10), there are consequently three longer and two shorter equatorial bonds and the abovementioned changes in the bond angles for **B**. In fact, a complex without a benzene ring, $[Cu(15C5)(H_2O)_2](ClO_4)_2$, possesses a reverse trend; that is, three shorter and two longer equatorial bonds and a larger ∠O(1)-Cu-O(5) angle, while smaller ∠O(2)-Cu-O(3) and ∠O(3)-Cu-O(4) [4]. The structure is thermodynamically stable because of the increasing numbers of shorter bonds. On the contrary, the structure of **A**, which does not possess any d orbitals, is little affected by vibronic interactions, and the bond lengths and angles do not much change.

Since the effective radius reported for Cu(II) (0.87Å) is close to that of Mg(II) (0.86Å) [16], it is reasonable to consider that when a small amount of Mg(II) is replaced by Cu(II) in **A**, it causes little change in the molecular structure. Thus it is easy to understand that the Cu(II) ion doped in the **A** matrix, which is in a form of $[Cu(B15C5)(H_2O)_2](ClO_4)_2$ but has the same conformation as **A**, is subjected to a stronger equatorial perturbation and weaker axial ones compared

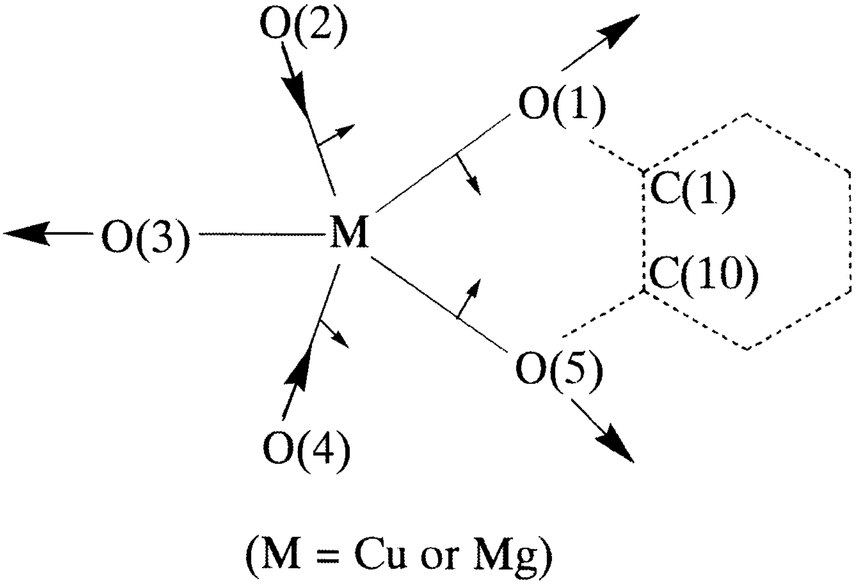

FIGURE 3 Possible changes in the equatorial coordination bond distances and angles caused by e_2' vibration modes.

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with the Cu(B15C5) complex in frozen 60% $HClO_4$ which is considered to have the same conformation as **B**. Therefore, from the viewpoint of crystal field theory, the energy gap between $3d_{z^2}$ orbital and $3d_{x^2-y^2}$ or $3d_{xy}$ orbital becomes smaller in the Cu(B15C5) complex in the dilute crystal, and the influence of $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals in the ground-state will increase. As a result, the ESR spectrum of the Cu(II) ion doped in the **A** matrix exhibits a larger anisotropy. Actually the Cu(II) ion doped in the **A** matrix shows larger coupling constants of perpendicular components, the smaller parallel component, and particularly a larger g_z value than the Cu(B15C5) complex in 60% $HClO_4$ (the g_z value obtained from the single crystal ESR measurements is indeed larger than that of a free electron [6]). These observations show that the ground-state deviates from a pure $3d_{z^2}$ one, and also implies perturbation in the equatorial positions related to $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals. Thus, the stronger equatorial perturbation results in much more mixing of the $3d_{x^2-y^2}$ and/or $3d_{xy}$ orbital into the ground-state. In an extreme case if an equatorial perturbation becomes stronger than an axial one, an ESR spectrum due to a $3d_{x^2-y^2}$ and/or $3d_{xy}$ ground-state doublet would be observed.

According to the results of Swalen *et al.* [17], the ground-state Kramers doublet wavefunctions can be expressed as follows,

$$\psi^{\alpha} = \mathrm{ad}_{z^2}\alpha + \mathrm{bd}_{x^2-y^2}\alpha + \mathrm{icd}_{xy}\alpha - \mathrm{idd}_{yz}\beta - \mathrm{ed}_{zx}\beta, \qquad (1a)$$

$$\psi^{\beta} = \mathrm{i}(\mathrm{ad}_{z^2}\beta + \mathrm{bd}_{x^2-y^2}\beta - \mathrm{icd}_{xy}\beta - \mathrm{idd}_{yz}\alpha + \mathrm{ed}_{zx}\alpha), \qquad (1b)$$

where α and β are the spin functions. The coefficients a ~ e represent a contribution of each d orbital, and are satisfied with the normalization condition. In addition, relationships between the above coefficients and ESR parameters can be written as follows 17],

$$g_z = 2 - 4d^{2}\,{}^{-\,4e2} + 8bc + 4de \qquad (2a)$$

$$g_x = 2 - 4c^2 - 4e^2 + 4\sqrt{3}ad - 4ce + 4bd \qquad (2b)$$

$$g_y = 2 - 4c^2 - 4d^2 + 4\sqrt{3}ae - 4be + 4cd \qquad (2c)$$

$$\begin{aligned} A_z = P\{&8bc + 4de + (6\xi - \kappa)(1 - 2d^2 - 2e^2) \\ &- 3\xi[4c^2 + 4b^2 - d^2 - e^2 + \sqrt{3}a(d+e) + 3(d-e)(c-b)]\} \end{aligned} \qquad (3a)$$

$$\begin{aligned} A_x = P\{&4\sqrt{3}ad - 4ec + 4bd + (6\xi - \kappa)(1 - 2c^2 - 2e^2) \\ &- 3\xi[(\sqrt{3}a + b)^2 - c^2 + 4d^2 - e^2 - \sqrt{3}a(e+2c) + 3dc - 3be + 3de]\} \end{aligned} \qquad (3b)$$

$$\begin{aligned} A_y = P\{&4\sqrt{3}ae + 4dc - 4be + (6\xi - \kappa)(1 - 2c^2 - 2d^2) \\ &- 3\xi[(\sqrt{3}a - b)^2 - c^2 - d^2 + 4e^2 - \sqrt{3}a(d-2c) - 3ce + 3bd + 3de]\} \end{aligned} \qquad (3c)$$

where $\xi = 2/21$. P and κ represent the dipolar term and the Fermi contact term, respectively.

In the present study, the Kramers doublet wavefunctions and the bonding parameters (P and κ) of the Cu(B15C5) complex doped in the **A** matrix and in frozen solution were evaluated based on the ESR parameters listed in Table II. Since (*2*) and (*3*) are nonlinear simultaneous equations, an iteration procedure as well as a least-squares method was used with a program GS-ORBITAL for the calculation. The results obtained are summarized in Table V. The coefficient a, which is approximately equal to 1.0, reveals that the main component in the ground-state is a $3d_{z^2}$ orbital for each case. However, the coefficients b and c of the Cu(II) ion doped in the **A** matrix are significantly increased compared to Cu(B15C5) complex in frozen solution, while coefficients e and d do not show any important change. This result is in excellent agreement with the abovementioned conclusion derived based on the vibronic interaction theory.

TABLE V Coefficients of the Kramers Doublet Wavefuctions and Bonding Parameters for the Cu(B15C5) Complex in Diluted Crystal and in Frozen Solution.

	a	b	c	d	e	P[a]	κ
in the Mg(B15C5) matrix	0.9877	0.1315	0.0377	0.0581	0.0482	329	0.2498
in frozen 60% $HClO_4$	0.9957	0.0570	0.0011	0.0553	0.0479	284	0.1311

[a] P values in 10^{-4} cm^{-1}.

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One should also note that the bonding parameters P and κ for the Cu(B15C5) complex in 60% $HClO_4$ are very close to those reported previously for the Cu(B15C5) complex in the BF_3-ether-water system, in which the axial ligands are also H_2O molecules [3], although the parameters were obtained using different calculation methods. The smaller P value implies strong perturbation due to the axial, covalent Cu-O bond [4]. On the other hand, the P and κ values for the Cu(II) ion doped in the **A** matrix are markedly larger than those calculated for Cu(B15C5) complex in solution; the P value is close to the dipolar term of a free Cu(II) ion (360×10^{-4} cm^{-1}). [18] The larger P value indicates a decrease of the covalent nature in the axial Cu-O bond. That is to say, the axial Cu-O bond distances of the Cu(B15C5) complex doped in the Mg(B15C5) matrix become longer in comparison with Cu(B15C5) in the pure crystal or in solution. This deduction is completely supported by the X-ray analyses in the previous and present studies as stated above [4]. Thus, the calculation based on the Kramers doublet wavefunctions are consistent with the discussion in terms of vibronic interaction theory in the present case.

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