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Transition-metal Complexes of Pyrrole Pigments. IX.[1,2) Divalent and Trivalent Iron Chelates of Dipyrromethenes

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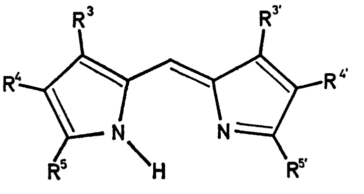
The iron chelates of polymethyl-substituted dipyrromethenes were prepared. The ferrous ion was found to form complexes having a ligand to metal ratio of 2 : 1 with 5,5′-substituted dipyrromethenes, 3,3′,5,5′-tetramethyl- and 3,3′,4,4′,5,5′-hexamethyl-dipyrromethene. On the other hand, the ferric ion gave a complex having a 3 : 1 molar ratio of ligand to metal with a 5,5′-unsubstituted ligand, 3,3′,4-trimethyldipyrromethene. The complexes were studied by means of visible and IR spectroscopy as well as by magnetic susceptibility measurements. The iron(II) chelates were confirmed to be of high spin type with distorted tetrahedral structure (D_2), while the iron(III) chelate demonstrated a low spin character with hexacoordination. The strong ligand-field bands of the latter complex was ascribed to the trigonally distorted octahedral coordination (D_3) along with a high covalent nature of metal-ligand bonds.

In connection with metal complexes of macrocyclic pyrrole pigments which occur naturally and play an eminent role in biochemical catalysis, we have investigated metal complexes of synthetic pyrrole pigments of open chain structure from the viewpoint of coordination stereochemistry.[2–9) These pyrrole derivatives include dipyrromethenes and biladienes with various substituents. We clarified that substituent groups placed at the 5 and 5′ positions of dipyrromethenes in the divalent transition-metal complexes yielded a significant steric hindrance among the substituents in the same complex, so that no planar complexes were obtained even with copper(II) and nickel(II) having a good tendency of planar coordination.

For a transition metal in a highly stabilized trivalent state, however, a hexacoordinated bisdipyrromethene complex with an additional anionic ligand can be obtained. This was exemplified by the characterization of acetatobis(3,3′,5,5′-tetramethyldipyrromethenato)chromium(III).[2) The chromium complex undergoes a significant distortion along the C_2-axis due to the steric effect of the 5,5′-substituents. In contrast to the chromium system, the valency state of iron is more susceptible to the ligand-field effect as judged from its oxidation-reduction potential. In the present work, we have undertaken to elucidate the correlation between the valency state of iron in a complex and the nature of the 5,5′-substituents placed in the ligands with the use of 3,3′,4-trimethyl- (**1**), 3,3′,5,5′-tetramethyl- (**2**), and 3,3′,4,4′,5,5′-hexamethyl-dipyrromethene (**3**) as bidentate ligands.



1: $R^3=R^{3'}=R^4=CH_3$, $R^{4'}=R^5=R^{5'}=H$
2: $R^3=R^{3'}=R^5=R^{5'}=CH_3$, $R^4=R^{4'}=H$
3; $R^3=R^{3'}=R^4=R^{4'}=R^5=R^{5'}=CH_3$

Experimental

Ligands. *3,3′,4-Trimethyldipyrromethene hydrochloride*: A mixture of 3-methyl-2-formylpyrrole[10) (0.41 g), 3,4-dimethylpyrrole[10) (0.36 g), and dry ethyl ether (60 ml) was added dropwise to 40 ml of dry ethyl ether placed in a reaction flask under nitrogen atmosphere. The hydrogen chloride gas diluted with dry nitrogen was bubbled through the reaction mixture while the addition was continued for 20 min at an ice-sodium chloride temperature. Dry HCl gas was continuously introduced into the mixture until precipitation of the orange solid no longer took place. The precipitates were recovered by filtration and washed with 50 ml of dry ether. Recrystallization from acetone-chloroform gave reddish orange crystals; yield 0.70 g (82%). UV-($CHCl_3$): 280 sh (ε 1150), 286 (ε 1180), 306 (ε 884), 378 (ε 6680), 460 sh (ε 63100), and 468 nm (ε 72200). IR(KBr disk): 1621 cm^{-1}(pyrrole skeletal). NMR(CF_3CO_2H, TMS): δ 2.19 (3H, s, 4-$C\underline{H}_3$), 2.44, 2.53 (6H, each s, 3-$C\underline{H}_3$ and 3′-$C\underline{H}_3$), 6.61 (1H, br.s, 4′-$\underline{H}$), 7.77 (2H, s, 5-$\underline{H}$ and 5′-$\underline{H}$), and 7.84 (1H, s, –$C\underline{H}$=).

Found: C, 64.74; H, 6.88; N, 12.32%. Calcd for $C_{12}H_{15}N_2Cl$: C, 64.71; H, 6.79; N, 12.58%.

The synthesis of 3,3′,5,5′-tetramethyl- and 3,3′,4,4′,5,5′-hexamethyl-dipyrromethene has been described.[3)

Tris(3,3′,4-trimethyldipyrromethenato)iron(III). An aqueous solution (3 ml) containing ferric chloride hexahydrate (0.36 g) was added to a mixture of 3,3′,4-trimethyldipyrromethene hydrochloride (0.60 g) and methanol (180 ml). Crystalline precipitates of dark green luster were obtained from the dark reddish reaction mixture upon dropwise addition of aqueous ammonia (28%, 10 ml) with stirring. After being allowed to stand for 1 hr in a freezer, the crystalline solid was recovered and recrystallized from acetone as dark green crystals; yield 0.43 g (77%).

Found: C, 70.34; H, 6.54; N, 14.13%. Calcd for $C_{36}H_{39}N_6Fe$: C, 70.69; H, 6.44; N, 13.74%.

Bis(3,3′,5,5′-tetramethyldipyrromethenato)iron(II). Aqueous ammonia (28%, 10 ml) was added dropwise into a mixture of the hydrated ferrous chloride (1.2 g) dissolved in 30 ml of water and 3,3′,5,5′-tetramethyldipyrromethene (free base, 1.0 g) in 130 ml of ethanol. A crystalline solid of green luster was recovered after the reaction mixture had been allowed to stand for sometime in a freezer. Recrystallization from *n*-hexane gave green crystals; yield 0.58 g (51%).

Found: C, 68.79; H, 6.65; N, 12.24%. Calcd for $C_{26}H_{30}N_4Fe$: C, 68.72; H, 6.66; N, 12.33%.

Bis(3,3′,4,4′,5,5′-hexamethyldipyrromethenato)iron(II) A crystalline solid was obtained from 3,3′,4,4′,5,5′-hexamethyldipyrromethene (free base, 0.50 g) and the hydrated ferrous chloride (0.50 g) in a manner similar to the above iron(II) complex. Recrystallization from *n*-hexane-benzene gave green crystals; yield 0.45 g (82%).

Found: C, 70.33; H, 7.39; N, 10.92%. Calcd for $C_{30}H_{38}N_4Fe$: C, 70.58; H, 7.50; N, 10.98%.

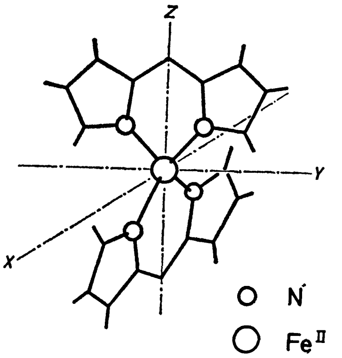
Physical Measurements. Electronic spectra covering the 250—2000 nm region were recorded on a Hitachi EPS-2 spectrophotometer for chloroform solutions at room temperature. Infrared spectra were measured with a JASCO DS-403G spectrophotometer by a Nujol mull technique. Magnetic susceptibility measurements of solid powdered samples were carried out with Gouy balance. Calibrations were made with use of fresh distilled water and cupric sulfate pentahydrate, while diamagnetic corrections were performed by using Pascal's constants.

Results and Discussion

The reactions of ferrous chloride with dipyrromethene ligands **2** and **3** resulted in the formation of the corresponding iron(II) complexes having a 2 : 1 ligand to metal ratio (bis-complex), while a ferric salt reacted with ligand **1** to give the 3 : 1 dipyrromethene-iron(III) complex (tris-complex). In the latter reaction, ferrous chloride was also utilized in place of the ferric salt to afford the same complex. On the other hand, the reactions of ferric chloride with ligands **2** and **3** failed to give any characteristic metal complex. For the dipyrromethene-iron chelate system, the trivalent iron state appears to be electronically more stable than the divalent state due to the chelate effect, unless other factors such as steric effect come into play. The absence of bulky substituent groups at the 5,5′-positions in one dipyrromethene ligand resulted in the formation of a tris-complex. When methyl groups are substituted at these positions, a significant steric interaction was generated among these substituents of different ligand molecules in the same complex to such an extent that the formation of a tris-complex is completely inhibited. This effect favors the formation of a neutral divalent iron complex, bis-complex.

A hexacoordinated chromium(III) complex was obtained with ligand **2** accompanied with acetate group as an additional anionic ligand.[2] Judging from the standard reduction potentials −0.41 and 0.77 V for chromium(III) and iron(III), respectively,[11] the trivalent state of chromium in a complex is intrinsically more stable than that of iron. The sterically crowded structure of hexacoordinated chromium(III) complex was relaxed by adopting the acetate ion as the third ligand.

The plausible structures for bis- and tri-complexes are illustrated schematically by **4** and **5**, respectively. A discussion will be made on the basis of these structures.



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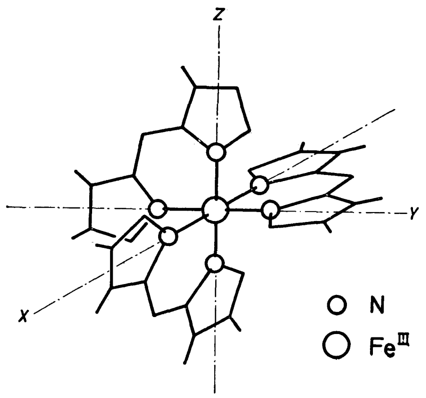

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Electronic Spectra. The electronic absorption spectra for the three iron complexes are shown in Fig. 1, covering the 250—2000 nm region. The absorption bands lying above 20000 cm^{-1} are attributed to charge transfer transitions from metal to ligand and $\pi \rightarrow \pi^*$ transitions within a ligand molecule. The ligand-field bands are observed in a region lying below 18000 cm^{-1} (Figs. 2 and 3) for tris(3,3′,4-trimethyldipyrromethenato)iron(III) and bis(3,3′,4,4′,5,5′-hexamethyldipyrromethenato)iron(II), respectively.

The coordination site symmetry for the tris-complex can be O_h with some minor trigonal distortion, if any. It is rather difficult to presume the spin state of iron(III) on the basis of spectral behavior alone. This is due to the fact that the ligand-field energy for the high spin state is frequently comparable to

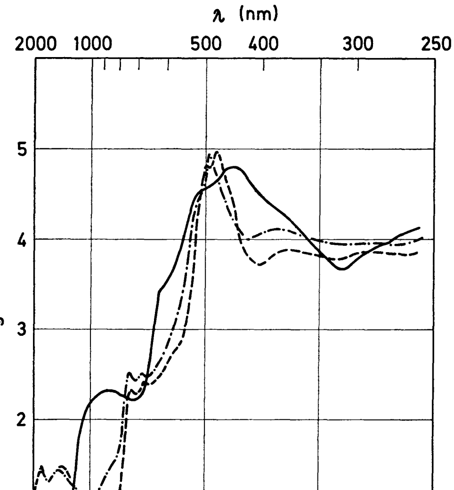

Fig. 1. Electronic absorption spectra of iron chelates in chloroform at room temperature: ——, tris-complex I; ----, bis-complex II; ·—·—, bis-complex III. Refer to the footnote of Table 1 for abbreviations.

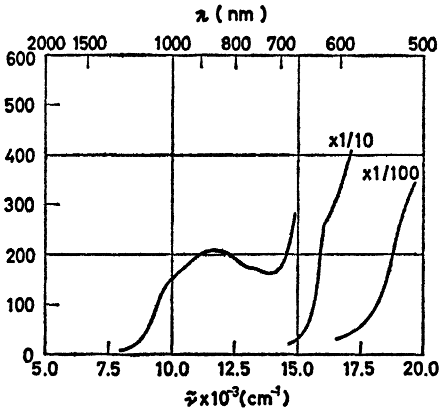

Fig. 2. Ligand-field spectrum for tris(3,3′,4-trimethyldipyrromethenato)iron(III) in chloroform at room temperature. Numbers in this figure (1/10 and 1/100) refer to the reduction factor of the absorption intensity.

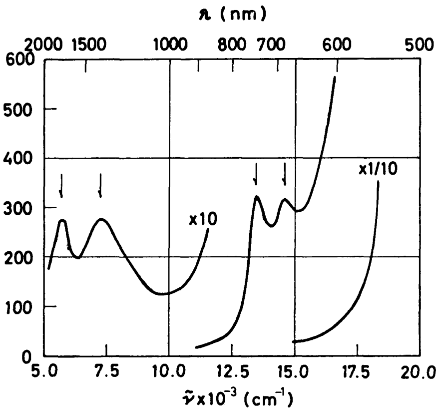

Fig. 3. Ligand-field spectrum for bis(3,3′,4,4′,5,5′-hexamethyldipyrromethenato)iron(II) in chloroform at room temperature. Numbers in this figure refer to the reduction (1/10) and enlarging (10) factors of the absorption intensity.

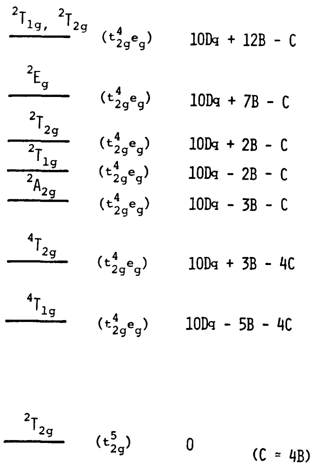

Fig. 4. The energy level scheme with configuration interaction for a low spin d^5 ion under O_h coordination symmetry.

Table 1. Ligand-field bands for dipyrromethene-iron chelates and their assignments[a)]

Chelate[b)]	Ligand-field band, cm^{-1} (ε)	Symmetry	Assignment
I[c)]	10000 sh (150)	O_h	$^2A_{2g} \leftarrow {}^2T_{2g}$
	11700 (208)		$^2T_{1g} \leftarrow {}^2T_{2g}$
	13200 sh (174)		$^2T_{2g} \leftarrow {}^2T_{2g}$
	16400 sh (2960)		$^2E_g \leftarrow {}^2T_{2g}$
II	5700 (26.0)	D_2	$^5B_2$, $^5B_3 \leftarrow {}^5A_{(1)}$, $^5A_{(2)}$
	7350 (29.4)		
	13600 (209)		$^5B_1 \leftarrow {}^5A_{(1)}$, $^5A_{(2)}$
	14700 (245)		
III	5680 (27.0)	D_2	$^5B_2$, $^5B_3 \leftarrow {}^5A_{(1)}$, $^5A_{(2)}$
	7250 (27.6)		
	13500 (318)		$^5B_1 \leftarrow {}^5A_{(1)}$, $^5A_{(2)}$
	14500 (314)		

a) Measured in chloroform at room temperature. b) I, tris(3,3′,4-trimethyldipyrromethenato)iron(III); II, bis(3,3′,5,5′-tetramethyldipyrromethenato)iron(II); III, bis(3,3′,4,4′,5,5′-hexamethyldipyrromethenato)iron(II).
c) Evaluated *Dq* and *B* values under O_h are 1440 and 600 cm^{-1}, respectively.

that for the low spin, and thermal equilibrium between these two states can be expected consequently. On the basis of the below-mentioned magnetic data, the energy level scheme for low spin state[12–14)] (Fig. 4) is adopted here for the elucidation of the spectrum.[15)] The ground state is $^2T_{2g}(t_{2g}^5, {}^2I)$ and can be split into $^2A_1$ and ^2E states under D_3 coordination symmetry. The spin-allowed excited levels with $t_{2g}^4e_g$ configuration are classified into three groups on the basis of the magnitude of energy separation: $^2A_{2g}$, $^2T_{1g}$, $^2T_{2g}(^2I)$; $^2E_g(^2I)$; and higher excited levels. The assignments of ligand-field bands with self-consistency are listed in Table 1. In spite of the satisfactory assignments of these bands, their absorption intensity is apparently too strong for the ordinary O_h coordination symmetry. The causes for this might be given as follows: a) distortion from O_h to D_3 to release the steric strain generated within a complex molecule; and b) d-p orbital mixing through strong covalent interaction between ligand and metal. Both *Dq* and *B* values were evaluated as shown in Table 1. The Racah parameter (*B*) for the complex is much smaller than the free ion value (~1300 cm^{-1}), indicating a strong nephelauxetic effect.

Cobalt(II) complexes with substituted dipyrromethenes exhibit distortion from regular tetrahedral coordination toward planar to an extent that the 5,5′-substituents do not generate any detectable steric effect within a complex molecule.[6)] The covalent nature of the coordinate bond may cause a tendency for a tetracoordinated complex to distort toward planar geometry. A similar state of affairs can be expected in the present case, and the bis-complex may assume tetrahedral coordination along with some minor distortion toward planar geometry. Thus, the D_2 local symmetry around iron(II) is tentatively assigned to these complexes. The distortion may arise partly from the skeletal structure of ligand molecule. As has been found for bisdipyrromethenato-copper(II) and -nickel(II) by X-ray diffraction measurements,[16,17)] the N-

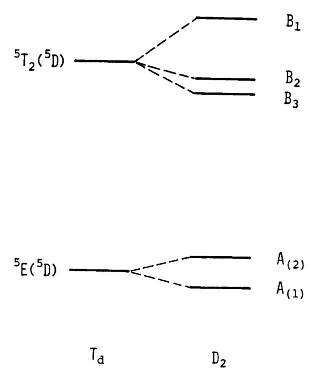

Fig. 5. The energy level schemes of direct concern for a high spin d^6 ion under T_d and D_2 symmetries.

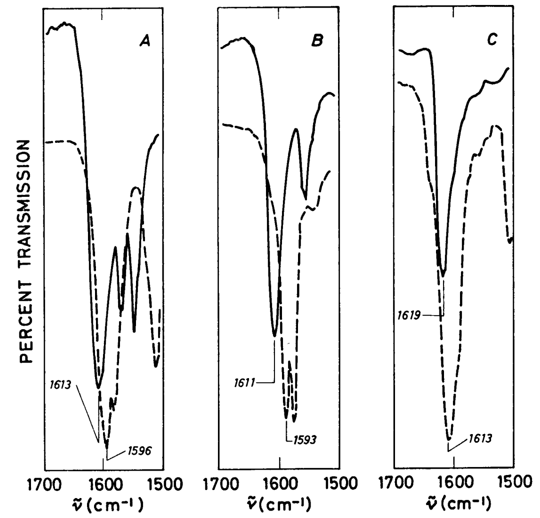

Fig. 6. Infrared spectra of iron chelates (----) and dipyrromethene free base (——) by a Nujol mull technique: A, 3,3′,5,5′-tetramethyldipyrromethene and its iron(II) chelate; B, 3,3′,4,4′,5,5′-hexamethyldipyrromethene and its iron(II) chelate; C, 3,3′,4-trimethyldipyrromethene and its iron(III) chelate. Number refers to the skeletal vibrational mode of the pyrrole rings.

M–N angle within a chelate ring is slightly smaller than the tetrahedral angle. This gives rise to the distortion toward two-fold axial symmetry. The energy level schemes for $T_d({}^5D)$ and $D_2({}^5D)$ are illustrated in Fig. 5. The possibility of being in the low spin state was excluded on the basis of the fact that the ligand field generated by the present ligands is not strong enough to make spin-pairing for d^6 ion under tetrahedral symmetry as in the case for the corresponding cobalt(II) complexes.[6)] This was approved by the magnetic susceptibility measurements described in the following.

If the magnitude of energy separation between $A_{(1)}$ and $A_{(2)}$ levels does not differ widely from that of the thermal energy at the temperature of measurement, a thermal pumping effect which provides some population in $A_{(2)}$ level can be expected. This effect may give two groups of ligand-field bands, each consisting of two absorption peaks with a smaller separation; $B_1 \leftarrow A_{(1)}$, $A_{(2)}$ and B_2, $B_3 \leftarrow A_{(1)}$, $A_{(2)}$. These assignments for the present bis-complexes are summarized in Table 1. A higher energy band in each group, attributable to the transition from $A_{(1)}$ level, shows a greater broadness relative to the lower one (Fig. 3). This is most likely due to vibronic coupling with the vibrational levels of larger energy separation for $A_{(1)}$ level, providing wider phonon wings.

Vibrational Spectra. The IR absorption spectra for the iron chelates, covering the 1500—1700 cm^{-1} region, are shown in Fig. 6. A strong band appearing in the 1600 cm^{-1} range is assigned to the skeletal stretching mode of the pyrrole rings.[3,6,8,9)] A slight shift of this band to lower energy is observed for each ligand upon metal-coordination.

In the far-infrared region 700—200 cm^{-1}, the bis-complexes showed absorption peaks of medium intensity in the 400—350 cm^{-1} range in a manner similar to those observed for the cobalt(II), nickel(II), and copper(II) chelates of some dipyrromethenes.[3)] This band can be associated with the metal-ligand (M–N) stretching mode since the corresponding band for each free ligand is absent: 388 cm^{-1} for bis(3,3′,5,5′-tetramethyldipyrromethenato)iron(II) and 368 cm^{-1} for bis(3,3′,4,4′,5,5′-hexamethyldipyrromethenato)iron(II). On the other hand, we failed to assign such a vibrational mode to the tris-complex.

Magnetic Susceptibilities. The results of magnetic susceptibility measurements are listed in Table 2. It became obvious that the tris-complex holds a spin-paired d^5 system, even though μ_{eff} value is no doubt larger than the spin-only value. The effective magnetic moments for some low-spin iron(III) complexes formed with cyano, ethylenediamine,[13)] tertiary arsine,[14)] and substituted xanthates[18)] were found to lie in a 2.2—2.5 range at ordinary temperature. However, there remains some ambiguity as to whether thermal population on the high spin state is still allowed. Further study on the behavior of magnetic susceptibility with variation of temperature is required for clarification of this state of affairs. The bis-complexes apparently

Table 2. Molar magnetic susceptibilities (χ_M) and magnetic moments (μ_{eff}) for dipyrromethene-iron chelates at room temperature

Chelate[a)]	Electronic configuration	Temp, °K	$10^6\times\chi_M$, CGS	$10^6\times\chi_M^{cor}$, CGS	μ_{eff}, BM	$[4S(S+1)]^{1/2}$	No. of unpaired electrons
I	d^5	297—298	2132—2176	2479—2523	2.43—2.45	1.73	1
II	d^6	297	10670—11520	10930—11770	5.10—5.20	4.90	4
III	d^6	299	10250—10430	10550—10730	5.03—5.07	4.90	4

a) See Table 1, footnote b) for abbreviations.

hold a high spin state. The effective magnetic moments are slightly larger than the spin-only value. This difference may arise from the incomplete quenching of orbital angular momentum.

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