Transition-metal Complexes of Pyrrole Pigments. XI. Zinc(II) Chelates of Some Dipyrromethenes*

Yukito Murakami and Kazunori Sakata

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

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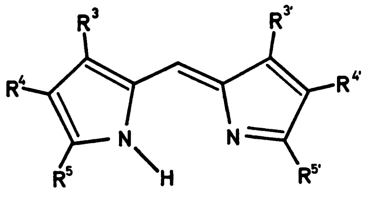
The zinc(II) chelates of five dipyrromethenes which have methyl substituents to a various extent, as well as that of 5,5'-diphenyldipyrromethene, have been prepared. The behaviors of methyl resonances upon metal-coordination were classified into three cases: (1) a down-field shift, but not greater than that of the corresponding ligand hydrochloride (3,3'-C$\underline{H}_3$); (2) nearly no change in chemical shift (4,4'-C$\underline{H}_3$); and (3) a profound up-field shift, the methyl resonance of the corresponding ligand hydrochloride showing a down-field shift on the contrary (5,5'-C$\underline{H}_3$). A marked change in chemical shift for the methine proton upon zinc(II)-coordination is related to conjugation in the chelate ring—the presence of aromaticity. As a whole, methyl resonances for the zinc chelates are consistent with the tetrahedral coordination geometry. Electronic absorption peaks for the zinc chelates, which were located in the lowest energy region with the highest intensity, were assigned to the intra-ligand $\pi \rightarrow \pi^*$ transition and the metal→ligand charge-transfer as well. Vibrational absorption bands appearing in the 1600 cm^{-1} range and in the 400—350 cm^{-1} region have been assigned to the skeletal stretching mode of the dipyrromethene moiety and the metal-ligand stretching mode, respectively, for the zinc chelates.

In order to make a further exploration into the coordination ability of various pyrrole pigments, the zinc(II) chelates of six dipyrromethenes (**1**—**6**) have been prepared in this work. From our structural investigations on various divalent metal chelates of substituted dipyrromethenes, cobalt(II) was found to coordinate tetrahedrally to dipyrromethene molecules.[1—3] In connection with the coordination behavior of cobalt(II) ion, the zinc(II) ion, which has a good tendency of typical tetrahedral coordination, was employed to yield the corresponding dipyrromethene complexes. The structural aspects of the present zinc(II) complexes as well as dipyrromethene ligands were investigated primarily by means of NMR spectroscopy. An additional information was also obtained by electronic and vibrational spectroscopy. Although Fergusson *et al.* carried out NMR studies on zinc(II), cadmium(II), mercury(II), and palladium(II) complexes of some dipyrromethenes,[4,5] their information is rather limited due to non-systematic utilization of dipyrromethene ligands with respect to substituent groups. The present study provides a thorough information on the proton resonance signals due to methyl groups substituted at all positions of the dipyrromethene skeleton as well as on their correlations.



1: $R^3=R^{3'}=R^4=R^{4'}=CH_3$, $R^5=R^{5'}=H$
2: $R^3=R^{3'}=R^5=CH_3$, $R^4=R^{4'}=R^{5'}=H$
3: $R^3=R^4=R^5=CH_3$, $R^{3'}=R^{4'}=R^{5'}=H$
4: $R^3=R^{3'}=R^5=R^{5'}=CH_3$, $R^4=R^{4'}=H$
5: $R^3=R^{3'}=R^4=R^{4'}=R^5=R^{5'}=CH_3$
6: $R^5=R^{5'}=C_6H_5$, $R^3=R^{3'}=R^4=R^{4'}=H$

Experimental

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

Metal Chelates. *Bis(3,3',4,4'-tetramethyldipyrromethenato)zinc(II)*: Zinc chloride (anhydrous, 50 mg) dissolved in 2 ml of water was added with stirring to an ethanol (15 ml) solution of the ligand hydrochloride (0.1 g) at room temperature. After addition of 3% aqueous ammonia (0.5 ml), the mixture was heated at 80 °C for 2 min with stirring and subsequently allowed to cool down to room temperature. Repeated recrystallization from chloroform-ethanol gave olive-green crystals; yield 41 mg (42%).

Found: C, 67.34; H, 6.58; N, 12.03%. Calcd for $C_{26}H_{30}N_4Zn$: C, 67.31; H, 6.52; N, 12.08%.

Bis(3,3',5-trimethyldipyrromethenato)zinc(II): The reaction of the ligand hydrochloride (0.1 g) and zinc chloride (anhydrous, 80 mg), following the above procedure, gave reddish orange crystals; yield 57 mg (58%).

Found: C, 65.85; H, 5.79; N, 12.88%. Calcd for $C_{24}H_{26}N_4Zn$: C, 66.13; H, 6.01; N, 12.86%.

Bis(3,4,5-trimethyldipyrromethenato)zinc(II): The reaction of the ligand hydrochloride (0.4 g) and zinc chloride (anhydrous, 0.26 g), following the above procedure, gave olive-green crystals; yield 0.25 g (64%).

Found: C, 65.88; H, 5.93; N, 12.99%. Calcd for $C_{24}H_{26}N_4Zn$: C, 66.13; H, 6.01; N, 12.86%.

Bis(3,3',5,5'-tetramethyldipyrromethenato)zinc(II): The reaction of the ligand hydrochloride (0.1 g) and zinc chloride (anhydrous, 50 mg), following the above procedure, gave orange crystals; yield 63 mg (64%).

Found: C, 67.17; H, 6.57; N, 12.00%. Calcd for $C_{26}H_{30}N_4Zn$: C, 67.31; H, 6.52; N, 12.08%.

Bis(3,3',4,4',5,5'-hexamethyldipyrromethenato)zinc(II): A mixture of the ligand hydrochloride (0.1 g), zinc acetate dihydrate (80 mg), and urea (0.8 g) in 15.5 ml ethanol was refluxed for 2 hr and subsequently allowed to cool down to room temperature. Repeated recrystallization from benzene gave orange crystals; yield 68 mg (70%).

Found: C, 69.49; H, 7.25; N, 10.97%. Calcd for $C_{30}H_{38}N_4Zn$: C, 69.29; H, 7.37; N, 10.78%.

Bis(5,5'-diphenyldipyrromethenato)zinc(II): A mixture of the ligand (free base, 0.5 g) and zinc acetate dihydrate (0.26 g) in 45 ml of ethanol was refluxed for 2 hr, and subsequently

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* Contribution No. 322 from this Department.

Part X: Y. Murakami, K. Sakata, K. Harada, and Y. Matsuda, This Bulletin, **47**, 3021 (1974).

Table 1. NMR data for dipyrromethenes and zinc(II) chelates[a]

Ligand	Form	Assignment (ppm)					Abbreviation
		$5,5'\text{-C}\underline{\text{H}}_3$	$4,4'\text{-C}\underline{\text{H}}_3$	$3,3'\text{-C}\underline{\text{H}}_3$	$\text{-C}\underline{\text{H}}\text{=}$	Pyrrole-ring proton	
1	HCl salt		2.06	2.31	7.30	7.63	**1**-HCl
	Zn chelate		1.95	2.23	7.13	7.13	**1**-Zn
2	HCl salt	2.68		2.39	7.21	7.70, 6.30	**2**-HCl
	Free base	2.31		2.26, 2.21	6.76	7.09, 6.08	**2**
	Zn chelate	1.89		2.37, 2.31	7.16	7.23, 6.19, 6.02	**2**-Zn
3	HCl salt	2.67	2.00	2.27	7.16	7.67, 7.06, 6.45	**3**-HCl
	Free base	2.27	1.90	2.05	6.63	7.04, 6.55, 6.23	**3**
	Zn chelate	1.88	1.85	2.20	7.10	7.26, 6.98, 6.31	**3**-Zn
4	HCl salt	2.62		2.35	7.08	6.14	**4**-HCl
	Free base	2.32		2.21	6.71	5.96	**4**
	Zn chelate	1.96		2.31	7.02	5.98	**4**-Zn
5	HCl salt	2.58	1.97	2.24	7.02		**5**-HCl
	Free base	2.27	1.91	2.10	6.62		**5**
	Zn chelate	1.90	1.90	2.21	6.98		**5**-Zn

a) Measured in chloroform-*d* with TMS as an internal reference.

allowed to cool down to room temperature. Repeated recrystallization from chloroform–ethanol gave olive-green crystals; yield 0.39 g (70%).

Found: C, 76.39; H, 4.69; N, 8.33%. Calcd for $C_{42}H_{30}N_4Zn$: C, 76.89; H, 4.61; N, 8.54%.

Spectral Measurements. A Varian A-60 spectrometer was used to obtain NMR spectra in chloroform-*d* at room temperature. Chemical shifts were reported in ppm from internal TMS and calibrated by the use of chloroform signal as the secondary reference. Ultraviolet and visible spectra in chloroform were recorded on a Hitachi Model EPS-2 spectrophotometer at room temperature. Infrared and far-infrared spectra covering the 4000—200 cm^{-1} range were measured with a JASCO Model DS-403G grating spectrophotometer at room temperature, where Nujol mull technique was adopted.

Results and Discussion

NMR Spectra. *Methyl Group Resonances*: *(a) Ligands.* The hydrochloride of 3,3′,5-trimethyldipyrromethene (**2**–HCl) showed methyl-proton peaks at 2.68 and 2.39 ppm with 1 : 2 ratio of signal intensity. Thus, the former signal was assigned to methyl-protons placed at the 5-position, while the latter to those at the 3- and 3′-positions. On the basis of these assignments, all the methyl resonances have been assigned for dipyrromethene hydrochlorides as listed in Table 1. A positive charge on the hydrochloride forms of dipyrromethenes is apparently delocalized throughout the dipyrromethene skeleton according to these data. The removal of positive charge results in the up-field shift of methyl resonances as shown in Table 1 for the free-base forms.*

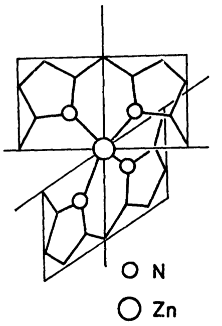

Fig. 1. Plausible spatial arrangement of the ligand molecules around zinc(II).

(b) Zinc Chelates. The metal nucleus in various zinc complexes generally demonstrates the tetrahedral coordination geometry by utilizing its (4s)(4p)^3 hybrid orbitals. The coordination geometry for the dipyrromethene chelates is shown schematically in Fig. 1. Consequently, the methyl groups substituted at the 5- and 5′-positions are to be placed in the shielding zone provided by a pyrrole ring as well as a chelate ring of another dipyrromethene moiety in the same chelate molecule. The behaviors of methyl resonances upon metal-coordination can be classified into three cases relative to those of the corresponding ligands (free base): (1) a down-field shift but not greater than the methyl resonance of the corresponding ligand hydrochloride ($3,3'\text{-C}\underline{\text{H}}_3$); (2) nearly no change in chemical shift, even though that of the corresponding ligand hydrochloride shows down-field shift ($4,4'\text{-C}\underline{\text{H}}_3$); and (3) a profound up-field shift, the methyl resonance of the corresponding ligand hydrochloride showing a down-field shift on the contrary ($5,5'\text{-C}\underline{\text{H}}_3$). All the down-field shifts can be attributed to the deshielding effect due to positive charge provided by either proton or zinc(II). The tetrahedral coordination geometry undoubtedly gives out the unique behavior of methyl resonances classified as (3). An apparent non-variation

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* Fergusson *et al.*[4] assigned the methyl resonances: $3,3'\text{-C}\underline{\text{H}}_3$, δ 2.58 and $5,5'\text{-C}\underline{\text{H}}_3$, 2.45 for 4,4′-diethoxycarbonyl-3,3′,5,5′-tetramethyldipyrromethene (free base); $3'\text{-C}\underline{\text{H}}_3$, δ 2.62 and $5'\text{-C}\underline{\text{H}}_3$, 2.46 for 3,4′-diethoxycarbonyl-5-chloro-3′,4,5′-trimethyldipyrromethene. Their assignments for $3(3')\text{-C}\underline{\text{H}}_3$ and $5(5')\text{-C}\underline{\text{H}}_3$ should be interchanged in reference to our present study.

of methyl resonances classified as (2) seems also due to some structural coordination effect—minor shielding effect.

Methine Group Resonances: A marked change in chemical shift for the methine proton upon zinc(II)-coordination should be directly related to conjugation in the chelate ring. The methine proton is significantly deshielded on protonation as observed for the porphyrin nucleus.[6] This is attributed to delocalization of a positive charge throughout the dipyrromethene molecule, which leaves out a partial positive charge on the methine carbon atom. The proton NMR investigations of acetylacetonate and porphyrin complexes have shown that no deshielding of the methine proton could be detected.[7,8,9] Consequently, the behavior of methine group resonances for the present zinc(II) chelates can be cited as an evidence for the presence of aromaticity in the chelate ring due to coordinate bonds of significant covalent character. In conclusion, the methyl resonances for the zinc chelates are consistent with the tetrahedral geometry as depicted in Fig. 1.

Electronic Spectra. Visible and ultraviolet spectra for the ligands in free base and hydrochloride forms as well as for the zinc chelates are shown in Figs. 2 through 4 for the selected cases. The ligands in free base forms show the most intense $\pi \rightarrow \pi^*$ band in the lowest energy range (Table 2). The $\pi \rightarrow \pi^*$ transition energy decreases as a number of methyl groups substituted in the dipyrromethene skeleton increases (Fig. 5). This phenomenon can be attributed to the hyperconjugation effect due to methyl groups. Upon protonation to a pyrrole-nitrogen (hydrochloride species), the $\pi \rightarrow \pi^*$

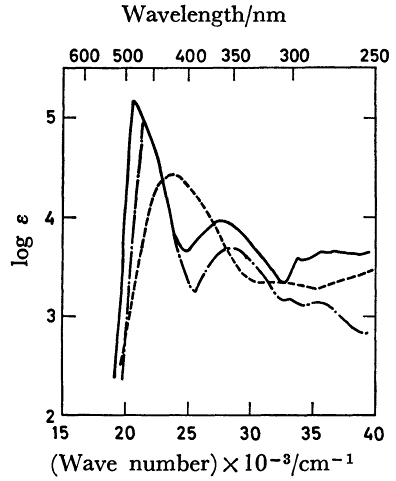

Fig. 2. Electronic absorption spectra for 3,3′,5-trimethyldipyrromethene and the zinc(II) chelate in chloform at room temperature: ——, zinc(II) chelate; —·—, ligand hydrochloride; - - - -, ligand free base.

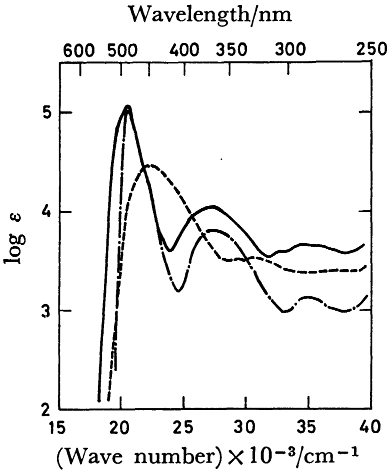

Fig. 3. Electronic absorption spectra for 3,3′,4,4′,5,5′-hexamethyldipyrromethene and the zinc(II) chelate in chloroform at room temperature: ——, zinc(II) chelate; —·—, ligand hydrochloride; - - - -, ligand free base.

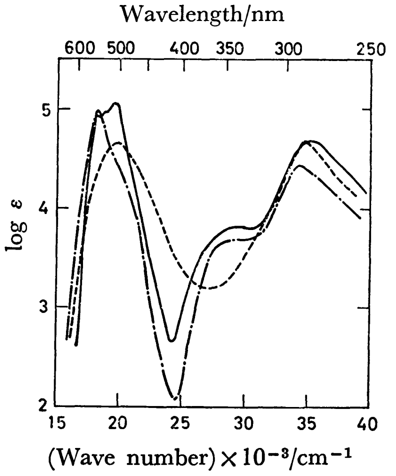

Fig. 4. Electronic absorption spectra for 5,5′-diphenyldipyrromethene and the zinc(II) chelate in chloroform at room temperature: ——, zinc(II) chelate; —·—, ligand hydrochloride; - - - -, ligand free base.

TABLE 2. ELECTRONIC ABSORPTION BANDS APPEARING IN THE LOWEST ENERGY RANGE FOR DIPYRROMETHENE LIGANDS AND ZINC(II) CHELATES[a]

Ligand	Form	Transition energy in cm⁻¹ (ε)
1	Free base	23300(28000)
	HCl salt	20900(68900)
	Zn chelate	20000(120000), 20700(93800)
2	Free base	23700(26200)
	HCl salt	21500(91900)
	Zn chelate	20700(144000), 22000sh(70600)
3	Free base	25200(23200)
	HCl salt	21400(64500)
	Zn chelate	20600(97300), 21800sh(75900)
4	Free base	22700(32300)
	HCl salt	21200(109000)
	Zn chelate	20500(166000), 21300sh(100000)
5	Free base	22300(29400)
	HCl salt	20500(107000)
	Zn chelate	19800sh(84400), 20500(117000), 21100sh(65300)
6	Free base	19500(44400)
	HCl salt	18100(94700)
	Zn chelate	18100(84700), 18900sh(95200), 19600(114000)

a) Measured in chloroform at room temperature.

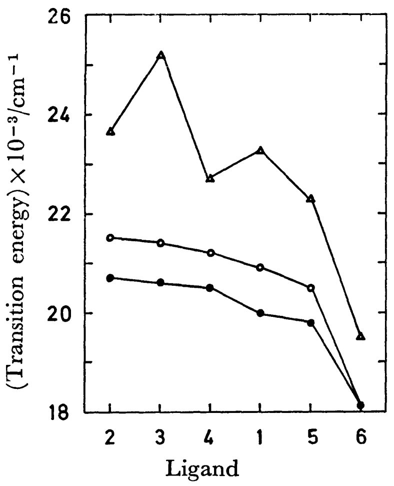

Fig. 5. Correlations between lowest electronic transition energy and nature of substituent groups in the dipyrromethene skeleton for ligand free bases(△), ligand hydrochlorides(○), and zinc(II) chelates(●): a number of methyl group increases from left to right (except **6**).

band further shift to a lower energy region (Figs. 3—5) along with an increase in its intensity. In a manner as pointed out by Corwin and Brunings for di-*N*-methyldipyrromethenes,[10,11] the steric interaction between *N*-protons in di-*N*-protonated dipyrromethenes seems to give out a significant effect on their electronic structure, thus raising the occupied π-energy levels relative to the free-base ligands. The intensity increase may be attributed to the polarity effect provided by the presence of a positive charge in the dipyrromethene skeleton. The effect of methyl-substitution (red-shift) is seen to be similar to that observed for the free-base ligands (Fig. 5). The electronic transition appearing in the lowest energy region for the zinc chelates are accompanied with multi-peaks (Table 2, Figs. 2—4), often along with a slight red-shift relative to that for the corresponding ligand hydrochlorides. The bands may be assigned to the $\pi \rightarrow \pi^*$ transition of similar origin as described for the ligands. On the other hand, the metal→ligand charge-transfer transitions, as generally observed for transition-metal complexes in a similar energy region, may be expected to appear in this region. Thus, we do hold the possibility of co-occurrence of charge-transfer and $\pi \rightarrow \pi^*$ transitions in the same range, although Fergusson *et al.* simply assigned these bands to the intra-ligand $\pi \rightarrow \pi^*$ transition and a band in the 28000 cm^{-1} range to the metal→ligand charge-transfer.

Vibrational Spectra. A strong band due to the skeletal stretching mode of the dipyrromethene moiety appears in the 1600 cm^{-1} range as listed in Table 3 for the free ligands and the corresponding zinc chelates. A slight shift of this band to lower energy is observed for each ligand upon metal-coordination.

Table 3. Infrared absorption band assigned to the skeletal stretching mode of the dipyrromethene moiety for ligands and zinc chelates

Ligand	Form	IR band in cm^{-1}
1	Free base	1619
	Zn chelate	1610
2	Free base	1622
	Zn chelate	1603
3	Free base	1625
	Zn chelate	1605
4	Free base	1613
	Zn chelate	1599
5	Free base	1611
	Zn chelate	1596
6	Free base	1618
	Zn chelate	1612

In the far-infrared region, 700—200 cm^{-1}, there was observed 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), iron(II), and manganese(II) chelates of some dipyrromethenes.[1,2,12,13] This band can be associated with the metal-ligand stretching mode: **3**-Zn, 383 cm^{-1}; **4**-Zn, 386 cm^{-1}; **5**-Zn, 363 cm^{-1}. We refrained from assigning a band of this origin for some zinc chelates due to the complexity of absorption spectra caused by ligand-nature.

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