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Transition-metal Complexes of Pyrrole Pigments. X.*,[1] Divalent and Trivalent Manganese Chelates of Dipyrromethenes

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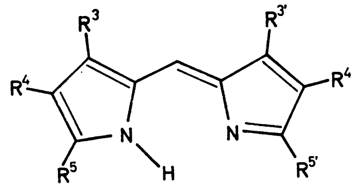
The solution spectra of two tris(dipyrromethenato)manganese(III) complexes and of one bis(dipyrromethenato)manganese(II) as well as the diffuse reflectance spectrum for the latter were examined. The high spin state was confirmed for all the manganese complexes by magnetic susceptibility measurements. For the tris-complexes, one broad low energy band (~9500 cm^{-1}) is assigned to the $^5A_{1g}\leftarrow{}^5B_{1g}$ transition and one pair of higher energy bands (~14000 cm^{-1}) are attributed to the $^5B_{2g}\leftarrow{}^5B_{1g}$ and $^5E_g\leftarrow{}^5B_{1g}$ transitions for a D_{4h} symmetry as a consequence of Jahn-Teller effect. In the bis-complex, manganese(II) is placed in a tetrahedral ligand field and one group of ligand-field bands lying below 16000 cm^{-1} are assigned to: $^4T_1(^4G)\leftarrow{}^6A_1(^6S)$, $^4T_2(^4G)\leftarrow{}^6A_1(^6S)$, and ^4E, $^4A_1(^4G)\leftarrow{}^6A_1(^6S)$ in an increasing order of energy. The exceedingly high intensity of these bands is ascribed to the covalent nature of coordinate bonds. A strong IR band due to the skeletal stretching mode of the dipyrromethene moiety was observed in the 1600 cm^{-1} range and shifted slightly toward lower energy upon metal-coordination.

Our previous investigations on the structural aspects of the first transition-metal complexes of dipyrromethenes have clarified the three major facts. Firstly, metal ions, which are in the divalent state of favorable stability, form the metal chelates of a 2 : 1 molar ratio of ligand to metal without any other additional ligand. These bis-complexes have a distorted tetrahedral structure, and the extent of this distortion very much depends on the coordination behavior of a central metal and the bulkiness of 5,5′-substituents in a ligand. If the central metals have an electronic configuration favorable for the planar coordination (*e.g.*, Cu(II) and Ni(II)), the yielded complexes come close to the planar geometry to an extent that the steric interaction between 5- and 5′-substituent groups of different ligand molecules in the same complex allows. Consequently, the structure of these complexes depends on the bulkiness of the substituent groups placed at 5- and 5′-positions.[2] On the other hand, when the electronic configuration of the central metals is in favor of the formation of tetrahedral geometry (*e.g.*, Co(II)), the bulkiness of 5,5′-moieties is not significant factor controlling the coordination structure. The covalent nature of coordinate bonds in these cases tends to distort the geometry from regular tetrahedron toward planar.[2]

Secondly, the central metals, which possess the slightly stable trivalent state relative to the divalent, yield tris-complexes with dipyrromethene ligands having no bulky 5,5′-substituents. However, when either or both of these positions are occupied with methyl or bulkier groups, only bis-complexes are obtained. An appropriate example is seen for the iron chelate system.[1]

Thirdly, the reaction of a metal ion, the trivalent state of which is much more stable than the divalent, and a 5,5′-substituted dipyrromethene gives only a complex of the distorted octahedral structure. This type of complex consists of two dipyrromethene molecules and an additional ligand, as observed for chromium(III) by the formation of acetatobis(3,3′,5,5′-tetramethyldipyrromethenato)chromium(III).[3]

In the present work, the correlation between the valency state of manganese in a complex and the nature of the 5,5′-substituents placed in the ligands is to be elucidated by employing 3,3′,4-trimethyl- (**1**), 3,3′,4,4′-tetramethyl- (**2**), and 3,3′,5,5′-tetramethyldipyrromethene (**3**) as bidentate ligands.



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

Experimental

Ligands. The synthetic procedures for the present ligands have been described previously.[1,2,4]

Tris(3,3′,4-trimethyldipyrromethenato)manganese(III). 3,3′,4-Trimethyldipyrromethene hydrochloride (0.4 g) and manganese dichloride tetrahydrate (0.2 g) were suspended in 100 ml of methanol. Crystalline precipitates of green luster developed from the dark reddish reaction mixture upon dropwise addition of dilute aqueous ammonia. The precipitates were recovered by filtration after the mixture being allowed to stand in a freezer for some time. The crystalline solid was extracted with chloroform. After evaporation of the solvent *in vacuo*, the residue was recrystallized from ethanol-chloroform as fine crystals of green luster; yield 0.10 g (36%).

Found: C, 70.11; H, 6.39; N, 13.47%; mol wt (osmometry),[5] 610. Calcd for $C_{36}H_{39}N_6Mn$: C, 70.79; H, 6.45; N, 13.76%; mol wt, 610.7.

Tris(3,3′,4,4′-tetramethyldipyrromethenato)manganese(III). Dilute aqueous ammonia was added dropwise into the suspension of 3,3′,4,4′-tetramethyldipyrromethene hydrochloride (0.15 g) and manganese dichloride tetrahydrate (0.07 g) in 40 ml of methanol. Reddish orange precipitates developed immediately. After heating on a water-bath (75 °C) for one minute, the reaction mixture was allowed to stand in a freezer for some time. The crystalline solid of green luster was recovered and extracted with chloroform. To the extract was added the same volume of acetone to precipitate fine crystals of green luster; yield 0.06 g (44%).

Found: C, 68.17; H, 6.79; N, 11.80%; mol wt,[5] 590.

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* Contribution No. 317 from this Department.

Table 1. Molar magnetic susceptibilities (χ_M) and magnetic moments (μ_{eff}) for dipyrromethene-manganese chelates at room temperature

Chelate	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
Tris-complex[a]	293.7	9525	9872	4.82	4.90	4
Bis-complex[b]	297.0	14234	14489	5.87	5.92	5

a) Tris(3,3',4-trimethyldipyrromethenato)manganese(III). b) Bis(3,3',5,5'-tetramethyldipyrromethenato)manganese(II).

Calcd for $C_{39}H_{45}N_6Mn$: C, 71.76; H, 6.95; N, 12.88%; mol wt, 652.3.

Bis(3,3',5,5'-tetramethyldipyrromethenato)manganese(II).[6] Six ml of an aqueous solution of manganese dichloride tetrahydrate (0.12 g) was mixed with an ethanol solution (20 ml) containing 3,3'5,5'-tetramethyldipyrromethene (free base, 0.12 g). Aqueous ammonia (28%, 2 ml) was added dropwise into the solution with stirring. Developed precipitates of green luster was recovered after the reaction mixture being allowed to stand in a freezer for one day. The solid was recrystallized from *n*-hexane as fine crystals of green luster; yield 0.10 g (88%).

Found: C, 68.68; H, 6.68; N, 12.23%; M+, 453.[7] Calcd for $C_{26}H_{30}N_4Mn$: C, 68.86; H, 6.69; N, 12.12%; mol wt, 453.58.

Physical Measurements. Electronic spectra covering the 7000—30000 cm^{-1} range were recorded on a Hitachi EPS-2 spectrophotometer for chloroform solutions at room temperature. Since bis(3,3',5,5'-tetramethyldipyrromethenato)-manganese(II) gradually decomposed in chloroform for long standing, its spectral measurement was performed immediately after the solution was prepared. Diffuse reflectance spectrum for the bis-complex was measured by a Hitachi EPU-2 spectrophotometer equipped with a R-3 reflectance attachment, MgO being used as a reference sample. Infrared spectra in the range of 200—4000 cm^{-1} were measured with a JASCO DS-403G spectrophotometer by a Nujol mull technique. Magnetic susceptibility measurements of solid samples were carried out by the Faraday method. Calibrations were made by the aid of Hg[Co(NCS)$_4$], while diamagnetic corrections were performed by using Pascal's constants.

Results and Discussion

The reaction of the manganese(II) salt with 5,5'-unsubstituted dipyrromethenes (**1** and **2**) resulted in the formation of the corresponding manganese(III) complexes having a ligand to metal ratio of 3 : 1 (tris-complex), while the same metal salt reacted with 5,5'-dimethyl-substituted ligand **3** to give the 2 : 1 dipyrromethene-manganese(II) complex (bis-complex). For the dipyrromethene-manganese chelate system, the trivalent manganese state appears to be electronically more stable than the divalent due to the ligand-field stabilization effect brought about by octahedral coordination unless other factors such as steric effects come into play. The introduction of methyl groups at 5,5'-positions gives out a significant steric interaction 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. Similar state of affairs has been observed for the dipyrromethene-iron chelate system.[1]

Magnetic Susceptibilities. The results of magnetic susceptibility measurements are listed in Table 1. It became apparent that the tris-complexes as well as the bis-complex hold a spin-free state. It is quite interesting to note that the present tris-complexes are in a high-spin ground state on the contrary to the low-spin state of the corresponding tris-complex of iron(III).[1]

Electronic Spectra. The electronic absorption

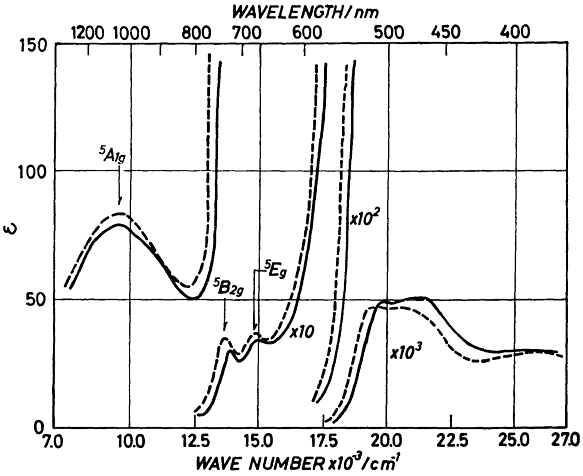

Fig. 1. Electronic absorption spectra of manganese(III) chelates of dipyrromethenes in chloroform at room temperature: ——, 3,3',4-trimethyldipyrromethene; - - - -, 3,3',4,4'-tetramethyldipyrromethene. Numbers in this figure (10, 10^2, and 10^3) refer to the enlarging factors of the absorption intensity.

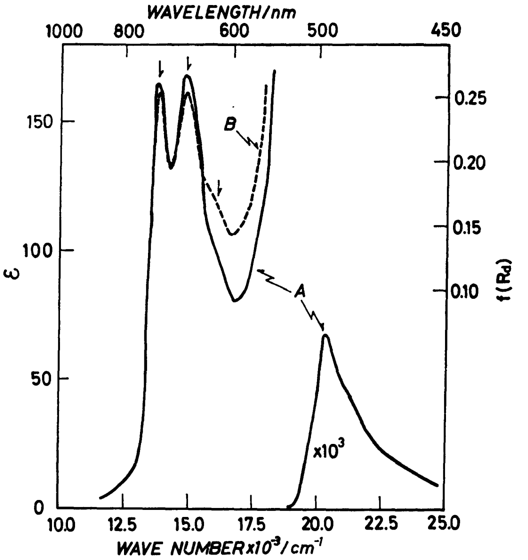

Fig. 2. Electronic spectra of bis(3,3', 5, 5'-tetramethyldipyrromethenato) manganese(II) at room temperature: A, absorption spectrum in chloroform; B, diffuse reflectance spectrum.

Table 2. Spectroscopic data and ligand-field parameters for some high-spin manganese(III) complexes at room temperature

Ligand	Complex type	Medium	Ligand-field bands, $cm^{-1}(\varepsilon)$			Ligand-field parameter, cm^{-1}			Ref.
			$^5A_{1g}\leftarrow{}^5B_{1g}$	$^5B_{2g}\leftarrow{}^5B_{1g}$	$^5E_g\leftarrow{}^5B_{1g}$	Dq	Ds	Dt	
1	$Mn(L)_3$	Chloroform	9410(78)	13750(297)	14900(338)	1375	1510	675	This work
2	$Mn(L)_3$	Chloroform	9450(84)	13580(350)	14800(370)	1358	1520	670	This work
Tropolonate	$Mn(L)_3$	Chloroform	9090(89)	15875(248)	17545(318)	1587	1535	590	8
2,4-Pentanedione	$Mn(L)_3$	Cyclohexane	9520(110)	17900(200)	21500	1790	1875	405	a)
Oxalate	$K_3Mn(L)_3$	Reflectance	9100	19050	20400	1905	1495	625	a)
F	K_3MnL_6	Reflectance	9000	17800	19400	1740	1600	520	b)

a) J. P. Fackler, Jr., T. S. Davis, and I. D. Chawla, *Inorg. Chem.*, **4**, 130 (1965). b) G. C. Allen, G. A. M. El-Sharkawy, and K. D. Warren, *ibid.*, **10**, 2538 (1971).

spectra for the tris-complexes are shown in Fig. 1, while the absorption and diffuse reflectance spectra for the bis-complex in Fig. 2. Lower intensity bands lying below 16000 cm^{-1} are apparently due to ligand-field transitions for all the manganese complexes in reference to the ligand-field bands for the other transition metal complexes previously studied.[1,2,4]

Ligand-field spectrum for each tris-complex consists of one broad band at 9500 cm^{-1} and one pair of bands in the 14000 cm^{-1} range. The electronic configuration [core]$3d^4$ (spin-free) produces E_g ground state in fields of octahedral symmetry. This state is susceptible to Jahn-Teller forces which causes the removal of the orbital degeneracy. The existence of a lower energy band at 9500 cm^{-1} and the correlation between this and the coexisting higher energy bands can not be elucidated reasonably in terms of other phenomena, such as spin-orbit coupling, solvent interaction, *etc.*, which may cause the removal of degeneracy. An electronic splitting of this magnitude can occur only if sizable effective distortions of the nuclear geometry from a regular tetrahedron. Jahn-Teller effects of this nature provide distortion to D_{4h} symmetry along with the removal of the E_g degeneracy. Thus, transitions may occur between components of the E_g (under O_h) ground state and from the ground state to the components of T_{2g}, which is less seriously split (Fig. 3). The broadness of the low-energy band (~9500 cm^{-1}) can also be attributed to the nature of potential energy surfaces for Jahn-Teller split E_g state.[8] Similar spectral behaviors have been observed for some manganese(III) complexes,[8] *e.g.*, tris(tropolonato)manganese(III), tris(2,4-pentanediono)manganese(III), potassium hexafluoromanganate, *etc.* It is not obvious whether the Jahn-Teller effects cause static or dynamic splitting of the E_g ground state for these manganese(III) complexes. Nevertheless, under assumption that the ground state becomes B_{1g} due to the effective D_{4h} field with axial elongation (Fig. 3), the transition energies can be represented as follows.[9]

$$E(^5A_{1g}\leftarrow{}^5B_{1g}) = 4Ds + 5Dt$$

$$E(^5B_{2g}\leftarrow{}^5B_{1g}) = 10Dq$$

$$E(^5E_g\leftarrow{}^5B_{1g}) = 3Ds - 5Dt + 10Dq$$

Spectral assignments and the ligand-field parameters thus evaluated are summarized in Table 2 along with some reference data from literatures.

Ligand-field spectrum for the bis-complex consists of three bands in a region lying below 16000 cm^{-1} as shown in Fig. 2. The tetrahalomanganate(II) complexes have been shown to assume tetrahedral coordination and their spectra analyzed[10] quantitatively by the aid of the secular equations of Tanabe and Sugano.[11] Similar interpretation would be applied to the present bis-complex, since structural require-

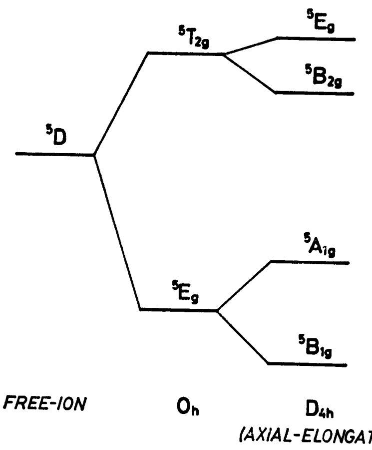

Fig. 3. Energy level diagrams for high-spin d^4 configuration under O_h and D_{4h} symmetries (not to scale).

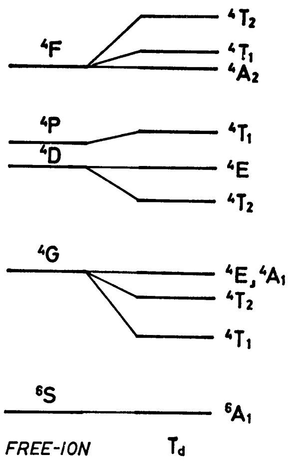

Fig. 4. Energy level diagram for high-spin d^5 configuration under T_d symmetry (not to scale).

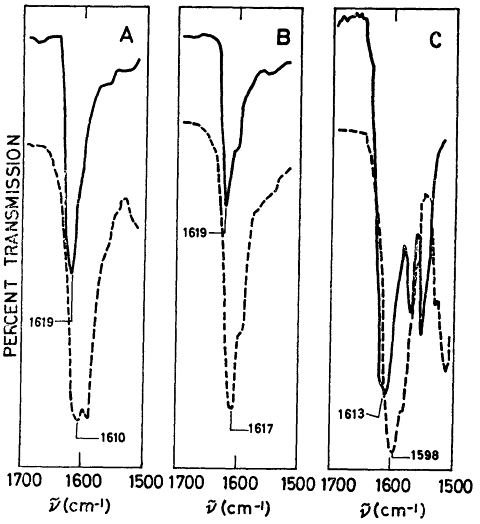

Fig. 5. Infrared spectra of manganese chelates (- - - -) and dipyrromethene free base (——) by a Nujol mull technique: A, 3,3′,4-trimethyldipyrromethene and its manganese(III) chelate; B, 3′3′,4,4′-tetramethyldipyrromethene and its manganese(III) chelate; C, 3,3′,5,5′-tetramethyldipyrromethene and its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

ment of the present dipyrromethene ligand forces manganese(II) to occupy a tetrahedral ligand field. The present ligand-field bands are tentatively assigned as follows (refer to Fig. 4).

$^4T_1(^4G) \leftarrow {}^6A_1(^6S)$: 13800 cm^{-1} (ε 165)
$^4T_2(^4G) \leftarrow {}^6A_1(^6S)$: 14900 cm^{-1} (ε 168)
^4E, $^4A_1(^4G) \leftarrow {}^6A_1(^6S)$: 16100 cm^{-1} (ε ~97 sh)

Since the higher energy ligand-field bands are hidden in the present case due to the presence of high intensity bands attributable to charge-transfer and ligand $\pi \rightarrow \pi^*$ transitions, the critical spectral analysis, to an extent as performed for the tetrahalomanganate system, was not attempted.

In spite of these interpretation for the bis-complex, absorption intensity of these bands is exceedingly high for the ordinary spin-forbidden transitions. If covalent nature of the coordinate bond increases, the orbital angular momentum for the ground state cannot be referred to pure A_1 state any longer. Thus, this interaction tends to act in favor of transition probability increase.[12] In addition, the covalent interaction may provide any tendency to distort a tetrahedrally coordinated complex toward planar geometry as postulated for other dipyrromethene complexes of divalent first-transition metals.[2,3]

Vibrational Spectra. The IR absorption spectra for manganese chelates, covering the 1500—1700 cm^{-1} region, are shown in Fig. 5. A strong band due to the skeletal stretching mode of the dipyrromethene moiety appears in the 1600 cm^{-1} range. These bands show a slight shift upon metal-coordination.

In the far-infrared region, 700—200 cm^{-1}, the bis-complex shows an absorption peak of medium intensity in the 400—350 cm^{-1} range in a manner similar to the cobalt(II), nickel(II), copper(II), and iron(II) chelates of some dipyrromethenes reported previously.[1,2] This band can be associated with the metal-ligand (M—N) stretching mode: 379 cm^{-1} for bis(3,3′,5,5′-tetramethyldipyrromethenato)manganese(II). On the other hand, we failed to assign such a vibrational mode to the tris-complexes.

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References

1) Part IX: Y. Murakami, Y. Matsuda, K. Sakata, and K. Harada, This Bulletin, **47**, 458 (1974).

2) Y. Murakami, Y. Matsuda, and K. Sakata, *Inorg. Chem.*, **10**, 1728 (1971).

3) Y. Murakami, Y. Matsuda, and K. Iiyama, *Chem. Lett.*, **1972**, 1069.

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

5) A Hitachi Model 115 vapor pressure osmometer was used to measure the molecular weight of a sample dissolved in chloroform.

6) Preparation of this metal chelate was aided by Mr. Kiyotaka Iiyama of this Laboratory.

7) The mass spectral analysis was carried out on a JEOL JMS-01SG spectrometer.

8) T. S. Davis, J. P. Fackler, and M. J. Weeks, *Inorg. Chem.*, **7**, 1994 (1968).

9) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York (1962).

10) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, **84**, 167 (1962).

11) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

12) Since the absorption intensity of these bands is much high for the ordinary spin-forbidden transitions, there exists some opinion against these assignments given above. Our interpretation will be confirmed by means of ESR study in the near future.