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Transition-metal Complexes of Pyrrole Pigments. II.[1] Cobalt(II) and Nickel(II) Complexes of 1,19-Dideoxy-8,12-dicarbethoxy-1,3,7,13,17,19-hexamethylbiladiene-ac

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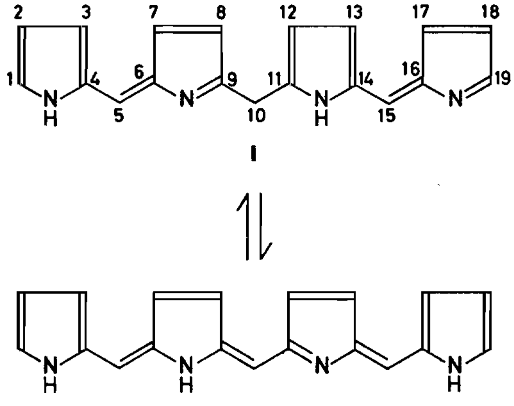
The cobalt(II) and nickel(II) complexes of 1,19-dideoxy-8,12-dicarbethoxy-1,3,7,13,17,19-hexamethylbiladiene-ac have been synthesized in this work and investigated by near-ultraviolet, visible, near-infrared and nmr measurements as well as vapor-pressure osmometry and mass spectroscopy for molecular weight determination. The ligand-field bands for these metal complexes have provided valuable information on their geometry around the central metal atoms. Namely, the cobalt complex assumes approximately the tetrahedral configuration, although more strict analysis of the ligand-field bands has been made in terms of C_{2v} symmetry. On the other hand, the nickel atom is subjected to the square-planar ligand-field in the complex. This conclusion has been further supported by nmr study. As for the overall structure of these metal complexes, the cobalt complex has been found to be dimeric while the nickel complex to be monomeric with a ligand to metal ratio of 1:1.

Introduction

The bile pigments, the breakdown products of the haem of haemoglobin, are the typical compounds possessing a linear tetrapyrrolic structure, each of the four pyrrole rings of which are bridged by a single carbon atom. Since these linear tetrapyrrolic compounds in general may behave as tetradentate ligands, they may form various polynuclear metal chelate compounds. In spite of these possibilities few investigation in this field has been carried out up to the present time. In connection with the chemistry of bilirubin, one of the bile pigments, the present investigation initiates the work on the various metal complexes of biladienes by means of electronic, vibrational and nmr spectroscopy. Dolphin *et al.* synthesized nickel(II) and cobalt(II) complexes of 1,19-dideoxy-8,12-diethyl-1,2,3,7,13,17,18,19-octamethylbiladiene-ac as intermediates in the synthesis of the corresponding corrin complexes.[2] They assigned a dimeric structure to the cobalt complex in which each cobalt atom attained tetrahedral configuration from both nmr and mass spectroscopy, while a monomeric planar structure was suggested for the nickel(II) complex from the nmr study.

This paper reports the synthesis and the structural properties of cobalt(II) and nickel(II) complexes of 1,19-dideoxy-8,12-dicarbethoxy-1,3,7,13,17,19-hexamethylbiladiene-ac, one of the 1,19-dideoxylbiladienes-ac (**I**), as examined by near-ultraviolet, visible, near-infrared and nmr measurements.



I

II

Experimental Section

Spectral Measurements. The visible and near-infrared absorption spectra for the ligand and the complexes in chloroform were recorded on a Hitachi Model EPS-2 spectrophotometer. The nmr spectra in chloroform-d and carbon tetrachloride for the nickel·chelate and the free ligand were measured on a Varian Model A-60 spectrometer using tetramethylsilane as an internal reference. The mass spectra were taken on a JEOL JMS-01SG mass spectrometer.

3,3′-Dicarbethoxy-4,4′-dimethyldipyrromethane. A 1-g sample of 3,3′-dicarbethoxy-4,4′-dimethyl-5,5′-dicarboxydipyrromethane[3,4] was placed in a sublimation apparatus and heated at 180-210° on an oil-bath for

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(1) Part I of this series: Y. Murakami and K. Sakata, *Inorg. Chim. Acta*, *2*, 273 (1968).

(2) D. Dolphin, R. L. N. Harris, J. L. Huppatz, A. W. Johnson, and I. T. Kay, *J. Chem. Soc.* (*C*), 30 (1966).

(3) A. H. Corwin, W. A. Bailey, and P. Viohl, *J. Am. Chem. Soc.*, *64*, 1270 (1942).

(4) H. Fischer and P. Halbig, *Ann. Chem.*, *447*, 134 (1926).

about 10 hr *in vacuo*. The sublimation product was recrystallized from ethanol to give 400 mg (51%) of colorless needles: m.p. 175.5-180° (lit.,[4] m.p. 173°); mol. wt. calcd. for $C_{17}H_{22}N_2O_4$ 318.16, mass analysis 318.16. Signals in the 60-MHz nmr spectrum were at $\delta(CCl_4)$ 1.37 (6 protons, triplet, assigned to methyl protons of the ethoxycarbonyl groups, J = 7 cps), 2.11 (6 protons, singlet, assigned to methyl protons of the 4,4'-dimethyl group), 4.28 (4 protons, quartet, assigned to methylene protons of the ethoxycarbonyl groups, J = 7 cps), 4.35 (2 protons, singlet, assigned to methylene protons of the bridging methylene group), and 6.22 (2 protons, singlet, assigned to ring protons at the 5,5'-positions).

Anal.[5] Calcd. for $C_{17}H_{22}N_2O_4$: C, 64.13; H, 6.97; N, 8.80. Found: C, 64.05; H, 7.01; N, 8.77.

2-Formyl-3,5-dimethylpyrrole. A 17.4-g sample of phosphoryl chloride was added dropwise to 8.5 g of N,N-dimethylformamide with stirring in 10 min at 5° and below. Into this solution was added 25 ml of dichloroethane and then 9.1 g of 2,4-dimethylpyrrole[6] dissolved in 25 ml of dichloroethane with sufficient stirring in 1 hr at 10°. After the reaction mixture being refluxed for 15 min, 75 g of sodium acetate tetrahydrate dissolved in 100 ml of water was added at room temperature. Then, the mixture was refluxed again for 15 min. The organic layer was separated and the aqueous layer was extracted three times with each 100 ml portion of ethyl ether. The combined mixture of organic layer and ether extracts was washed with concd sodium carbonate solution and dried over calcium sulfate. The solid material recovered from this mixture was recrystallized from petroleum ether and purified by sublimation *in vacuo*: yield 9.9 g (84%); m.p. 90-92°. Signals in the 60-MHz nmr spectrum appeared at $\delta(CCl_4)$ 2.29 (3 protons, singlet, assigned to methyl protons at the 3-position), 2.33 (3 protons, singlet, assigned to methyl protons at the 5-position), 5.78 (1 proton, singlet, assigned to ring proton at the 4-position), and 9.45 (1 proton, singlet, assigned to formyl proton).

1,19-Dideoxy-8,12-dicarbethoxy-1,3,7,13,17,19-hexamethylbiladiene-ac. To a mixture of each 2-g sample of 2-formyl-3,5-dimethylpyrrole and of 3,3'-dicarbethoxy-4,4'-dimethyldipyrromethane in 200 ml of methanol was added concd hydrochloric acid dropwise at 5° and below until no further precipitation was noticed. After the mixture was allowed to stand for one day, the reddish violet crystals were recovered. This product was recrystallized from chloroform to give 2.4 g of the hydrochloride. The biladiene free base was obtained by treatment of the hydrochloride suspended in methanol with concd ammonia: m.p. 170-171° (decomp.); mol. wt. calcd. for $C_{31}H_{36}N_4O_4$ 528.27, mass analysis 528.30. The nmr data are listed in Table II.

Anal. Calcd. for $C_{31}H_{36}N_4O_4$: C, 70.43; H, 6.86; N, 10.60. Found: C, 70.44; H, 6.93; N, 10.21.

1,19-Dideoxy-8,12-dicarbethoxy-1,3,7,13,17,19-hexamethylbiladiene-ac Complexes. The nickel(II) complex was prepared by adding 150 mg of nickel chloride hexahydrate in 10 ml of methanol to the suspension of 50 mg of the biladiene and 50 mg of sodium acetate in 40 ml of methanol while heating on a water-bath. After standing for one day at room temperature, dark reddish crystals were recovered and recrystallized from chloroform-methanol: yield 60 mg; m.p. 194-195° (decomp.); mol. wt. calcd. for $C_{31}H_{34}N_4O_4Ni$ 586.36, mass analysis 584.66, osmometric method[7] 580. The nmr data are listed in Table II.

Anal. Calcd. for $C_{31}H_{34}N_4O_4Ni$: C, 63.61; H, 5.85; N, 9.57; Ni, 10.0. Found: C, 63.54; H, 5.90; N, 9.62; Ni, 10.6.[8]

The cobalt(II) complex was produced by refluxing a mixture of 50 mg of the biladiene, 50 mg of sodium acetate and 150 mg of cobalt chloride hexahydrate in methanol (35 ml) for 1 hr. The green crystalline material was recrystallized from chloroform-methanol: yield 20 mg; m.p. $\nless$ 275°; mol. wt. calcd. for $(C_{31}H_{34}N_4O_4Co)_2$ 1171.15, osmometric method 1050.

Anal. Calcd. for $C_{31}H_{34}N_4O_4Co$: C, 63.59; H, 5.85; N, 9.57; Co, 10.1. Found: C, 63.05; H, 6.04; N, 9.28; Co, 10.9.[8]

Results and Discussion

Electronic Spectra. The visible and near-infrared spectra for the biladiene free base and the corresponding nickel and cobalt complexes are shown in Figure 1. 1,9-Dideoxy-8,12-dicarbethoxy-1,3,7,13,17 19-hexamethylbiladiene-ac shows five absorption bands, maxima of which are located at 425, 490, 590 (shoulder), 760 and 840 (shoulder) mμ. The absorption bands at 425 and 495 mμ are attributed to the $\pi \rightarrow \pi^*$ transitions of structure **I**. On the other hand, the intensity of the two bands appearing in the higher wavelength region show a characteristic temperature-dependence most likely due to thermal prototropy.[9] Since 1,19-dideoxy-8,12-diethyl-1,2,3,7,13,17,18,19-octamethylbilatriene-abc has been reported[10] to demonstrate the lowest energy transition in the visible region at 705 mμ with ε-value of 12,000, these bands at 760 and 840 mμ are tentatively assigned to the $\pi \rightarrow \pi^*$ transitions of structure **II** which is in equilibrium with **I**.

The cobalt complex shows eight absorption bands in the 300-2000 mμ range in chloroform. The bands in a higher energy region — 28,000 and 26,000 cm^{-1} — are considered to be due to the $\pi \rightarrow \pi^*$ transitions for which the ligand part is responsible. The strongest band at 20,500 cm^{-1} ($\varepsilon = 1.24 \times 10^5$) is attributed to the intramolecular charge transfer transition. The ligand-field bands in a lower energy region are listed in Table I together with the data on some

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(5) The elemental analyses were performed at the Microanalysis Center of Kyushu University.

(6) A. H. Corwin and R. H. Krieble, *J. Am. Chem. Soc.*, 63, 1829 (1941).

(7) A vapor pressure osmometer Model 301 A of Mechrolab, Inc., Mountain View, Calif. was used.

(8) The metal analisis was performed on a Nippon Jarrell-Ash atomic absorption spectrophotometer.

(9) Y. Murakami, Y. Kohno, and Y. Matsuda, unpublished results.

(10) E. Bullock, R. Grigg, A. W. Johnson, and J. W. F. Wasley, *J. Chem. Soc.*, 2326 (1965).

Table I. Ligand-field bands for cobalt complexes of some pyrrole pigments in chloroform[a]

Ligand[b] BLD[c]	TEDP	HDP	TRDP	Assignment
8330 (64.5) 10,750 (68.8)	8000 sh (50) 10,000 (67)	8100 sh (41) 10,300 (76)	7700 sh (25) 10,300 (59)	${}^4A_2(F) \longrightarrow {}^4T_1(F)$
13,550 (302) 14,600 (312) 16,300 sh (1610)	13,200 (336) 14,400 (304) 16,700 sh (1350)	13,000 (482) 14,000 (410) 15,900 sh (1590) 17,200 sh (3700)	13,400 (314) 14,500 (305) 16,300 sh (1420) 17,500 sh (2080)	${}^4A_2(F) \longrightarrow {}^4T_1(P)$

[a] Band positions are expressed in wavenumbers (cm^{-1}) and measured at room temperature; extinction coefficients are given in bracket after the band positions. [b] Abbreviation for the ligands: BLD, 1,19-dideoxy-8,12-dicarbethoxy-1,3,7,13,17,19-hexamethylbiladiene-ac; TEDP, 3,3′,5,5′-tetramethyldipyrromethene; HDP, 3,3′,4,4′,5,5′-hexamethyldipyrromethene; TRDP, 3,4,5-trimethyldipyrromethene. [c] Spectral parameters for the BLD complex: Δ = 5122 cm^{-1}, B' = 637 cm^{-1}, and β = 0.83.

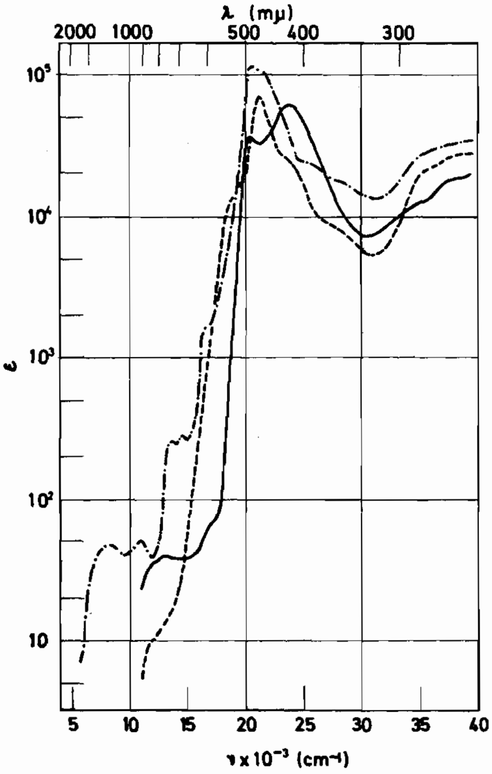


Figure 1. Electronic absorption spectra in chloroform: ——, 1,19-dideoxy-8,12-dicarbethoxy-1,3,7,13,17,19-hexamethylbiladiene-ac (free base); —·—·—, the cobalt complex; - - - - -, the nickel complex.

dipyrromethene complexes reported previously.[1] The band position and the corresponding intensity of the present complex are quite similar to those observed for the dipyrromethene complexes in their magnitude. Since the dipyrromethene complexes were concluded to assume a tetrahedral configuration around the central metal atom, the cobalt atom in the present complex is also placed approximately in a tetrahedral ligand-field with the spectral assignments listed in Table I. When a distortion of the tetrahedral configuration to a lower symmetry D_{2d} is attained, T_1-state is split into A_2 and E. This E-state is further split into B_1 and B_2 as symmetry goes down to C_{2v}. In fact, the ligand-field bands are grouped into two kinds of transitions in terms of T_d-symmetry as listed in Table I, and each is composed of two or three bands. Thus, these ${}^4A_2 \rightarrow {}^4T_1$ transitions in T_d ligand-field are now considered to be composed of three transitions in C_{2v} field; ${}^4A_2 \rightarrow {}^4B_1$, ${}^4A_2 \rightarrow {}^4B_2$, and ${}^4A_2 \rightarrow {}^4A_2$. The present ligand-field spectrum is, therefore, analyzed in terms of C_{2v} ligand-field: the assignments and the energy correlations are shown in Figure 2. The modulus of the ligand-field strength and the effective value of the Racah inter-electronic repulsion integral are evaluated for the T_d ligand-field as shown in Table I.

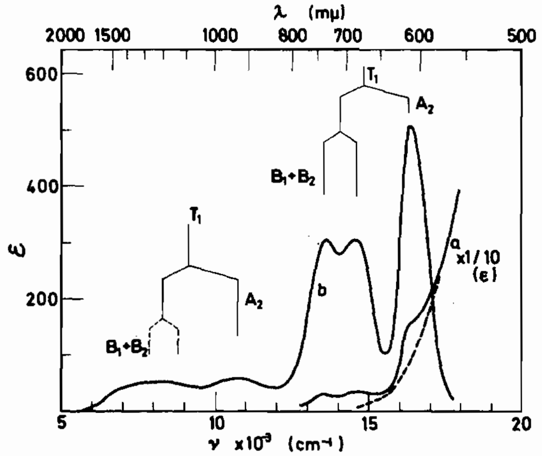
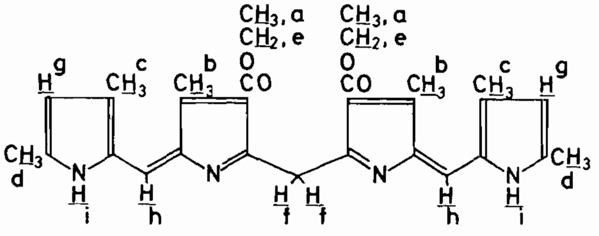


Figure 2. Ligand-field spectrum of the cobalt complex of 1,19-dideoxy-8,12-dicarbethoxy-1,3,7,13,17,19-hexamethylbiladiene-ac and energy correlation diagram. Curve b, absorption spectrum only due to ligand-field transitions, was obtained by substracting the absorption due to charge-transfer transition (shown by the broken line of curve a); curve a, observed absorption spectrum, was reduced in its intensity to 1/10 of the real magnitude.

The nickel complex demonstrates the strongest band at 21,000 cm^{-1} (ε = 7.36$\times$10^4) in the 300-2000 mμ range. This is attributed to the intramolecular charge transfer transition. In a higher energy region up to 300 mμ, there were observed two shoulder bands at 23,800 and 27,400 cm^{-1} which are assignable to the $\pi \rightarrow \pi^*$ transitions of the ligand part. Below 21,000 cm^{-1}, a broad weak band at 13,200 cm^{-1} and a more intense shoulder band at 18,500 cm^{-1} were observed. These bands are undoubtedly attributed to the ligand-field transitions.

Table II. Proton chemical shifts for BLD and the nickel complex

	Solvent	δ, ppm								
BLD	CCl_4	1.32	2.08	2.18	2.42	4.26	4.69	5.85	6.65	11.13
Ni complex	$CDCl_3$	1.39	1.98	2.18	2.57	4.33	4.87	5.93	7.00	—
Assignment		a	d	c	b	e	f	g	h	i



Since no ligand-field transitions seem to occur below 10,000 cm^{-1}, the biladiene-nickel(II) complex of the present study assumes approximately a square planar configuration around the central metal atom.[11]

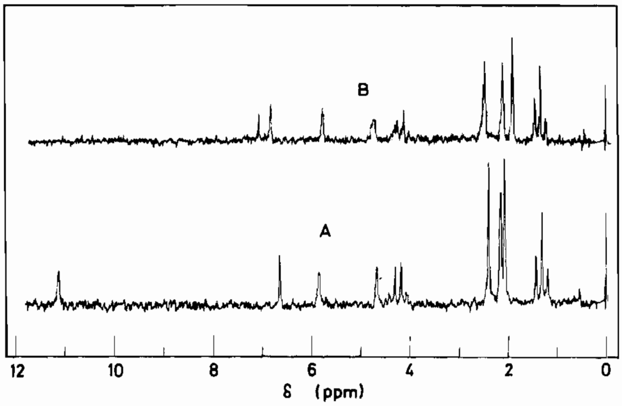
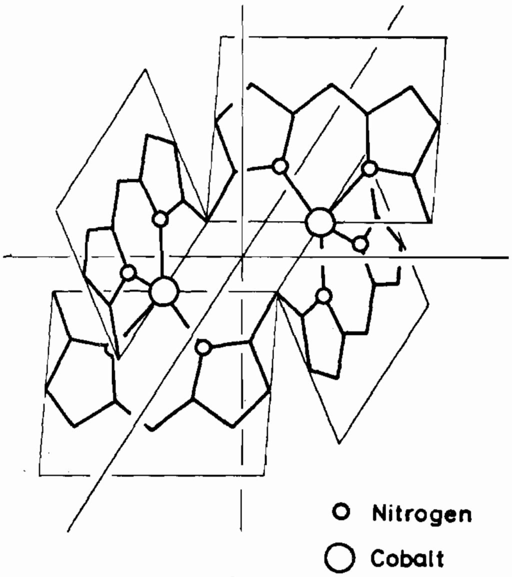


Figure 3. Nmr spectra of 1,19-dideoxy-8,12-dicarbethoxy-1,3,7,13,17,19-hexamethylbiladiene-ac in CCl_4 (A) and the corresponding nickel complex in $CDCl_3$ (B); TMS as an internal reference.

Nmr Spectrum of the Nickel Complex. The nmr spectra for the biladiene free base and the corresponding nickel complex are shown in Figure 3 and their assignments are listed in Table II. The signal for protons attached to the pyrrole-type nitrogen was found to disappear upon coordination, and all other proton signals except the 2.08 ppm signal of the free ligand shifted downfield. as well. The methyl protons at the 7- and 13-positions may be deshielded by the presence of carbonyl groups at the 8- and 12-positions. These methyl protons, therefore, give a resonance signal in the lowest field among all the methyl-group protons. The methyl groups at the 1- and 19-positions (α-position to the pyrrolic nitrogen) are considered to provide a proton signal in a higher field relative to the methyl groups at the 3- and 17-positions (β-position to the pyrrolic nitrogen). The 3,3′-dimethyl group of 3,5,3′-trimethyldipyrromethane provided their proton signal at 2.16 ppm in δ-value, while the 5-methyl group at 2.12 ppm. This result may support the above assignments. After all, the nickel atom is placed primarily in a square-planar ligand-field in the present complex, in agreement with the conclusion based on the ligand-field spectrum, and no extensive steric interaction between the methyl groups at the 1- and 19-positions seems to be present.

Structure of the Metal Complexes. The ligand-field analysis of electronic spectrum for the cobalt complex indicates that the cobalt atom is placed approximately in a tetrahedral ligand-field, although the strict ligand-field symmetry seems to be somewhat lowered. The elemental analysis of this complex is consistent with ligand to metal ratio of 1:1 with no additional ions or species. In addition, the molecular weight determination by means of vapor pressure osmometer provided the evidence of binuclear chelate formation. In fact, the inspection by means of a molecular model suggests that formation of the mononuclear complex with tetrahedral configuration around the cobalt atom is prohibited by steric reason. As a result, the most plausible structure for the binuclear cobalt complexes is depicted schematically as shown by **III**. This type of structure is consistent with the one proposed by Dolphin *et. al.*[2] for the 1,19-dideoxy-8,12-diethyl-1,2,3,7,13,17,18,19-octamethylbiladiene-ac complex, alhough they did not provide any ligand-field data.



III

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(11) A. B. P. Lever, « Inorganic Electronic Spectroscopy, » Elsevier Publishing Co., Amsterdam, 1968, p. 343.

The elemental analysis of the nickel complex is consistent with ligand to metal ratio of 1:1 with no additional species. The molecular weight determined by the aid of vapor pressure osmometer and mass spectrometer indicates a mononuclear nature of the complex. As for the steric configuration around the central nickel atom, both ligand-field spectrum and availability of the nmr spectrum are consistent with the square planar coordination. Since coordination of the nickel ion to the present biladiene resulted in only a slight up-field shift of proton signals of the 1- and 19-methyl groups, the steric repulsion between these two methyl groups seems to be too minor to cause any significant distortion from the square-planarity around the metal atom.

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