Studies on Mixed Chelates. XV. An ESR Investigation of Solvatochromic Copper(II) Complexes with Various *N*-Alkylated Ethylenediamines and *β*-Diketonates

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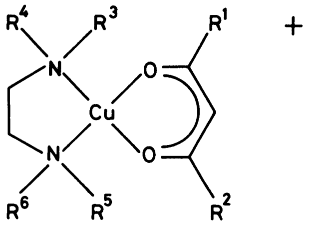
(Received May 5, 1987)

ESR spectra were obtained for frozen solutions of copper(II) mixed chelate complexes, [Cu(diam)(dike)]-ClO_4, having various *N*-alkylated ethylenediamines (diam) and *β*-diketonate ligands (dike). The ESR *g*-factor ($g_{/\!/}$) determined from apparently axial signals may be correlated by a decreasing function to pK_a of dikeH or diam ligand for the series of [Cu(tmen)(dike)]$^+$ or [Cu(diam)(acac)]$^+$, respectively. On the other hand, the $g_{/\!/}$ values gradually increased when the former series of complexes were dissolved in more strongly coordinating solvents, and a relationship was found between $g_{/\!/}$ and Donor Number of the solvent. These trends are regarded as ligand substituent effect and solvent effect on the $g_{/\!/}$ factor, and are analyzed using a crystal field model of a C_{2v} symmetry.

Previous studies from this laboratory showed that a series of mixed chelate complexes of copper(II), [Cu(diam)(dike)]$^+$, in which diam and dike designate *N*-alkylated ethylenediamines and *β*-diketonates, respectively (Structure I), possesses an interesting coloring behavior in organic solutions.[1] Namely, in the case of [Cu(tmen)(acac)]ClO_4 (R^1—R^6=CH_3), for instance, the color of the solutions ranges from reddish violet (in nitrobenzene) through azure (in formamide) to green (in piperidine) and it follows the donor ability of the solvent. This has been quantitatively revealed by the linear relationship between the wavenumber of the visible absorption maximum and Donor Number (DN) of the solvent.[2–4]

Demonstration of such a remarkable solvatochromism has exemplified an application of this complex as a teaching tool or a color indicator for solvent parameters.[4] On the other hand, interpretation of this solvent effect on the electronic spectra of [Cu(diam)(dike)]$^+$ in solution has been limited to rather qualitative terms. Information on the structure of the complexes and the nature of solvent interaction is essential for full understanding of the chemistry of these mixed chelate complexes. We therefore conducted a new study on the electronic structure of [Cu(diam)(dike)]$^+$ complexes in solution by means of the ESR spectroscopy and attempted to find a correlation between the previously obtained absorption spectral data and the ESR parameters for the mixed chelate complexes. The ESR *g*-factors are under electronic effects of both diam and dike substituents and also of ligated solvent molecules. Both effects were interpreted using a simple crystal field model of C_{2v} symmetry, which is described in this paper.



Structure I

Experimental

Materials. Preparation of the complexes, [Cu(diam)(dike)]ClO_4, used in this study has been reported elsewhere.[2] Our choice of the perchlorate salts is based on the fact that perchlorate ion does not coordinate to the mixed chelate cation in the solvents used in this study.[5] Table 1 provides a list of two series of complexes prepared, [Cu(tmen)(dike)]- and [Cu(diam)(acac)]ClO_4, and organic solvents used.

Measurements. Solvents used for ESR measurements were dried and purified by conventional methods. All of the solvents were added with tetrabutylammonium tetrafluoroborate (TBAB, 0.1 mol dm^{-3}) for the purpose of improving ESR resolution. ESR spectra were obtained for frozen solutions containing 5×10^{-3} mol dm^{-3} of complexes at 123 K in the X-band region using a JEOL JES-FE2XG spectrometer equipped with a 100 kHz magnetic field modulation. The ESR parameters were determined directly from the spectra, with the magnetic field calibrated using a standard Mn^{2+} sample (supplied by JEOL together with a computer program, GVALUE, for calculating *g*-values). Reported values involve errors within ±0.003 for $g_{/\!/}$ values and $\pm3\times10^{-4}$ cm^{-1} for $A_{/\!/}$ values. The $g_{/\!/}$ was positioned at the center of four hyperfine peaks due to the Cu nucleus, three of which from lower magnetic field were well resolved.

Results and Discussion

ESR Data for [Cu(diam)(dike)]$^+$. The X-band ESR spectra obtained for the series of [Cu(diam)(dike)]$^+$ complexes are typically of nearly axial type. An example is shown in Fig. 1. The apparent $g_{/\!/}$

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Table 1. List of Complexes and Solvents Used in This Study

Complex	[Cu(tmen)(dike)]ClO_4			
	dike a)	R^1	R^2	pK_a of dikeH b)
1	hfac	CF_3	CF_3	6.0
2	tfac	CF_3	CH_3	8.8
3	acac	CH_3	CH_3	12.7
4	dipm	$C(CH_3)_3$	$C(CH_3)_3$	15.9

Complex	[Cu(diam)(acac)]ClO_4					
	diam a)	R^3	R^4	R^5	R^6	pK_a of diam c)
3	tmen	CH_3	CH_3	CH_3	CH_3	14.7
5	asym-dmen	CH_3	CH_3	H	H	15.7
6	asym-deen	C_2H_5	C_2H_5	H	H	16.4
7	sym-deen	C_2H_5	H	C_2H_5	H	17.1
8	teen	C_2H_5	C_2H_5	C_2H_5	C_2H_5	—

Solvent	Abbreviation	Mark (in Figs. 2 and 3)	DN d)
1,2-Dichloroethane	DCE	○	0
Nitromethane	NM	△	2.7
Acetonitrile	AN	□	14.1
Acetone	AC	●	17.0
Methanol	MeOH	▲	19
N,*N*-Dimethylformamide	DMF	■	26.6
Dimethyl sulfoxide	DMSO	▽	29.8

a) The following abbreviations were used for the ligands: hfac=1,1,1,5,5,5-hexafluoroacetylacetonate, tfac=1,1,1-trifluoroacetylacetonate, acac=acetylacetonate, dipm=dipivaloylmethanate, tmen=*N*,*N*,*N*′,*N*′-tetramethylethylenediamine, asym-dmen=*N*,*N*-dimethylethylenediamine, asym-deen=*N*,*N*-diethylethylenediamine, sym-deen=*N*,*N*′-diethylethylenediamine, teen=*N*,*N*,*N*′,*N*′-tetraethylethylenediamine. b) Reference 6. c) "Stability Constants Supplement No. 1," The Chemical Society, London (1971). d) DN: Donor Number of the solvent (see text and Reference 1).

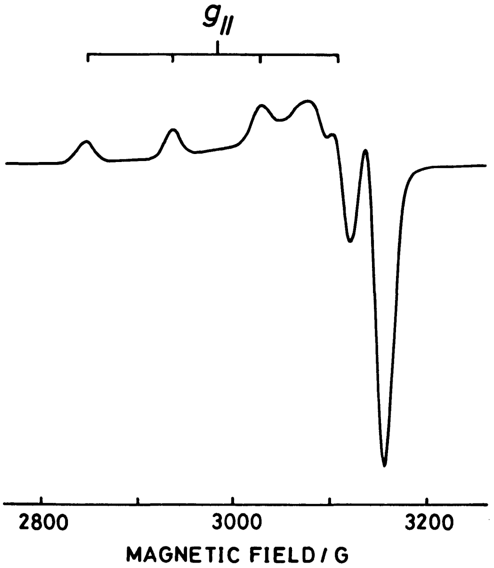

Fig. 1. ESR spectrum of [Cu(tmen)(acac)]$^+$ in acetonitrile containing 0.1 mol dm^{-3} of TBAB (ESR recorded at 123 K).

values can be determined from the spectra and fall in the range between 2.21 and 2.27, while the apparent $g_{\perp}$ values are found around g=2.0. As discussed below, theory predicts a slightly rhombic spectrum rather than an axial spectrum and simulation might yield two g-values resolved for the $g_{\perp}$ region. However, we focus our attention to the $g_{\parallel}$ values alone in this paper. Table 2 lists the observed $g_{\parallel}$ and $A_{\parallel}$ values for all of the complexes studied in seven different solvents.

In analyzing the trend in g-values, two correlations are noted: (1) $g_{\parallel}$ vs. ligand basicity (in the same solvent) and (2) $g_{\parallel}$ vs. solvent basicity (for the same ligand pair). With regard to the first relationship, Fig. 2 compiles plots of $g_{\parallel}$ values against pK_a of *β*-diketones and *N*-alkylated ethylenediamines. The pK_a of *β*-diketone varies widely upon substitution of R^1 and R^2 groups and is known to represent ligand basicity of *β*-diketonate.[6] The general trend noted in Fig. 2 is that, for each of the solvents, $g_{\parallel}$ value of the complex decreases as the *β*-diketonate ligand becomes more basic or more strongly coordinating. In addition, it appears that curvature of the fitted lines increases across DCE→DMSO in the order of increasing donor ability of the solvent. Substitution on the diam ligands has little effect on the $g_{\parallel}$ factor. Perhaps substitution of R^3—R^6 groups, which are not as remote as R^1 and R^2 groups, involves more than just electronic effect.

Table 2. ESR Parameters Determined for Various Solutions of Cu(II) Mixed Chelate Complexes

Complex	$g_{//}$ ($\lvert A_{//}\rvert/10^{-4}$ cm^{-1})						
	DCE	NM	AN	AC	MeOH	DMF	DMSO
1	2.231	2.237	2.239	2.246	2.242	2.260	2.264
	(190)	(185)	(183)	(182)	(183)	(188)	(180)
2	2.226	2.224	2.228	2.237	2.236	2.238	2.240
	(190)	(187)	(187)	(187)	(189)	(191)	(191)
3	2.219	2.218	2.220	2.228	2.226	2.225	2.233
	(192)	(192)	(188)	(190)	(189)	(190)	(190)
4	2.214	2.215	2.216	2.223	2.223	2.224	2.226
	(193)	(193)	(189)	(190)	(190)	(190)	(192)
5	2.220	2.221	2.225	2.228	2.227	2.230	2.233
	(195)	(192)	(191)	(190)	(190)	(185)	(188)
6	2.217	2.223	2.225	2.229	2.230	2.228	2.236
	(189)	(184)	(186)	(185)	(186)	(179)	(181)
7	2.220	2.222	2.227	2.228	2.230	2.232	2.232
	(191)	(191)	(189)	(190)	(189)	(183)	(188)
8	2.210	2.216	2.227	2.224	2.226	2.234	2.242
	(196)	(186)	(182)	(186)	(186)	(175)	(178)

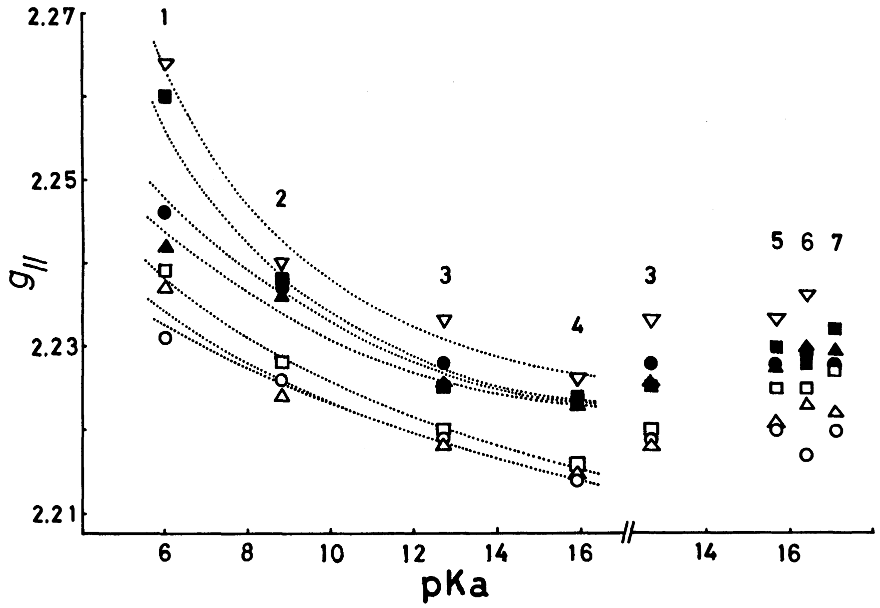

Fig. 2. Plots of $g_{//}$ values against pK_a of dikeH or diam for the series of [Cu(tmen)(dike)]$^+$ (left) or [Cu(diam)(acac)]$^+$ (right) dissolved in different solvents.

On the other hand, Fig. 3 plots $g_{//}$ values for the series of four complexes, [Cu(tmen)(dike)]$^+$, against solvent Donor Number (DN). A general trend can be seen; for the same complex, the $g_{//}$ value increases as the solvent property changes from noncoordinating to strongly coordinating (increase in DN). Again the curvature of the fitted lines becomes greater across dipm→hfac, here in the order of decreasing in-plane ligand basicity.

Symmetry of [Cu(diam)(dike)]$^+$ and Copper d-Orbital Sequence. The molecular structure of [Cu(diam)(dike)]$^+$ is shown schematically in Fig. 4, together with the coordinate system. It is safely assumed that the complex belongs to the point group C_{2v}. It should be noted that with this choice of coordinate system z axis remains as the unique symmetry axis so that a standard character table can be used, although the geometrical chelate plane is now in xz plane rather than more conventional xy plane. Thus each of the d-orbital wave functions is labelled as shown in Fig. 4.

Other workers have discussed the structure of Schiff base complexes of copper(II) as belonging to $C_{2v}(x)$ point group,[7,8] in which the coordinate system

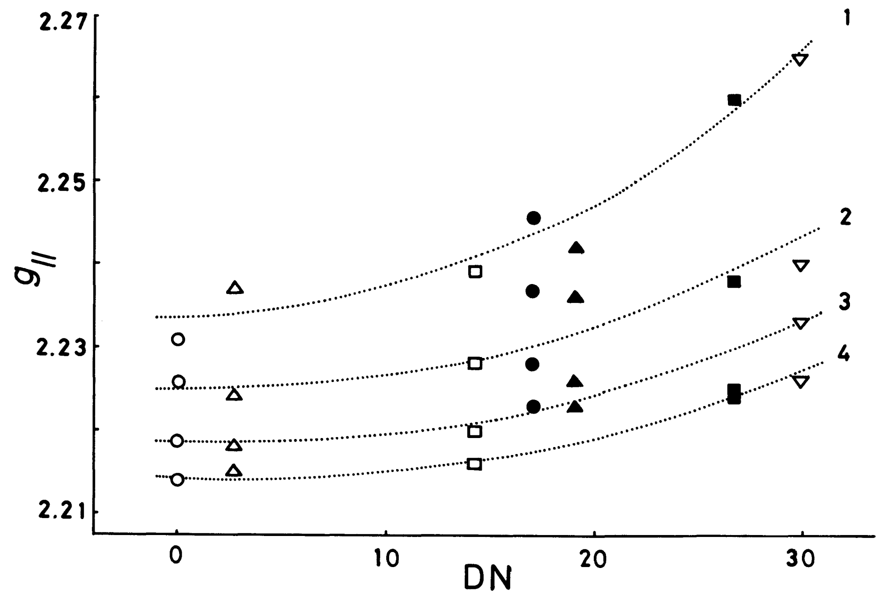

Fig. 3. Plots of $g_{/\!/}$ values against solvent Donor Number (DN) for the series of [Cu(tmen)(dike)]$^+$ complexes.

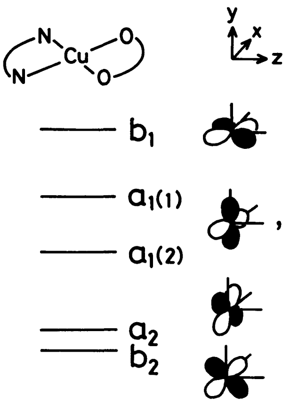

Fig. 4. Structure, coordinate system, and expected d-orbital pattern for [Cu(diam)(dike)]$^+$.

appears more familiar, with z axis perpendicular to the geometrical chelate plane but no longer being the twofold axis. The mixed chelate complex [Cu(diam)(dike)]$^+$ used to be approximated, for convenience, to have D_{4h} symmetry indistinguishing N–N and O–O donor sets.[1] In the present paper, we use the strict C_{2v} representations particularly for the purpose of explaining the solvent effect observed in this study.

Work is in progress towards acquiring single crystal electronic spectral data on [Cu(diam)(dike)]$^+$ that we can use for sequencing the d-orbitals split under the C_{2v} crystal field. As yet, we have to make the most reasonable estimates for the orbital energies. The ground state is undoubtedly B_1 with d_{xz} orbital singly occupied. The d_{xy} (a_2) and d_{yz} (b_2) orbitals would have similar energies; they correspond to the e_g orbitals in the D_{4h} approximation. The remaining d_{z^2} and $d_{x^2-y^2}$ (a_1) should mix with each other under the crystal field;

$$a_1(1) = a\cdot d_{z^2} + b\cdot d_{x^2-y^2} \tag{1}$$

$$a_1(2) = b\cdot d_{z^2} - a\cdot d_{x^2-y^2} \tag{2}$$

in which a and b are the mixing coefficients. Then the g-values are related to the excited state energies via the orbital reduction parameters k_x, k_y, and k_z by the equations;

$$g_y = 2.0023 - 2\lambda k_y{}^2\left[\frac{(\sqrt{3}a-b)^2}{E(a_1(1))} + \frac{(a+\sqrt{3}b)^2}{E(a_1(2))}\right] \tag{3}$$

$$g_x = 2.0023 - \frac{2\lambda k_x{}^2}{E(d_{xy})}. \tag{4}$$

$$g_z = 2.0023 - \frac{2\lambda k_z{}^2}{E(d_{yz})} \tag{5}$$

where λ is the spin-orbit coupling constant (-828 cm^{-1}). For the present purpose, however, it suffices to note that the spin-orbit coupling between the ground B_1 term and excited A_1 terms should include contributions from both d_{z^2} and $d_{x^2-y^2}$ orbitals. This is the major consequence of lowering the symmetry from approximate D_{4h} to the more precise C_{2v} (z axis in chelate plane). Under a condition that $\sqrt{3}a=b$ or $a=-\sqrt{3}b$, the expression for g_y is reduced to the one involving the energy of "$d_{z^2-x^2}$" orbital, which is equivalent to the results of $C_{2v}(x)$ treatment.[7,8] Since the precise symmetry of the crystal field in [Cu(diam)(dike)]$^+$ is unknown, we leave the mixing coefficients a and b as undetermined parameters.

According to the above model, the most likely energy sequence of the d-orbitals in [Cu(diam)(dike)]$^+$ is $d_{xz} > a_1(1)$, $a_1(2) \gtrsim d_{yz} \approx d_{xy}$ and the three g-values are expected to follow the order; $g_y > g_x \approx g_z$. Comparison with actual ESR signals, which are nearly of axial type, indicates that $g_y = g_{\parallel}$. The dependences of $g_{\parallel}$ values on ligand basicity and on solvent can now be explained in terms of changes in $E(a_1(1))$ and/or $E(a_1(2))$ in the expression for g_y.

Interpretation of Substituent and Solvent Effects on the $g_{\parallel}$ Values. Figure 5(A) illustrates how the d-orbital energies of $[Cu(tmen)(dike)]^+$ complexes are affected by increasing the basicity of dike ligand. Most notable change is a rise in b_1 orbital (d_{xz}) energy since the orbital lobes are directed towards the ligand. This should bring about an increase in both $E(a_1(1))$ and $E(a_1(2))$ and consequently a decrease in the $g_{\parallel}$ value, following Eq. 3. If pK_a of the β-diketones are linearly related to the energy terms as in the case of $[Cu(dike)_2]$ complexes,⁶⁾ the $g_{\parallel}$ values would be inversely proportional to the pK_a as long as crystal field model is appropriate. The relationships demonstrated in Fig. 2 can be reasonably taken as the inverse proportionality and lend support to the above model.

Figure 5(B) illustrates how the d-orbital energies of $[Cu(diam)(dike)]^+$ are affected upon coordination of solvent molecules (S) along the y axis, bringing about the solvent effect on the $g_{\parallel}$ values. To simplify the discussion, the mixing coefficients a and b in Eqs. 1 and 2 are assumed to be 1 and 0, respectively (mixing is negligibly small). Then the expression for g_y is reduced to the following.

$$g_y = 2.0023 - 2\lambda k_y{}^2\left[\frac{3}{E(d_{z^2})}+\frac{1}{E(d_{x^2-y^2})}\right] \qquad (6)$$

The d_{z^2} orbital is placed above $d_{x^2-y^2}$ in the Figure since it has some "in-plane" lobal character, though not directed to the donor atoms. At any rate, it should be noted that the primary effect of coordination of the solvent is to increase the energy of $d_{x^2-y^2}$ orbital. The d_{z^2} orbital would also rise and, as an overall effect, the decreased $E(a_1)$ terms should yield larger $g_{\parallel}$ values. Degree of the changes in energy is dependent on coordinating ability of the solvent, for which DN can be a reasonable measure. Thus the plots of $g_{\parallel}$ values vs. DN of solvents, shown in Fig. 3, follow the relationship in Eq. 3.

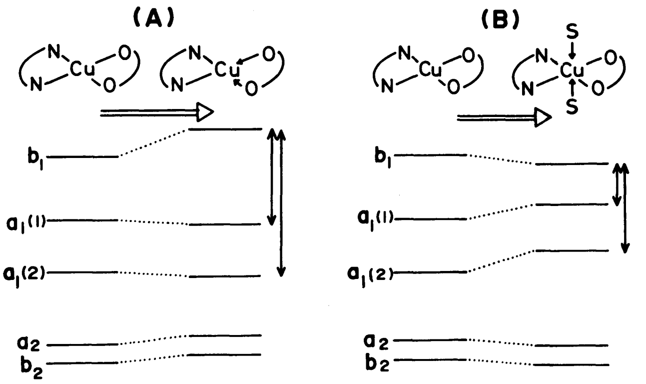

Fig. 5. The efffects of varying the substituents of dike ligand (A) and of changing the solvent (B) on the relative energies of d-orbitals in $[Cu(diam)(dike)]^+$. Horizontal arrow shows increase in the ligand basicity (O→ in A) or the degree of solvation (S→ in B), i.e., the coordination power of dike ligand or the solvent molecules increases from left to right. Vertical arrows indicate the energy terms which appear in the $g_{\parallel}$ expression.

ESR parameters of $[Cu(dike)_2]$ have been extensively investigated by other workers.⁶,⁹,¹⁰⁾ In most of these studies, an MO scheme has been favorably employed. Solvent-dependency of the ESR parameters of these complexes was particularly difficult to explain, since under D_{4h} symmetry the spin-orbit coupling relates $g_{\parallel}$ to the energy difference between $d_{x^2-y^2}$ and d_{xy}, both of which have only the in-plane lobal component. Effect of axial coordination was interpreted as an indirect effect on the energy of the highest $d_{x^2-y^2}$ orbital and/or on bonding characters in the complexes.

In contrast, the present model explains the solvent effect as a direct consequence of coordination. There may seem to be little inadequacy in D_{4h} approximation for the present CuN_2O_2 chelate complexes at first, but recognizing the fact that the lowering symmetry results in mixing of in-plane and axial d-orbitals along x, y, and z axes is important in the explanation of the remarkable solvent effect, both on the ESR parameters and on electronic spectra.

Comparison with Absorption Spectral Data. Finally, the information from the ESR spectroscopy is to be compared to the electronic spectral data obtained previously. The energies for solution absorption

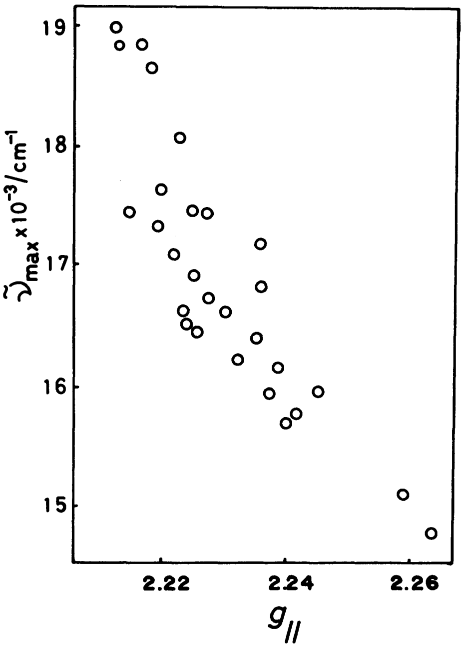

Fig. 6. Correlation between the energies of absorption spectral maxima ($\tilde{\nu}_{max}$) and ESR $g_{\parallel}$ values for the series of $[Cu(tmen)(dike)]^+$ complexes in solution.

spectral maxima are plotted against $g_{/\!/}$ values in Fig. 6. The 28 data points (the series of four complexes $[Cu(tmen)(dike)]^+$ in seven solvents) fall in a region on the plot that suggests the overall linear relationship between $\tilde{\nu}_{max}$ and $g_{/\!/}$. It is clear at least that the d–d band observed in the visible region for solutions consists of $B_1 \rightarrow A_1$ transition(s). Due to the remarkable solvatochromism, the visible band at around 550 nm used to be arbitrarily assigned to $B_{1g} \rightarrow E_g$ transition under D_{4h} symmetry, which appeared to be most affected by changing degrees in solvation, despite the fact that the energy of this transition may well extend into the ultraviolet region.[11] Precise band assignment is not possible until absorption spectrum of a single crystal has been analyzed but in the meantime the C_{2v} crystal field model seems to adequately explain both absorption spectral and ESR spectral properties of $[Cu(diam)(dike)]^+$ series.

This work was partially supported by a Grant-in-Aid for Scientific Research No. 59430009 from the Ministry of Education, Science and Culture. The authors would like to thank Dr. Makoto Chikira of Chuo University for helpful discussion.

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11) The electronic absorption spectra of $[Cu(diam)(dike)]ClO_4$ in organic solvents typically contain one visible band and a noticeable shoulder (390—400 nm) at the foot of intense ultraviolet absorption. If an estimated value for g_x of 2.03 and one for k_x^2 of 0.5[7] are used to calculate the energy of d_{xy} orbital, it follows that the corresponding transition should appear around 340 nm.