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## Transition Metal Complexes of Pyrrole Pigments. IV.<sup>1</sup> Electronic and Vibrational Spectra of Cobalt(II), Nickel(II), and Copper(II) Complexes of Some Substituted Dipyrromethenes

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Received November 16, 1970

The cobalt(II), nickel(II), and copper(II) complexes of 3,3',5-trimethyl-, 3,3',4,4'-tetramethyl-, and 5,5'-diphenyldipyrromethene were prepared and investigated by means of electronic and vibrational spectroscopy. The energy level diagrams for metal d electrons were evaluated in terms of a point-charge ligand-field model as a function of the dihedral angle between the ligand planes ( $2\omega$ ) in  $D_2$  symmetry. Upon reviewing the ligand-field spectra for the copper complexes of both present and previous studies, the ligand-field band appearing in the 9000–13,000-cm<sup>-1</sup> range was found to shift to lower energy as the bulkiness of 5,5' substituents increased: 3,3',4,4'-tetramethyl- (I)  $\sim$  3,3',5-trimethyl- (II)  $\sim$  3,4,5-trimethyl- (III)  $>$  3,3',5,5'-tetramethyl- (IV)  $\sim$  3,3',4,4',5,5'-hexamethyl- (V)  $>$  5,5'-diphenyl- (VI). From the point-charge calculation, the ligand-field bands appearing in the visible region were assigned to  $B_2 \leftarrow B_1$ ,  $B_3 \leftarrow B_1$ ,  $A \leftarrow B_1$ , and  $A' \leftarrow B_1$  transitions in an increasing order of energy, and the dihedral angle  $2\omega$  was predicted to vary in a range 63–73°. Meanwhile, variation of the 5,5' substituents in their bulkiness did not result in any remarkable change in the ligand-field transition energies for the cobalt complexes. Under the assumption of  $D_2$  symmetry, the ligand-field bands in the 7000–10,000-cm<sup>-1</sup> range were assigned to the transitions  $B_1(F) \leftarrow A$ ,  $B_2(F) \leftarrow A$ , and  $B_3(F) \leftarrow A$  while those in the 12,000–17,000-cm<sup>-1</sup> range were attributed to  $B_1(P) \leftarrow A$ ,  $B_2(P) \leftarrow A$ , and  $B_3(P) \leftarrow A$  transitions in an increasing order of energy. The lower energy ligand-field band (6000–8000 cm<sup>-1</sup>) for the nickel complexes was found to shift to lower energy as the bulkiness of 5,5' substituents increased. The complexity of the energy level diagram of the nickel complexes is due to the splitting of the ground state  $T_1$  ( $T_d$ ) into  $B_1$ ,  $B_2$ , and  $B_3$  ( $D_2$ ). Thus, a satisfactory analysis of the ligand-field bands was not performed. The skeletal stretching mode of the pyrrole rings in the 1600-cm<sup>-1</sup> range provided some additional information on the nature of the coordinate bond.

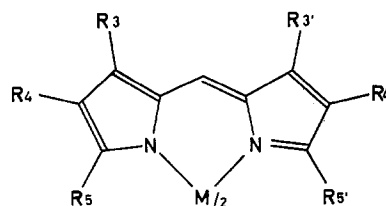
### Introduction

In our previous study on the dipyrromethene complexes,<sup>2</sup> the structural properties of cobalt(II), nickel(II), and copper(II) complexes of 3,4,5-trimethyl-, 3,3',5,5'-tetramethyl-, and 3,3',4,4',5,5'-hexamethyl-dipyrromethene were investigated by means of electronic and vibrational spectroscopy. The results seem to indicate that the copper complexes assume the tetragonally distorted tetrahedral configuration, while the nickel and cobalt complexes are approximately tetrahedral. In addition, the removal of the 5-methyl group of the dipyrromethene moiety in the copper complexes allows a twisting toward planarity.

A recent X-ray diffraction study by Elder and Penfold<sup>3</sup> revealed the stereochemistry of coordination for bis(3,3',5,5'-tetramethyl-4,4'-dicarboxy-dipyrromethenato)copper(II). The molecule was shown to possess distorted  $D_2$  symmetry with the dihedral angle between the chelate rings of 68°. Another single-crystal X-ray diffraction method has been applied by Cotton, DeBoer, and Pipal<sup>4</sup> to the structural determination of bis(3,3',5,5'-tetramethyldipyrromethenato)nickel(II). As a result, the molecule was shown to have an approximately  $D_2$  structure, in which the dihedral angle between the least-squares planes formed by the two ligands is 76.3°.

Since the steric repulsion between substituent groups at the 5,5' positions on one ligand and those on the other has much to do with the stereochemistry of coordination as the above crystallographic data indicate, the cobalt(II), nickel(II), and copper(II) complexes of three different dipyrromethenes with substituents of

various degrees of bulkiness in the 5,5' positions, as shown in I, II, and VI, were prepared and investigated



I,  $R_3 = R_3' = R_4 = R_4' = \text{CH}_3$ ,  $R_5 = R_5' = \text{H}$   
 II,  $R_3 = R_3' = R_5 = \text{CH}_3$ ,  $R_4 = R_4' = R_5' = \text{H}$   
 VI,  $R_3 = R_3' = R_4 = R_4' = \text{H}$ ,  $R_5 = R_5' = \text{C}_6\text{H}_5$

in the present work by means of electronic and vibrational spectroscopy. The energy level diagrams for metal d electrons were evaluated by means of point-charge ligand-field model, in which the dihedral angle between the ligand planes was varied. These energy diagrams as well as the crystal structural data reported by the two research groups were employed to postulate the plausible molecular structures for the present complexes.

### Experimental Section

**3,3',5-Trimethyldipyrromethene.**—A 1.0-g sample of 3-methyl-2-formylpyrrole<sup>5</sup> dissolved in 40 ml of dry ethyl ether was added dropwise at room temperature in 1 hr into a mixture of 60 ml of dry ethyl ether and 1.0 g of 2,4-dimethylpyrrole<sup>6</sup> with stirring while HCl gas was bubbled through the reaction mixture. After being allowed to stand for 1 hr at room temperature, the reddish orange crystals were separated from the mixture and recrystallized from methanol; yield 1.8 g (88%). This hydrochloride was converted to the free base through neutralization with aqueous ammonia; mp 74.5–75.5° dec.

**3,3',4,4'-Tetramethyldipyrromethene.**—A mixture of 3,4-dimethylpyrrole<sup>5</sup> (310 mg), 3,4-dimethyl-2-formylpyrrole<sup>5</sup> (460 mg), and dry ethyl ether (40 ml) was added dropwise with stirring

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(4) F. A. Cotton, B. G. DeBoer, and J. R. Pipal, *Inorg. Chem.*, **9**, 783 (1970).

(5) G. M. Badger, R. L. N. Harris, and R. A. Jones, *Aust. J. Chem.*, **17**, 1022 (1964).

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into 40 ml of dry ethyl ether which was maintained under nitrogen atmosphere and at approximately  $-15^{\circ}$ . During the course of addition, HCl gas diluted with dry nitrogen gas was continuously introduced into the reaction mixture. The reddish precipitates were separated from the mixture and recrystallized from ethanol-chloroform, giving reddish needlelike crystals; yield 0.72 g (93%). This hydrochloride was converted to the free base by adding aqueous NaOH solution into its aqueous solution; mp  $103.5-105.5^{\circ}$  dec.

**5,5'-Diphenyldipyrromethene.**—2-Formyl-5-phenylpyrrole was prepared from  $\alpha$ -phenylpyrrole by referring to the procedure employed for the formylation of 3,5-diphenylpyrrole.<sup>7,8</sup> A 520-mg sample of 2-formyl-5-phenylpyrrole dissolved in 100 ml of dry ethyl ether was added dropwise with stirring in 1 hr at room temperature into a mixture of 430 mg of 2-phenylpyrrole<sup>9</sup> and 100 ml of dry ethyl ether. During this procedure, HCl gas was continuously bubbled through the reaction mixture. Then, this reaction mixture was allowed to stand for 1 hr at room temperature. Violet needlelike crystals of the dipyrromethene hydrochloride were recovered and washed with 50 ml of dry ethyl ether; yield 950 mg (95%). This material was dissolved in chloroform, neutralized with triethylamine, and then washed with water. The solid material, which was recovered by evaporating the solution to dryness, was recrystallized from acetone-petroleum ether (bp  $40-60^{\circ}$ ) to obtain the free base; mp  $161-162^{\circ}$  dec.

**3,3',5-Trimethyldipyrromethene Complexes.**—Bis(3,3',5-trimethyldipyrromethenato)cobalt(II) was prepared by addition of aqueous ammonia in a mixture of the dipyrromethene hydrochloride in ethanol and cobalt chloride hexahydrate in water, followed by heating at  $80^{\circ}$  for 2 min. Crystalline solid was recovered from the cooled mixture, and then recrystallized from chloroform-ethanol, giving bluish green crystals. *Anal.*<sup>10</sup> Calcd for  $C_{24}H_{26}N_4Co$ : C, 67.12; H, 6.10; N, 13.05. Found: C, 66.88; H, 6.00; N, 13.08.

Bis(3,3',5-trimethyldipyrromethenato)nickel(II) was synthesized and recrystallized in a manner similar to that described for the corresponding cobalt complex (nickel chloride hexahydrate was employed as a metal salt), yielding green crystals. *Anal.* Calcd for  $C_{24}H_{26}N_4Ni$ : C, 67.16; H, 6.11; N, 13.06. Found: C, 67.47; H, 6.21; N, 13.35.

Bis(3,3',5-trimethyldipyrromethenato)copper(II) was prepared from the dipyrromethene hydrochloride and copper chloride dihydrate in a manner similar to those described above and recrystallized from *n*-hexane, giving bluish green crystals. *Anal.* Calcd for  $C_{24}H_{26}N_4Cu$ : C, 66.41; H, 6.04; N, 12.91. Found: C, 66.28; H, 6.10; N, 12.81.

**3,3',4,4'-Tetramethyldipyrromethene Complexes.**—Bis(3,3',4,4'-tetramethyldipyrromethenato)cobalt(II) was prepared by the method similar to that described above for the cobalt(II) complex, giving bluish green crystals. Since the observed values of elemental analysis were not in satisfactory agreement with the calculated ones, purification of the complex has been attempted by means of repeated recrystallization from a wide variety of solvents as well as column chromatographic separation. Both methods, however, failed to give satisfactory results. The mass spectroscopic analysis<sup>11</sup> of the product indicated the predominant abundance of the desired complex. Thus, this product containing a minor impurity was used to obtain a qualitative ligand-field spectrum.

Bis(3,3',4,4'-tetramethyldipyrromethenato)nickel(II) was obtained in a manner similar to those described above for the nickel complex, giving green crystals. *Anal.* Calcd for  $C_{26}H_{30}N_4Ni$ : C, 68.29; H, 6.61; N, 12.25. Found: C, 68.03; H, 6.72; N, 12.13.

Bis(3,3',4,4'-tetramethyldipyrromethenato)copper(II) was prepared through the procedure similar to that employed for the above copper complex and recrystallized from chloroform-ethanol, giving green crystals. *Anal.* Calcd for  $C_{26}H_{30}N_4Cu$ : C, 67.58; H, 6.54; N, 12.13. Found: Co, 67.73; H, 6.63; N, 11.99.

**5,5'-Diphenyldipyrromethene Complexes.**—Bis(5,5'-diphenyl-

dipyrromethenato)cobalt(II) was obtained by refluxing a mixture of the dipyrromethene free base and cobalt acetate hexahydrate in ethanol for 2 hr. Crystalline solid was separated from the cooled mixture and recrystallized from chloroform-ethanol, giving green crystals. *Anal.* Calcd for  $C_{42}H_{30}N_4Co$ : C, 77.65; H, 4.65; N, 8.63. Found: C, 77.45; H, 4.71; N, 8.46.

Bis(5,5'-diphenyldipyrromethenato)nickel(II) was prepared in a manner similar to that described for the corresponding cobalt complex (nickel acetate hexahydrate was used as a metal salt), giving olive green crystals. *Anal.* Calcd for  $C_{42}H_{30}N_4Ni$ : C, 77.67; H, 4.66; N, 8.63. Found: C, 77.03; H, 4.67; N, 8.45.

Bis(5,5'-diphenyldipyrromethenato)copper(II) was synthesized and purified in a manner as described for the corresponding cobalt and nickel complexes (copper acetate monohydrate was utilized as a metal salt), giving olive green crystals. *Anal.* Calcd for  $C_{42}H_{30}N_4Cu$ : C, 77.10; H, 4.62; N, 8.57. Found: C, 76.56; H, 4.61; N, 8.53.

**Spectral Measurements.**—Near-ultraviolet, visible, and near-infrared spectra in chloroform were recorded on a Hitachi Model EPS-2 spectrophotometer at room temperature. Infrared spectra were measured with a JASCO Model DS-403G grating spectrophotometer at room temperature by means of a Nujol mull technique.

## Results and Discussion

**Calculation of Ligand-Field Splittings.**—In reference to the crystal structural data reported on bis(3,3',5,5'-tetramethyl-4,4'-dicarbethoxydipyrromethenato)copper(II)<sup>3</sup> and bis(3,3',5,5'-tetramethyldipyrromethenato)nickel(II),<sup>4</sup> the point-charge model was established as shown in Figure 1 to evaluate the energy levels

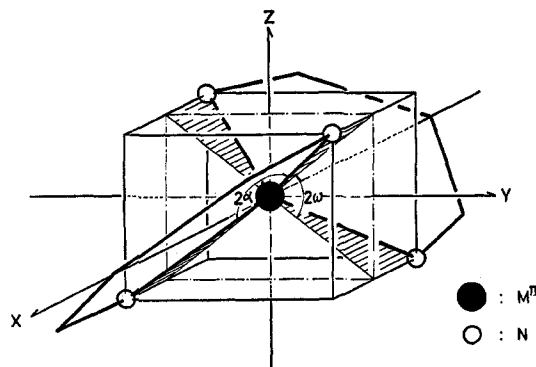


Figure 1.—Schematic representation of the point-charge model:  $2\alpha$ , the bond angle involving the metal atom within each chelate ring;  $2\omega$ , the dihedral angle between two chelate rings.

as a function of angle  $\omega$ , where  $2\alpha$  and  $2\omega$  are defined as a bond angle involving the copper atom within each chelate ring and a dihedral angle between two chelate rings, respectively. Angle  $2\alpha$  was considered to be constant in the calculation under the assumption that the 5,5' substituents do not generate any detectable distortion effect on the metal chelate rings; the reported  $2\alpha$  values for single crystals of the copper and nickel complexes<sup>3,4</sup> were employed for the calculation of energy levels of the corresponding metal complexes.

The ligand-field potential, which arises from the arrangement of negative charges of magnitude  $Ze_i$  placed at four points in space about the central metal ion at a distance  $a$ , may be represented by eq 1.<sup>12</sup> The

(12) See for example: H. Watanabe, "Operator Methods in Ligand Field Theory," Prentice-Hall, Englewood Cliffs, N. J., 1966, Chapter 4; W. Low, "Paramagnetic Resonance in Solids," Academic Press, New York N. Y., 1960.

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(9) T. Severin and B. Brück, *Chem. Ber.*, **98**, 3847 (1965).

(10) All the elemental analyses were performed at the Microanalysis Center of Kyushu University.

(11) Measurement of the mass spectrum was carried out by a JEOL JMS-01SG mass spectrometer of the Research Institute of Yoshitomi Pharmaceutical Co., Ltd., whose courtesy is greatly acknowledged.

TABLE I  
 LIGAND-FIELD BANDS FOR DIPYRRROMETHENE COMPLEXES AND THEIR ASSIGNMENTS<sup>a, b</sup>

| Metal            | Ligand <sup>c</sup> |                  |                  |                  |                  |                                | Assignment   |                                    |
|------------------|---------------------|------------------|------------------|------------------|------------------|--------------------------------|--|------------------------------------|
|                  | I                   | II               | III              | IV               | V                | VI                             | $D_2$  | $T_d$                              |
| Co <sup>II</sup> | 6,200 sh            | 7,800 sh (29)    | 6,600 sh (9.2)   | 6,700 sh (24)    | 6,300 sh (12)    | 7,800 sh (13)                  | $B_1 \leftarrow A$<br>$B_2 \leftarrow A$<br>$B_3 \leftarrow A$ | ${}^4T_1(F) \leftarrow {}^4A_2(F)$ |
|                  | 8,470               | 8,770 sh (41)    | 8,500 sh (34)    | 8,200 sh (53)    | 8,100 sh (50)    | 8,800 sh (17)                  |  |                                    |
|                  | 10,200 sh           | 10,200 (55)      | 10,400 (59)      | 10,000 (67)      | 10,300 (76)      | 10,000 (26)                    |  |                                    |
|                  | 13,300              | 13,500 (266)     | 13,400 (314)     | 13,200 (336)     | 13,000 (482)     | 12,300 (639)                   | $B_1 \leftarrow A$<br>$B_2 \leftarrow A$<br>$B_3 \leftarrow A$ | ${}^4T_1(P) \leftarrow {}^4A_2(F)$ |
|                  | 14,500              | 14,500 (265)     | 14,500 (305)     | 14,400 (304)     | 14,000 (410)     | 13,300 (499)                   |  |                                    |
|                  | 16,500 sh           | 16,500 (1240)    | 16,300 (1420)    | 16,900 sh (1885) | 16,300 sh (2700) | 16,700 sh (20,400)             |  |                                    |
|                  |                     |                  | 17,500 (2080)    |                  | 16,900 sh (3480) |                                |  |                                    |
|                  |                     |                  |                  | 17,700 sh (4220) |                  |                                |  |                                    |
| Ni <sup>II</sup> | 8,120 (13)          | 7,300 (24)       | 7,140 (21)       | 6,300 (26)       | 6,300 (34)       | 6,100 (17)                     |  | ${}^2A_2(F) \leftarrow {}^2T_1(F)$ |
|                  |                     | 12,300 sh (60)   | 11,600 sh (73)   | 11,000 sh (48)   | 7,700 sh (24)    |                                |  |                                    |
|                  | 11,200 (82)         | 13,000 (361)     | 13,200 (453)     | 13,200 (453)     | 12,700 (574)     | 11,800 (759)                   |  |                                    |
|                  | 12,930 (143)        | 14,200 (338)     | 14,200 (412)     | 13,850 (474)     | 13,300 (557)     | 13,300 sh (500)                |  | ${}^2T_1(P) \leftarrow {}^2T_1(F)$ |
|                  | 15,600 sh (583)     |                  |                  | 15,000 sh (225)  | 15,500 (273)     | 15,900 sh (40,500)             |  |                                    |
| Cu <sup>II</sup> | 12,750 sh (132)     | 12,600 (227)     | 12,600 (245)     | 10,900 (278)     | 10,400 (282)     | 8,850 (456)                    | $B_2, B_3 \leftarrow B_1$                                      |                                    |
|                  | 14,000 sh (165)     |                  |                  |                  |                  |                                |  |                                    |
|                  | 16,400 sh (1320)    | 17,100 sh (1750) | 17,500 sh (2210) | 16,500 sh (1550) | 16,200 sh (1930) | 14,700 (2600)<br>15,600 (2490) | $A, A' \leftarrow B_1$   |                                    |

<sup>a</sup> Band positions are expressed in wave numbers ( $\text{cm}^{-1}$ ) and molar extinction coefficients are given in parentheses after the band positions. <sup>b</sup> Measured at room temperature in chloroform. <sup>c</sup> I, 3,3',4,4'-tetramethyldipyrrromethene; II, 3,3',5-trimethyldipyrrromethene; III, 3,4,5-trimethyldipyrrromethene; IV, 3,3',5,5'-tetramethyldipyrrromethene; V, 3,3',4,4',5,5'-hexamethyldipyrrromethene; VI, 5,5'-diphenyldipyrrromethene.

$$V(r, \theta, \phi) = \sum_{n=0}^{\infty} \sum_{m=n}^{-n} A_{nm} r^n Y_{nm}(\theta, \phi) \quad (1)$$

$$A_{nm} = \frac{4\pi}{2n+1} (-1)^m \sum_{i=1}^4 Z e_i \alpha^{-(n+1)} Y_{n-m}(\theta_i, \phi_i)$$

distribution of the electrons of a central metal ion in the vicinity of these point charges was neglected. The summation in eq 1 is to be carried out for  $n = 2$  and 4, because we are interested only in the 3d wave functions and the potential due to  $n = 0$  is not responsible for the splitting of energy levels derived from the same spectroscopic term. The  $Y_{nm}$  functions are spherical harmonics, in which  $\theta_i$  and  $\phi_i$  specify the angles to the four negative charges fixed in space at a specified dihedral angle  $2\omega$ ;  $r$ ,  $\theta$ , and  $\phi$  stand for the spherical coordinates to represent the location of a d electron in reference to the central metal nucleus. The spherical coordinates  $\theta_i$  and  $\phi_i$  can be related to angles  $\alpha$  and  $\omega$  by eq 2.

$$\begin{aligned} \cos \theta_i &= \sin \omega \sin \alpha \\ \sin \theta_i \cos \phi_i &= \cos \alpha \\ \sin \theta_i \sin \phi_i &= \cos \omega \sin \alpha \end{aligned} \quad (2)$$

Angle  $2\omega$  was varied in the range  $0^\circ \leq 2\omega \leq 90^\circ$ . The symmetry of coordination around the central metal atom is  $D_{2h}$  at  $2\omega = 0^\circ$ ,  $D_{2d}$  at  $2\omega = 90^\circ$ , and  $D_2$  in between. Now,  $A_{nm}$  values are represented as functions of  $\omega$  and  $\alpha$

$$A_{44} = A_{4-4} = Z(\sqrt{35\pi}/3\sqrt{2})ea^{-5} \times (\cos^4 \alpha - \cos^2 \alpha \sin^2 \alpha \cos^2 \omega + \sin^4 \alpha \cos^4 \omega)$$

$$A_{42} = A_{4-2} = Z(\sqrt{10\pi}/3)ea^{-5} \times (7 \sin^2 \alpha \sin^2 \omega - 1)(\cos^2 \alpha - \sin^2 \alpha \cos^2 \omega)$$

$$A_{40} = Z(\sqrt{\pi}/3)ea^{-5}(35 \sin^4 \alpha \sin^4 \omega - 30 \sin^2 \alpha \sin^2 \omega + 3)$$

$$A_{22} = A_{2-2} = Z(2\sqrt{6\pi}/\sqrt{5})ea^{-3}(\cos^2 \alpha - \sin^2 \alpha \cos^2 \omega)$$

$$A_{20} = Z(4\sqrt{\pi}/\sqrt{5})ea^{-3}(3 \sin^2 \alpha \sin^2 \omega - 1)$$

$$A_{4\pm 3} = A_{4\pm 1} = A_{2\pm 1} = 0$$

Each ligand-field potential term in eq 1,  $V_{nm} = r^n Y_{nm}(\theta, \phi)$ , is replaced by the equivalent operator.<sup>12</sup> The

$V_{nm}$  terms can be shown as

$$V_{44} + V_{4-4} = (3\sqrt{35}/16\sqrt{2\pi})\beta r^4(L_+^4 + L_-^4)$$

$$V_{42} + V_{4-2} = (3\sqrt{5}/16\sqrt{2\pi})\beta r^4\{[7L_z^2 - L(L+1) - 5](L_+^2 + L_-^2) + (L_+^2 + L_-^2) \times [7L_z^2 - L(L+1) - 5]\}$$

$$V_{40} = (3/16\sqrt{\pi})\beta r^4[35L_z^4 - 30L(L+1)L_z^2 + 25L_z^2 - 6L(L+1) + 3L^2(L+1)^2]$$

$$V_{22} + V_{2-2} = (\sqrt{15}/4\sqrt{2\pi})\alpha r^2(L_+^2 + L_-^2)$$

$$V_{20} = (\sqrt{5}/4\sqrt{\pi})\alpha r^2[3L_z^2 - L(L+1)]$$

where  $\bar{r}^2$  and  $\bar{r}^4$  are the average radial values of the second and fourth power of the d-orbital distance from the nucleus. In the present work, the  $\bar{r}^4/a^4$  to  $\bar{r}^2/a^2$  ratio was varied in a range 0.64–4.0 for calculations. The proportionality factors  $\alpha$  and  $\beta$  depend on the d-electron configuration and the corresponding spectroscopic term; these values needed for the present calculations are found elsewhere.<sup>12</sup> The ligand-field splitting energy is now calculated by solving the secular equation<sup>13</sup>

$$\left| \sum_{\substack{n=2,4 \\ m}} (\langle L_{zi} A_{nm} V_{nm} L_{zj} \rangle) - E \langle L_{zi} | L_{zj} \rangle \right| = 0 \quad (3)$$

where  $\langle L_{zi} |$  and  $|L_{zj} \rangle$  stand for angular momentum eigenfunctions and the matrix elements between different angular momentum states have no meaning for calculation.

**Electronic Spectra.**—The electronic spectral data for ligand-field transitions and the assignments for these absorption bands are summarized in Table I together with the data for the previously reported complexes, which were reinvestigated in this work.

(a) **Copper(II) Complexes.**—By referring to the spectral data in Table I and to the electronic spectra for the copper complexes of the present dipyrromethenes shown in Figure 2, the ligand-field effect of the substituents placed in positions 5 and 5' may be stated

(13) The numerical calculation was carried out on a Facom 230-60 electronic computer of the Computer Center of Kyushu University.

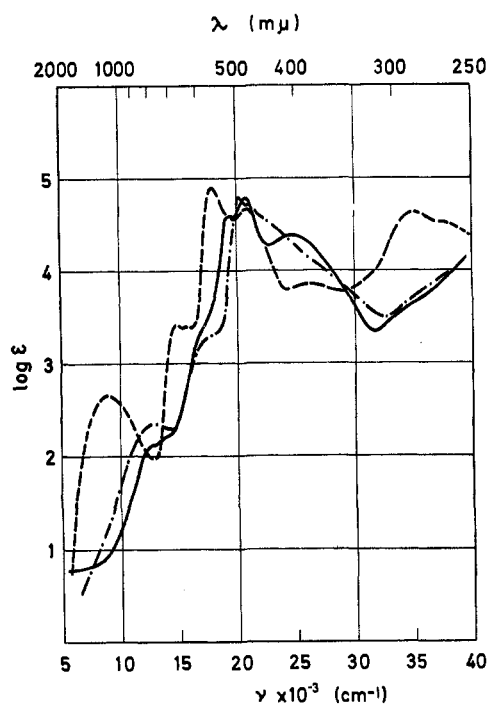


Figure 2.—Electronic absorption spectra of copper(II) complexes of dipyrromethenes in chloroform at room temperature: —, 3,3',4,4'-tetramethyldipyrromethene; ---, 3,3',5-trimethyldipyrromethene; - · - · - ·, 5,5'-diphenyldipyrromethene.

in the following manner. As the bulkiness of substituents increases, the ligand-field band appearing in the lowest energy region (9000–13,000  $\text{cm}^{-1}$ ) was found to shift to lower energy: 3,3',4,4'-tetramethyl (I)  $\sim$  3,3',5-trimethyl (II)  $\sim$  3,4,5-trimethyl (III)  $>$  3,3',5,5'-tetramethyl (IV)  $\sim$  3,3',4,4',5,5'-hexamethyl (V)  $>$  5,5'-diphenyl (VI). On the other hand, the absorption intensity of this band increases as the steric disturbance due to substituents increases: I  $<$  II  $<$  III  $<$  IV  $\sim$  V  $\ll$  VI. Thus, the substituent effect on the ligand field around the copper atom was found to be greatest with phenyl groups placed at positions 5 and 5' among other groups at the same positions.

According to the X-ray diffraction study carried out for the single crystal of the 3,3',5,5'-tetramethyl-4,4'-dicarboxyldipyrromethene complex, bond angles involving the copper atom within the chelate rings are constrained by the ligand geometry to a mean value of  $97^\circ$  and the twist of the chelate rings from coplanarity is  $68^\circ$ . The energy levels were evaluated as a function of the dihedral angle  $2\omega$  by means of the point-charge model as described above. The best fit of the theoretical calculation to the experimental data was obtained for the  $\bar{r}^4/a^4$  to  $\bar{r}^2/a^2$  ratio of 0.64. The energy term for the ground state is  $B_1(d_{xy})$  as seen in Figure 3. When we take  $2\omega = 68^\circ$  for the substitution of methyl groups at positions 5 and 5', the ligand-field bands appearing in the 10,000- $\text{cm}^{-1}$  region and in the 16,000- $\text{cm}^{-1}$  region for the complexes of 3,3',5,5'-tetramethyldipyrromethene and of 3,3',4,4',5,5'-hexamethyldipyrromethene may be assigned to the  $B_2, B_3 \leftarrow B_1$  transition and the A,  $A' \leftarrow B_1$  transition, respectively. Substitution of only one methyl group in either position 5 or 5' shifted the corresponding absorption bands to the 12,000- $\text{cm}^{-1}$  range and to the 17,000- $\text{cm}^{-1}$  range, respectively, as seen for the 3,4,5- and 3,3',5-trimethyldipyr-

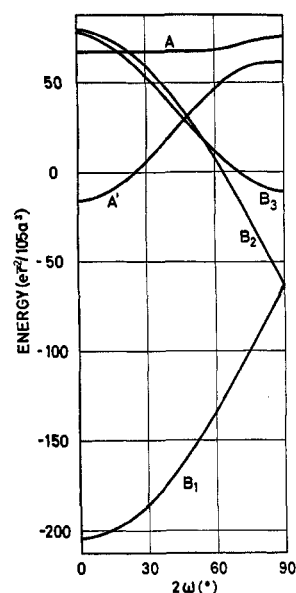


Figure 3.—Splitting of the  ${}^2D$  term of  $d^9$  electronic configuration in the ligand field of  $D_2$  symmetry as a function of the dihedral angle  $2\omega$ . Relative energies on the vertical axis are shown in the units of  $e^2/105a^3$ . The bond angle involving the copper atom within each chelate ring is fixed at  $97^\circ$  and the  $\bar{r}^4/a^4$  to  $\bar{r}^2/a^2$  ratio is set at 0.64 for this diagram.

romethene complexes. By employing the above reference for the  $\omega$  and transition energy relation, the dihedral angle  $2\omega$  was estimated to be approximately  $63^\circ$ . Since the 3,3',4,4'-tetramethyldipyrromethene complex demonstrated the ligand-field bands at 12,750  $\text{cm}^{-1}$  and in the 14,000–16,000  $\text{cm}^{-1}$  range, substitution with one methyl group at either position 5 or 5' does not result in any drastic distortion in molecular geometry. Meanwhile, introduction of phenyl groups to positions 5 and 5' resulted in remarkable shifts of these ligand-field bands to lower energy. By referring to the energy diagram shown in Figure 3, the dihedral angle was estimated to be about  $73^\circ$ . The calculated ligand-field energies for transitions  $B_2 \leftarrow B_1$ ,  $B_3 \leftarrow B_1$ ,  $A \leftarrow B_1$ , and  $A' \leftarrow B_1$  in an increasing order of energy are shown in Figure 4 for the representative complexes from this and previous studies. The ground-state energy level  $B_1$  is increasingly destabilized as the coordination symmetry distorted from planarity to tetrahedron through the increase of dihedral angle from 0 to  $90^\circ$  as seen in Figure 3.<sup>14</sup>

(b) **Cobalt(II) Complexes.**—Variation of the 5,5' substituents in their bulkiness does not result in any remarkable change in the ligand-field transitions as can be seen in Figure 5 and in Table I. Thus, these dipyrromethene complexes seem to be nearly in the state of tetrahedral coordination around the cobalt atom as described in our previous paper,<sup>2</sup> so that the bulky substituents placed in positions 5 and 5' do not generate any profound steric disturbance which may result in a change of coordination stereochemistry. Only one comment can be made for their absorption intensities. In the case of the 5,5'-diphenyldipyrromethene complex, the bands appearing in the 7000–10,000- $\text{cm}^{-1}$  range were found to be less intense while those in the

(14) The present discussion is based on the assumption that the dihedral angle ( $2\omega$ ) retains the same value in solution as that in the solid state. Although this assumption is not warranted because of the lack of spectral data for the solid state, these authors believe that the errors in the predicted dihedral angles should not be significant.

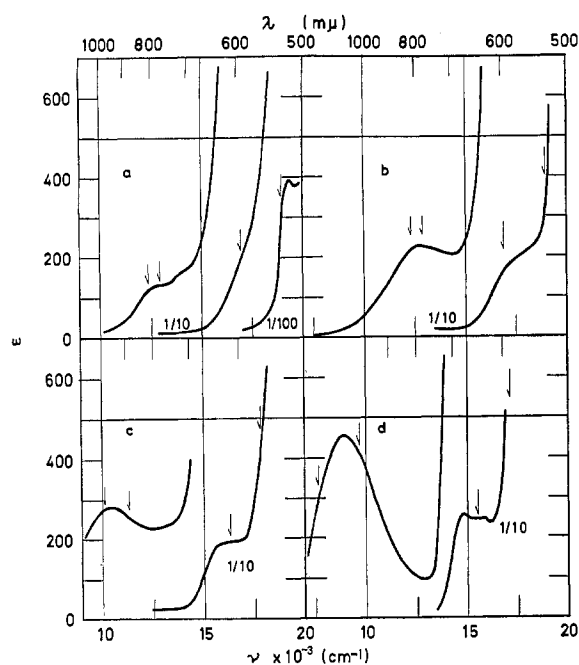


Figure 4.—Ligand-field spectra for some copper(II)-dipyrromethene complexes in chloroform at room temperature: (a) bis(3,3',4,4'-tetramethyldipyrromethenato)copper(II); (b) bis(3,3',5-trimethyldipyrromethenato)copper(II); (c) bis(3,3',4,4',-5,5'-hexamethyldipyrromethenato)copper(II); (d) bis(5,5'-diphenyldipyrromethenato)copper(II). Arrows indicate the calculated ligand-field transition energies based on the energy diagram shown in Figure 3. Numbers in this figure (1/10 and 1/100) refer to the reduction factor of the absorption intensity.

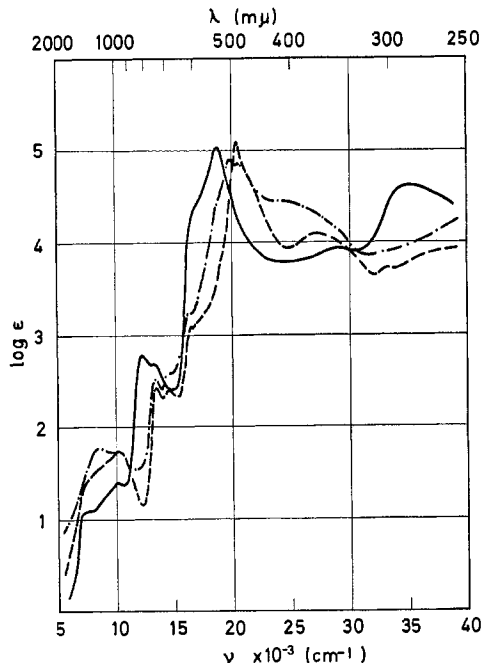


Figure 5.—Electronic absorption spectra of cobalt(II) complexes of dipyrromethenes in chloroform at room temperature: —, 3,3',4,4'-tetramethyldipyrromethane; ----, 3,3',5-trimethyldipyrromethane; — · —, 5,5'-diphenyldipyrromethane. The absorption spectrum for bis(3,3',4,4'-tetramethyldipyrromethenato)cobalt(II) is not strictly quantitative due to the reason given in the Experimental Section.

12,000–17,000-cm<sup>-1</sup> range were more intense than those corresponding bands for other complexes as can be seen in Table I. Since the single-crystal X-ray diffraction study for any dipyrromethene complex has not

been reported so far, no definite angles of  $\alpha$  and  $\omega$  can be established. Thus, bond angles involving the cobalt atom within the chelate rings were simply assumed to be 90° for the energy level calculation by referring to the crystal structures reported for some dipyrromethene complexes of copper<sup>3</sup> and nickel.<sup>4</sup> The energy level diagram was, then, established in a manner as mentioned for the copper complexes through employment of the point-charge model. The energy minima for the ground state are attained either at  $2\omega = 0$  or 90° as seen in Figure 6. Judging from the molecular struc-

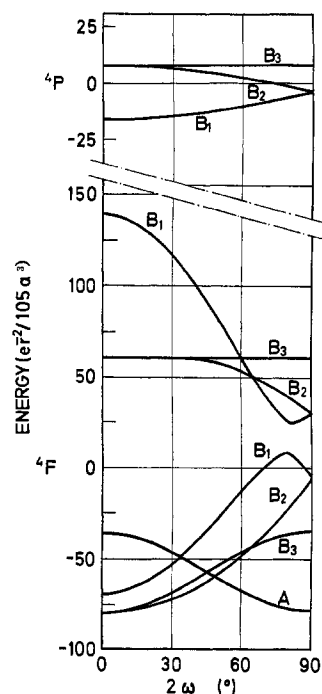


Figure 6.—Splitting of the <sup>4</sup>F and <sup>4</sup>P terms of d<sup>4</sup> electronic configuration in the ligand field of *D*<sub>3</sub> symmetry as a function of the dihedral angle  $2\omega$ . Relative energies on the vertical axis are shown in the units of  $er^2/105a^3$ . The bond angle involving the cobalt atom within each chelate ring is fixed at 90° and the  $\bar{r}^4/a^4$  to  $\bar{r}^2/a^2$  ratio is set at 1.0 for this diagram.

tures determined for some copper<sup>3</sup> and nickel<sup>4</sup> complexes, the dihedral angle  $2\omega$  is considered to be greater than 45°. The distortion from *T*<sub>d</sub> to *D*<sub>2</sub> symmetry results in the splitting of *T*<sub>1</sub> levels into *B*<sub>1</sub>, *B*<sub>2</sub>, and *B*<sub>3</sub>. As can be seen in Figure 5, there exist three bands in the 7000–10,000-cm<sup>-1</sup> range, two bands in the lower energy region, and one band in most cases in the higher energy region of the 12,000–17,000-cm<sup>-1</sup> range. These results are, therefore, consistent with the above distortion of molecular structure. Thus, the former three bands are assigned to the transitions from *A* to *B*<sub>1</sub>, *B*<sub>2</sub>, and *B*<sub>3</sub> levels derived from *T*<sub>1</sub>(<sup>4</sup>F) in *T*<sub>d</sub> symmetry, respectively, while the latter three bands are attributed to the transitions from *A* to *B*<sub>1</sub>, *B*<sub>2</sub>, and *B*<sub>3</sub> from *T*<sub>1</sub>(<sup>4</sup>P) in *T*<sub>d</sub>, respectively. This state of affairs can be seen in Figure 7, where the analysis of ligand-field bands for the 3,3',5-trimethyldipyrromethene complex is illustrated. According to the energy level diagram shown in Figure 6, the *B*<sub>1</sub> and *B*<sub>2</sub> levels are to be converged into the doubly degenerate *E* level (*D*<sub>2d</sub> symmetry) at the dihedral angle  $2\omega = 90^\circ$ . The present system is not consistent with this extreme case. In conclusion, therefore, distortion from regular tetrahedral structure seems to be signifi-

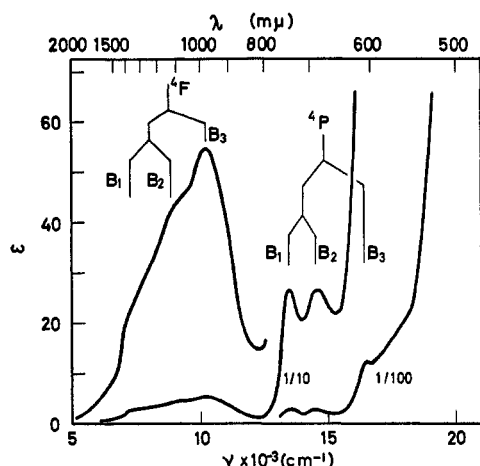


Figure 7.—Ligand-field spectrum for bis(3,3',5-trimethyldipyrrromethenato)cobalt(II) and energy correlation diagram in  $D_2$  symmetry. Numbers in this figure (1/10 and 1/100) refer to the reduction factor of the absorption intensity.

cant ( $2\omega < 90^\circ$ ) to an extent that the 5,5' substituents do not generate any detectable steric effect on the coordination stereochemistry.

(c) **Nickel Complexes.**—As can be seen in Figure 8

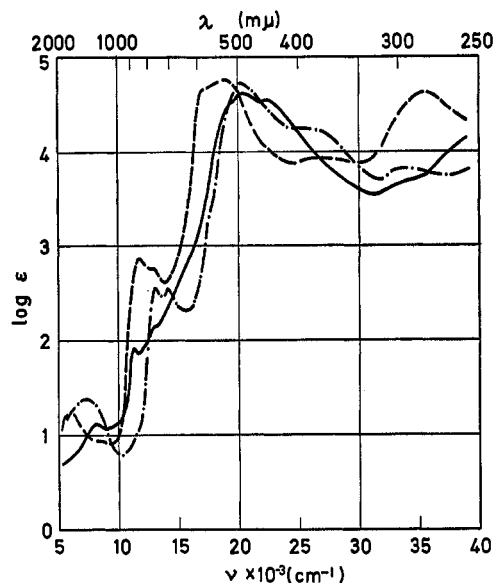


Figure 8.—Electronic absorption spectra of nickel(II) complexes of dipyrromethenes in chloroform at room temperature: —, 3,3',4,4'-tetramethyldipyrrromethane; ---, 3,3',5-trimethyldipyrrromethane; - · - ·, 5,5'-diphenyldipyrrromethane; · · · ·, free ligand.

and in Table I, the ligand-field band appearing in the lowest energy region ( $6000\text{--}8000\text{ cm}^{-1}$ ) was found to shift to lower energy in the following manner as the bulkiness of 5,5' substituents increases:  $I > II > III > IV \sim V > VI$ . On the other hand, the ligand-field bands observed in the higher energy region ( $11,000\text{--}15,000\text{ cm}^{-1}$ ) do not shift in a parallel manner. In our previous paper,<sup>2</sup> the lower energy band was assigned to the  ${}^3A_2(F) \leftarrow {}^3T_1(F)$  transition in  $T_d$  symmetry, while the group of higher energy was attributed to the  ${}^3T_1(P) \leftarrow {}^3T_1(F)$  transition in the same symmetry.

The molecular structure of the 3,3',5,5'-tetramethyldipyrrromethene complex as determined by the single-crystal X-ray diffraction study<sup>4</sup> belongs to  $D_2$  sym-

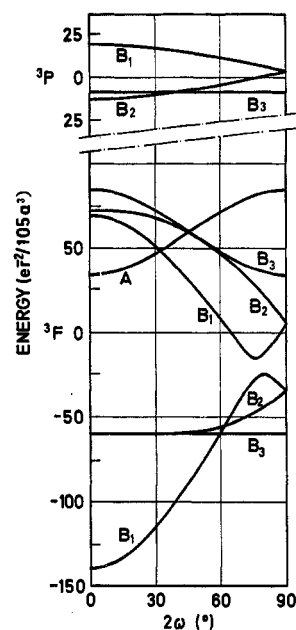


Figure 9.—Splitting of the  ${}^3F$  and  ${}^3P$  terms of  $d^8$  electronic configuration in the ligand field of  $D_2$  symmetry as a function of the dihedral angle  $2\omega$ . Relative energies on the vertical axis are shown in the units of  $e^2/r^2/105a^3$ . The bond angle involving the nickel atom within each chelate ring is fixed at  $94^\circ$  and the  $r^4/a^4$  to  $r^2/a^2$  ratio is set at 1.0 for this diagram.

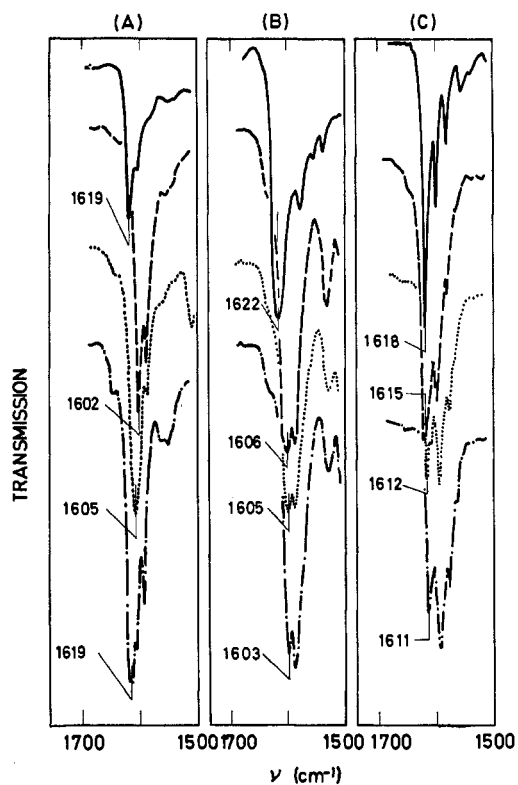


Figure 10.—Infrared spectra of bivalent metal complexes of dipyrromethenes (Nujol mull method): (A) 3,3',4,4'-tetramethyldipyrrromethene; (B) 3,3',5-trimethyldipyrrromethene; (C) 5,5'-diphenyldipyrrromethene; —, free ligand; ---, copper(II) complex; · · · ·, nickel(II) complex; - · - ·, cobalt(II) complex. Number refers to the skeletal vibrational mode of the pyrrole rings.

metry. The bond angles involving the nickel atom within the chelate rings are approximately  $94^\circ$  and the dihedral angle between the ligand planes is  $76.3^\circ$ . Therefore, distortion from  $T_d$  symmetry may result in

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.<sup>15</sup> 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.*,<sup>4</sup> the point-charge model shown in Figure 1 may be employed to evaluate the energy level diagram as a function of angle  $\omega$ , where the dihedral angle  $2\alpha$  was simply assumed to be constant ( $2\alpha = 94^\circ$ ). Upon consulting the energy level diagram thus evaluated (Figure 9), the  $B_3$  level becomes the ground state for the dihedral angle greater than  $60^\circ$ . 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  $\text{cm}^{-1}$ ) and the higher energy ones (11,000–15,000  $\text{cm}^{-1}$ ) 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  $A_1 \leftarrow B_3$ ;  $B_3(P)$

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

$\leftarrow B_2$ ,  $B_3(P) \leftarrow B_1$ ,  $B_1(P) \leftarrow B_2$ ,  $B_2(P) \leftarrow B_1$ ,  $B_2(P) \leftarrow B_3$ , 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- $\text{cm}^{-1}$  range was assigned to the skeletal stretching mode of the pyrrole rings as suggested previously.<sup>2</sup> 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,<sup>2</sup> and its magnitude with respect to metal species for each ligand treated in this and previous studies follows the sequence in an increasing order:  $\text{Cu} < \text{Ni} \lesssim \text{Co}$ . 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.

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## Transition Metal Complexes of Pyrrole Pigments. V.<sup>1</sup> An Electron Spin Resonance Study of Copper(II)-Dipyrromethene Complexes

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Received November 16, 1970

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  $-150$ ,  $122^\circ$ , and room temperature. As the dihedral angle between the chelate rings ( $2\omega$ ) 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  $2\omega - \lambda_0/\lambda_{\text{eff}}$  correlation indicates. In reference to the spin-Hamiltonian parameters obtained for both  $^{63}\text{Cu}$  hyperfine interaction and  $^{14}\text{N}$  superhyperfine interaction, the coordinate bond was concluded to gain greater  $\sigma$ -bonding character with the decrease of the dihedral angle  $2\omega$ . 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  $2\omega$  would be less than that predicted on the basis of ligand-field transition energies ( $63^\circ$ ).

### 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.<sup>1,2</sup>

In the meantime, Elder and Penfold<sup>3</sup> 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  $68^\circ$ . 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.<sup>1</sup> 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

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(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).