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Transition-metal Complexes of Pyrrole Pigments. XVII. Preparation and Spectroscopic Properties of Corrole Complexes†

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Nickel(II), copper(II), and cobalt(III) complexes were prepared with corroles; 2,3,7,8,12,13,17,18-octaethylcorrole (OEC), 2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrole (MEC), and 8,12-bis[2-(ethoxycarbonyl)ethyl]-2,3,7,13,17,18-hexamethylcorrole (PMC). For the coordination with nickel and copper ions, the corroles acted as dianionic ligands to yield electrically neutral complexes. These complexes exhibited metalloporphyrin-like electronic spectra, while they showed spectra which bear a much closer resemblance to those for metalloporphyrins as the anionic complexes were formed upon addition of alkali. The corroles coordinate to tervalent cobalt as trianionic ligands to form neutral complexes, which were reduced to the corresponding cobalt(II) complexes with sodium hydroborate. These reduced species gave a unique set of *g*-values ($g_1 \gg g_2 > g_3$) for the complexes of macrocyclic ligands with conjugated double bond system. The plausible coordination geometry as well as the structural properties of the corrole ligands has been discussed.

Corrole (**1**) and tetradehydrocorrin (**2**) are unique macrocyclic tetrapyrroles, having a highly conjugated π-electron system like porphyrin and phthalocyanine. However, the direct linkage between A and D pyrrole rings involved in the former two macrocycles acts to provide a deformation effect on the macrocyclic skeleton so that those rings can not take complete planar structure. A significant structural difference between corrole and tetradehydrocorrin is in orbital hybridization of carbon atoms at 1- and 19-positions. The particular atoms concerned are considered to possess sp^2 hybrid orbitals for corrole while sp^3 for tetradehydrocorrin. Thus, it is interesting to shed light on the unique electronic structure of corrole and the possible consequences of ring deformation in its coordination with transition-metal ions. The synthesis of corrole and its cobalt(III), nickel(II), and copper(II) complexes was reported first by Johnson *et al.*[1,2] However, they did not investigate the electronic structure of these complexes in any detail by spectroscopic means.

Three corroles having different peripheral substituents were employed in the present study; *i.e.*, 2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrole (MEC), 2,3,7,8,12,13,17,18-octaethylcorrole (OEC), and 8,12-bis[2-(ethoxycarbonyl) ethyl]-2,3,7,13,17,18-hexamethylcorrole (PMC). The corresponding linear tetrapyrroles, biladiene-ac dihydrobromides, underwent cyclization to afford the corroles under irradiation with visible light. The metal complexes were prepared directly from biladiene-ac's by template reaction as functioned by metal ions. Stereochemistry and electronic structures have been discussed for both ligands and complexes.

Experimental

Electronic absorption spectra were recorded on a Hitachi EPS-2 spectrophotometer at room temperature; chloroform was used as solvent unless otherwise stated. ESR spectra were obtained with a JEOL JES-ME-3 X-band spectrometer equipped with 100-kHz field modulation unit; a standard MgO/Mn(II) sample calibrated with a NMR magnetometer was employed for calibration of the magnetic field. NMR spectra were taken on a Varian A-60 spectrometer for chloroform-*d* solutions; tetramethylsilane being used as an internal reference.

1,19-Dideoxy-2,3,17,18-tetramethyl-7,8,12,13-tetraethylbiladiene-ac dihydrobromide and 1,19-dideoxy-2,3,7,8,12,13,17,18-octaethylbiladiene-ac dihydrobromide were obtained as described previously.[3]

1,19-Dideoxy-8,12-bis[2-(ethoxycarbonyl)ethyl]-2,3,7,13,17,18-hexamethylbiladiene-ac Dihydrobromide. Aqueous ammonia (28%) was added dropwise to a suspension of 3,3′-bis[2-(ethoxycarbonyl)ethyl]-4,4′-dimethyl-5,5′-dicarboxydipyrromethane[4] (5.0 g) and 2-formyl-3,4-dimethylpyrrole[5] (2.65 g) in methanol (200 ml) until a clear solution was obtained. Aqueous hydrobromic acid (47%, 25 ml) was added to the mixture in one portion at 120 °C. After being refluxed for 1 min, the dark red solution was allowed to stand in a freezer for 1 h. The product was recovered, washed with water, methanol, and ether, and then recrystallized from chloroform to give red crystals with green luster; yield 6.9 g (86%), mp>300 °C. UV$_{max}$ (CHCl$_3$): 370, 427, 455, and 518 nm. IR (KBr): 1608 (biladiene skeletal str.) and 1722 cm^{-1} (C=O str.). NMR (CF$_3$CO$_2$H): δ 1.38 (6H, t, J=7.0 Hz, -CH$_2$CH$_2$CO$_2$CH$_2$C$\underline{\text{H}}_3$), 2.18, 2.43, and 2.46 (18H, s, -CH$_3$ on pyrrole ring), 2.23—3.27 (8H, m, -C$\underline{\text{H}}_2$C$\underline{\text{H}}_2$CO$_2$C$_2$H$_5$), 4.35 (4H, q, J=7.0 Hz, -CH$_2$CH$_2$-CO$_2$C$\underline{\text{H}}_2$CH$_3$), 4.75 (2H, s, -CH$_2$- at 10-position), 7.66 (2H, s, -CH=), 8.01 (2H, d, J=4.0 Hz, 1- and 19-H), 11.39 (2H, br s, NH), and 11.55 (2H, br s, N$^+$H).

2,3,17,18-Tetramethyl-7,8,12,13-tetraethylcorrole (MEC). A mixture of 1,19-dideoxy-2,3,17,18-tetramethyl-7,8,12,13-tetraethylbiladiene-ac dihydrobromide (200 mg) and methanol (100 ml) was heated to obtain a homogeneous solution, to which 28% aqueous ammonia (4 ml) was added subsequently. The refluxing green solution was irradiated with a 200-W tungsten lamp for 1 h, and then allowed to stand in a freezer for 2 h. Dark fine crystals were recovered and recrystallized from chloroform–methanol to give purple needles; yield 90 mg (61%). IR (Nujol mull): 3350 cm^{-1} (N–H str.).

Found: C, 79.41; H, 8.15; N, 11.98%. Calcd for C$_{31}$-H$_{38}$N$_4$: C, 79.77; H, 8.22; N, 12.01%.

The following two corroles were prepared by similar photocyclization of the corresponding biladiene-ac dihydrobromides.

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2,3,7,8,12,13,17,18-Octaethylcorrole (OEC): purple needles, yield 19%. IR (Nujol mull): 3345 cm^{-1} (N–H str.). Found: C, 79.38; H, 8.68; N, 11.03%. Calcd for $C_{35}H_{46}N_4$: C, 80.40; H, 8.89; N, 10.72%.

8,12-Bis[2-(ethoxycarbonyl)ethyl]-2,3,7,13,17,18-hexamethylcorrole (PMC): purple needles, yield 51%. IR (KBr): 3360 cm^{-1} (N–H str.). Found: C, 71.90; H, 7.29; N, 9.65%. Calcd for $C_{35}H_{42}N_4O_4$: C, 72.14; H, 7.27; N, 9.61%.

Pyridine(2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrolato)cobalt(III) [Co(MEC)Py] and (2,3,7,8,12,13,17,18-octaethylcorrolato)cobalt(III) [Co(OEC)] were prepared as described previously.[3)]

Pyridine{8,12-bis[2-(ethoxycarbonyl)ethyl]-2,3,7,13,17,18-hexamethylcorrolato}cobalt(III) [Co(PMC)Py] was prepared by essentially the same procedure as employed for the preparation of Co(MEC)Py and obtained as purple prisms; yield 43%. IR (Nujol mull): 1603 (pyridine skeletal str.) and 1728 cm^{-1} (C=O str.). Found: C, 67.71; H, 6.08; N, 10.68%. Calcd for $C_{40}H_{44}N_5O_4Co$: C, 66.94; H, 6.18; N, 9.76%.

(2,3,17,18-Tetramethyl-7,8,12,13-tetraethylcorrolato)cobalt(III) [Co(MEC)]. A solution of pyridine(2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrolato)cobalt(III) (100 mg) in chloroform (4 ml) was refluxed for 3 min. Hot methanol (12 ml) was added to the solution, which was subsequently allowed to stand in a freezer for 2 h. Dark precipitates were recovered and washed with methanol to give glittering black prisms; yield 80 mg (92%).

Found: C, 71.43; H, 6.59; N, 11.37%. Calcd for $C_{31}H_{35}N_4Co$: C, 71.24; H, 6.76; N, 10.72%.

(2,3,17,18-Tetramethyl-7,8,12,13-tetraethylcorrolato)nickel(II) [Ni(MEC)]. A mixture of 1,19-dideoxy-2,3,17,18-tetramethyl-7,8,12,13-tetraethylbiladiene-ac dihydrobromide (300 mg), nickel(II) acetate tetrahydrate (300 mg), methanol (50 ml), and 28% aqueous ammonia (6 ml) was irradiated with a 200-W tungsten lamp for 20 min. The green solution turned to red and finally to dark brown. The reaction mixture was then allowed to stand at 0 °C overnight, and precipitates were recrystallized from chloroform–methanol (2:1 v/v) to give glittering dark green prisms; yield 100 mg (40%), mp>250 °C.

Found: C, 70.83; H, 6.66; N, 10.66%. Calcd for $C_{31}H_{36}N_4Ni$: C, 71.13; H, 6.95; N, 10.71%.

{8,12-Bis[2-(ethoxycarbonyl)ethyl]-2,3,7,13,17,18-hexamethylcorrolato}nickel(II) [Ni(PMC)] was prepared in a manner similar to that employed for the preparation of Ni(MEC): yield 57%, *m/e* 638 (M$^+$).

(2,3,17,18-Tetramethyl-7,8,12,13-tetraethylcorrolato)copper(II) [Cu(MEC)]. A mixture of 1,19-dideoxy-2,3,17,18-tetramethyl-7,8,12,13-tetraethylbiladiene-ac dihydrobromide (315 mg) and copper(II) acetate monohydrate (300 mg) in methanol (150 ml) was stirred at room temperature for 10 min. Precipitates were washed with methanol and recrystallized from chloroform–methanol (2:1 v/v) to give reddish brown needles; yield 50 mg (19%), mp>250 °C.

Found: C, 70.41; H, 6.60; N, 10.55%. Calcd for $C_{31}H_{36}N_4Cu$: C, 70.48; H, 6.88; N, 10.61%.

{8,12-Bis[2-(ethoxycarbonyl)ethyl]-2,3,7,13,17,18-hexamethylcorrolato}copper(II) [Cu(PMC)] was prepared by essentially the same procedure as employed for the preparation of Cu(MEC): yield 47%, *m/e* 643 (M$^+$).

Results and Discussion

Electronic Spectra. Characteristic transition energies and the corresponding molar absorption coefficients (ε) are summarized in Table 1 for the three corrole ligands. The strong absorption bands in the region of 24000—26000 cm^{-1} are presumably due to transitions similar to those observed for porphyrins as B-band. The nature of transitions for the bands in the region of 15000—19000 cm^{-1} is presumably similar to that for Q-bands of porphyrins. The electronic transitions, which result in B- and Q-bands, have not been characterized because multiple transitions with similar energies were observed in these regions due to lower symmetry of the corrole skeleton relative to the porphyrin framework.

The nickel(II) and copper(II) complexes of MEC and PMC were obtained as electrically neutral molecules without additional ligand or counter ion. This fact indicates that the corroles coordinate to nickel(II) and copper(II) as dianionic ligands. The complexes exhibited metalloporphyrin-like spectra, but a number of absorption bands is larger for the corrole complexes than for the corresponding metalloporphyrins. Both nickel(II) and copper(II) complexes of corrole showed much sharper absorption bands upon addition of sodium hydroxide to their DMSO solutions. The characteristic absorption bands are summarized in Table 2 along with molar absorption coefficients for the neutral complexes. The absorption bands for each complex are obviously classified into the following groups: group A, weak bands with transition energy less than 10000 cm^{-1}; group B, bands with intermediate intensity in the region of 10000—20000 cm^{-1}; and group C, very intense bands with high transition energy (greater than 20000 cm^{-1}).

TABLE 1. ELECTRONIC ABSORPTION BANDS FOR CORROLES IN CHLOROFORM AT ROOM TEMPERATURE

Corrole	MEC	OEC	PMC
Absorption maxima/cm^{-1} (ε)	14700^{sh} (1000)	14700^{sh} (1220)	
	16800 (14840)	16800 (19860)	16900 (18800)
	18100 (13280)	18200^{sh} (17160)	18200 (17300)
	18600 (13840)	18600 (19020)	18600 (17200)
			19500^{sh} (8120)
	20000^{sh} (6700)	20000^{sh} (7720)	20000^{sh} (7050)
	20800^{sh} (5040)	21100^{sh} (4780)	20900^{sh} (4720)
	24540 (94800)	24400 (103200)	24600 (106000)
	25100 (116600)	25100 (116200)	25100 (129000)
	30300^{sh} (20800)	30300^{sh} (20600)	30700^{sh} (18200)
	36400^{sh} (14900)	36400^{sh} (15040)	36000^{sh} (14800)

TABLE 2. ELECTRONIC ABSORPTION BANDS FOR NICKEL(II) AND COPPER(II) COMPLEXES OF MEC AT ROOM TEMPERATURE

Complex	Ni(MEC)[a]	[Ni(MEC)]$^-$ [b]	Cu(MEC)[a]	[Cu(MEC)]$^-$ [b]
	8330^{sh} (574)		10600^{sh} (590)	
	11900 (1310)		11600 (661)	
	15200 (9870)	15600	14900^{sh} (1060)	
	16700 (3840)	17000		
Absorption maxima/cm^{-1} (ε)		18000	18200 (10000)	17600
		19000	19800^{sh} (7580)	18800
	23500^{sh} (35300)			
	26000 (42200)	24900	25100 (87700)	24000
	27800 (58800)			
			35800 (26800)	

a) Measured in chloroform. b) Measured in *N*,*N*-dimethylformamide in the presence of NaOH.

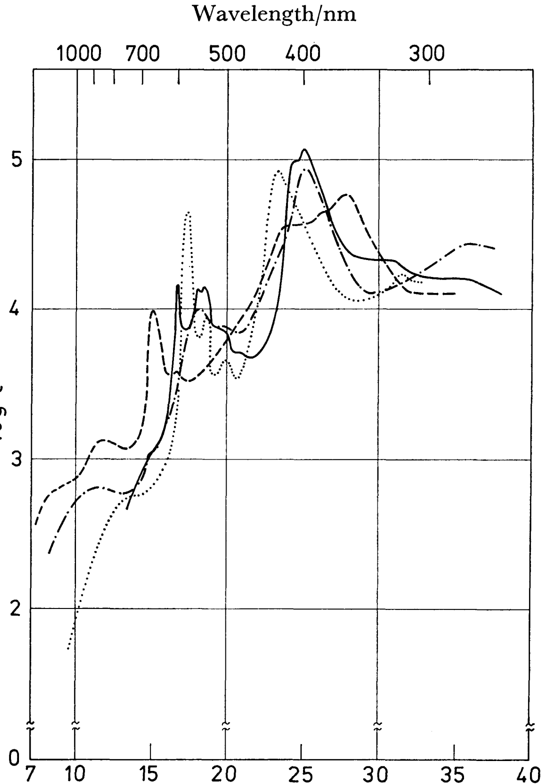
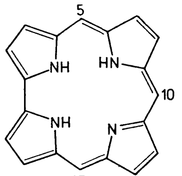
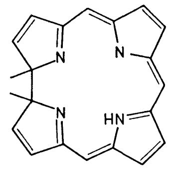


Fig. 1. Electronic absorption spectra of MEC and its metal complexes at room temperature.
——: Metal-free MEC in $CHCl_3$, ----: Ni^{II}(MEC) in $CHCl_3$, —·—: Cu^{II}(MEC) in $CHCl_3$, ······: Co^{III}(MEC) in pyridine.



1



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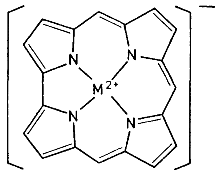

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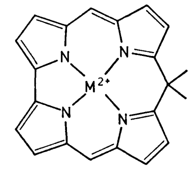

4

The local structure about the central metal may be assumed to be square planar with slight distortion. For such cases, the d-d transitions of nickel(II) and copper(II) are generally expected to appear in the region of 10000—20000 cm^{-1}. The absorption bands classified as group A are, therefore, not attributed to d-d transitions, but rather to charge-transfer transitions. The absorption bands of group B have molar absorption coefficients larger than 1000; they are too large to be assigned to d-d transitions. These bands may be attributed to π-π^* transitions which have similar character as those for the Q-bands of metalloporphyrins. The absorption bands of group C are attributed to transitions from π- to higher π^*-orbitals, corresponding to B-bands of metalloporphyrins. The neutral nickel(II) complex exhibited at least three absorption bands in the B-band region while the corresponding copper(II) complex showed only one band. However, this high energy band for the copper complex is very broad so that it must consist of two or more unresolved absorptions. The corresponding absorption band for the anionic complexes, [Ni(MEC)]$^-$ and [Cu(MEC)]$^-$, is remarkably sharp in a manner as observed for metalloporphyrins.

Above observation indicates a large difference in π-conjugation between anionic and neutral complexes. Nine double bonds of the corrole macrocycle (**1**) seem to be conjugated throughout the whole molecule for the anionic complex[6] (**3**) while the protonated structure (the neutral complex) interferes with such a conjugation effect. Structures of the neutral complexes are not established at present, but most plausibly shown by **4**.

Cobalt complexes with the corrole ligands were isolated only in the tervalent cobalt state as Co(corrole) and Co(corrole)Py. We reported previously the following equilibria in solution.[3]

$$n\text{Co(corrole)} \rightleftharpoons [\text{Co(corrole)}]_n \qquad (1)$$

$$\mathrm{Co(corrole)} \xrightleftharpoons{\mathrm{Py}} \mathrm{Co(corrole)Py} \xrightleftharpoons{\mathrm{Py}} \mathrm{Co(corrole)(Py)_2} \qquad (2)$$

Thus, an absorption spectra for the bis(pyridine) adduct can be obtained directly in the presence of excess pyridine. Electronic spectral data for the cobalt(III) complexes in pyridine are summarized in Table 3. For both complexes, absorption bands in the region of 12000—15000 $\mathrm{cm^{-1}}$ are attributed to charge-transfer transitions while higher energy bands are attributed to Q- and B-type transitions.

NMR Spectra. Proton NMR chemical shifts for the selected absorptions of Co(MEC)Py and Co(PMC)Py are listed in Table 4 along with the corresponding data for dicyano(8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrinato)cobalt(III) and dicyano(8,12-diethyl-1,2,3,7,13,17,18,19-octamethyl-AD-bisdehydrocorrinato)cobalt(III) [abbreviated as $\mathrm{Co(TDHC)(CN)_2}$ and $\mathrm{Co(BDHC)(CN)_2}$, respectively]. The meso-protons at 5-, 10-, and 15-positions and methyl-protons at 2-, 3-, 17-, and 18-positions provide an useful information: these signals shift to lower field in going from $\mathrm{Co(BDHC)(CN)_2}$ to $\mathrm{Co(TDHC)(CN)_2}$, Co(MEC)Py, and Co(PMC)Py; those protons involved in the corrole complexes resonate at the lowest field. The result indicates that the significant ring current effect is exercised undoubtedly by the corrole ring on the peripheral protons. The axial pyridine ligand in the corrole complexes is placed in a shielding zone of the ring current, and the pyridine protons resonate at a considerable higher field (δ 5.06—6.30) relative to those in $\mathrm{Co(NH_3)_5Py}$ (δ 7.75—8.33 in $\mathrm{D_2O}$).[8]

TABLE 3. ELECTRONIC ABSORPTION BANDS FOR COBALT(III) COMPLEXES IN PYRIDINE AT ROOM TEMPERATURE

Ligand	MEC	OEC
	13300^{sh} (530)	12500^{sh} (377) 15200 (1000)
Absorption maxima/$\mathrm{cm^{-1}}$ (ε)	17300 (43800) 18500 (8660) 19900 (4520)	17200 (56500) 18500 (10800) 19800 (6080)
	23400 (79200)	23500 (11300)

TABLE 4. PROTON NMR CHEMICAL SHIFTS FOR THE COBALT(III) COMPLEXES OF CORROLES AND DEHYDROCORRINS AT ROOM TEMPERATURE[a)]

Complex	Medium	δ CH₃ (2, 3, 17, 18)	δ =CH- (5, 15)	δ =CH- (10)
Co(MEC)Py	$\mathrm{CS_2}$	3.47, 4.30	8.43	8.08
Co(PMC)Py	$\mathrm{CS_2}$	3.31, 3.48, 3.92[b)]	9.20	8.99
$\mathrm{Co(TDHC)(CN)_2}$[c)]	$\mathrm{CDCl_3}$	2.36, 2.48	6.99	6.95
$\mathrm{Co(BDHC)(CN)_2}$[d)]	$\mathrm{CDCl_3}$	2.11, 2.29	5.97	5.91

a) Chemical shifts needed for discussion are given. b) One of the three values must be attributed to methyl protons at 7- and 13-positions. c) As for preparation, see: D. Dolphin, R. L. N. Harris, J. L. Huppatz, A. W. Johnson, I. T. Kay, *J. Chem. Soc., C*, **1966**, 30. d) Cited from Ref. 7.

Table 5 summarizes chemical shifts for metal-free OEC and 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP). OEC exhibits a deshielding effect on the imino-protons and a shielding effect on the meso-protons, but such effects are more pronounced for OEP. This is most plausibly caused by the deviation of the corrole skeleton from ideal planar configuration, which results in reduction of the extent of π-conjugation compared with porphyrins.

Except for the case of OEC, the metal-free corroles showed only broad NMR signals, presumably caused by paramagnetic contamination. This was confirmed by the presence of a sharp ESR signal at $g=2.0$. The paramagnetic species responsible for the observation is presumably radical species of corrole itself generated during photo-cyclization of biladiene-ac's. It is not clear at present whether the formation of such species is influenced by the nature of substituents or simply a matter of slight difference in experimental conditions. The paramagnetic species disappeared upon addition of thiophenol.

ESR Spectra. Copper(II) complexes of the corroles exhibited ESR spectra typical of the planar coordination structure. The X-band ESR spectrum for neutral Cu(MEC) at 77 K is shown in Fig. 2.

TABLE 5. PROTON NMR CHEMICAL SHIFTS FOR OEC AND OEP MEASURED IN CHLOROFORM-*d* AT ROOM TEMPERATURE

Compound	δ NH	δ =CH-	δ CH₃	δ CH₂
OEC	−2.47	9.39, 9.22[a)]	1.75	3.82
OEP	−3.78	10.00	1.89	4.11

a) For 5- and 15-positions, 9.39; for 10-position, 9.22.

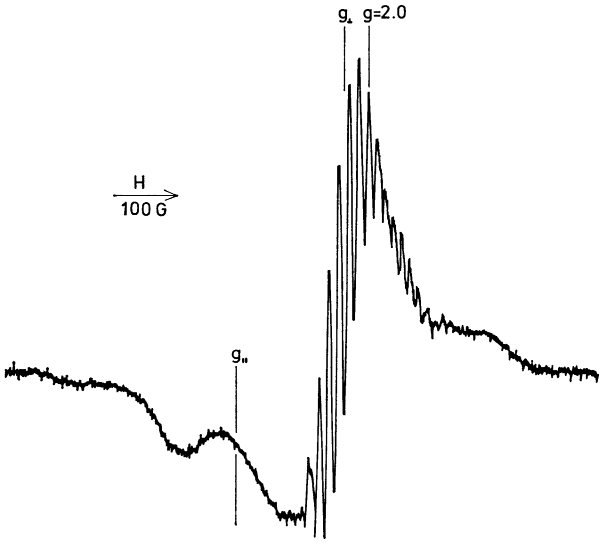

Fig. 2. ESR spectrum of $\mathrm{Cu^{II}(MEC)}$ in benzene–xylene (4: 6 v/v) at 77 K.

Table 6. Spin Hamiltonian parameters for the copper(II) complexes of macrocyclic ligands

Complex	$g_{\parallel}$	$g_{\perp}$	$\frac{A_{\parallel}^{Cu}\times 10^4}{cm^{-1}}$	$\frac{A_{\parallel}^{N}\times 10^4}{cm^{-1}}$	$\frac{A_{\perp}^{N}\times 10^4}{cm^{-1}}$	Medium
Cu(MEC)	2.145	2.021	208	15.8	14.2	Metal-free MEC[c]
Cu(MEC)	2.152	2.030	240	17.3	16.1	Benzene-xylene (4:6 v/v)[d]
Cu(PMC)	2.148	2.023	207	15.6	13.0	Metal-free PMC[c]
Cu(PMC)	2.146	2.030	246	16.9	16.0	Benzene-xylene (4:6 v/v)[d]
Cu(TPP)[a]	2.193	2.071	202	14.5	16.1	Metal-free TPP[c]
Cu(PC)[b]	2.160	2.045	218	18.6	15.5	Metal-free PC[c]

a) Cited from Ref. 9. b) Cited from Ref. 10. c) Measured at 293 K. d) Measured at 77 K.

Spin Hamiltonian parameters for MEC and PMC complexes are summarized in Table 6 along with those for the copper complexes of 5,10,15,20-tetraphenylporphine (TPP) and phthalocyanine (PC). As mentioned earlier, the complexes would possess planar structure with slight rhombic distortion. Rhombic parameters (g_1, g_2, and g_3), however, were not obtained because of the complexity of the spectra in the perpendicular component range. The parameters were evaluated, in any event, for pseudo-tetragonal coordination having C_{4v} local symmetry around the copper atom. Both $g_{\parallel}$ and $g_{\perp}$ for the corrole complexes are significantly smaller than those for the TPP and PC complexes. This observation reflects the deformation of the corrole complexes from planar structure. As mentioned above, the extent of π-conjugation in the neutral complex is much lower than that for metalloporphyrins. In addition, the direct linkage of A and D pyrrole rings stands in favor of such deformation.

A remarkable medium effect on hyperfine splitting constants was observed: the complexes gave larger A-values in frozen solution (benzene–xylene, 4:6 v/v) relative to those for the samples diluted with the corresponding metal-free corroles, while g-values were not affected significantly by the nature of media. The complexes also gave larger A^N-values in frozen solutions compared with those in the solid matrices. These facts suggest that both extent of mixing of 4s orbital with $3d_{x^2-y^2}$ and covalent character of the coordinate bonds are more pronounced in solution state rather than in the matrix of metal-free ligand. Lack of d-d transition energies makes it difficult to evaluate the effect of host structure quantitatively. The neutral copper(II) complexes presumably have a molecular geometry different from those of the corresponding anionic complexes and metal-free ligands. Thus, the neutral complexes are subjected to deformation in the matrices of metal-free corroles which tends to raise the molecular symmetry, while their coordination geometry is less affected in organic solvents. Such deformation is responsible for reduction of the covalency of coordinate bonds and of the mixing of s-orbital with $d_{x^2-y^2}$. Meanwhile, the anionic copper(II) complexes, which have more extensive π-conjugation system relative to the neutral ones, may be stabilized upon protonation to yield the latter complexes because the internal strain provided by the direct A-D linkage is relaxed through such a process (refer to **4**).

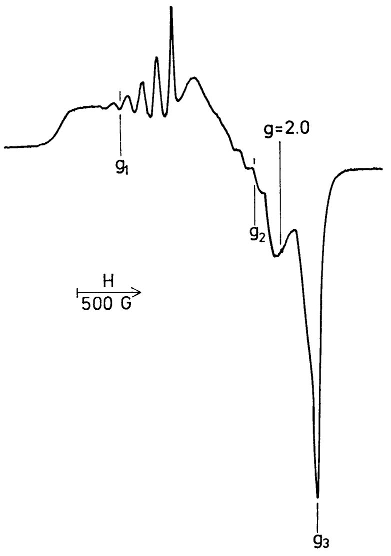

Fig. 3. ESR spectrum of $[Co^{II}(MEC)]^-$ in DMF at 77 K.

The cobalt(II) complexes, generated by reduction of the corresponding cobalt(III) complexes with $NaBH_4$ in *N,N*-dimethylformamide(DMF), showed intense ESR signals at 77 K as shown in Fig. 3. The samples did not give such ESR signals at room temperature due to short spin-lattice relaxation time of the low spin d^7 configuration. An ESR spectrum for the pyridine adduct of a reduced cobalt complex was observed upon addition of pyridine to the DMF solution (Fig. 4); except for the appearance of an additional superhyperfine splitting due to the nitrogen nucleus of pyridine, the spectra of both adduct and pyridine-free complex are essentially identical. The spin Hamiltonian parameters for $S=1/2$ and $I=7/2$ were obtained as summarized in Table 7. The spectral feature suggests that the cobalt(II) complexes assume a rhombic symmetry at the coordination site. Since the spectral features of both Figs. 3 and 4 bear a close resemblance to each other as stated above, the spatial arrangement of cobalt and four pyrrole-nitrogen atoms remains practically unchanged regardless of pyridine coordination. Since the superhyperfine splitting shown in Fig. 4 consists of three lines, the coordination of pyridine takes place only at the fifth coordination site; suggesting strongly a pyramidal structure for the original corrole complex with the cobalt atom placed at the top so that pyridine can approach to the metal from only one side of the molecular plane. The

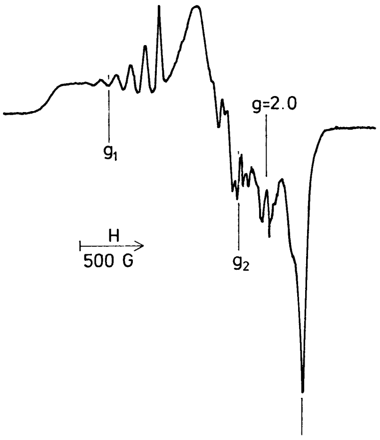

Fig. 4. ESR spectrum of $[Co^{II}(MEC)]^-$ in DMF at 77 K; pyridine was added.

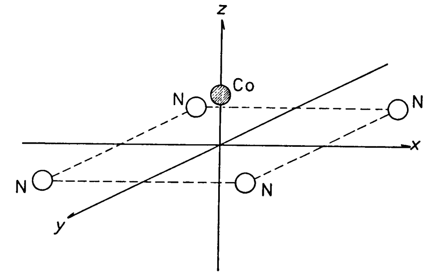

Fig. 5. Coordination geometry around the cobalt atom for C_{4v} local symmetry; four nitrogen atoms are placed in xy-plane while the cobalt atom is displaced upward from xy-plane along z-axis.

four nitrogen atoms involved in the corrole complexes can not occupy vertices of square even if they are placed on the same plane, because the A and D pyrrole rings are linked directly. The coordination site around the cobalt atom assumes, therefore, C_s local symmetry, distorted from C_{4v}.

The cobalt(II)-corrole complexes provide g-values of $g_1 \gg g_2 > g_3$ as seen in Table 7. Cobalt(II) complexes other than the corrole complexes, given in Table 7, require g-values of $g_1 = g_2 \gg g_3$; local symmetry of C_{4v}. The coordination geometry around the cobalt atom for C_{4v} local symmetry is shown in Fig. 5. Four nitrogen atoms are placed in xy-plane on lines bisecting angles between x and y axes. Therefore, a d-orbital with the largest contribution to σ coordinate bonds is d_{xy} which occupies the highest energy level among d-orbitals. The hole formalism represents the ground state for d^7 configuration by one of the following four configurations: $(d^2_{xy}, d_{x^2-y^2})$, (d^2_{xy}, d_{z^2}), (d^2_{xy}, d_{xz}), and (d^2_{xy}, d_{yz}); the last two configurations are degenerate in C_{4v} while referred to different energy states in C_s. g-Values are represented as shown in Table 8 for the above hole configurations. A relation, $g_{xx} \simeq g_{yy} > g_{zz} = 2$, is obtained for the ground state configuration of (d^2_{xy}, d_{z^2}). Co(II)(TPP) in TPP matrix and Co(II)(PC) diluted with Zn(II)(PC) are included in this category (refer to Table 7). The ground-state configuration can not be established for the corrole complexes on the basis of g-values alone. Nevertheless, either (d^2_{xy}, d_{xz}) or (d^2_{xy}, d_{yz}) is referred to the ground state judging from their coordination geometry. For either of the configurations, the relative magnitude of g-values depends on the energies of excited configurations. Since (d^2_{xy}, d_{xz}) and (d^2_{xy}, d_{yz}) are transformed into each other by interchange of x and y axes, we discuss the situation for the former as the ground state.

Suppose the following correlations are satisfied.

$$E(d_{xy}, d^2_{xz}) \gg E(d^2_{xy}, d_{yz}) \tag{3}$$

Table 7. Spin Hamiltonian parameters for the cobalt(II) complexes of macrocyclic ligands at 77 K

Complex	g_1	g_2	g_3	$A_1^{Co} \times 10^4$ / cm^{-1}	$A_2^{Co} \times 10^4$ / cm^{-1}	$A_3^{Co} \times 10^4$ / cm^{-1}	$A_2^{N} \times 10^4$ / cm^{-1}	Medium
Co(MEC)	3.236	2.263	1.847	181	104			DMF
Co(MEC)Py	3.223	2.206	1.848	180	113		17.2	DMF
Co(PMC)	3.242	2.214	1.841	181	108			DMF
Co(PMC)Py	3.225	2.147	1.854	172	97.9		17.4	DMF
Co(TPP)[a]	2.505[c]		2.034[d]	115[c]		92[d]		metal-free TPP
Co(PC)[b]	2.422[c]		2.007[d]	116[c]		66[d]		Zn(PC)

a) Cited from Ref. 9. b) Cited from Ref. 11. c) Perpendicular component. d) Parallel component.

Table 8. Representation of g-values for the ground state configurations based on hole formalism[a)]

Hole configuration for the ground state	Δg_{xx}	Δg_{yy}	Δg_{zz}
$(d^2_{xy}, d_{x^2-y^2})$	$-2\lambda/\Delta E(d^2_{xy}, d_{yz})$	$-2\lambda/\Delta E(d^2_{xy}, d_{xz})$	$8\lambda/\Delta E(d^2_{xy}, d_{x^2-y^2})$
(d^2_{xy}, d_{z^2})	$-6\lambda/\Delta E(d^2_{xy}, d_{yz})$	$-6\lambda/\Delta E(d^2_{xy}, d_{xz})$	0
(d^2_{xy}, d_{xz})	$2\lambda/\Delta E(d_{xy}, d^2_{xz})$	$-2\lambda/\Delta E(d^2_{xy}, d_{x^2-y^2})$ $-6\lambda/\Delta E(d^2_{xy}, d_{z^2})$	$-2\lambda/\Delta E(d^2_{xy}, d_{yz})$

a) ΔE denotes an energy difference between ground state and excited state configurations, the latter being given in parentheses after ΔE; $\Delta g_{ii} = g_{ii} - g_0$.

$$E(d_{xy}^2,\ d_{x^2-y^2}) > E(d_{xy}^2,\ d_{yz}) \qquad (4)$$

$$E(d_{xy}^2,\ d_{z^2}) \gg E(d_{xy}^2,\ d_{yz}) \qquad (5)$$

g-Values are interrelated by Eq. 6.

$$g_{zz} \gg g_{yy} > g_{xx} \qquad (6)$$

On the other hand, a relationship among g-values is provided by Eq. 8 for an energy correlation given by Eq. 7.

$$E(d_{xy}^2,\ d_{yz}) \simeq E(d_{xy}^2,\ d_{z^2}) \qquad (7)$$

$$g_{yy} \gg g_{zz} > g_{xx} \qquad (8)$$

If (d_{xy}^2, d_{xz}) is referred to the ground state, either of the above conditions [(3), (4), and (5); or (7)] must be satisfied in order to observe the g-value correlation for the present corrole complexes: $g_1 \gg g_2 > g_3$ (refer to Table 7); other ground-state configurations listed in Table 8 are not consistent with this relation.

The cobalt atom is displaced most plausibly from the plane of the four pyrrole-nitrogen atoms to yield a pyramidal geometry as stated earlier. Under such circumstances, d_{xz} and d_{yz} orbitals contribute extensively to the formation of σ-antibonding orbitals. Although strong out-of-plane pπ-dπ interactions between cobalt and pyrrole-nitrogen atoms may be in favor of the present experimental sequence of g-values, such interactions are expected for all the complexes cited in Table 7. Thus, the π-bonding effect does not explain the difference in interrelation of g-values among these complexes.

Conclusion

Corrole involves a significant internal strain in its macrocyclic skeleton due to the direct linkage between A and D pyrrole rings. This strain may cause deviation of the skeleton from complete planar configuration and consequently results in reduction of the extent of π-conjugation compared to porphyrin. Such an internal strain effect seems to be relaxed to some extent through formation of the bivalent metal complexes, in which corrole acts as a dianionic ligand. The π-conjugation throughout the whole complex molecule is interfered with by the presence of a methylene group at 10-position. Such bivalent metal complexes of neutral charge were transformed into anionic complexes upon losing a proton of 10-position with base.

Corrole is coordinated to the tervalent cobalt as a trianionic ligand. The cobalt(II) complex, generated by reduction of the corresponding cobalt(III) complex with $NaBH_4$, must assume C_s local symmetry at the coordination site; the cobalt atom is placed at the top of a pyramidal structure. Either (d_{xy}^2, d_{xz}) or (d_{xy}^2, d_{yz}) is referred to the ground state configuration (hole) with extensive contribution of d_{xz} and d_{yz} to the formation of σ-antibonding orbitals. The interrelation of experimental g-values ($g_1 \gg g_2 > g_3$) is consistent with such circumstances along with requirement given by (3), (4), and (5); or (7).

References

1) A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, **1965**, 1620.

2) M. Conlon, A. W. Johnson, W. R. Overend, D. Rajapaksa, and C. M. Elson, *J. Chem. Soc.*, *Perkin Trans. 1*, **1973**, 2281.

3) Y. Murakami, S. Yamada, Y. Matsuda, and K. Sakata, *Bull. Chem. Soc. Jpn.*, **51**, 123 (1978).

4) Y. Murakami, K. Sakata, Y. Tanaka, and T. Matsuo, *Bull. Chem. Soc. Jpn.*, **48**, 3622 (1975).

5) G. M. Badger, R. L. N. Harris, and R. A. Jones, *Aust. J. Chem.*, **17**, 1022 (1964).

6) N. S. Hush, J. M. Dyke, M. L. Williams, and I. S. Woolsey, *J. Chem. Soc.*, *Dalton Trans.*, **1974**, 395.

7) Y. Murakami, Y. Aoyama, and S. Nakanishi, *Chem. Lett.*, **1977**, 991.

8) D. K. Lavallee, M. D. Baughman, and M. P. Phillips, *J. Am. Chem. Soc.*, **99**, 718 (1977).

9) J. M. Assour, *J. Chem. Phys.*, **43**, 2477 (1965).

10) C. M. Guzy, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc.*, *A*, **1969**, 2299.

11) J. M. Assour and W. K. Kahn, *J. Am. Chem. Soc.*, **87**, 207 (1965).