the splittings of ligand-field bands as observed in our study. General features of these assignments performed in the present study in terms of T_d symmetry are in a good agreement with those for the ordinary tetrahedral nickel complexes.[15] The symmetry descent to D_2 makes the energy level diagram more complex for the nickel ion than for other metal ions treated in this work. This is due to the splitting of the ground state $T_1(T_d)$ into B_1, B_2, and B_3 levels (D_2). In reference to the crystal structure reported by Cotton, *et al.*,[4] the point-charge model shown in Figure 1 may be employed to evaluate the energy level diagram as a function of angle ω, where the dihedral angle 2α was simply assumed to be constant ($2\alpha = 94°$). Upon consulting the energy level diagram thus evaluated (Figure 9), the B_3 level becomes the ground state for the dihedral angle greater than 60°. Both B_1 and B_2 levels from $T_1(F)$ lie rather close to the ground state B_3, and transitions from these levels to higher excited states at ordinary temperature may be expected. If we stick to the above assignments in the T_d approximation, the lower energy band (6000–8000 cm^{-1}) and the higher energy ones (11,000–15,000 cm^{-1}) need to be referred to the group of transitions in the following manner, respectively: $A_1 \leftarrow B_1$, $A_1 \leftarrow B_2$, and $A_1 \leftarrow B_3$; $B_3(P) \leftarrow B_2$, $B_3(P) \leftarrow B_1$, $B_1(P) \leftarrow B_2$, $B_2(P) \leftarrow B_1$, $B_2(P) \leftarrow B_3$, and $B_1(P) \leftarrow B_3$. It could be possible to find out some energy relations from Figure 9 which are in a relatively good agreement with the experimental data as far as their trends are concerned; adequacy of such assignments may not be explained in a clear-cut manner at present. A satisfactory assignment and explanation for these ligand-field bands wait further study.

Vibrational Spectra.—In the ordinary infrared region, a strong band appearing in the 1600-cm^{-1} range was assigned to the skeletal stretching mode of the pyrrole rings as suggested previously.[2] Although this band is sensitive to metal coordination relative to other absorption bands appearing in the NaCl region, the spectral shift of this band to lower frequency upon metal coordination is quite small as shown in Figure 10. This small spectral shift may be attributed to the ligand nature as described in our previous paper,[2] and its magnitude with respect to metal species for each ligand treated in this and previous studies follows the sequence in an increasing order: $\mathrm{Cu} < \mathrm{Ni} \lesssim \mathrm{Co}$. This order has been reversed only for the 3,3′,4,4′-tetramethyldipyrromethene complexes. Thus, the absence of bulky substituents at positions 5 and 5′ would give some significant change in the nature of coordinate bonds. Such a sudden change in coordination behavior was not detected in the corresponding ligand field spectra.

[15] A. B. P. Lever, "Inorganic Electronic Spectroscopy," American Elsevier, New York, N. Y., 1968, Chapter 9.

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Transition Metal Complexes of Pyrrole Pigments. V.[1] An Electron Spin Resonance Study of Copper(II)–Dipyrromethene Complexes

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The six copper(II)–dipyrromethene complexes were investigated by means of esr spectroscopy to provide necessary information on the behavior of d electrons under the ligand field of D_2 symmetry. The measurements were carried out in xylene–benzene at −150, 122°, and room temperature. As the dihedral angle between the chelate rings (2ω) in one molecule decreases, the observed $g_\perp$ and $g_\parallel$ values decrease concomitantly. This correlation provides an evidence for the increase of orbital excitation energies with the distortion from tetrahedron toward square planarity in coordination geometry. Such distortion also results in an increase of d-electron delocalization as the 2ω–$\lambda_0/\lambda_{\mathrm{eff}}$ correlation indicates. In reference to the spin-Hamiltonian parameters obtained for both ^{63}Cu hyperfine interaction and ^{14}N superhyperfine interaction, the coordinate bond was concluded to gain greater σ-bonding character with the decrease of the dihedral angle 2ω. These hyperfine splitting terms as well as the experimental g values for bis(3,3′,4,4′-tetramethyldipyrromethenato)copper(II) seem to indicate that the dihedral angle 2ω would be less than that predicted on the basis of ligand-field transition energies (63°).

Introduction

The analysis of ligand-field bands for the transition metal complexes of porphyrins has not been successful, because these bands generally overlap with the $\pi \rightarrow \pi^*$ bands due to the highly conjugated porphyrin system. In a close approximation to the state of affairs existing in the porphyrin complexes as far as the nature of their coordinate bonds is concerned, various dipyrromethene complexes have been chosen for study and investigated by means of electronic and vibrational spectroscopy.[1,2]

In the meantime, Elder and Penfold[3] determined the structure of bis(3,3′,5,5′-tetramethyl-4,4′-dicarbethoxydipyrromethenato)copper(II), in which the molecule possesses approximately D_2 symmetry with the dihedral angle between the chelate rings of 68°. The energy level diagram for the copper d electrons was evaluated in our previous work by means of point-charge ligand-field model, where the dihedral angle between the ligand planes was varied.[1] We then analyzed the ligand-field spectra by referring to the energy level diagram as well as to the above crystal structural information and postulated that the dihedral angle between the chelate

[1] Part IV: Y. Murakami, Y. Matsuda, and K. Sakata, *Inorg. Chem.*, **10**, 1728 (1971).

[2] Y. Murakami and K. Sakata, *Inorg. Chim. Acta*, **2**, 273 (1968).

[3] M. Elder and B. R. Penfold, *J. Chem. Soc. A*, 2556 (1969).

TABLE I

SPIN-HAMILTONIAN PARAMETERS FOR SOME COPPER(II)–DIPYRROMETHENE COMPLEXES[f]

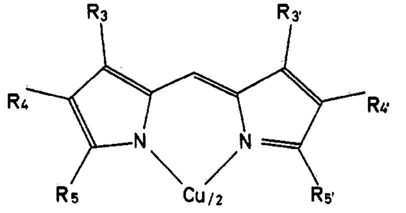
Complex	$g_\parallel$[a]	$g_\perp$[b]	g_z^0(calcd)	g_x^0(calcd)	g_y^0(calcd)	$g_\parallel$(calcd)	$g_\perp$(calcd)	$\bar{g}$[c]	$10^4 \times \lvert A_\parallel^{Cu}\rvert$,[a] cm^{-1}	$10^4 \times \lvert \bar{A}^{Cu}\rvert$, cm^{-1}	$10^4 \times \lvert A_\parallel^{N}\rvert$,[a] cm^{-1}	$10^4 \times \lvert A_\perp^{N}\rvert$,[a] cm^{-1}	2ω,[e] deg
I	2.224	2.039	2.356	2.125	2.067	2.404	2.130	2.113	154	58.6,[c] 55.6[d]	11.2	13.1	63
II	2.248	2.050				2.379	2.132	2.132	136	56.1,[c] ...	9.8	11.2	63
III	2.245	2.057				2.388	2.132	2.132	136	56.2,[c] ...	9.8	11.2	63
IV	2.272	2.062	2.376	2.147	2.079	2.402	2.152	2.130	108	..., 82.3[d]	...	9.3	68
V	2.278	2.062				2.409	2.159	2.129	108	..., 83.1[d]	...	9.3	68
VI	2.279	2.070	2.400	2.170	2.103	2.433	2.188	2.130	103	..., ...	...	7.9	73

[a] Measured at −150° in xylene–benzene (6:4). [b] Measured at −150° in xylene–benzene (6:4); obtained by taking a center of the resonance peak holding hyperfine structure in the upper field. [c] Measured at room temperature in xylene–benzene (6:4). [d] Measured at 122° in xylene–benzene (6:4). [e] Estimated dihedral angle between the chelate rings.[1] [f] g^0 values were calculated using theoretical excitation energies derived from the point-charge model; both $g_\parallel$(calcd) and $g_\perp$(calcd) values were evaluated using experimental excitation energies.

rings would vary from 63 to 73° as the substitutions in the 5,5′ positions change from two hydrogens to two bulky phenyl groups. As also approved by the point-charge calculation, the square-planar coordination attains the largest ligand-field stabilization for d^9 configuration. The ground state is increasingly destabilized as the coordination geometry deviates from planarity toward tetrahedral. Accordingly, it became interesting to investigate the nature of coordinate bonds under the influence of ligand field distorted from the stable square-planar coordination.

Bates, *et al.*,[4] studied the paramagnetic resonance of bis(5,5′-dibromodipyrromethenato)copper(II) in its single crystalline form. Their resonance spectrum showed no resolved hyperfine structure from the copper nuclear spin. Although they attributed the lack of hyperfine splittings to a small admixture of $4p_z$ orbital with the $3d_{xy}$ ground state in a tetrahedral ligand field, this is most likely due to the insufficient magnetic dilution.

In the present work, the six copper(II)–dipyrromethene complexes (I–VI)[5] were investigated by means of electron spin resonance spectroscopy to provide some further information on the behavior of d electrons under the distorted ligand field produced in these pyrrole pigment complexes. Another purpose of this study was to find out the correlation between the nature of coordinate bonds and the degree of distortion from tetrahedral coordination.



I, $R_3 = R_{3'} = R_4 = R_{4'} = CH_3$, $R_5 = R_{5'} = H$

II, $R_3 = R_{3'} = R_5 = CH_3$, $R_4 = R_{4'} = R_{5'} = H$

III, $R_3 = R_4 = R_5 = CH_3$, $R_{3'} = R_{4'} = R_{5'} = H$

IV, $R_3 = R_{3'} = R_5 = R_{5'} = CH_3$, $R_4 = R_{4'} = H$

V, $R_3 = R_{3'} = R_4 = R_{4'} = R_5 = R_{5'} = CH_3$

VI, $R_3 = R_{3'} = R_4 = R_{4'} = H$, $R_5 = R_{5'} = C_6H_5$

Experimental Section

Materials.—Preparation of the copper(II)–dipyrromethene complexes employed in this work has been described in our previous papers.[1,2]

Esr Measurements.—The esr spectra were recorded on a JEOL JES-ME-3X X-band spectrometer equipped with a 100-kHz field modulation unit. All samples were measured in xylene–benzene (6:4) at −150, 122°, and room temperature, the concentration of copper complexes being maintained in a range of 1×10^{-4} *M*. The glasses obtained in the lower temperature experiments (−150°) in benzene did not provide well-resolved spectra, due to the lack of homogeneity. The manganese ion diffused thermally into magnesium oxide was employed to establish the standard reference signals for measurements. The maximum possible error for the reported *g* values is less than ±0.0001, and those for $A_\parallel^{Cu}$ values and other coupling constants in Table I are not more than $\pm 0.5 \times 10^{-4}$ and $\pm 0.05 \times 10^{-4}$ cm^{-1}, respectively.

Results

Xylene–Benzene Solutions at Room and Higher Temperatures.—Some representative esr spectra measured at 122° and room temperature are shown together in Figure 1. At room temperature, each of the spectra for I, II, and III consists of four resonance peaks. Since these hyperfine splittings caused by the interaction with the copper atom are distorted in their shapes from the complete symmetry due to insufficient motional narrowing, the evaluated *g* values were not equivalent to those calculated by $(g_\parallel + 2g_\perp)/3$ based on the data at low temperature. As the measuring temperature was raised to 122°, the single resonance peak was observed for II and III. On the other hand, in the resonance measurements for I the hyperfine splitting is still retained at this temperature, although the symmetry of the band shape was improved. The reason for this averaging effect on the hyperfine interaction observed for complexes II and III is not obvious at this moment, although some intramolecular interaction would be a probable cause. The complexes IV, V, and VI demonstrated a single symmetric resonance peak for each even at room temperature and four hyperfine resonance peaks as temperature was lowered below −50°. Although a spectral behavior similar to that at room temperature was observed at 122° for VI, a family of four resonance bands was detected for each of the remaining two complexes, IV and V, at this elevated temperature. The following spectral observations for the latter complexes (IV and V) seem to indicate that the copper complexes of some other nature are formed at elevated temperatures in a reversible manner: (1) the observed *g* values are slightly smaller than the

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[4] C. A. Bates, W. S. Moore, K. J. Stanley, and K. W. H. Stevens, *Proc. Phys. Soc.*, **79**, 73 (1962).

[5] The six dipyrromethene complexes are as follows: I, bis(3,3′,4,4′-tetramethyldipyrromethenato)copper(II); II, bis(3,3′,5-trimethyldipyrromethenato)copper(II); III, bis(3,4,5-trimethyldipyrromethenato)copper(II); IV, bis(3,3′,5,5′-tetramethyldipyrromethenato)copper(II); V, bis-(3,3′,4,4′,5,5′-hexamethyldipyrromethenato)copper(II); VI, bis(5,5′-diphenyldipyrromethenato)copper(II). The above numbering system is to be adopted throughout this paper.

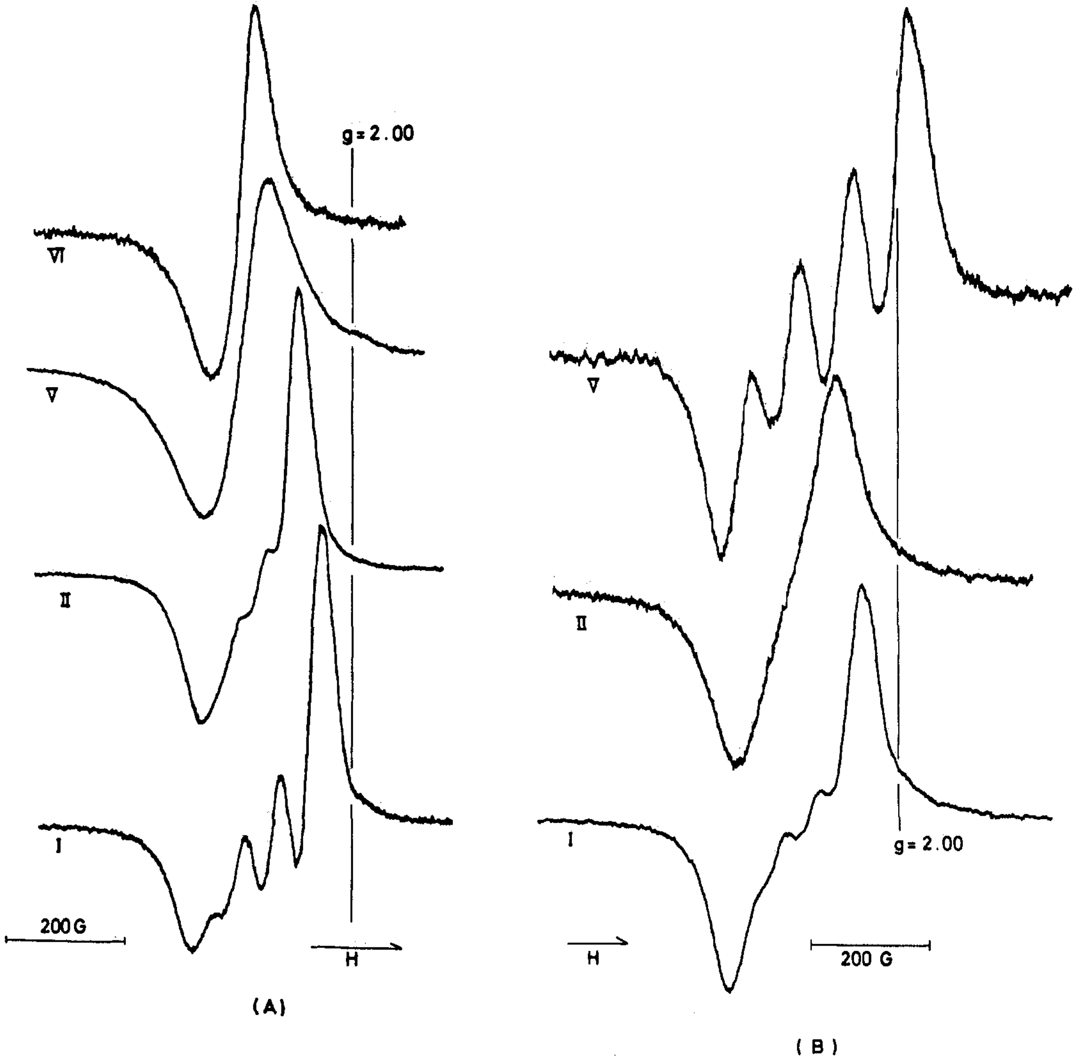

Figure 1.—Esr spectra of copper(II)–dipyrromethene complexes in xylene–benzene (6:4): (A) at room temperature; (B) at 122°. Ligands: I, 3,3′,4,4′-tetramethyldipyrromethene; II, 3,3′,5-trimethyldipyrromethene; V, 3,3′,4,4′,5,5′-hexamethyldipyrromethene; VI, 5,5′-diphenyldipyrromethene.

corresponding values at room temperature, (2) the $\bar{A}^{\mathrm{Cu}}$ values are much larger than the corresponding values estimated at lower temperatures, (3) the motional narrowing is already sufficient at room temperature, and (4) the hyperfine splittings observed at 122° disappeared at approximately 50° as temperature decreased and only single resonance peak was detected; this phenomenon was found to occur in a reversible manner.

Xylene–Benzene Solutions at Low Temperature.—The esr spectra measured at $-150°$ are shown in Figure 2 for some representative complexes. These resonance spectra are of anisotropic nature and consist of four almost equally spaced peaks, which may be attributed to the hyperfine interaction with the copper atom ($I = {}^3/_2$) and are observed in the $g_\parallel$ positions. In addition, the lower field peak in the $g_\parallel$ position for complexes I, II, and III has a superhyperfine structure due to four equivalent nitrogen donor atoms. In the $g_\perp$ positions, the sharp hyperfine structure, due to the interaction with the copper atom as well as with the nitrogen nuclei, was observed for all the metal complexes with the exception of VI and consists of over ten lines. These hyperfine structures are not well resolved as observed in the $g_\parallel$ positions.

Discussion

g Values.—In accordance with the X-ray diffraction study on bis(3,3′,5,5′-tetramethyl-4,4′-dicarbethoxydipyrromethenato)copper(II), the molecule has a D_2 symmetry property around the central metal atom. The schematic representation of the molecular structure for a copper(II)–dipyrromethene complex in general can be drawn as shown in Figure 1 of our preceding paper.[1] By employing the point-charge model which was established in this figure, the energy levels for 3d electrons were evaluated previously by varying a dihedral angle between the two chelate rings (2ω). Analysis of the ligand-field bands with the aid of this energy level diagram indicated the variation of the dihedral angle, which was brought about by change of the 5,5′ substituents, may be expected in a range: $60° \lesssim 2\omega \lesssim 75°$. The d-electron wave functions for the ground state B_1 (d_{xy}) and the excited states may be represented as

$$\langle \mathrm{B}_1| = (1/\sqrt{2})(\langle 2| - \langle \overline{2}|) \tag{1}$$

$$\langle \mathrm{B}_2| = (1/\sqrt{2})(\langle 1| - \langle \overline{1}|) \tag{2}$$

$$\langle \mathrm{B}_3| = (1/\sqrt{2})(\langle 1| + \langle \overline{1}|) \tag{3}$$

$$\langle \mathrm{A}| = (\alpha/\sqrt{2})(\langle 2| + \langle \overline{2}|) + (1 - \alpha^2)^{1/2}\langle 0| \tag{4}$$

$$\langle \mathrm{A}'| = (\beta/\sqrt{2})(\langle 2| + \langle \overline{2}|) + (1 - \beta^2)^{1/2}\langle 0| \tag{5}$$

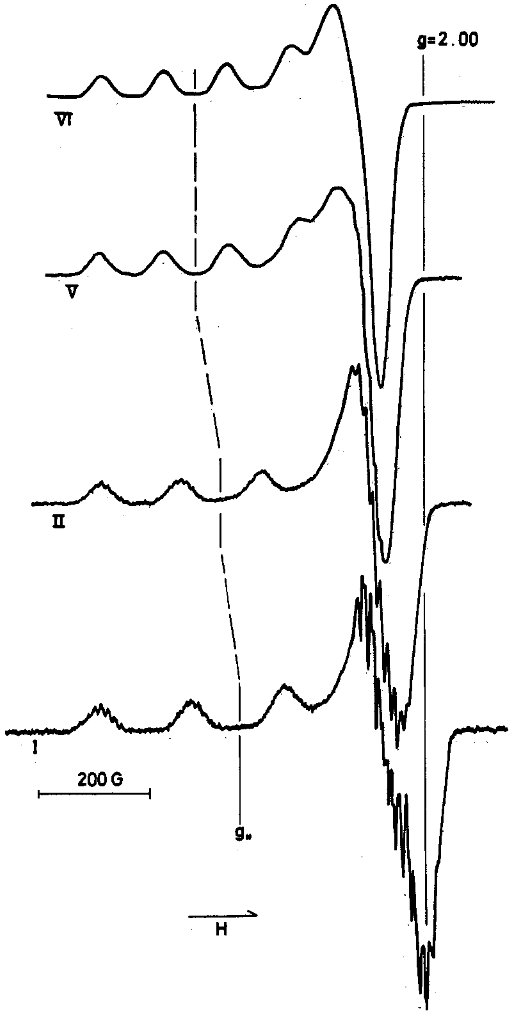

Figure 2.—Esr spectra of copper(II)-dipyrromethene complexes in xylene-benzene (6:4) at −150°. Ligands: I, 3,3′,4,4′-tetramethyldipyrromethene; II, 3,3′,5-trimethyldipyrromethene; V, 3,3′,4,4′,5,5′-hexamethyldipyrromethene; VI, 5,5′-diphenyldipyrromethene.

where

$$\alpha^2 + \beta^2 = {}^1/_2$$

For 60° $\lesssim 2\omega \lesssim$ 80°, the spin-orbit coupling constant λ_0 is much smaller than the orbital excitation energies (ΔE). Thus, the first-order perturbation can be applied to our system for evaluation of Δg values

$$\Delta g_z = g_z - g_0 = -16\lambda_0(\alpha^2/\Delta E_{\mathrm{A}} + \beta^2/\Delta E_{\mathrm{A}'}) \quad (6)$$

$$\Delta g_x = g_x - g_0 = -2\lambda_0/\Delta E_{\mathrm{B}_2} \quad (7)$$

$$\Delta g_y = g_y - g_0 = -2\lambda_0/\Delta E_{\mathrm{B}_3} \quad (8)$$

where the ΔE's are orbital excitation energies to the levels suffixed to them, the B_1 level being the ground state. The calculated Δg curves based on the energy level diagram reported in our previous paper[1] are shown as a function of the dihedral angle 2ω in Figure 3, along with the plots of experimental $\Delta g_\parallel$ and $\Delta g_\perp$ values for the present complexes. This figure also includes the plots of $\Delta g_\parallel$ and $\Delta g_\perp$ values which were evaluated by the aid of experimental excitation energies obtained from the corresponding ligand-field spectra,[1] assumptions being $\Delta E_{\mathrm{A}} = \Delta E_{\mathrm{A}'}$ and $\Delta E_{\mathrm{B}_2} = \Delta E_{\mathrm{B}_3}$. The observed g value increases as the corresponding ΔE, evaluated from the ligand-field spectra, decreases. These experimental trends may well be explained by the relationships 6–8. On the other hand, all the g values obtained experimentally are always smaller than the corresponding calculated g values as can be seen in Table I. Since we adopted a spin-orbit coupling constant in the free ion state for the evaluation of g values, the discrepancy between the observed and the calculated g values is apparently attributed to the practical decrease of $|\lambda|$ value in the complexes. The effective λ values (λ_{eff}) for the present complexes can be evaluated by the aid of eq 6–8 provided that the same experimental ΔE value is used for each set of calculated and observed g values. Then, the following relation is derived

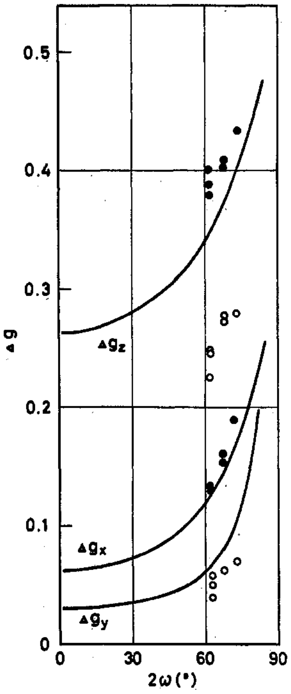

Figure 3.—The correlations between Δg values and dihedral angle (2ω). Solid lines indicate the theoretical curves calculated on the basis of a point-charge ligand-field model. Open circles refer to the experimental $\Delta g_\parallel$ (upper family) and $\Delta g_\perp$ values (lower family), while solid circles refer to the calculated $\Delta g_\parallel$ (upper family) and $\Delta g_\perp$ values (lower family) by using experimental orbital excitation energies.

$$\lambda_0/\lambda_{\mathrm{eff}} = \Delta g_{\mathrm{calcd}}/\Delta g_{\mathrm{obsd}} \quad (9)$$

The ratio $\lambda_0/\lambda_{\mathrm{eff}}$ may provide a reasonable measure for d-electron delocalization through coordinate bonding. In other words, the greater this ratio is, the more the covalency of coordinate bonds is attained. As can be seen in Table II, the $\lambda_0/\lambda_{\mathrm{eff}}$ value is greater than the

TABLE II

ANALYTICAL DATA EVALUATED IN CONNECTION WITH SPIN-HAMILTONIAN PARAMETERS

Complex	$\Delta g_{\mathrm{calcd}}/\Delta g_{\mathrm{obsd}}$ $\parallel$	$\perp$	$10^4P(-\kappa - {}^4/_7)$, cm^{-1}	$10^4P\Delta g_\parallel$, cm^{-1}	$10^2 f_s$
I	1.80	3.33	−241	87	2.48
II	1.52	2.64	−232	96	2.12
III	1.58	2.32	−231	95	2.12
IV	1.47	2.45	−214	106	1.8
V	1.47	2.56	−216	108	1.8
VI	1.55	2.69	−211	108	1.5

corresponding $\lambda_0/\lambda_{\parallel\mathrm{eff}}$. Thus, the B_2 and B_3 levels seem to secure a greater delocalization effect than the A levels. Furthermore, as the correlation between the dihedral angle and the $\lambda_0/\lambda_{\mathrm{eff}}$ value indicates, the departure from the tetrahedron toward the square planarity in coordination geometry gives greater delocalization.[6] The g value for complex I is much smaller than expected from the molecular geometry based on the ligand-field bands. This fact, therefore, suggests that the dihedral angle would be practically smaller than 63° for this complex.

The more satisfactory elucidation of the correlation[7] between covalency of coordinate bonds and g values in terms of molecular orbital language is now in progress in our laboratories and will appear in the forthcoming paper.

Hyperfine Coupling Constants.—The hyperfine interaction with the copper nucleus becomes increasingly favored as the dihedral angle between ligand planes gets smaller. This state of affairs is evident as seen in Table I. The hyperfine coupling constant in the $g_{\parallel}$ direction can be expressed approximately by

$$A_{\parallel}^{\mathrm{Cu}} \approx P(-\kappa - {}^{4}/_{7} + \Delta g_{\parallel}) \qquad (10)$$

where

$$P = 2g_{\mathrm{N}}\beta_0\beta_{\mathrm{N}}\langle r^{-3}\rangle$$

The κ is the isotropic Fermi-contact term for the copper atom and was assigned to be 0.43 for the free ion;[8,9] β_0 and β_{N} are the Bohr and nuclear magnetons, and g_{N} is the nuclear g factor. P was estimated to be 388×10^{-4} cm^{-1}.[10] The estimated isotropic term $P(-\kappa - {}^{4}/_{7})$ by the aid of eq 10 and the anisotropic $P\Delta g_{\parallel}$ values are listed in Table II for the six complexes.

An increase of the dihedral angle 2ω results in the decrease of isotropic term and the concomitant increase of anisotropic term. As the distortion of the coordination geometry proceeds toward planarity, the s character of the odd d electron and consequently the σ-bonding strength of the coordinate bonds increase. These anisotropic and isotropic terms listed in Table II suggest that the smaller dihedral angle would be plausible for complex I than expected from its ligand-field spectrum.

Superhyperfine Coupling Constants.—The coupling constants for the superhyperfine interaction with the nitrogen donor atoms in both $g_{\parallel}$ and $g_{\perp}$ directions are limited in a range $(8\text{–}14) \times 10^{-4}$ cm^{-1}. The resonance spectra for IV–VI are not resolved enough to determine $A_{\parallel}^{\mathrm{N}}$ values. For the rest of the complexes, both $A_{\parallel}^{\mathrm{N}}$ and $A_{\perp}^{\mathrm{N}}$ were evaluated as shown in Table I and the former was found to be less than the corresponding latter value.

The isotropic nitrogen splitting parameter due to the 2s contribution is represented

$$A^{\mathrm{N}} = (16/3)\pi\gamma_{\mathrm{N}}\beta_0\beta_{\mathrm{N}}f_{\mathrm{s}}|\rho(0)|^2 \qquad (11)$$

where f_{s} is the effective fraction of unpaired spin in a nitrogen 2s orbital and $|\rho(0)|^2$ is the 2s electron density at the nucleus of the nitrogen atom; γ_{N} is the gyromagnetic ratio of the ^{14}N nucleus. Each $A_{\parallel}^{\mathrm{N}}$ value obtained for I–III is not so much different in its magnitude from the corresponding $A_{\perp}^{\mathrm{N}}$. Thus, we may employ the $A_{\perp}^{\mathrm{N}}$ value as the approximate A^{N} value for our present discussion. Using $\gamma_{\mathrm{N}} = 0.404$ and $|\rho(0)|^2 = 33.4 \times 10^{24}$ cm^{-3},[11] we evaluated f_{s} values as listed in Table II. Since σ covalency of the coordinate bonds in general increases with the increase of s character of the donor orbital, the coordinate bonds gain greater σ-bonding character as the dihedral angle 2ω is reduced.

As understood from the data on $A_{\parallel}^{\mathrm{N}}$ and $A_{\perp}^{\mathrm{N}}$ summarized in Table I, these values suddenly increase by removing the second methyl group from the 5,5′ positions of the dipyrromethene moiety (as going from either II or III to I). This fact seems to indicate that the dihedral angle 2ω would be less than that predicted on the basis of ligand-field transition energies,[1] in conformity with the prediction derived from the investigation of the hyperfine interaction described above.

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[6] A correlation of spin–orbit coupling constants between the free ion value and the effective value for a complex has been put forward as $\lambda_{\mathrm{eff}} \approx 0.75\lambda_0$ for the square-planar copper complex: W. Schneider and P. Baccini, *Helv. Chim. Acta*, **52**, 1955 (1969).

[7] The d-electron delocalization through coordinate bonding was discussed here in terms of an effective spin–orbit coupling interaction based on the point-charge model. Since the present analysis does not include σ-bonding and π-bonding interaction through coordinate bond formation, the present discussion has rather limited scope.

[8] A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc., Ser. A*, **230**, 206 (1951).

[9] D. Kivelson and R. Neiman, *J. Chem. Phys.*, **35**, 149 (1961).

[10] B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).

[11] A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 35 (1958).