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Transition-metal Complexes of Pyrrole Pigments. XII. Optical and Magnetic Resonance Spectra of the Cobalt(II) and Nickel(II) Complexes of 1,19-Disubstituted Tetradehydrocorrins[†]

Yukito MURAKAMI, Kazunori SAKATA, Yasuhiro TANAKA, and Tadashi MATSUO

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

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The cobalt(II) and nickel(II) complexes of 1,19-dimethyl- and 1,19-diethoxycarbonyltetradehydrocorrins were prepared by the template reaction as functioned by metal ions from the corresponding 1,19-disubstituted 1,19-dideoxybiladiene-ac's. The absorption bands appearing in the energy region greater than 15000 cm^{-1} were attributed to the $\pi \rightarrow \pi^*$ transitions within a ligand molecule. The ligand-field bands were observed in the lower energy region (<15000 cm^{-1}) for the cobalt(II) complexes in which cobalt(II) assumes the C$_{2v}$ coordination symmetry: $^2A_1 \leftarrow {}^2A_1$, $^2A_2 \leftarrow {}^2A_1$, $^2B_2 \leftarrow {}^2A_1$, and $^2B_1 \leftarrow {}^2A_1$ in an increasing order of energy. The vibrational spectra provided evidences for the formation of the tetradehydrocorrin complexes with perchlorate ion as the counter ion. The angular methyl groups placed at the 1- and 19-positions of tetradehydrocorrins showed the abnormally large up-field shift (2.0 ppm) of their proton signal relative to the parent biladiene-ac's due to the magnetic anisotropy of the adjacent pyrrole rings A and D. For a 1,19-diethyoxycarbonyltetradehydrocorrin complex, the 1,19-substituents were also placed in the shielding zone of the neighboring pyrrole rings. In the case of the cyclized 2,8,12,18-tetra(2-ethoxycarbonylethyl) derivative, the ethyl ester groups of the 2,18-substituents were presumably placed in a conformational space different from that occupied by those of the 8,12-substituents according to the proton NMR behaviors. The parent biladiene-ac which carries ethoxycarbonyl groups at the 1,19-positions caused a up-field shift of its methine (at bridge positions) proton signal upon cyclization due to the loss of electronic conjugation of carbonyl groups with pyrrole rings, in consistent with the vibrational data. The ESR spectra were measured in chloroform–benzene (2 : 1) at 77 K in the presence and absence of pyridine. The cobalt(II) complexes were identified as of low-spin square-planar type with the unpaired electron in the cobalt d_{z^2} orbital. The coordination capability of 2-ethoxycarbonylethyl groups, which are directly bound to the pyrrole rings in the cyclized metal complex system, was also suggested.

Much work has been carried out on vitamin B$_{12}$ model compounds of the cobaloxime type to obtain some information which may throw light on the chemistry of vitamin B$_{12}$ itself.[1,2] On the other hand, 1,19-disubstituted tetradehydrocorrins have a ring structure which is closely related to the corrin ring of vitamin B$_{12}$. The cobalt complexes are of particular interest since these are the direct analogs of the vitamin B$_{12}$ complexes. Hush and Woolsey studied the electronic and ESR spectra of the cobalt(II) and nickel(II) complexes of 1,19-diethoxycarbonyltetradehydrocorrins[3,4] without assignments of ligand-field bands observable in the electronic spectra.

On account of the increasing interest in the chemistry and structural feature of vitamin B$_{12}$, we report in this paper the results of electronic spectra of the cobalt(II) and nickel(II) complexes of 1,19-dimethyl- and 1,19-diethoxycarbonyltetradehydrocorrins with ligand-field interpretations as well as vibrational spectra of the complexes. The detailed NMR studies for the nickel(II) complexes and the ESR data for the cobalt(II) are also provided. The metal complexes of 1,19-disubstituted tetradehydrocorrins (**2**) were prepared by the template reaction as functioned by metal ions from the corresponding 1,19-disubstituted 1,19-dideoxybiladiene-ac's (**1**).

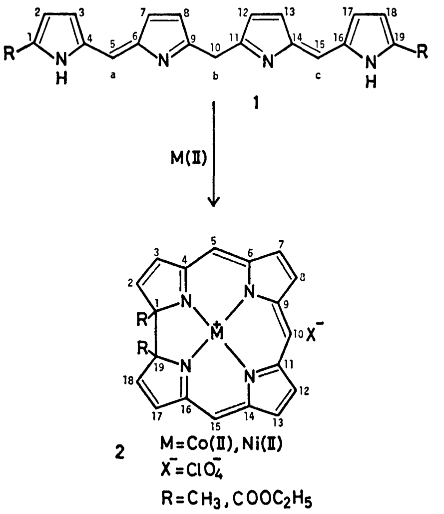

Chart 1.

Experimental

1,19-Dideoxy-1,3,7,8,12,13,17,19-octamethylbiladiene-ac Dihydrobromide (3). Prepared after Johnson *et al.*[5] from 3,3',4,4'-tetramethyl-5,5'-dicarboxydipyrromethane[6,7] (14.0 g) and 2-formyl-3,5-dimethylpyrrole[8] (11.5 g) in methanol (1150 ml) and aqueous ammonia (3.3 ml, 28%), the resulting solution being treated with aqueous hydrobromic acid (33 ml, 47%). The product was recrystallized from chloroform as red prisms with a green luster; yield 18.1 g (66%). UV(CHCl$_3$): 19200(ε 2.05×10^5), 20400 sh(ε 3.58×10^4), 22100(ε 2.10×10^4), 23500 sh(ε 9.20×10^3), 27100(ε 1.37×10^4), and 34400 cm^{-1}(ε 2.73×10^3). IR(Nujol mull): 1611 cm^{-1}(biladiene skeletal str.). Found: C, 56.41; H, 6.05; N, 9.49%. Calcd for $C_{27}H_{34}Br_2N_4$: C, 56.46; H, 5.97; N, 9.75%.

1,19-Dideoxy-1,2,3,7,8,12,13,17,18,19-decamethylbiladiene-ac Dihydrobromide (4). Prepared as above[9] from 3,3',4,4'-tetramethyl-5,5'-dicarboxydipyrromethane (1.5 g) and 2-

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[†] Contribution No. 377 from this Department. Part XI: Y. Murakami and K. Sakata, This Bulletin, **47**, 3025 (1974).

formyl-3,4,5-trimethylpyrrole[10,11] (0.75 g) in methanol (150 ml) and aqueous ammonia (0.2 ml, 28%). The resulting solution was treated with aqueous hydrobromic acid (3 ml, 47%) and the product was recrystallized from chloroform-light petroleum as red prisms; yield 1.4 g (67%).

1,19-Dideoxy-8,12-di(2-ethoxycarbonylethyl)-1,2,3,7,13,17,18,19-octamethylbiladiene-ac Dihydrobromide (**5**). 3,3′-Di(2-ethoxycarbonylethyl)-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid (**6**) was first prepared as follows. Dibenzyl 3,3′-di(2-ethoxycarbonylethyl)-4,4′-dimethyldipyrromethane-5,5′-dicarboxylate[12] (10 g) was hydrogenated in dry tetrahydrofuran (250 ml) and triethylamine (0.5 g) over 10% palladium-carbon (1.25 g) for 2 h. Saturated aqueous sodium hydrogen carbonate was added to the resulting mixture and tetrahydrofuran was removed *in vacuo* from the filtrate. The precipitates obtained by the addition of acetic acid were recovered and washed repeatedly with water; white powder, yield 6.1 g (85%), mp>300 °C. IR(KBr disk): 1710 (ester C=O str.), and 1656 cm^{-1} (carboxyl C=O str.). NMR (H_2O-KOH, tetramethylammonium chloride): δ 1.56 (2H, s, $-C\underline{H}_2-$(bridge)), 0.64 (4H, q $J=7.0$ Hz, 3,3′-$CH_3C\underline{H}_2$-$OCOCH_2CH_2$–), -0.18—-0.46 (8H, m, 3,3′-$CH_3CH_2OCOC\underline{H}_2C\underline{H}_2$–), -0.75 (6H, s, 4,4′-$C\underline{H}_3$), and -1.85 (6H, t $J=7.0$ Hz, 3,3′-$C\underline{H}_3CH_2OCOCH_2CH_2$–).

The biladiene-ac dihydrobromide (**5**) was prepared[13] from **6** (1.51 g) and 2-formyl-3,4,5-trimethylpyrrole (0.68 g) in ethanol (7 ml) and aqueous hydrobromic acid (1 ml, 47%). The product was washed and recrystallized from chloroform–light petroleum (bp 80—100 °C) as red needles; yield 1.03 g (40%), mp>300 °C. IR(KBr disk): 1732 (ester C=O str.), 1616 (biladiene skeletal str.), and 1245 cm^{-1} (C–O–C str.). Found: C, 56.90; H, 6.41; N, 7.09%. Calcd for $C_{37}H_{50}Br_2N_4O_4$: C, 57.37; H, 6.51; N, 7.23%.

1,19-Dideoxy-2,8,12,18-tetra(2-ethoxycarbonylethyl)-1,3,7,13,17,19-hexamethylbiladiene-ac Dihydrobromide[13] (**7**). A mixture of 3,3′-di(2-ethoxycarbonylethyl)-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid (2.31 g), aqueous ammonia (0.4 ml, 28%), and methanol (50 ml) was refluxed with stirring. After addition of 3-(2-ethoxycarbonylethyl)-5-formyl-2,4-dimethylpyrrole[13] (2.23 g) dissolved in methanol (20 ml) and aqueous hydrobromic acid (3.5 ml, 47%) subsequently, the reaction mixture was refluxed for another 15 min with stirring. Upon cooling the mixture in a refrigerator overnight, the crystalline solid was recrystallized from chloroform–acetone to give red needles; yield 2.8 g (59%), mp>300 °C. IR(KBr disk): 1728 (ester C=O str.), 1610 (biladiene skeletal str.), and 1237 cm^{-1} (C–O–C str.).

1,19-Dideoxy-1,19-diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethylbiladiene-ac Dihydrobromide[14] (**8**). A mixture of phosphorus oxychloride (13 ml) and *N,N*-dimethylformamide (100 ml) was added dropwise into 3,4-dimethyl-2-ethoxycarbonylpyrrole[6] (20.8 g) which was dissolved in *N,N*-dimethylformamide (200 ml) and cooled with ice-water. An aqueous solution (700 ml) of anhydrous sodium acetate (44 g) was added into the reaction mixture, which was heated at 70—80 °C for 1 h subsequently. After being allowed to stand overnight in a refrigerator, the crystalline solid was recovered and recrystallized from *i*-octane to give colorless plates of 3,4-dimethyl-2-ethoxycarbonyl-5-formylpyrrole; yield 19.4 g (79.8%), mp 107.5—108.0 °C (lit,[15] mp 106—108 °C). IR(Nujol mull): 3320 (N–H str.), 1692, 1656 (C=O str.), and 1265 cm^{-1} (C–O–C str.). NMR(CCl_4, TMS): δ 1.39 (3H, t $J=7.0$ Hz, 2-$C\underline{H}_3CH_2OCO$–), 2.23, 2.27 (6H, each s, 3-$C\underline{H}_3$ and 4-$C\underline{H}_3$), 4.38 (2H, q $J=7.0$ Hz, 2-$CH_3C\underline{H}_2$-OCO–), 9.77 (1H, s, 5-$C\underline{H}O$), and 10.03 (1H, s, 1-$\underline{H}$).

Into a mixture of 3,4-dimethyl-2-ethoxycarbonyl-5-formylpyrrole (2.05 g), 3,3′,4,4′-tetramethyldipyrromethane-5,5′-dicarboxylic acid (1.3 g) and glacial acetic acid (25 ml) was added aqueous hydrobromic acid (5.5 ml, 47%) with stirring. The mixture was warmed at 40—43 °C for 40 min and allowed to stand in a refrigerator overnight. The crystalline solid was washed with acetic acid and ethyl ether subsequently to give reddish brown needles; yield 2.35 g (72.4%), mp>300 °C. IR(Nujol mull): 1705, 1712 (ester C=O str.), and 1604 cm^{-1} (biladiene skeletal str.).

1,3,7,8,12,13,17,19-Octamethyltetradehydrocorrinatocobalt(II) Perchlorate. Air was bubbled through a mixture of biladiene-ac dihydrobromide (**3**) (0.5 g), cobalt acetate tetrahydrate (0.5 g), and ethanol (30 ml) at room temperature for 6 h. The mixture was concentrated to *ca.* 10 ml *in vacuo*, and subsequently an aqueous solution (10 ml) of sodium perchlorate monohydrate (0.5 g) was added into it. The precipitates were separated and recrystallized from methanol-acetone to give dark brown needles; yield 0.29 g (59%), mp>300 °C. Found: C, 56.82; H, 5.12; N, 9.84%. Calcd for $C_{27}H_{29}ClCoN_4O_4$: C, 57.10; H, 5.15; N, 9.87%.

1,3,7,8,12,13,17,19-Octamethyltetradehydrocorrinatonickel(II) Perchlorate. A mixture of biladiene-ac dihydrobromide (**3**) (0.5 g), nickel acetate tetrahydrate (0.5 g), and ethanol (7 ml) was heated at 60 °C for 30 min. The stream of air was bubbled through the reaction mixture into which anhydrous sodium acetate (0.5 g) was added in advance. An aqueous solution (7.5 ml) of sodium perchlorate monohydrate (1 g) was added in the reaction mixture which was subsequently kept in a refrigerator overnight. The recovered crystalline solid was recrystallized from chloroform to give dark violet needles; yield 0.135 g (68%). Found: C, 56.90; H, 5.24; N, 10.00%. Calcd for $C_{27}H_{29}ClN_4NiO_4$; C, 57.12; H, 5.15; N, 9.87%.

1,2,3,7,8,12,13,17,18,19-Decamethyltetradehydrocorrinatocobalt(II) Perchlorate. Prepared from biladiene-ac dihydrobromide (**4**) (2.3 g) and cobalt acetate tetrahydrate (2.3 g) in ethanol (200 ml) after Melent'eva *et al.*[9] The product was recrystallized from methanol–acetone to give dark brown prisms of golden luster; yield 1.42 g (62%). Found: C, 58.27; H, 5.62; N, 9.53%. Calcd for $C_{29}H_{33}ClCoN_4O_4$: C, 58.44; H, 5.58; N, 9.40%.

1,2,3,7,8,12,13,17,18,19-Decamethyltetradehydrocorrinatonickel(II) Perchlorate. Prepared from biladiene-ac dihydrobromide (**4**) (1.4 g) and nickel acetate tetrahydrate (1.4 g) in the presence of anhydrous sodium acetate (1.4 g) and ethanol (200 ml) after Melent'eva *et al.*[9] The product was recrystallized from methanol–acetone to give dark brown needles; yield 0.83 g (60%). Found: C, 58.77; H, 5.73; N, 9.52%. Calcd for $C_{29}H_{33}ClN_4NiO_4$: C, 58.47; H, 5.58; N, 9.40%.

8,12-Di(2-ethoxycarbonylethyl)-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrinatocobalt(II) Perchlorate. Prepared from biladiene-ac dihydrobromide (**5**) (0.287 g) and cobalt acetate tetrahydrate (0.30 g in 3 ml H_2O) in ethanol (100 ml) after Johnson *et al.*[13] The crystalline solid was washed with ethyl ether (100 ml) and *n*-hexane (40 ml) successively and recrystallized from dichloromethane–*n*-hexane to give reddish brown needles; yield 0.075 g (27%), mp 225.0—225.2 °C (lit.,[13] mp 181—183 °C). Found: C, 58.15; H, 5.96; N, 6.98%. Calcd for $C_{37}H_{45}ClCoN_4O_8$: C, 57.85; H, 5.91; N, 7.29%.

8,12-Di(2-ethoxycarbonylethyl)-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrinatonickel(II) Perchlorate. Prepared from biladiene-ac dihydrobromide (**5**) (0.52 g) and nickel acetate tetrahydrate (0.60 g) in the presence of anhydrous sodium acetate (0.60 g) and ethanol (15 ml) after Johnson *et al.*[13] The product was recrystallized from ethanol–light petroleum (bp 80—100 °C) to give violet needles; yield 0.37 g (71%), mp 243.2—244.3 °C (lit.,13) mp 243—244 °C). Found: C, 58.08; H, 5.83; N, 7.21%. Calcd for $C_{37}H_{45}ClN_4NiO_8$: C, 57.87; H, 5.91; N, 7.30%.

2,8,12,18-Tetra(2-ethoxycarbonylethyl)-1,3,7,13,17,19-hexamethyltetradehydrocorrinatocobalt(II) Perchlorate. Prepared from biladiene-ac dihydrobromide (**7**) (1.0 g) and cobalt acetate tetrahydrate (1.0 g in 10 ml H_2O) in ethanol (200 ml) after Johnson *et al.*13) The crystalline solid was washed with ethyl ether (100 ml) and recrystallized from ethanol-light petroleum (bp 80—100 °C) to give dark reddish needles; yield 0.50 g (48%), mp 139.9—141.7 °C (lit.,13) mp 175 °C). Found: C, 56.85; H, 6.03; N, 5.89%. Calcd for $C_{45}H_{57}ClCON_4O_{12}$: C, 57.48; H, 6.11; N, 5.96%.

2,8,12,18-Tetra(2-ethoxycarbonylethyl)-1,3,7,13,17,19-hexamethyltetradehydrocorrinatonickel(II) Perchlorate. Prepared from biladiene-ac dihydrobromide (**7**) (1.0 g) and nickel acetate tetrahydrate (1.0 g) in the presence of anhydrous sodium acetate (1.0 g) and ethanol (50 ml) after Johnson *et al.*13) The product was recrystallized from ethanol-light petroleum (bp 80—100 °C) to give reddish violet needles; yield 0.56 g (56%), mp 162.4—165.6 °C (lit.,13) mp 169—170 °C). Found: C, 57.70; H, 5.97; N, 6.16%. Calcd for $C_{45}H_{57}ClN_4NiO_{12}$: C, 57.49; H, 6.11; N, 5.96%.

*1,19-Diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethyltetradehydrocorrinatocobalt(II) Perchlorate.*14) An aqueous solution (25 ml) of cobalt acetate tetrahydrate (5.0 g) was added into an ethanol suspension (500 ml) of biladiene-ac dihydrobromide (**8**) (5.0 g). Air was introduced into the reaction mixture at room temperature for 2 hr with continuous stirring, which was subsequently concentrated to a half volume. After addition of an aqueous solution (30 ml) of sodium perchlorate monohydrate (5.0 g), the reaction mixture was allowed to stand in a refrigerator for 3 hr. The crystalline solid was washed with ethyl ether and recrystallized from acetone–*n*-hexane to give brown pillar-like crystals of golden luster; yield 4.2 g (85%), mp>300 °C. Found: C, 55.89; H, 5.46; N, 7.92%. Calcd for $C_{33}H_{37}ClCoN_4O_8$: C, 55.67; H, 5.24; N, 7.87%.

*1,19-Diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethyltetradehydrocorrinatonickel(II) Perchlorate.*14) A methanol solution (10 ml) of nickel acetate tetrahydrate (2.0 g) was added into a methanol suspension (200 ml) of biladiene-ac dihydrobromide (**8**) (2.0 g). The mixture was refluxed for 2 hr while air was continuously bubbled through it, and then concentrated to a half volume. After addition of an aqueous solution (100 ml) of sodium perchlorate monohydrate (2.0 g), the reaction mixture was allowed to stand overnight in a refrigerator. The crystalline product was recrystallized from acetone–*n*-hexane to give brown pillar-like crystals; yield 1.7 g (86%), mp>300 °C. Found: C, 55.53; H, 5.20; N, 7.76%. Calcd for $C_{33}H_{37}ClN_4NiO_8$: C, 55.67; H, 5.24; N, 7.89%.

Spectral Measurements. Electronic spectra covering the 5000—40000 cm^{-1} region were recorded on a Hitachi EPS-2 spectrophotometer for chloroform solutions at room temperature. Vibrational spectra were measured with a JASCO DS-403G spectrophotometer by Nujol mull and KBr disk methods. A Varian A-60 spectrometer was used to obtain NMR spectra in trifluoroacetic acid at room temperature. Chemical shifts were reported in ppm from internal TMS and calibrated by the use of chloroform signal as the external reference. ESR spectra were recorded on a JEOL JES-ME-3 X-band spectrometer equipped with a 100K Hz field modulation unit. All samples were measured in chloroform-benzene (2 : 1) at 77 K, concentrations being maintained in the 10^{-2} M range. The manganese ion diffused into magnesium oxide was used to obtain the standard reference signals for measurements.

Results and Discussion

Electronic Spectra. The electronic spectra of the cobalt(II) and nickel(II) complexes are shown in Figs. 1 and 2, respectively, and the absorption bands appearing in the energy region greater than 15000 cm^{-1} are reasonably attributed to the $\pi\rightarrow\pi^*$ transitions within a ligand molecule. The general features of the spectra arising from the $\pi\rightarrow\pi^*$ transitions are similar to those observed for metal porphyrins16,17) and corrins.18) An extremely intense band is observed around 28000 cm^{-1} analogous to the Soret band of porphyrins, with a weaker series of bands in the 15000—25000 cm^{-1} region comparable with the α and β bands of metal porphyrins. Hush and his associates have established on the basis of PPP-SCF π-electron calculations 4,19) that the absorption bands of metal corroles appearing in the similar energy region arise from the $\pi\rightarrow\pi^*$ transitions of the corrole ligand. The $\pi\rightarrow\pi^*$ transition energies for the present cobalt(II) and nickel(II) complexes are summarized together in Table 1.

The nickel(II) complexes do not show any significant absorption in the region lying below 15000 cm^{-1}. This spectral behavior is consistent with the square planar coordination of nickel(II).20) Due to the presence of intense $\pi\rightarrow\pi^*$ absorption bands in the higher energy region, we failed to assign ligand-field transition bands for the nickel(II) complexes.

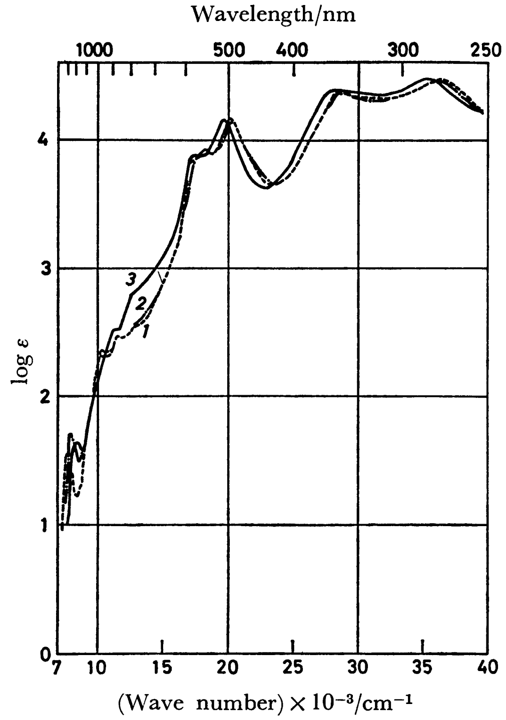

Fig. 1. Electronic absorption spectra of the tetradehydrocorrinatocobalt(II) perchlorates in chloroform at room temperature. Ligands: **1**, 1,2,3,7,8,12,13,17,18,19-decamethyltetradehydrocorrin; **2**, 8,12-di(2-ethoxycarbonylethyl)-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrin; **3**, 1,19-diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethyltetradehydrocorrin.

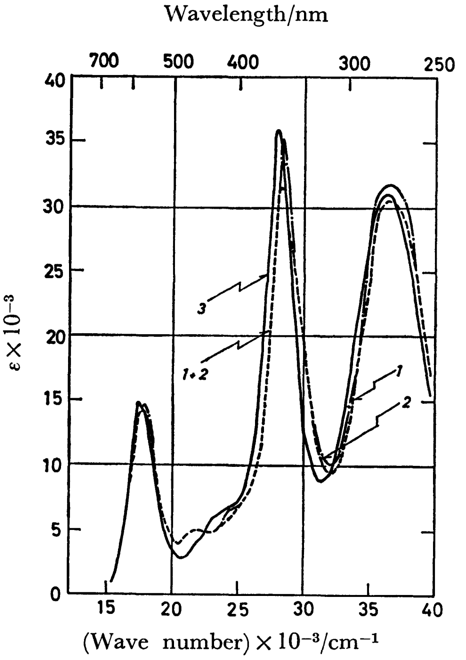

Fig. 2. Electronic absorption spectra of the tetradehydrocorrinatonickel(II) perchlorates in chloroform at room temperature. See Fig. 1 for numbering of the ligands.

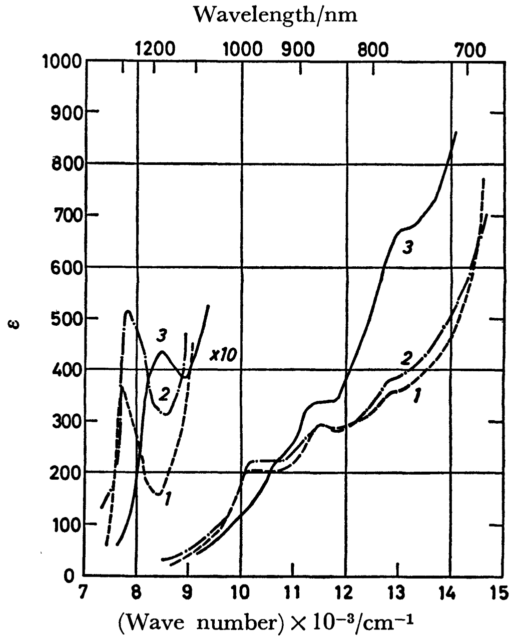

Fig. 3. Ligand-field spectra of the tetradehydrocorrinatocobalt(II) perchlorates in chloroform at room temperature. See Fig. 1 for numbering of the ligands.

The absorption spectra of the cobalt(II) complexes in the lower energy region (below 15000 cm^{-1}) are shown in Fig. 3. Nishikawa and Yamada pointed out that the ligand-field band appeared at around 8000 cm^{-1} is characteristic of the square planar low-spin cobalt(II) complexes.[21)] The present cobalt(II) complexes show a distinct absorption band in the similar energy region. Meanwhile, Nishida and Kida[22)] and Engelhardt and Green[23)] as well have carried out ligand-field calculations for tetragonal low-spin d^7 complexes using a d^3 hole ligand-field model. We employed a energy level correlation different from these proposed by the former investigators on the basis of band-splitting behavior of the present spectra, and the ligand-field bands are assigned under the assumption of C$_{2v}$ coordination

Table 1. Electronic absorption bands due to $\pi \rightarrow \pi^*$ transitions for the cobalt(II) and nickel(II) complexes of 1,19-disubstituted tetradehydrocorrins[a)]

Ligand[b)]	Transition energy in cm^{-1} (ε)			
	Co(II)		Ni(II)	
I	17600 sh (6590)	18400 (7950)	18200 (14400)	22200 (5070)
	20400 (13500)	28600 (20300)	25000 sh (6290)	28500 (27600)
	36100 (27600)		36500 (27700)	
II	17500 sh (7080)	18200 (8190)	17900 (14200)	21700 (4990)
	20100 (14400)	28400 (23400)	25000 sh (6520)	28300 (31400)
	36100 (29400)		36500 (30500)	
III	17500 sh (7420)	18300 (8230)	17900 (14500)	21700 (4990)
	20200 (13800)	28400 (23900)	24400 sh (6490)	28400 (34100)
	35700 (29300)		36400 (31700)	
IV	17500 sh (7650)	18200 (8190)	17700 (14300)	21700 sh (5900)
	20100 (13000)	28400 (23100)	25000 sh (9160)	28200 (32300)
	35300 (29900)		36000 (32100)	
V	17400 (7670)	18200 sh (7580)	17400 (14600)	21700 sh (3810)
	19700 (14300)	28200 (23700)	23300 sh (6000)	27900 (34900)
	35200 (29700)		36200 (31000)	

a) Measured in chloroform at room temperature. All the metal complexes are in the perchlorate salt form.
b) I, 1,3,7,8,12,13,17,19-octamethyltetradehydrocorrin; II, 1,2,3,7,8,12,13,17,18,19-decamethyltetradehydrocorrin; III, 8,12-di(2-ethoxycarbonylethyl)-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrin; IV, 2,8,12,18-tetra(2-ethoxycarbonylethyl)-1,3,7,13,17,19-hexamethyltetradehydrocorrin; V, 1,19-diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethyltetradehydrocorrin.

Table 2. Ligand-field bands for the tetradehydrocorrinatocobalt(II) perchlorates[a,b]

Ligand[c]					Assignment	
I	II	III	IV	V	C_{2v}	D_{4h}
7840(49.0)	7700(36.2)	7800(51.0)	8000(111)	8500(43.4)	$^2A_1 \leftarrow {}^2A_1$	$^2B_{2g} \leftarrow {}^2A_{1g}$
10400(238)	10200(202)	10200(221)	10200 sh (390)	10600 sh (217)	$^2A_2 \leftarrow {}^2A_1$	$^2E_g \leftarrow {}^2A_{1g}$
11800 sh (361)	11500(291)	11500(293)	11500 sh (620)	11300 sh (327)	$^2B_2 \leftarrow {}^2A_1$	
12800 sh (432)	12800 sh (351)	12800 sh (377)	12800 sh (921)	13000 sh (670)	$^2B_1 \leftarrow {}^2A_1$	$^2B_{1g} \leftarrow {}^2A_{1g}$

a) Band positions are expressed in cm^{-1} and molar extinction coefficients are given in parentheses after the band positions. b) Measured in chloroform at room temperature. c) See Table 1 for numbering of the ligands.

symmetry in consistent with the spectral feature shown in Fig. 3, as listed in Table 2.

Vibrational Spectra. The characteristic IR bands, which are meaningful for the present discussion, are summarized in Table 3 for metal-free biladiene-ac's and tetradehydrocorrin complexes. A strong absorption band observed at around 1600 cm^{-1} for a biladiene-ac dihydrobromide can be attributed to the stretching mode of the dipyrromethene skeleton. The similar spectral feature has been observed for dipyrromethenes,[24—29] tripyrrene-b, and bilene-b.[30] This characteristic band loses its intensity to a large extent as seen in Fig. 4 upon formation of the tetradehydrocorrin macrocycle in a manner as observed for the porphyrin system.[31] The change in absorption intensity may be due to the structural nature of the macrocycle which is nearly fixed in one plane. This structural effect would inhibit the independent skeletal vibration of each pyrrole ring and consequently diminish its IR activity.

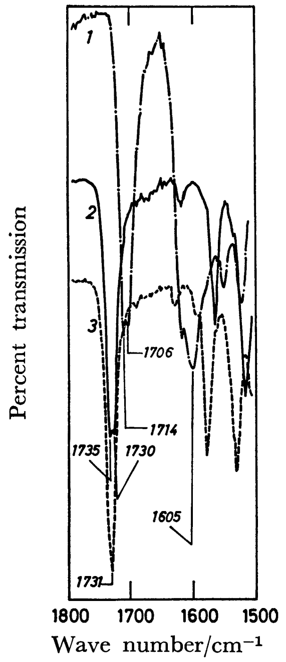

Fig. 4. Infrared spectra of biladiene-ac dihydrobromide and tetradehydrocorrin complexes by a Nujol mull technique: **1**, 1,9-dideoxy-1,19-diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethylbiladiene-ac dihydrobromide; **2**, 1,19-diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethyltetradehydrocorrinatocobalt(II) perchlorate; **3**, 1,19-diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethyltetradehydrocorrinatonickel(II) perchlorate.

Since the carbonyl group of 2-ethoxycarbonylethyl in the biladiene-ac's does not have any electronic interaction with the pyrrole rings due to the structural reasons, the corresponding stretching mode is not affected by metal coordination as seen in spectra for the corresponding metal tetradehydrocorrins (III and IV in Table 3). On the other hand, the ethoxycarbonyl groups of 1,19-dideoxy-1,19-diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethylbiladiene-ac lose their electronic conjugation with the pyrrole rings upon formation of the tetradehydrocorrin ring. Consequently, the C=O stretching band due to these carbonyl groups, which is observed in a relatively low frequency region for the biladiene-ac, is shifted to higher frequency upon metal coordination (V is Table 3).

A strong broad absorption at around 1080 cm^{-1} was observed for all the metal complexes and attributed to the stretching vibrational mode of perchlorate ion.[32] Since no splitting of this characteristic band was detected, the perchlorate group in the present metal complexes may be present not as a coordinated group but as a simple isolated ion.[33] Another peak due to the perchlorate group was observed at about 620 cm^{-1}, which may be attributed to its bending vibration.[33]

NMR Spectra. The NMR data for the 1,19-dideoxybiladiene-ac's and the corresponding tetradehydrocorrinatonickel(II) complexes are summarized in Table 4. The methyl-proton peak observed in the lowest field (2.72—2.77 ppm) for the biladiene-ac's is shifted to up-field by about 2.0 ppm upon cyclization along with nickel(II)-coordination (I—IV in Table 4). The abnormally large up-field shift is most likely associated with the angular methyl groups of the 1- and 19-positions.[15] The angular methyl groups placed at the 1- and 19-positions of tetradehydrocorrin are subjected to the shielding effect caused by the magnetic anisotropy of the adjacent pyrrole rings A and D. The proton signals for other methyl groups directly bound to the pyrrole rings show the down-field shift upon cyclization to form the tetradehydrocorrin macrocycle. These down-field shifts can be attributed to the deshielding effect due to positive charge provided by nickel(II) as well as to the additional anisotropy by the macrocyclic ring system. A similar behavior of methyl resonances has been observed for the zinc(II) chelates of dipyrromethenes.[29]

In the case of the cyclized 1,19-diethoxycarbonyl derivative, the 1,19-substituents are also placed in the shielding zone of the neighboring pyrrole rings as

TABLE 3. CHARACTERISTIC IR ABSORPTION BANDS FOR THE COBALT(II) AND NICKEL(II) COMPLEXES OF 1,19-DISUBSTITUTED TETRADEHYDROCORRINS AND THE PARENT BILADIENE-AC'S[a,b]

Ligand[c]	Form	IR band (cm^{-1})	Assignment
I′	2 HBr	1613 (s)	$\nu_{C=C,\ C=N}$ (dipyrromethene skeletal)
I	Co^{II} chelate	1614 (w)	$\nu_{C=C,\ C=N}$ (macrocyclic skeletal)
		1095 (s br)	$\nu_{ClO_4^-}$
		622 (s)	$\delta_{ClO_4^-}$
I	Ni^{II} chelate	1621 (w)	$\nu_{C=C,\ C=N}$ (macrocyclic skeletal)
		1085 (s br)	$\nu_{ClO_4^-}$
		622 (s)	$\delta_{ClO_4^-}$
II′	2 HBr	1613 (s)	$\nu_{C=C,\ C=N}$ (dipyrromethene skeletal)
II	Co^{II} chelate	1622 (w)	$\nu_{C=C,\ C=N}$ (macrocyclic skeletal)
		1088 (s br)	$\nu_{ClO_4^-}$
		621 (s)	$\delta_{ClO_4^-}$
II	Ni^{II} chelate	1625 (w)	$\nu_{C=C,\ C=N}$ (macrocyclic skeletal)
		1092 (s br)	$\nu_{ClO_4^-}$
		622 (s)	$\delta_{ClO_4^-}$
III′	2 HBr	1730 (s)	$\nu_{C=O}$ (ester)
		1618 (s)	$\nu_{C=C,\ C=N}$ (dipyrromethene skeletal)
III	Co^{II} chelate	1726 (s)	$\nu_{C=O}$ (ester)
		1623 (w)	$\nu_{C=C,\ C=N}$ (macrocyclic skeletal)
		1086 (s br)	$\nu_{ClO_4^-}$
		622 (s)	$\delta_{ClO_4^-}$
III	Ni^{II} chelate	1727 (s)	$\nu_{C=O}$ (ester)
		1630 (w)	$\nu_{C=C,\ C=N}$ (macrocyclic skeletal)
		1079 (s br)	$\nu_{ClO_4^-}$
		622 (s)	$\delta_{ClO_4^-}$
IV′	2 HBr	1728 (s)	$\nu_{C=O}$ (ester)
		1611 (s)	$\nu_{C=C,\ C=N}$ (dipyrromethene skeletal)
IV	Co^{II} chelate	1725 (s)	$\nu_{C=O}$ (ester)
		1622 (w)	$\nu_{C=C,\ C=N}$ (macrocyclic skeletal)
		1090 (s br)	$\nu_{ClO_4^-}$
		621 (s)	$\delta_{ClO_4^-}$
IV	Ni^{II} chelate	1726 (s)	$\nu_{C=O}$ (ester)
		1632 (w)	$\nu_{C=C,\ C=N}$ (macrocyclic skeletal)
		1088 (s br)	$\nu_{ClO_4^-}$
		622 (s)	$\delta_{ClO_4^-}$
V′	2 HBr	1714 (s) 1706 (s)	$\nu_{C=O}$ (ester)
		1605 (s)	$\nu_{C=C,\ C=N}$ (dipyrromethene skeletal)
V	Co^{II} chelate	1735 (s) 1730 (s)	$\nu_{C=O}$ (ester)
		1623 (w)	$\nu_{C=C,\ C=N}$ (macrocyclic skeletal)
		1080 (s br)	$\nu_{ClO_4^-}$
		621 (s)	$\delta_{ClO_4^-}$
V	Ni^{II} chelate	1731 (s)	$\nu_{C=O}$ (ester)
		1631 (w)	$\nu_{C=C,\ C=N}$ (macrocyclic skeletal)
		1084 (s br)	$\nu_{ClO_4^-}$
		621 (s)	$\delta_{ClO_4^-}$

a) Measured by the Nujol mull method at room temperature. b) Relative intensities: s, strong; w, weak; br, broad. c) See Table 1 for numbering of the ligands I through V.

I′, 1,19-dideoxy-1,3,7,8,12,13,17,19-octamethylbiladiene-ac; II′, 1,19-dideoxy-1,2,3,7,8,12,13,17,18,19-decamethylbiladiene-ac; III′, 1,19-dideoxy-8,12-di(2-ethoxycarbonylethyl)-1,2,3,7,13,17,18,19-octamethylbiladiene-ac; IV′, 1,19-dideoxy-2,8,12,18-tetra(2-ethoxycarbonylethyl)-1,3,7,13,17,19-hexamethylbiladiene-ac; V′ 1,19-dideoxy-1,19-diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethylbiladiene-ac.

TABLE 4. PROTON NMR DATA FOR THE NICKEL(II) COMPLEXES OF 1,19-DISUBSTITUTED TETRADEHYDROCORRIRS AND THE PARENT BILADIENE-AC'S[a,b]

Ligand[c]	Form	$\text{-C}\underline{\text{H}}_3$ (ester)	$\text{-C}\underline{\text{H}}_3$					$\text{-C}\underline{\text{H}}_2\text{-}$ (ester)	$\text{-C}\underline{\text{H}}_2\text{-}$	$\text{-C}\underline{\text{H}}_2\text{C}\underline{\text{H}}_2\text{-}$	$\text{-C}\underline{\text{H}}\text{=}$		H N
			1,19	2,18	3,17	7,13	8,12				5,15	10	
I	2 HBr		2.74		2.38	2.46	2.25		4.53		7.48		6.43
I	Ni^{II} chelate		0.80		2.65	2.71	2.61				7.60	7.65	7.80 7.81
II′	2 HBr		2.73	2.12	2.36	2.36	2.24		4.47		7.43		
II	Ni^{II} chelate		0.81	2.55	2.61	2.66	2.61				7.55	7.49	
III′	2 HBr	1.39(3)	2.72	2.12	2.40	2.40		4.36(4)	4.64	3.00(m)	7.46		
III	Ni^{II} chelate	1.37(3)	0.77	2.59	2.65	2.72		4.38(4)		3.10(3) 3.59(3)	7.62	7.74	
IV′	2 HBr	1.38(3)	2.77		2.44	2.44		4.36(4)	4.68	3.00(m)	7.51		
IV	Ni^{II} chelate	1.35(3) 1.46(3)	0.79		2.65	2.71		4.30(4) 4.53(4)		3.07(3) 3.46(3)	7.63	7.79	
V′	2 HBr	1.52(3)		2.50	2.43	2.43	2.18	4.60(4)	4.87		7.85		
V	Ni^{II} chelate	1.10(3)		2.58	2.63	2.83	2.63	4.07(4)			7.55	7.77	

a) Measured in trifluoroacetic acid with TMS as an internal reference; chemical shifts are given in ppm. b) Multiplicity of a proton signal is given in parentheses after δ-value ($J=7.0$ Hz). c) See Tables 1 and 3 for numbering of the ligands.

observed for the angular methyl groups mentioned above. Thus, the methylene-proton peaks ($CH_3C\underline{H}_2$-OCO–) and the methyl-proton signals ($C\underline{H}_3CH_2OCO$–) show up-field shifts by 0.5 and 0.4 ppm, respectively, upon cyclization. The magnitude of up-field shifts for these ethyl groups is much smaller than those observed for the angular methyl groups. This is primarily due to the fact that the ethyl ester groups are placed further from the adjacent pyrrole rings, which provide magnetic anisotropy, relative to the angular methyls.

In the case of the cyclized 2,8,12,18-tetra(2-ethoxycarbonylethyl) derivative (IV in Table 4), the proton signals for ester-methylene ($CH_3C\underline{H}_2OCOCH_2CH_2$–) and ester-methyl ($C\underline{H}_3CH_2OCOCH_2CH_2$–) of the 2-ethoxycarbonylethyl group were observed as quintet and quartet, respectively. These peaks were analyzed as the overlaps of two quartet and of two triplet, respectively, for the quintet and quartet signals. This seems to indicate that the ethyl ester groups of the 2,18-substituents are placed in a conformational space different from that occupied by those of the 8,12-substituents. Consequently, one type of these ethyl ester groups secures the magnetic anisotropy effect due to the macrocyclic ring system in a manner different from the other.

The cyclization of biladiene-ac's, which do not carry any carbonyl group in conjugation with the pyrrole rings, causes a down-field shift of the proton signal due to the 5- and 15-methine groups. Another proton peak was observed in a lower field relative to the above one for the same tetradehydrocorrins along with the disappearance of the proton signal due to the 10-methylene group of the biladiene-ac precursors. Only exception is noticed in the case of tetradehydrocorrin complex II (see Table 4): the reversed relation of these proton signals is observed although the reason for this is not obvious at present. These down-field shifts may be attributed to the presence of aromaticity in the chelate rings as well as the electron-withdrawing effect of nickel(II) as observed previously for the zinc(II) complexes of dipyrromethenes[29] and bilene-b.[30] Meanwhile, the biladiene-ac precursor which carries ethoxycarbonyl groups at the 1,19-positions causes an up-field shift of its methine proton signal upon cyclization (V′ and V in Table 4) on the contrary. Since the strong electronic conjugation of carbonyl groups placed at the 1- and 19-positions is lost upon formation of the tetradehydrocorrin ring, the electron density at the 5- and 10-carbons is increased significantly as a whole. This result is consistent with the corresponding IR spectral behavior.

ESR Spectra. The ESR spectrum of 1,19-diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethyltetradehydrocorrinatocobalt(II) perchlorate observed in chloroform–benzene at 77 K is shown in Fig. 5 as an example for those of the cobalt(II) complexes of 1,19-disubstituted tetradehydrocorrins. In this spectrum, a set of eight cobalt hyperfine lines on the parallel component of the g-tensor ($g_{/\!/}$), which lie at higher fields, with a g-value close to spin free. The low-field set of hyperfine lines that belongs to the perpendicular component of the g-tensor ($g_\perp$) is not clearly resolved. Thus, unambiguous analysis of these low-field lines is difficult and the evaluated $g_\perp$ values would involve some minor errors. In any case, the ESR spectra indicate that the present cobalt(II) complexes are of low-spin square-planar type with an unpaired electron in the cobalt d_{z^2} orbital. The similar spectral features have also been observed for the complexes derived from porphyrins,[34,35] phthalocyanin,[36] vitamin B_{12} and related compounds,[37–39] and Schiff bases.[40]

In the presence of a few drops of pyridine in the chloroform–benzene solution, the spectrum shown in Fig. 5 is transformed into that in Fig. 6. Since a triplet nitrogen superfine coupling due to axial coordination of a pyridine molecule is observed on the parallel cobalt hyperfine lines, it may be concluded that the unpaired electron of cobalt(II) is certainly in the d_{z^2}

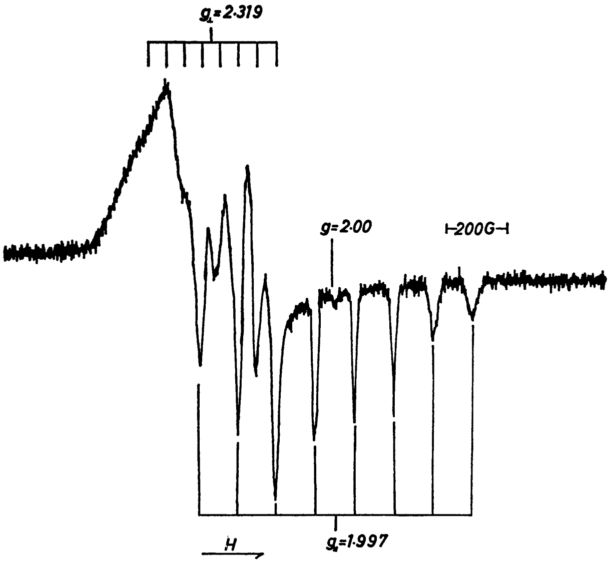

Fig. 5. ESR spectrum of 1,19-diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethyltetradehydrocorrinatocobalt(II) perchlorate in chloroform-benzene(2 : 1) at 77 K.

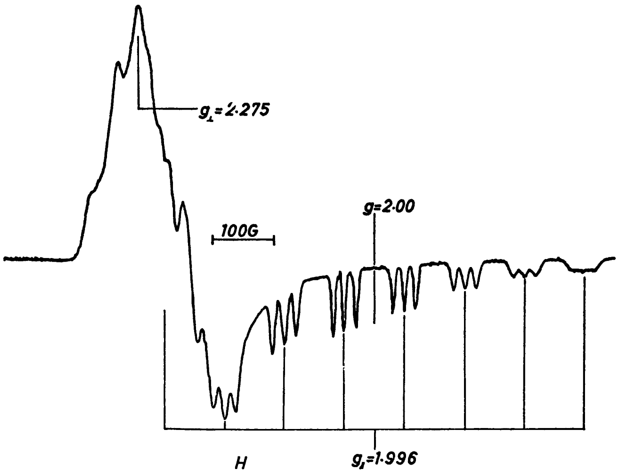

Fig. 6. ESR spectrum of 1,19-diethoxycarbonyl-2,3,7,8,12,13,17,18 - octamethyltetradehydrocorrinatocobalt(II) perchlorate in chloroform–benzene (2 : 1) at 77 K upon addition of pyridine.

orbital.

The ESR spectra were analyzed in terms of the spin Hamiltonian given by Eq. (1).

$$\mathscr{H}_{\rm s} = \beta_{\rm e}[g_{/\!/}H_{\rm z}S_{\rm z} + g_{\perp}(H_{\rm x}S_{\rm x}+H_{\rm y}S_{\rm y})] + A_{/\!/}S_{\rm z}I_{\rm z} + A_{\perp}(S_{\rm x}I_{\rm x}+S_{\rm y}I_{\rm y}) \tag{1}$$

For the unpaired electron in the d_{z^2} orbital, the g factors of second-order calculations are[34)]

$$g_{/\!/} = 2.0023 - 3(\lambda/\Delta)^2 \tag{2}$$

$$g_{\perp} = 2.0023 + 6(\lambda/\Delta) - 6(\lambda/\Delta)^2 \tag{3}$$

where λ is the spin-orbit coupling for Co(II), and Δ is the excitation energy from the degenerated d_{xz} and d_{yz} orbitals to the d_{z^2} orbital. The first-order $A_{/\!/}$ and $A_{\perp}$ components of hyperfine interaction are given as:[4)]

$$A_{/\!/} = P[4/7-K+6/7(\lambda/\Delta)] \tag{4}$$

$$A_{\perp} = P[-2/7-K+45/7(\lambda/\Delta)] \tag{5}$$

where $P=g_{\rm e}\beta_{\rm e}g_{\rm n}\beta_{\rm n}\langle d_{z^2}|1/r^3|d_{z^2}\rangle$ and K is the Fermi contact interaction term. The spin Hamiltonian parameters evaluated according to Eqs. (2) through (5) are summarized in Table 5. The $g_{/\!/}$ values are quite similar in magnitude to those reported by Hush and Woolsey[3,4)] for 1,19-diethoxycarbonyltetradehydrocorrinatocobalt(II) complexes, but the $g_{\perp}$ components are somewhat different from those evaluated by them and seem to be quite sensitive to the solvent environment. The decrease in A-tensor components along with the coordination of a pyridine molecule suggests that an unpaired electron in the d_{z^2} orbital of cobalt(II) is delocalized through the coordinate bond formed between cobalt(II) and pyridine nitrogen. The formation of similar penta-coordinated cobalt(II) complexes of square pyramidal structure with axial coordination of pyridine has been reported for the $\alpha,\beta,\gamma,\delta$-tetra($p$-methoxyphenyl)porphine complex, and the vitamine B_{12} and related complexes.[37–39)] On the other hand, the cobalt(II) complexes derived from phthalocyanin,[36)] and dimethylglyoxime[39)] were found to take up two pyridine molecules at their axial positions. The reason for the difference in coordination

Table 5. Spin hamiltonian parameters for the cobalt(II) complexes of 1,19-disubstituted tetradehydrocorrins[a,b)]

Ligand	Added base	$g_{/\!/}$	$g_{\perp}$	$A_{/\!/}^{\rm Co}\times10^4$ (cm^{-1})	$A_{\perp}^{\rm Co}\times10^4$ (cm^{-1})	$A_{/\!/}^{\rm N}\times10^4$ (cm^{-1})	λ/Δ	$P\times10^4$ (cm^{-1})	K	$(P/P_0)\times100$[c)] (%)
I		1.998	2.286	126	69		0.0379	98.1	−0.746	38.6
I	pyridine	1.995	2.270	93.2	45[d)]	18.9	0.0493	96.8	−0.421	38.1
II		1.999	2.295	128	70		0.0332	94.3	−0.817	37.1
II	pyridine	1.995	2.274	97.9	48[d)]	19.2	0.0493	100	−0.449	39.3
III		1.991	2.259	135	69		0.0614	161	−0.320	63.4
III	pyridine	1.989	2.267	91.5	48[d)]	17.3	0.0666	117	−0.268	46.1
IV		1.992	2.278	133	72		0.0586	142	−0.416	55.9
IV	pyridine	1.990	2.263	89.7	49[d)]	17.5	0.0640	104	−0.345	40.9
V		1.997	2.319	120	70		0.0420	90.7	−0.783	35.7
V	pyridine	1.996	2.275	98.2	46[d)]	19.2	0.0458	100	−0.451	39.3

a) Measured in chloroform-benzene (2 : 1) at 77 K; concentration, 10^{-2}—10^{-3} M. b) Maximum possible errors: g, ±0.005; $A_{/\!/}^{\rm Co}$, $\pm0.5\times10^{-4}$ cm^{-1}; $A_{\perp}^{\rm C}$, $\pm5\times10^{-4}$ cm^{-1}, $A_{/\!/}^{\rm N}$, $\pm0.05\times10^{-4}$ cm^{-1}. c) P_0 for the free cobalt(II) ion, 2.54×10^{-2} cm^{-1}. d) Estimated from line width.

behavior of pyridine molecule is not clear at present.

The P/P_0 values listed in Table 5 may be referred to as a measure for the degree of covalency of coordinate bonds, P_0 being as for the free cobalt(II) ion (254×10^{-4} cm^{-1} [41]). When the tetradehydrocorrin carries more than two groups of 2-ethoxycarbonylethyl (III and IV in Table 5), the P/P_0 value becomes relatively large compared to other analogous complexes given in Table 5. This seems to suggest that the 2-ethoxycarbonylethyl groups have a coordination interaction with cobalt(II) at the axial positions and can be replaced by a pyridine molecule along with the formation of the corresponding penta-coordinated complex.

Meanwhile, the present tetradehydrocorrinatocobalt(II) complexes which underwent reaction with $NaBH_4$ in dimethylformamide did not show any ESR signal, most likely due to the formation of the diamagnetic cobalt(I) complexes.

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