Transition-metal Complexes of Pyrrole Pigments. Part VII.[1] Cobalt(II) and Zinc(II) Chelates of Some Tripyrrene-*b* and Bilene-*b* Ligands

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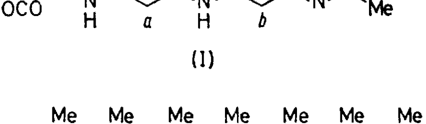
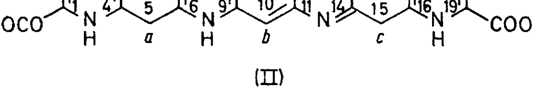
The cobalt(II) and zinc(II) chelates of 1′,6-diethoxycarbonyl-1,2,3,4,5,6′-hexamethyltripyrrene-*b* and 1,19-diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethyl-1,19-dideoxybilene-*b* in a ligand to metal ratio of 2:1 were prepared and investigated by electronic, i.r., and n.m.r. spectroscopy. A co-ordination geometry close to a regular tetrahedron (D_2 symmetry) around the metal atoms was assigned to these chelates.

BILENE-*b*'s and tripyrrene-*b*'s have gained credit as being useful intermediates for the preparation of corrin or tetradehydrocorrin compounds.[2] As a continuation of our studies on the pyrrole pigment complexes, the above tri- and tetra-pyrrolic compounds were adopted as ligands in the present work.



(I)



(II)

Since some transition-metal ions act as catalysts in cyclisation reactions of polypyrrolic compounds, studies on the co-ordination behaviour of metal ions with these non-cyclic pyrrole compounds may provide useful information for these catalytic cyclisation mechanisms. In addition, these pyrrole pigments are considered dipyrromethene compounds with bulky substituents at the 5,5′-positions or either. Thus, the effects of bulky groups on the co-ordination geometry are to be evaluated in reference to the previously studied dipyrromethene complexes.[1,3,4] Practically, the cobalt(II) and zinc(II) chelates of 1′,6-diethoxycarbonyl-1,2,3,4,5,6′-hexa methyltripyrrene-*b* (I) and 1,19-diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethyl-1,19-dideoxybilene-*b* (II) were prepared and investigated by means of electronic, i.r., and n.m.r. spectroscopy.

EXPERIMENTAL

1′,6-*Diethoxycarbonyl*-1,2,3,4,5,6′-*hexamethyltripyrrene*-b *Hydrobromide*.—3,3′,4,4′-Tetramethyl-5-ethoxycarbonyl-5′-formyldipyrromethane[5] (2·0 g) and 2,4-dimethyl-3-ethoxycarbonylpyrrole[6] (1·4 g) were suspended in methanol (15 ml). Aqueous hydrobromic acid (2 ml; 47%) was added at 20° and the mixture was stirred at 20—25° for 3 h. The reddish product was separated, washed with methanol, and then recrystallised from methanol–chloroform (3·2 g, 91%) (Found: C, 58·6; H, 6·45; N, 7·65%; M^+, 451. $C_{26}H_{34}N_3O_4Br$ requires C, 58·65; H, 6·45; N, 7·9%; $C_{26}H_{33}N_3O_4$

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requires M, 451), $\lambda_{max.}$ (chloroform) 490 nm (ε 69 400). The corresponding hydrochloride was also obtained by using aqueous hydrochloric acid (35%) in place of hydrobromic acid.

1,19-*Diethoxycarbonyl*-2,3,7,8,12,13,17,18-*octamethyl*-1,19-*dideoxybilene*-b *Hydrobromide*.—(*a*) 3,3′,4,4′-Tetramethyl-5-ethoxycarbonyl-5′-formyldipyrromethane (790 mg) and 3,3′,4,4′-tetramethyl-5-ethoxycarbonyldipyrromethane [4] (870 mg) were suspended in methanol (60 ml). Aqueous hydrobromic acid (0·5 ml; 47%) was added at room temperature and the stirring was continued for 30 min. The reddish product which separated from the mixture was washed with methanol and recrystallised from methanol–chloroform (1·75 g, 95%).

(*b*) Aqueous hydrobromic acid (0·5 ml; 47%) was added at reflux temperature into the suspension of 3,3′,4,4′-tetramethyl-5-ethoxycarbonyl-5′-formyldipyrromethane (720 mg) in methanol (40 ml). The mixture was stirred under reflux for 1·5 and then cooled to room temperature. The reddish product was separated, washed with methanol, and recrystallised from methanol–chloroform (640 mg, 82%) (Found: C, 61·75; H, 6·85; N, 8·75%; M^+, 558. $C_{33}H_{43}O_4N_4Br$ requires C, 61·95; H, 6·8; N, 8·75%; $C_{33}H_{42}O_4N_4$ requires M, 558), $\lambda_{max.}$ (chloroform) 509 nm (ε 58 900).

1′,6-*Diethoxycarbonyl*-1,2,3,4,5,6′-*hexamethyltripyrrene*-b *Chelates*.—(a) *Cobalt*(II) *chelate*. The tripyrrene-*b* hydrochloride (170 mg), cobalt(II) acetate tetrahydrate (80 mg), aqueous ammonia (1 ml; 28%), and ethanol (14 ml) were heated under reflux for 45 min. The solvent was removed and the n-hexane (50 ml) mixture refluxed for 30 min. Then, the filtrate and the n-hexane extracts were combined, concentrated to 50 ml and kept in a freezer overnight. The product was washed with n-hexane and recrystallised from n-pentane as green plates (60 mg, 36%), (Found: C, 65·7; H, 6·8; N, 8·7. $C_{52}H_{64}N_6O_8Co$ requires C, 65·05; H, 6·7; N, 8·75%).

(b) *Zinc*(II) *chelate*. The tripyrrene-*b* hydrochloride (400 mg), zinc(II) acetate dihydrate (180 mg), aqueous ammonia (4 ml; 28%), and ethanol (110 ml) were heated under reflux for 45 min. The solvent was removed and the residue was refluxed for 2·5 h in n-hexane (150 ml). The solvent was removed from the filtrate and the residue was recrystallised from ethanol as an orange solid (240 mg, 60%). Upon treatment with n-pentane the product was obtained as glittering green plates (Found: C, 64·55; H, 6·7; N, 8·7. $C_{52}H_{64}N_6O_8Zn$ requires C, 64·6; H, 6·75; N, 8·7%).

1,19-*Diethoxycarbonyl*-2,3,7,8,12,13,17,18-*octamethyl*-1,19-*dideoxybilene*-b *Chelates*.—(a) *Cobalt*(II) *chelate*. The bilene-*b* hydrobromide (2·5 g), cobalt(II) acetate tetrahydrate (1·0 g), aqueous ammonia (10 ml; 28%), and ethanol (300 ml) were heated under reflux for 40 min with vigorous stirring. The hot mixture was filtered and the resulting filtrate was kept in a freezer overnight. The separated product (1·68 g, 61%) was recrystallised from ethanol as glittering green plates (Found: C, 67·45; H, 7·05; N, 9·65. $C_{66}H_{82}N_8O_8Co$ requires C, 67·5; H, 7·05; N, 9·55%).

(b) *Zinc*(II) *chelate*. This metal chelate was obtained by the similar procedure and recrystallised from ethanol–chloroform as an orange solid (150 mg, 65%) (Found: C, 66·85; H, 6·95; N, 9·4. $C_{66}H_{82}N_8O_8Zn$ requires C, 67·15; H, 7·0; N, 9·5%).

Spectral Measurements.—Electronic spectra in chloroform were recorded on a Hitachi EPS2 spectrometer at room temperature. I.r. spectra were measured with a JASCO DG403G spectrophotometer at room temperature in chloroform as well as by the Nujol mull technique. Varian A60 and JEOL JNMPS100 spectrometers were used to obtain n.m.r. spectra in [$^2H_1$]chloroform at room temperature.

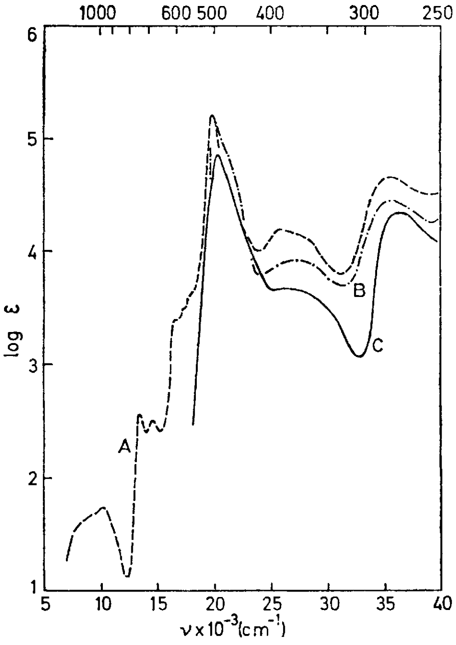


FIGURE 1 Electronic absorption spectra of the 1′,6-diethoxycarbonyl-1,2,3,4,5,6′-hexamethyltripyrrene-*b* chelates in chloroform at room temperature: A, cobalt(II); B, zinc(II); C, the ligand hydrochloride

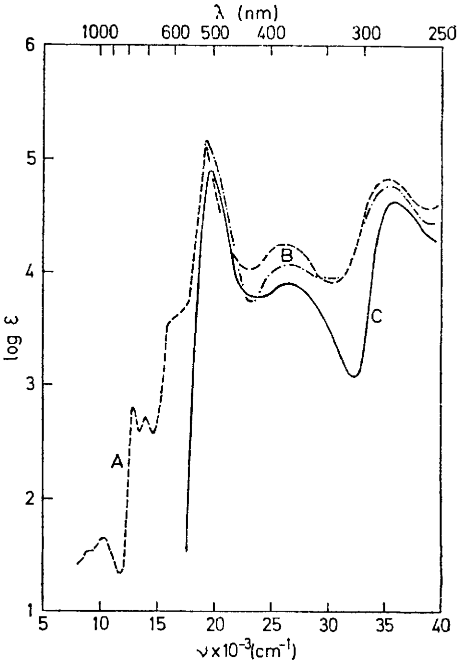


FIGURE 2 Electronic absorption spectra of the 1,19-diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethyl-1,19-dideoxybilene-*b* chelates in chloroform at room temperature: A, cobalt(II); B, zinc(II); C, the ligand hydrochloride

RESULTS AND DISCUSSION

Electronic Spectra.—The electronic spectra covering the 6000—35 000 cm^{-1} region are shown in Figures 1 and 2 for tripyrrene-*b* and bilene-*b* chelates, respectively. Only the cobalt(II) chelates show ligand-field bands in a region lying below 18 000 cm^{-1}. These spectral data for the cobalt chelates and their assignments are listed in Table 1. The general feature of these ligand-field spectra is nearly the same as those observed for other dipyrromethene–cobalt(II) chelates previously studied by us.[1,3,4] Consequently, the cobalt atom assumes the co-ordination configuration of D_2 symmetry upon minor distortion from the regular tetrahedral geometry.

TABLE 1

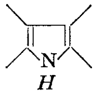
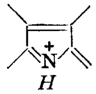
Ligand-field bands for cobalt(II) chelates and their assignments [a,b]

Ligand [c] (I)	Ligand [c] (II)	Assignment D_2	Assignment T_d
ca. 7700sh	*ca.* 7700sh	$B_1 \longleftarrow A$	
9300sh (46)	9000sh (34)	$B_2 \longleftarrow A$	$^4T_1(F) \longleftarrow {}^4A_2(F)$
10 200 (54)	10 300 (46)	$B_3 \longleftarrow A$	
13 400 (364)	12 800 (649)	$B_1 \longleftarrow A$	
14 500 (325)	13 900 (521)	$B_2 \longleftarrow A$	$^4T_1(P) \longleftarrow {}^4A_2(F)$
16 500sh (2500)	16 100sh (3660)	$B_3 \longleftarrow A$	
17 200sh (3050)	16 800sh (4300)		
18 000sh (4250)	17 400sh (4820)		

[a] Band positions are expressed in cm^{-1} and molar extinction coefficients are given in parentheses after the band positions. [b] Measured at room temperature in chloroform. [c] (I) 1′,6-diethoxycarbonyl-1,2,3,4,5,6′-hexamethyltripyrrene-*b*; (II), 1,19-diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethyl-1,19-dideoxybilene-*b*.

TABLE 2

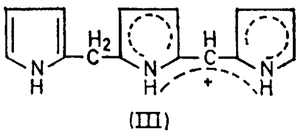
N.m.r. data for the zinc(II) chelates of tripyrrene-*b* and bilene-*b* [a]

Ligand [c]	Sample	Assignment [b] $-CH_3$ (ester)	$-CH_3$	$-CH_2-$ (ester)	$-CH_2-$	$-CH=$		
(I)	HBr salt [e]	1·36(3), 1·38(3)	2·00, 2·20, 2·26, 2·58, 2·89	4·26(4)	4·26	7·16	10·36	12·92, 13·28
	HCl salt [d]	1·36(3), 1·39(3)	2·04, 2·24, 2·26, 2·60, 2·89	4·30(4), 4·35(4)	4·25	7·31	10·91	13·83, 14·45
	Zn-chelate [d]	1·28(3), 1·30(3)	1·53, 1·77, 2·07, 2·12, 2·22, 2·52	4·21(4)	3·49	7·30	8·03	
(II)	HBr salt [d]	1·35(3)	2·00, 2·05,[f] 2·25	4·29(4)	4·33	7·13	10·2	13·2
	HCl salt [e]	1·35(3)	2·04, 2·07, 2·24, 2·26	4·30(4)	4·26	7·11	10·73	13·84
	Zn-chelate [e]	1·29(3)	1·53, 1·70, 2·09, 2·18	4·24(4)	3·22	6·88	8·08	

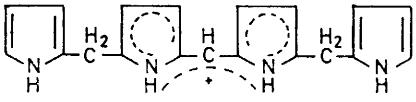
[a] Measured in [$^2H_1$]chloroform with Me_4Si as an internal reference; chemical shifts are shown in p.p.m. [b] Multiplicity of a proton signal is given in parentheses after δ-value (J = 7 Hz). [c] Ligand: (I) and (II) are the same as in Table 1. [d] 60 MHz measurement. [e] 100 MHz measurement. [f] Owing to low resolution, the signal did not give a splitting.

N.m.r. Spectra.—The n.m.r. data for the zinc(II) chelates and their assignments are listed in Table 2 together with those for the hydrochloride salts of ligands. As for the ligands, the presence of two *N*-protonated proton signals for the tripyrrene-*b* hydrochloride as well as a single signal of such character for the bilene-*b* salt may be ascribed to the mesomeric structures shown by (III) and (IV) for the former and the latter, respectively. Other characteristic behaviours of proton signals also support this prediction.

Almost all the proton signals listed in Table 2 shifted up-field upon co-ordination. The most significant behaviours in chemical shifts are as follows. The signal due to the non-co-ordinated pyrrole *N*-protons of the bilene-*b* shifted up-field as much as 2·7 p.p.m. (the ligand hydrochloride as a reference) upon co-ordination with zinc. This state of affairs can be visualised by depicting a molecular structure as shown in Figure 3. Since the zinc(II) ion assumes approximately a tetrahedral co-ordination, the pyrrole *N*-proton seems to be placed in the shielding zone of a co-ordinated pyrrole ring of the opposite ligand molecule. The molecular model for this



(III)



(IV)

TABLE 3

Characteristic i.r. bands for the cobalt(II) and zinc(II) chelates of tripyrrene-*b* and bilene-*b* [a,b,c]

(I)			(II)			
HCl	Co^{II}	Zn^{II}	HCl	Co^{II}	Zn^{II}	Assignment
3325m [d]	3470m [d]	3475m [d]	3340w [d]	3440m [d]	3440m [d]	N–H Stretching
3165w	3285m	3290m	3230w	3290m	3280m	
			3180w			
			3080w			
1707s	1693s	1693s	1707s	1686s	1685s	C=O Stretching
1684s	1668s	1670s	1678s	1668s	1668s	
1620s	1597s	1598s	1611s	1603s	1602s	Pyrrole skeletal
	1586s	1586s		1590sh	1588s	

[a] Measured by the Nujol mull method at room temperature; band positions are given in cm^{-1}. [b] Relative intensities: s, strong; m, medium; w, weak; sh, shoulder. [c] (I) and (II) (ligands) are the same as in Table 1; HCl stands for the hydrochloride of each ligand. [d] Assigned to N–H stretching mode due to free pyrrolic NH group on the basis of data for the bilene hydrochloride and its cobalt(II) chelate measured in chloroform.

zinc chelate predicts that this *N*-proton is located 2·5—3·0 Å above the pyrrole ring, thus a large magnetic anisotropy effect being expected. A 1·0 p.p.m. up-field shift of the bridging methylene-proton signal may be attributed to the shielding effect due to both co-ordinated and non-co-ordinated pyrrole rings of the opposite ligand molecule.

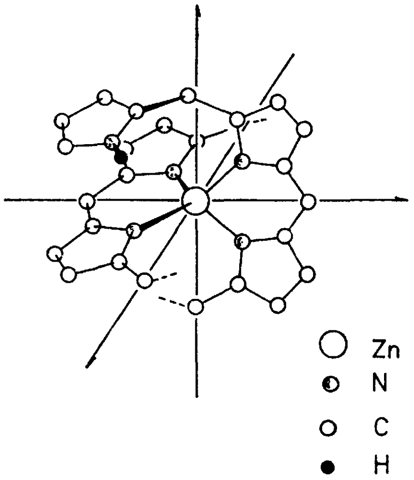


FIGURE 3 Plausible spatial arrangement of the ligand molecules around zinc(II)

An n.m.r. behaviour observed for the non-co-ordinating pyrrole *N*-protons and the bridging methylene-protons in the tripyrrene-*b* system was also the same and the similar structural elucidation can be applied to the tripyrrene–zinc(II) chelate.

I.r. Spectra.—The i.r. data assignable to N–H stretching, C=O stretching, and pyrrole skeletal vibrational modes are listed in Table 3. Both carbonyl and pyrrole skeletal bands shifted to lower frequency regions upon metal-co-ordination as is generally the case. In addition, the latter band resulted in splitting into two intense bands in the metal complexes. The higher energy band and the lower one are most likely due to free and co-ordinated pyrrole groups, respectively. A lower-energy shift of the skeletal vibrational band for the non-co-ordinating pyrrole ring upon chelation may be ascribed to the molecular packing effect.

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