

# Transition-metal Complexes of Pyrrole Pigments. I. Electronic and Vibrational Spectra of Cobalt(II), Nickel(II) and Copper(II) Complexes of Some Dipyrromethenes

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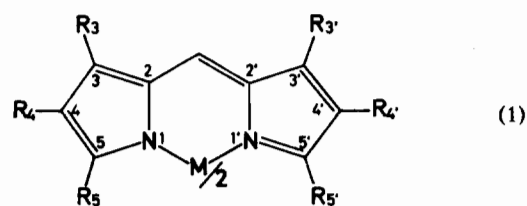
The cobalt(II), nickel(II), and copper(II) complexes of 3,4,5-trimethyl-, 3,3',5,5'-tetramethyl- and 3,3',4,4',5,5'-hexamethyldipyrromethene have been synthesized in this work and investigated by visible, near-infrared, infrared and far-infrared spectroscopy. The ligand-field bands for these metal complexes have provided valuable information on their geometry around the central metal atoms. Namely, the copper complexes assume the tetragonally distorted tetrahedral configuration while the nickel and cobalt complexes are approximately regular tetrahedral. Moreover, the removal of the 5'-methyl group of a dipyrromethene moiety in the copper complexes results in a significant structural alteration to the further flattened tetrahedron. In the far-infrared spectra, the prominent absorption peaks which can be associated with the metal-ligand stretching modes have been observed in the 400-350  $\text{cm}^{-1}$  range. In addition, strong bands appearing at  $\sim 1600 \text{ cm}^{-1}$  have been assigned to the pyrroles-skeletal stretching mode. After examination of these infrared spectral data, the strength of the coordinate bonds has been noticed to increase in the order:  $\text{Cu} < \text{Ni} \lesssim \text{Co}$ . The lowered strength of coordinate bonds for the copper complexes and the nature of coordinate bonds involved in the metal complexes of this work were discussed in connection with their stereochemistry.

## Introduction

The chemistry of porphyrins and metalloporphyrins has been extensively studied up to the present time in the light of their biological importance. In order to understand further the more detailed structural properties of metalloporphyrins and their related substances of biological significance and the nature of coordinate bonds involved therein, this series of work intends to investigate transition-metal complexes of various polynuclear pyrrole pigments by means of spectral and magnetic measurements. The present investigation initiates the work on the various metal complexes of substituted dipyrromethenes by means of electronic and vibrational spectroscopy. Porter<sup>1</sup> first dealt with some bivalent metal complexes of a

hexa-substituted dipyrromethene and precluded the possibility of forming a complex with a planar configuration because of inter-ligand repulsion between the 5- and 5'-substituents. Later, bivalent metal complexes of some dipyrromethenes were treated by Fergusson and Ramsay<sup>2</sup> and the tetrahedral configuration was assigned on the basis of ligand-field spectra, magnetic data and X-ray powder photographs. Ferguson and West<sup>3</sup> inferred the stereochemistry of nickel(II) chelates of five 4,4'- and 5,5'-substituted dipyrromethenes in the solid state, in pyridine and also in benzene in accordance with the experimental evidence of magnetic moments and ligand-field spectra: as the bulky substituents at the 5,5'-positions are lost, a complex may approach closer to a planar configuration in the solid state.

This paper reports 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'-hexamethyldipyrromethene (I) as examined by visible, near-infrared, infrared and far-infrared



a:  $\text{R}_3 = \text{R}_4 = \text{R}_5 = \text{CH}_3$ ,  $\text{R}_3' = \text{R}_4' = \text{R}_5' = \text{H}$

b:  $\text{R}_3 = \text{R}_3' = \text{R}_5 = \text{R}_5' = \text{CH}_3$ ,  $\text{R}_4 = \text{R}_4' = \text{H}$

c:  $\text{R}_3 = \text{R}_3' = \text{R}_4 = \text{R}_4' = \text{R}_5 = \text{R}_5' = \text{CH}_3$

measurements. The values for  $\Delta$ , the ligand-field strength, and  $B'$ , the Racah inter-electronic repulsion integral, have been calculated from solution spectra obtained both in chloroform and benzene.

## Experimental Section

**Spectral Measurements.** The visible and near-infrared spectra in chloroform and benzene were recorded on a Hitachi Model EPS-2 recording spectrophotometer. Some benzene-solution spectra were obtained

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(1) C. R. Porter, *J. Chem. Soc.*, 368 (1938).

(2) J. E. Fergusson and C. A. Ramsay, *J. Chem. Soc.*, 5222 (1965).

(3) J. Ferguson and B. O. West, *J. Chem. Soc. (A)*, 1565 (1966).

from solutions heated to 48-50° in a special cell holder. Infrared spectra in the region 4000-650 cm<sup>-1</sup> were taken on a Koken Model DS-301 spectrophotometer equipped with sodium chloride optics. The KBr disk method as well as the nujol mull technique was employed throughout measurements. A Hitachi Model EFI-L grating spectrophotometer was used to obtain the spectra in the 700-200 cm<sup>-1</sup> region. For these spectra, all the samples were measured as nujol mulls sandwiched between polyethylene film.

**3,3',5,5'-Tetramethyldipyrromethene.**<sup>4</sup> The hydrochloride of this material was prepared by the method of Corwin *et al.*<sup>5</sup> It was converted to the free base by neutralization with ammonia in aqueous solution, and recrystallized from acetone: m.p. 116.8-118.2° (lit.,<sup>5,6</sup> m.p. 116-118°).

**3,3',4,4',5,5'-Hexamethyldipyrromethene.** 2,3,4-Trimethylpyrrole was prepared through the combined procedures of each described by MacDonald,<sup>7</sup> Chu *et al.*<sup>8</sup> and Treibs *et al.*<sup>9</sup> A 6-g sample of the pyrrole dissolved in 40 ml of ethyl ether was added dropwise at room temperature into a mixture of 110 ml of ethyl ether and 6 ml of formic acid which was maintained under nitrogen atmosphere. At each addition of the pyrrole solution a sufficient amount of HCl gas was introduced. After the addition was completed in 5 hr, the reaction mixture was allowed to stand for 1 hr at room temperature. Then, the dipyrromethene hydrochloride was separated from the mixture as red crystals, yield 6 g (50%). The free base was prepared by neutralization of the aqueous solution of the hydrochloride with ammonia, and recrystallized from acetone: m.p. 167.5-168.4° (decomp.) (lit.,<sup>5,10</sup> m.p. 168-169°).

**3,4,5-Trimethyldipyrromethene.**  $\alpha$ -Pyrrole aldehyde was prepared by the method of Silverstein *et al.*<sup>11</sup> A 0.90-g sample of  $\alpha$ -pyrrole aldehyde in 50 ml of ethyl ether was added dropwise into the ethereal solution (25 ml) of 1.0 g of 2,3,4-trimethylpyrrole with stirring while HCl gas was bubbled through the reaction mixture. The reddish brown crystals separated from the mixture were recrystallized from methanol, yield 1.9 g (95%). This hydrochloride was converted to the free base by addition of ammonia into its aqueous solution, and recrystallized from acetone: m.p. 87.6-89.5° (decomp.).

**3,3',5,5'-Tetramethyldipyrromethene Complexes.**<sup>12</sup> Bis(3,3',5,5'-tetramethyldipyrromethenato)copper(II) was prepared by mixing the dipyrromethene hydrochloride in ethanol with a solution of copper acetate monohydrate and ammonia in water, and recrystallized from chloroform-ether as green needles.

*Anal.*<sup>13</sup> Calcd. for C<sub>26</sub>H<sub>30</sub>N<sub>4</sub>Cu: C, 67.58; H, 6.54; N, 12.12. Found: C, 67.44; H, 6.63; N, 12.04.

Bis(3,3',5,5'-tetramethyldipyrromethenato)cobalt(II) was prepared by mixing the dipyrromethene hydrochloride in ethanol with aqueous solutions of sodium acetate and of cobalt acetate tetrahydrate, and recrystallized from chloroform-*n*-hexane as green needles.

*Anal.* Calcd. for C<sub>26</sub>H<sub>30</sub>N<sub>4</sub>Co: C, 68.26; H, 6.61; N, 12.25. Found: C, 68.12; H, 6.61; N, 12.20.

Bis(3,3',5,5'-tetramethyldipyrromethenato)nickel(II) was obtained by a technique similar to that for the cobalt(II) complex with the use of nickel acetate tetrahydrate, and recrystallized from chloroform-*n*-hexane as green needles.

*Anal.* Calcd. for C<sub>26</sub>H<sub>30</sub>N<sub>4</sub>Ni: C, 68.30; H, 6.61; N, 12.27. Found: C, 68.23; H, 6.73; N, 12.09.

**3,3',4,4',5,5'-Hexamethyldipyrromethene Complexes.** Bis(3,3',4,4',5,5'-hexamethyldipyrromethenato)copper(II) was prepared by heating a suspension of the dipyrromethene hydrochloride, copper acetate monohydrate and sodium acetate in ethanol-water. The solution was heated under reflux for 30 min. and then cooled overnight; the dark green crystals were collected and recrystallized from benzene.

*Anal.* Calcd. for C<sub>30</sub>H<sub>38</sub>N<sub>4</sub>Cu: C, 69.53; H, 7.39; N, 10.81. Found: C, 69.27; H, 7.53; N, 10.54.

Bis(3,3',4,4',5,5'-hexamethyldipyrromethenato)cobalt(II) was synthesized in a similar manner as the corresponding copper chelate by employing cobalt acetate tetrahydrate; recrystallized from benzene as green crystals.

*Anal.* Calcd. for C<sub>30</sub>H<sub>38</sub>N<sub>4</sub>Co: C, 70.16; H, 7.46; N, 10.92. Found: C, 70.11; H, 7.43; N, 11.18.

Bis(3,3',4,4',5,5'-hexamethyldipyrromethenato)nickel(II) was obtained by the method of Ferguson and West;<sup>3</sup> recrystallized from benzene as olive-green crystals.

*Anal.* Calcd. for C<sub>30</sub>H<sub>38</sub>N<sub>4</sub>Ni: C, 70.19; H, 7.46; N, 10.92. Found: C, 70.45; H, 7.51; N, 11.11.

**3,4,5-Trimethyldipyrromethene Complexes.** Bis(3,4,5-trimethyldipyrromethenato)copper(II) was prepared by heating a mixture of the dipyrromethene hydrochloride dissolved in ethanol with sodium acetate and copper acetate monohydrate in water. The solution was heated at 80° for 2 min. and then cooled overnight; the precipitated chelate was recrystallized from *n*-hexane as dark green crystals.

*Anal.* Calcd. for C<sub>24</sub>H<sub>26</sub>N<sub>4</sub>Cu: C, 66.41; H, 6.04; N, 12.91. Found: C, 66.65; H, 6.24; N, 12.83.

Bis(3,4,5-trimethyldipyrromethenato)cobalt(II) was prepared by heating a mixture of the dipyrromethene hydrochloride in ethanol with an aqueous solution of cobalt acetate tetrahydrate at 80° for 2 min. after

(13) The elemental analyses of all the metal complexes were performed at the Microanalysis Center of Kyushu University.

(4) This material was prepared by Mr. Y. Kohno of this laboratory.  
(5) A. H. Corwin and R. H. Kriebel, *J. Am. Chem. Soc.*, **63**, 1829 (1941).

(6) R. W. Guy and R. A. Jones, *Aust. J. Chem.*, **18**, 363 (1965).

(7) S. F. MacDonald, *J. Chem. Soc.*, 4176 (1952).

(8) E. J. H. Chu and T. C. Chu, *J. Org. Chem.*, **19**, 266 (1954).

(9) A. Treibs and H. Derra-Scherer, *Ann. Chem.*, **589**, 196 (1954).

(10) A. W. Johnson, I. T. Kay, E. Markham, R. Price, and K. B. Shaw, *J. Chem. Soc.*, 3416 (1959).

(11) R. M. Silverstein, E. E. Ryskiewicz, C. Willard, and R. C. Koehler, *J. Org. Chem.*, **20**, 668 (1955).

(12) These metal complexes were prepared by Mr. Y. Kohno of this laboratory.

pH of the solution was adjusted with ammonia. The mixture was then cooled overnight and precipitated chelate was recrystallized from *n*-hexane as dark green crystals.

*Anal.* Calcd. for  $C_{24}H_{26}N_4Co$ : C, 67.12; H, 6.10; N, 13.05. Found: C, 67.47; H, 6.18; N, 12.49.

Bis(3,4,5-trimethyldipyrromethenato)nickel(II) was obtained by the method similar to that for the corresponding cobalt complex with the use of nickel chloride hexahydrate; recrystallized from *n*-hexane as olive-green crystals.

*Anal.* Calcd. for  $C_{24}H_{26}N_4Ni$ : C, 67.16; H, 6.11; N, 13.06. Found: C, 67.03; H, 6.38; N, 12.93.

## Results and Discussion

*Electronic Spectra.* The electronic spectral data for ligand-field transitions and the assignments for these absorption bands are summarized in Table I, and the corresponding spectral parameters calculated on the basis of ligand field theory are listed in Tables

II and III.

(a) *Copper(II) Complexes.*  $N,N'$ -Ethylenebis(4-amino-3-penten-2-ono)copper(II) in solution has been known to assume a square-planar configuration and to demonstrate a strong ligand-field band at approximately  $18,500\text{ cm}^{-1}$  in chloroform.<sup>14</sup> The ligand-field band for the tetrachlorocuprate anion was observed at  $8500\text{ cm}^{-1}$  and the same spectrum was obtained whether it is measured in the solid state or in solution.<sup>15</sup> The X-ray analysis of  $Cs_2CuCl_4$ <sup>16</sup> has shown that the  $CuCl_4^{2-}$  complex assumes a tetragonally distorted tetrahedral configuration. Other experimental evidence to support the flattened tetrahedron for  $CuCl_4^{2-}$  was supplied by means of ultraviolet and visible spectroscopy with polarized light.<sup>17</sup> Recently, the visible spectra of the copper-doped single crystals of ZnO, in which copper ions are surrounded by slightly distorted oxygen tetrahedra, have been obtained at different temperatures.<sup>18</sup> A sharp band located at  $5807\text{ cm}^{-1}$  was observed at  $78^\circ\text{K}$ . Thus, it seems more likely that copper complexes show their ligand-field bands at around  $6000\text{ cm}^{-1}$  if the copper ion assumes tetrahedral coordination.

**Table I.** Ligand-field bands for dipyrromethene complexes and their assignments <sup>a</sup>

Metal	Ligand						Assignment
	3,3',5,5'-Tetramethyl-dipyrromethene		3,3',4,4',5,5'-Hexamethyl-dipyrromethene		3,4,5-Trimethyl-dipyrromethene		
	Chloroform	Benzene	Chloroform	Benzene	Chloroform	Benzene	
Ni <sup>II</sup>	6300 (26) 11,100 sh	6250 (24) 11,100 sh	6330 (34)		7140 (21)	7140 (20)	<sup>3</sup> T <sub>1</sub> (F)→ <sup>3</sup> A <sub>2</sub> (F)
	12,700 (574) 13,850 (474) 15,200 sh (233)	12,600 (606) 13,700 (474) 15,200 sh (212)	12,300 (791) 13,300 (557) 14,700 sh (257)	12,200 (788) <sup>b</sup> 13,300 (553) 14,300 sh (252)	11,600 sh (73) 13,200 (453) 14,200 (412)	11,600 sh (79) 13,100 (581) 14,200 (490)	<sup>3</sup> T <sub>1</sub> (F)→ <sup>3</sup> T <sub>1</sub> (P)
	8000 sh (50) 10,000 (67)	8200 sh (34) 9900 (54)	8100 sh (41) 10,300 (76)	8000 sh (100) <sup>c</sup> 10,100 (137)	7700 sh (25) 10,300 (59)	7700 sh (24) 10,300 (59)	<sup>4</sup> A <sub>2</sub> (F)→ <sup>4</sup> T <sub>1</sub> (F)
	13,200 (336) 14,400 (304) 16,700 sh (1350)	13,100 (367) 14,100 (304) 16,400 sh (1350) 17,500 sh (2220)	13,000 (482) 14,000 (410) 15,900 sh (1590) 17,200 sh (3700)	12,700 (424) <sup>c</sup> 13,800 (339) 16,100 sh (2870) 17,500 sh (4180)	13,400 (314) 14,500 (305) 16,300 sh (1420) 17,500 sh (2080)	13,600 (408) 14,600 (413) 16,500 sh (1570) 17,600 sh (2350)	<sup>4</sup> A <sub>2</sub> (F)→ <sup>4</sup> T <sub>1</sub> (P)
Cu <sup>II</sup>	(6700 sh) 10,900 (278)	(6800 sh) 10,500 (283)	(6500 sh) 10,400 (282)	(7000 sh) <sup>b</sup> 10,000 (440)	(8200 sh) 12,600 (245)	(8200 sh) 12,300 (268)	<sup>2</sup> T <sub>2</sub> → <sup>2</sup> E(?)

<sup>a</sup> Band positions are expressed in wavenumbers ( $\text{cm}^{-1}$ ) and measured at room temperature unless otherwise stated; molecular extinction coefficients are given in brackets after the band positions <sup>b</sup> Data measured at  $48.0 \pm 1.0^\circ$ . <sup>c</sup> Data measured at  $50.0 \pm 1.0^\circ$ .

**Table II.** Spectral parameters for dipyrromethene complexes in chloroform solution

Ligand	Metal	$\nu_1$ ( $\text{cm}^{-1}$ )	$\nu_2$ ( $\text{cm}^{-1}$ )	$\Delta$ ( $\text{cm}^{-1}$ )	$B'$ ( $\text{cm}^{-1}$ )	$\beta^a$
3,3',5,5'-Tetramethyldipyrromethene	Ni <sup>II</sup>	13,300	6300	3422	731	0.71
	Co <sup>II</sup>	16,000	9400	5737	546	0.56
	Cu <sup>II</sup>	—	—	10,900	—	—
3,3',4,4',5,5'-Hexamethyldipyrromethene	Ni <sup>II</sup>	12,800	6330	3428	695	0.68
	Co <sup>II</sup>	16,000	9500	5825	535	0.55
	Cu <sup>II</sup>	—	—	10,400	—	—
3,4,5-Trimethyldipyrromethene	Ni <sup>II</sup>	13,600	7100	3995	759	0.74
	Co <sup>II</sup>	16,100	9800	6083	511	0.53
	Cu <sup>II</sup>	—	—	12,600	—	—

<sup>a</sup>  $\beta = B'/B$  where B is the free-ion value: Ni<sup>II</sup>,  $1030\text{ cm}^{-1}$ ; Co<sup>II</sup>,  $967\text{ cm}^{-1}$

(14) R. L. Belford and W. A. Yeranos, *Mol. Phys.*, **6**, 121 (1963).

(15) A. van der Avoird and P. Ros, *Theor. Chim. Acta*, **4**, 13 (1966).

(16) L. Helmholz and R. F. Krüh, *J. Am. Chem. Soc.*, **74**, 1176

(1952).

(17) S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **27**, 436 (1954).

(18) R. Pappalardo, *J. Mol. Spectrosc.*, **6**, 554 (1961).

**Table III.** Spectral parameters for dipyrromethene complexes in benzene solution

Ligand	Metal	$\nu_1$ (cm <sup>-1</sup> )	$\nu_2$ (cm <sup>-1</sup> )	$\Delta$ (cm <sup>-1</sup> )	B' (cm <sup>-1</sup> )	$\beta$
3,3',5,5'-Tetramethyldipyrromethene	Ni <sup>II</sup>	13,200	6250	3392	725	0.70
	Co <sup>II</sup>	16,200	9400	5713	564	0.58
	Cu <sup>II</sup>	—	—	10,500	—	—
3,3',4,4',5,5'-Hexamethyldipyrromethene	Ni <sup>II</sup>	12,800	—	—	—	—
	Co <sup>II</sup>	16,100	9400	5725	555	0.57
	Cu <sup>II</sup>	—	—	10,000	—	—
3,4,5-Trimethyldipyrromethene	Ni <sup>II</sup>	13,500	7100	3675	723	0.70
	Co <sup>II</sup>	16,200	9800	5902	593	0.61
	Cu <sup>II</sup>	—	—	12,300	—	—

Each of the symmetrically substituted dipyrromethene-copper(II) complexes investigated in this work shows one strong ligand-field band in the 10,000-11,000 cm<sup>-1</sup> range and a shoulder at longer wavelength side of this band as shown in Figure 1.

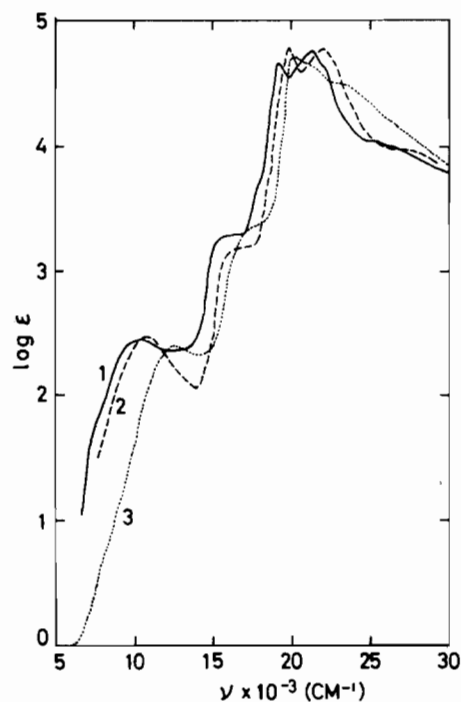


Figure 1. Electronic absorption spectra of copper(II) complexes of dipyrromethenes in chloroform: (1), 3,3',4,4',5,5'-hexamethyldipyrromethene; (2), 3,3',5,5'-tetramethyldipyrromethene; (3), 3,4,5-trimethyldipyrromethene.

Meanwhile, the asymmetrically substituted dipyrromethene-copper(II) complex, *i. e.*, bis(3,4,5-trimethyldipyrromethenato)copper(II), demonstrates its strong ligand-field band at around 12,500 cm<sup>-1</sup> and also a shoulder at longer wavelength side of this band. Thus, the ligand-field band is shifted to higher frequency by approximately 2500 cm<sup>-1</sup> upon substitution of the 5'-methyl group of the ligand moiety with a hydrogen. This result seems to indicate that the structure of the copper complex tends to approach closer to a square-planar configuration as the inter-ligand repulsion in the complex is reduced. The values for  $\Delta$  (10,000-12,500 cm<sup>-1</sup>) calculated under the assumption of a regular tetrahedral configuration

are much too large if these values are compared with those of the corresponding nickel(II) and cobalt(II) complexes of tetrahedral structure (3400-6000 cm<sup>-1</sup>). In conclusion, all the dipyrromethene-copper(II) complexes of the present study seem to assume the flattened tetrahedral structure around the metal atom.

(b) *Cobalt(II) Complexes.* The electronic spectra for the dipyrromethene-cobalt(II) complexes of the present study are quite similar in intensity and band-position to those obtained for the 3,3',5,5'-tetramethyl-4,4'-ethoxycarbonyldipyrromethene and the 5'-bromo-3,4',5-trimethyl-3',4'-diethoxycarbonyldipyrromethene complexes.<sup>2</sup> In a tetrahedral field, the bivalent cobalt may demonstrate three spin-allowed ligand-field transitions in increasing order of energies:  ${}^4A_2 \rightarrow {}^4T_2$ ,  ${}^4A_2 \rightarrow {}^4T_1(F)$ ,  ${}^4A_2 \rightarrow {}^4T_1(P)$ . The frequencies (cm<sup>-1</sup>) of these transitions are denoted here as  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  respectively in the above order, and the following relations can be derived from Tanabe and Sugano's formula.

$$\begin{aligned}\nu_1 &= \Delta \\ \nu_2 &= 1.5\Delta + 7.5B' - Q \\ \nu_3 &= 1.5\Delta + 7.5B' + Q \\ Q &= 1/2\{(0.6\Delta - 15B')^2 + 0.64\Delta^2\}^{1/2}\end{aligned}$$

where  $\Delta$  is the modulus of the ligand-field strength and  $B'$  is the effective value of the Racah inter-electronic repulsion integral. Selection of single energy values for  $\nu_2$  and  $\nu_3$  is necessarily arbitrary to a certain degree. As shown in Figure 2, each of the  $\nu_2$  bands is broad and involve at least two components. The  $\nu_3$  bands are also broad and exhibit a great deal of fine structure. The spin-orbit coupling may result in some splitting of these  $\nu_2$  and  $\nu_3$  bands as Stahl-Brada and Low<sup>19</sup> mentioned on a theoretical basis. Since the separation of the highest and lowest energy sub-bands of  $\nu_2$  and  $\nu_3$  is considerably greater than the value of  $6\lambda$ ,<sup>19</sup> even taking for  $\lambda$  the full free-ion value of 178 cm<sup>-1</sup>, the spin-orbit coupling alone can not provide reasonable account for these complicated features of the  $\nu_2$  and  $\nu_3$  bands. A satisfactory explanation for these observations waits further study, although a distortion of the tetrahedral configuration to a lower symmetry would give such complex splittings.

(19) R. Stahl-Brada and W. Low, *Phys. Rev.*, 113, 775 (1959).

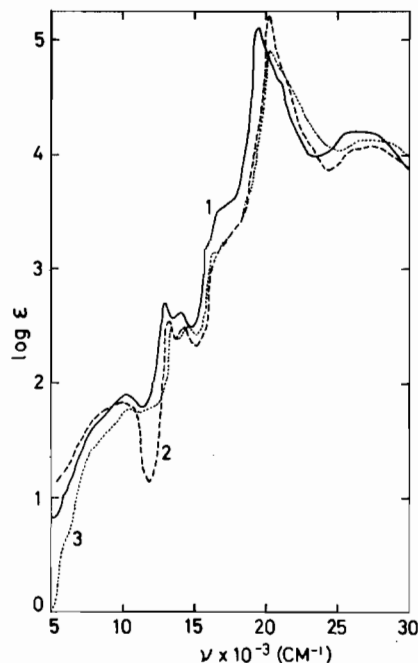


Figure 2. Electronic absorption spectra of cobalt(II) complexes of dipyrromethenes in chloroform: (1), 3,3',4,4',5,5'-hexamethyldipyrromethene; (2), 3,3',5,5'-tetramethyldipyrromethene; (3), 3,4,5-trimethyldipyrromethene.

In selecting energies for the  $\nu_2$  and  $\nu_3$  bands, the center of gravity of the total intensity was evaluated by visual estimation. Although Fergusson and Ramsay<sup>2</sup> have assigned two peaks located in the 13,000-14,000  $\text{cm}^{-1}$  and the 14,000-15,000  $\text{cm}^{-1}$  range to the  $\nu_3$  bands, this assignment can not give any reasonable value for  $B'$ .

In accordance with the above observation, the dipyrromethene-cobalt(II) complexes of the present study assume approximately a regular tetrahedral configuration around the central metal atom.

(c) *Nickel(II) Complexes.* The ligand-field spectra of the three complexes in solution are quite similar both in position and intensity to those examined by Fergusson and Ramsay<sup>2</sup> and Fergusson and West.<sup>3</sup> Since the general spectral feature of the present complexes is analogous to those of known tetrahedral nickel(II) complexes,<sup>20-23</sup> three ligand-field transitions are considered in increasing order of energies:  ${}^3T_1 \rightarrow {}^3T_2$ ,  ${}^3T_1 \rightarrow {}^3A_2$ ,  ${}^3T_1 \rightarrow {}^3T_1(P)$ . The frequencies of these transitions,  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  respectively in the above order, hold the following relations as derived from Tanabe and Sugano's matrix equation.

$$\nu_1 = -7.5B' + 0.5\Delta + Q$$

$$\nu_2 = -7.5B' + 1.5\Delta + Q$$

$$\nu_3 = 2Q$$

$$Q = 1/2\{(B' + \Delta)^2 + 16B'\Delta + 224B'^2\}^{1/2}$$

(20) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1958).

(21) F. A. Cotton and D. M. L. Goodgame, *J. Am. Chem. Soc.*, 82, 5771, 5774 (1960).

(22) F. A. Cotton, O. D. Faut and D. M. L. Goodgame, *J. Am. Chem. Soc.*, 83, 344 (1961).

(23) D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Am. Chem. Soc.*, 83, 4161 (1961).

As shown in Figure 3, the splitting of the  $\nu_3$  bands is appreciable. Thus, the center of gravity method was applied to the evaluation of the  $\nu_3$  values as employed for the corresponding cobalt complexes. The broad splitting of the  $\nu_3$  bands could be accounted for by spin-orbit coupling concept on the basis of the calculation carried out by Liehr and Ballhausen.<sup>24</sup> Nevertheless, a satisfactory account of these fine structures seem not to be provided at present.

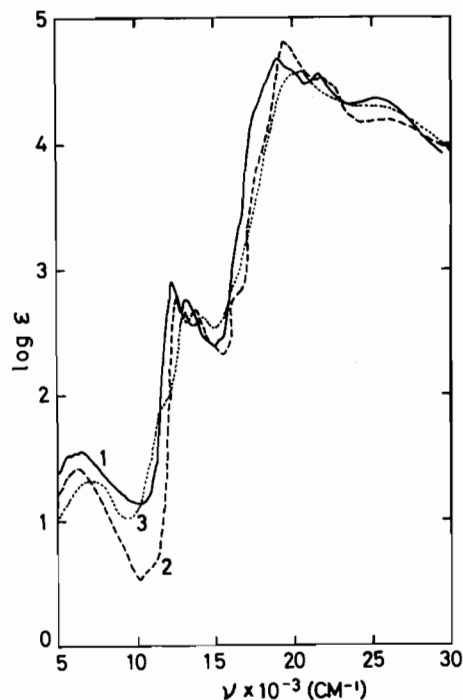


Figure 3. Electronic absorption spectra of nickel(II) complexes of dipyrromethenes in chloroform: (1), 3,3',4,4',5,5'-hexamethyldipyrromethene; (2), 3,3',5,5'-tetramethyldipyrromethene; (3), 3,4,5-trimethyldipyrromethene.

In summarizing the above results, the removal of a bulky substituent at the 5'-position of a dipyrromethene moiety in the copper complex resulted in a profound spectral change which means a significant structural alteration to the further flattened tetrahedron. By contrast, such changes in the ligand moiety do not produce any significant spectral variations for the corresponding nickel and cobalt complexes.

*Vibrational Spectra.* In the NaCl region, a strong band appearing at  $\sim 1600 \text{ cm}^{-1}$  can be assigned to the skeletal stretching mode of the pyrrole rings.<sup>25</sup> This band is most sensitive to metal-coordination among the absorption peaks appearing in this region. Nevertheless, the spectral shift of this band to lower frequency upon metal-coordination is rather small as shown in Figure 4. This is not unexpected because the high conjugation is already attained in the ligand moiety before a metal atom undergoes coordination and the formation of metal-ligand bonds may not give an appreciable effect on such conjugation. The

(24) A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (N. Y.)*, 6, 134 (1959).

(25) L. J. Boucher and J. I. Katz, *J. Am. Chem. Soc.*, 89, 1340 (1967).

magnitude of these frequency-shifts from the corresponding band of each ligand follows the sequence for the present metal complexes in an increasing order:  $\text{Cu} < \text{Ni} < \text{Co}$ .

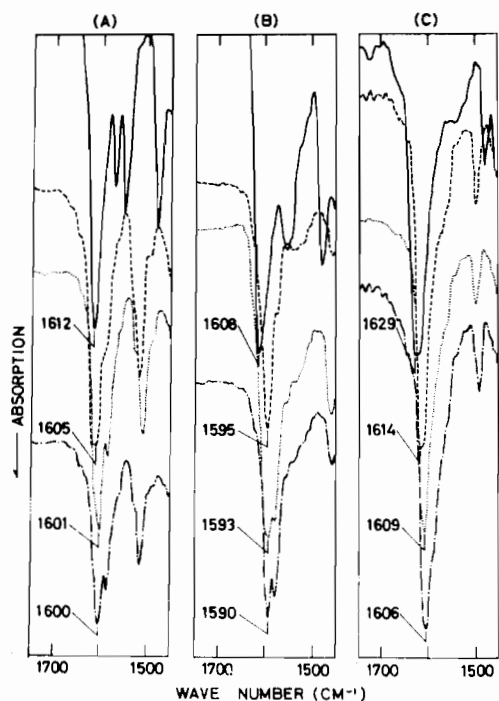


Figure 4. Infrared spectra of bivalent metal complexes of dipyrromethenes (KBr disk method): (A), 3,3',5,5'-tetramethyldipyrromethene; (B), 3,3',4,4',5,5'-hexamethyldipyrromethene; (C), 3,4,5-trimethyldipyrromethene; —, free ligand; ----, copper(II) complex; ·····, nickel(II) complex; — · —, cobalt(II) complex. Number refers to the skeletal vibrational mode of the pyrrole rings.

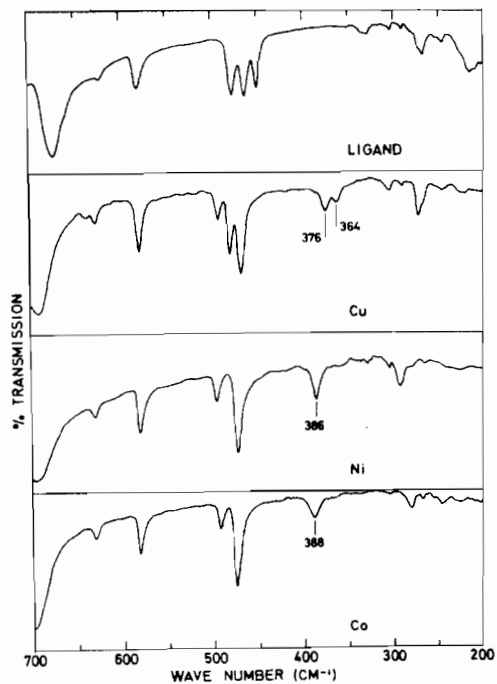


Figure 5. Far-infrared spectra of bivalent metal complexes of 3,3',5,5'-tetramethyldipyrromethene (nujol mull method). Number refers to the metal-ligand stretching mode.

In the far-infrared region,  $700\text{--}200\text{ cm}^{-1}$ , all the metal complexes show absorption peaks of medium intensity in the  $400\text{--}350\text{ cm}^{-1}$  range as seen in Figures 5 through 7. These bands can be associated with the metal-ligand (M–N) stretching modes because the corresponding band for each free ligand is evidently absent. These metal-dependent absorption peaks are

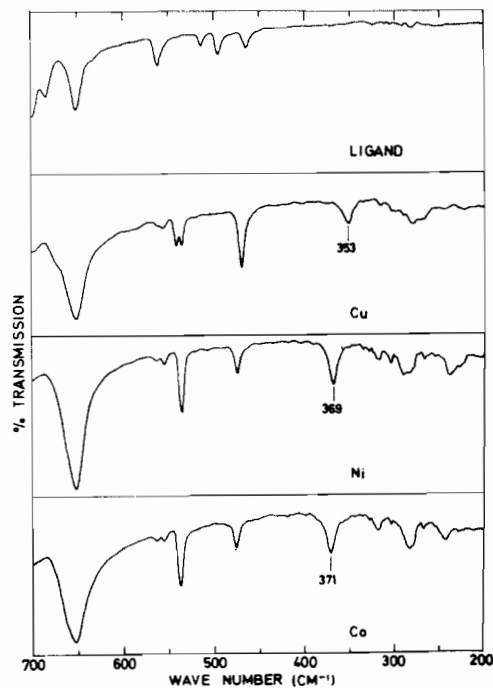


Figure 6. Far-infrared spectra of bivalent metal complexes of 3,3',4,4',5,5'-hexamethyldipyrromethene (nujol mull method). Number refers to the metal-ligand stretching mode.

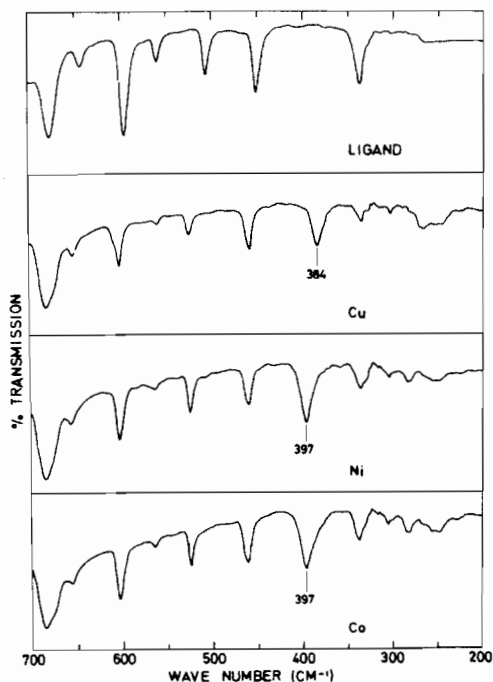


Figure 7. Far-infrared spectra of bivalent metal complexes of 3,4,5-trimethyldipyrromethene (nujol mull method). Number refers to the metal-ligand stretching mode.

shifted to lower frequencies by varying metal species in the sequence:  $\text{Co} \sim \text{Ni} > \text{Cu}$ . Recently, infrared spectral study of some metal ammine complexes and the normal coordinate analyses of these complexes have been carried out by Nakagawa and Shimanouchi.<sup>26</sup> The band appearing at  $318 \text{ cm}^{-1}$  for the hexaamminecobalt(II) complex and the one at  $330 \text{ cm}^{-1}$  for the hexaamminenickel(II) complex were assigned to the metal-nitrogen stretching vibration. Thus, the metal-nitrogen stretching vibrations for the present cobalt and nickel complexes appear in the higher frequency region relative to those for the corresponding ammine complexes. The high stability of the dipyrromethene complexes and the configurational change from octahedron to tetrahedron would be the cause for a somewhat higher frequency of the metal-nitrogen stretching mode. The  $420 \text{ cm}^{-1}$  band for the tetraamminecopper(II) complex was attributed to the metal-ligand stretching mode. The marked decrease of such a vibrational frequency is noted

(26) I. Nakagawa and T. Shimanouchi. *Spectrochim. Acta*, 22, 759 (1966).

here for the dipyrromethene complexes. As previously suggested by the study of ligand-field spectra for these copper complexes, the structure around the central metal atom has been distorted from the stable planar configuration to the flattened tetrahedral. This effect seems to be responsible for the weakened metal-nitrogen bonds in comparison with those bonds involved in the ammine complex and the corresponding cobalt and nickel complexes.

In summarizing the above infrared spectral data, the strength of the coordinate bonds increases in the following sequence among the bivalent metal complexes of each substituted dipyrromethene treated in this work:  $\text{Cu} < \text{Ni} \lesssim \text{Co}$ .

As for the effect of the ligand species on the nature of coordinate bonds, the strength of the metal-nitrogen bonds increases in the order: 3,3',4,4',5,5'-hexamethyl- < 3,3',5,5'-tetramethyl- < 3,4,5-trimethyl-dipyrromethene. This can be understood by investigating the absorption peaks in the  $400\text{-}350 \text{ cm}^{-1}$  region, and may be correlated with the extent of steric interaction among substituents.