November, 1981] © 1981 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, **54**, 3425—3432 (1981) 3425

Preparation and Physicochemical Properties of Tervalent Cobalt Complexes of Porphyrins

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(Received March 9, 1981)

Tervalent cobalt complexes of octaethylporphyrin (OEP) and tetraphenylporphyrin (TPP), $[Co^{III}(OEP)(H_2O)_2]X$ ($X=ClO_4$, BF_4), $[Co^{III}(OEP)(THF)_2]ClO_4$, $[Co^{III}(TPP)(H_2O)_2]X$ ($X=ClO_4$, BF_4), and $[Co^{III}(TPP)(H_2O)Y]$ (Y=Cl, Br, SCN, N_3) were synthesized. Molecular weight measurements indicate that only $[Co^{III}(TPP)(H_2O)_2]BF_4$ and $[Co^{III}(TPP)(H_2O)_2]ClO_4$ aggregate at higher concentrations in chloroform. In polar solvents such as methanol, all are monomeric. In nonpolar solvents, all the complexes show Soret bands at shorter wavelengths and somewhat paramagnetic ^1H NMR spectra; these anomalies are absent in polar solvents. Tetrafluoroborates and perchlorates react with ethyl vinyl ether smoothly to form 2,2-diethoxyethylcobalt(III) complexes which are easily converted to formylmethylcobalt(III) complexes. ^1H NMR and absorption spectra of the amine adducts prepared in this study, $[Co^{III}(OEP)(L)_2]ClO_4$ (L=pyridine, 2-methylimidazole) and $[Co^{III}(TPP)(L')_2]ClO_4$ (L'=pyridine, 4-cyanopyridine, 4-methylpyridine), indicate that the two amine molecules coordinate to the central cobalt atom. As regards redox potentials for the Co(III)/Co(II) couple as measured by cyclic voltammetry, the cobalt(III) porphyrins are categorized into three groups: (i) BF_4 and ClO_4 salts with redox potentials at about 0.7 V; (ii) halides and pseudohalides with those at 0.2—0.3 V; and (iii) bis(amine) adducts with those at −0.3—+0.1 V. In polar solvents, however, the redox potentials of (i) and (ii) are very similar to one another.

It is well known that the active site of vitamin B_{12} is the cobalt complex of the corrin ligand and that its coenzyme form and related alkylcobalamin are the only organometallic compounds hitherto found in nature. Since the discovery of the cobalt σ-bond between cobalt(III) and 5′-carbon of an adenine moiety through crystallographic studies by Hodgkin,1) a large number of model compounds have been synthesized to elucidate the basic chemistry of the cobalt-carbon bond in square planar macrocyclic systems.2–8) Metal complexes of porphyrin are particularly suitable for model studies on the structure and reaction of coenzyme B_{12}, because both porphyrin and corrin9) are of tetrapyrrole macrocycle. Since the rapture and recombination of the cobalt-carbon bond are key steps to achieve the enzymatic catalysis, main interes thas existed in the formation and cleavage of the cobalt-carbon bond by uni-, bi-, and tervalent metal complexes. The formation of the cobalt-carbon bond through nucleophilic reactions of Co(I) toward organic halides has been investigated in relation to the reaction of coenzyme B_{12}. Similar nucleophilic reactions of Co(I) species were found in porphyrin complexes of Rh(I)10) and Ir.11) On the other hand, another mode for the cobalt-carbon bond formation was recently found in an electrophilic reaction of coenzyme B_{12} having a tervalent cobalt atom12) with alkyl vinyl ether. Ogoshi *et al.*13) reported that a tervalent rhodium complex of porphyrin reacted with ethyl vinyl ether to give a rhodium-carbon bond. Silverman and Dolphin12) also showed a cobalt-carbon bond formation by the electrophilic reaction of cobalt(III) oxime with vinyl ether. Dolphin suggested the intermediacy of an olefin π-complex of cobalt(III) in the reaction. However, there has hitherto been no report about the electrophilic reaction of cobalt(III) porphyrins toward electron rich olefins. This is probably because tervalent cobalt atoms of usual cobalt(III) porphyrin complexes have no sufficient cationic character to cause the reaction. Thus, usual cobalt(III) porphyrins are six-coordinated by inclusion of halogens and/or amines in the coordination sphere, such as $[Co^{III}(porphyrin)(amine)_2]X$ and $[Co^{III}(porphyrin)(amine)X]$, and the electrophilicity or cationic character of the central cobalt(III) ion is thereby reduced. In order that cobalt(III) porphyrins should have sufficient electrophilicity to react with various organic nucleophiles, therefore, the electron-donating ability of the counter anion should be sufficiently weak. In this sense it was thought of utmost importance to compare cobalt(III) complexes of porphyrins having various types of axial ligands: weak ligands such as BF_4 and ClO_4 ions; intermediate ligand such as halides and pseudohalides; and strong ligands such as amines. Although active investigations14) have been made for bromides and chlorides and their amine adducts, for perchlorates only our research group15,16) has recently reported of syntheses and X-ray crystallographic data. This paper is concerned with synthetic methods, electrophilic reactions toward electron rich olefins, and redox potentials for various tervalent cobalt complexes of octaethylporphyrin and tetraphenylporphyrin, and discusses the relation between mode of coordination of counter anions to the central cobalt atom and physicochemical properties such as absorption and ^1H NMR spectra, particularly redox potentials of the cobalt atom.**

Experimental

Synthesis. *$[Co^{III}(OEP)(THF)_2]ClO_4$ (1)*: Octaethylporphyrinatocobalt(II) $Co^{II}(OEP)$, (100 mg) was dissolved in tetrahydrofuran (100 cm^3) containing 1 cm^3 of 70% perchloric acid. The reaction mixture was stirred for 24 h under an aerobic condition until black crystals

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** Abbreviations used are: OEP, octaethylporphyrin; TPP, $\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin; THF, tetrahydrofuran; py, pyridine; 2-MeIm, 2-methylimidazole; 4-CNpy, 4-cyanopyridine; 4-Mepy, 4-methylpyridine; TBAP, tetrabutylammonium perchlorate; TBAF, tetrabutylammonium fluoroborate; TBAB, tetrabutylammonium bromide; TBAC, tetra butylammonium chloride.

were precipitated. The crystals thus obtained were collected and washed with petroleum ether. Recrystallization from benzene–THF afforded reddish purple crystals (75 mg) in 53% yield. Found: C, 63.28; H, 7.43; N, 6.76%. Calcd for $C_{44}H_{60}N_4ClO_6Co$: C, 63.26; H, 7.24; N, 6.71%.

$[Co^{III}(OEP)(H_2O)_2]ClO_4$ (2): Recrystallization of **1** from benzene–dichloromethane saturated with water gave dark red, slightly hygroscopic crystals in a quantitative yield. Found: C, 59.00; H, 6.29; N, 6.99%. Calcd for $C_{36}H_{48}N_4ClO_6Co$: C, 59.46; H, 6.65; N, 7.70%.

$[Co^{III}(OEP)(H_2O)_2]BF_4$ (3): To a solution of Co^{II}(OEP) (100 mg) in methanol (100 cm^3) was added 10% tetrafluoroboric acid (2—3 cm^3) and the solution was stirred for several hours. Then the solvent was removed carefully under reduced pressure until fine purple crystals were precipitated. The crystals were collected, washed with water, and dried over P_2O_5 *in vacuo* to give **3** in 70% yield. Found: C, 61.62; H, 6.72; N, 7.87%. Calcd for $C_{36}H_{48}N_4BF_4O_2Co$: C, 60.51; H, 6.77; N, 7.84%.

$[Co^{III}(OEP)(py)_2]ClO_4$ (4): Recrystallization of **1** from benzene containing an excess amount of pyridine gave reddish purple crystals in almost a quantitative yield. Found: C, 64.56; H, 6.63; N, 9.69%. Calcd for $C_{46}H_{54}N_4ClO_4Co$: C, 65.05; H, 6.40; N, 9.89%.

$[Co^{III}(OEP)(2\text{-}MeIm)_2]ClO_4$ (5): Recrystallization of **1** from benzene–dichloromethane containing an excess amount of 2-methylimidazole afforded reddish purple crystals in a quantitative yield. Found: C, 61.94; H, 6.83; N, 12.90%. Calcd for $C_{44}H_{56}N_8ClO_4Co$: C, 61.78; H, 6.60; N, 13.10%.

$[Co^{III}(OEP)CH_2CH(OCH_2CH_3)_2]$ (6): To an ethanol solution (100 cm^3) of **1** (100 mg) were added vinyl ethyl ether (100 mg) and triethylamine (0.5 cm^3). The reaction mixture was stirred at room temperature until a fine powder was precipitated. The powder thus obtained was collected and recrystallized from benzene–dichloromethane to afford reddish purple crystals (64 mg) in 75% yield. Found: C, 71.47; H, 7.55; N, 8.07%. Calcd for $C_{42}H_{57}N_4O_2Co$: C, 71.16; H, 8.10; N, 7.90%.

$[Co^{III}(OEP)CH_2CHO]$ (7): A dichloromethane solution of **6** was treated with silica gel or allowed to stand for 1 d. The solvent was evaporated under reduced pressure. The residual solid was recrystallized from benzene to afford orange red crystals in almost a quantitative yield. Found: C, 71.14; H, 7.51; N, 8.46%. Calcd for $C_{38}H_{47}N_4OCo$: C, 71.90; H, 7.48; N, 8.84%.

$[Co^{III}(TPP)(H_2O)_2]ClO_4$ (8): To a suspension of Co^{II}(TPP) (100 mg) in methanol (100 cm^3) was added 10% perchloric acid (1—2 cm^3) and the solution was stirred for about 10 h to almost complete dissolution. The solvent was removed under reduced pressure. The residual solid was recrystallized from methanol–benzene to give reddish purple crystals in 75% yield. Found: C, 66.23; H, 3.77; N, 7.09%. Calcd for $C_{44}H_{40}N_4ClO_4Co$: C, 66.62; H, 4.32; N, 7.06%.

$[Co^{III}(TPP)(H_2O)_2]BF_4$ (9): To a solution of Co^{II}(TPP) (100 mg) in dioxane (100 cm^3) was added 10% tetrafluoroboric acid (2—5 cm^3) and the solution was stirred for about 1 h. Then the solvent was removed carefully under reduced pressure until fine crystals were precipitated. The crystals were collected, washed with water and dried over P_2O_5 *in vacuo* to give **9** in 65% yield. Found: C, 63.62; H, 4.42; N, 6.63%. Calcd for $C_{44}H_{36}N_4BF_4Co$: C, 63.63; H, 4.37; N, 6.75%.

$[Co^{III}(TPP)(H_2O)I]$ (10): A dichloromethane solution of **8** was washed with an aqueous sodium iodide solution several times and then with water and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residual solid was recrystallized from methanol to give reddish purple crystals in almost a quantitative yield. Found: C, 64.97; H, 4.08; N, 6.36%. Calcd for $C_{44}H_{30}N_4OICo$: C, 64.72; H, 3.70; N, 6.86%.

$[Co^{III}(TPP)(H_2O)Br]$ (11): To a suspension of Co^{II}(TPP) in methanol was added 10% hydrobromic acid and the mixture was stirred for 20 h. Methanol was removed under reduced pressure. The residual solid was recrystallized from methanol to give reddish purple crystals in a quantitative yield. Found: C, 68.38; H, 3.96; N, 7.29%. Calcd for $C_{44}H_{30}N_4OBrCo$: C, 68.31; H, 4.17; N, 7.41%.

$[Co^{III}(TPP)(H_2O)Cl]$ (12): This was synthesized by the method reported by Yamamoto *et al.*[14h,i]

$[Co^{III}(TPP)(H_2O)SCN]$ (13): This was prepared by the same procedure as for **10** except that KI was replaced by KSCN. Found: C, 72.73; H, 3.86; N, 9.50%. Calcd for $C_{45}H_{30}N_5OSCo$: C, 72.28; H, 4.04; N, 9.37%.

$[Co^{III}(TPP)(H_2O)N_3]$ (14): This complex also was prepared by the same procedure as for **10** but by using NaN_3 in place of KI. Found: C, 72.85; H, 4.12; N, 13.36%. Calcd for $C_{44}H_{30}N_7OCo$: C, 72.22; H, 4.13; N, 13.40%.

$[Co^{III}(TPP)(py)_2]ClO_4$ (15): Recrystallization of **8** from benzene–pyridine (10:1 vol/vol) gave reddish purple crystals in 80% yield. Found: C, 70.14; H, 4.33; N, 8.72%. Calcd for $C_{54}H_{38}N_6ClO_4Co$: C, 69.79; H, 4.12; N, 9.04%.

$[Co^{III}(TPP)(4\text{-}CNpy)_2]ClO_4$ (16): Recrystallization of **8** from benzene containing an excess amount of 4-cyanopyridine gave reddish purple crystals. Found: C, 68.37; H, 3.69; N, 11.39%. Calcd for $C_{56}H_{36}N_8ClO_4Co$: C, 68.68; H, 3.71; N, 11.44%.

$[Co^{III}(TPP)(4\text{-}Mepy)_2]ClO_4$ (17): Recrystallization of **8** from benzene containing an excess amount of 4-methylpyridine gave reddish purple crystals in a quantitative yield. Found: C, 70.78; H, 4.70; N, 9.19%. Calcd for $C_{56}H_{42}N_6ClO_4$: C, 70.25; H, 4.42; N, 8.78%.

$[Co^{III}(TPP)(py)_2]Cl$ (18): Recrystallization of **12** from benzene–pyridine (1:1 vol/vol) gave reddish purple crystals. Found: C, 74.73; H, 4.87; N, 9.67%. Calcd for $C_{54}H_{46}N_6ClCo$: C, 74.60; H, 4.87; N, 9.67%.

$[Co^{III}(TPP)(py)Cl]$ (19): This was prepared by the method previously reported,[14l] and also obtained from recrystallization of **18** from benzene–dichloromethane.

$[Co^{III}(TPP)CH_2CH(OCH_2CH_3)_2]$ (20): The procedure for preparation was the same as that described for octaethylporphyrin complex **6**. Found: C, 75.73; H, 4.92; N, 7.32%. Calcd for $C_{51}H_{45}N_4O_2Co$: C, 76.10; H, 5.64; N, 6.96%.

$[Co^{III}(TPP)CH_2CHO]$ (21): A dichloromethane solution of **20** was treated with silica gel as described for **7**. Found: C, 76.93; H, 4.42; N, 7.99%. Calcd for $C_{46}H_{35}N_4OCo$: C, 76.87; H, 4.91; N, 7.80%.

Molecular Weight. Molecular weights were measured by the vapour pressure osmometry at 31.5 °C in chloroform and methanol on a Knour vapour pressure osmometer.

Spectral Measurements. ^{1}H NMR spectra were obtained on Varian HA-100D and JEOL HM-100 spectrometers. Infrared spectra were measured on a Hitachi G-3 spectrometer and absorption spectra on a Hitachi model 200-10 spectrophotometer.

Cyclic Voltammetry. All solvents were dried and distilled before use. As a supporting electrolyte, tetrabutylammonium perchlorate (TBAP) was used after being subjected twice to crystallization from benzene. Cyclic voltammograms were obtained on a HA-104 potentiostat (Hokuto Denko) in combination with an HB-107A function generator. A three-electrode system was used which consisted of platinum working and counter electrodes and a commercial saturated calomel electrode (SCE) separated from the bulk of solution by a bridge filled with solvent and supporting electrolyte. The bridge had its solution changed periodically to avoid aqueous contaminants from entering the cell *via* the SCE. All solutions were purged of oxygen by passing purified nitrogen through them for 10 min just before taking cyclic voltammograms. After the degassing a blanket of nitrogen was kept over the solution. The half-wave potential $E_{1/2}$ was taken as that potential lying midway between the oxidation and reduction peaks for a given couple. All experiments were carried out at room temperature (20 °C) and the potentials reported refer to the SCE.

Results and Discussion

Synthesis. All the tervalent cobalt complexes were prepared generally by air oxidation of their corresponding bivalent cobalt complexes in the presence of aqueous acid.[14)] Perchlorate, tetrafluoroborate, bromide, and chloride salts of tetraphenylporphyrin complexes **8**, **9**, **11**, and **12** were obtained in methanol. Iodide and pseudohalide salts **10**, **13**, and **14** were obtained through anion exchange from the perchlorate salt. The bis(tetrahydrofuran) adduct of the perchlorate salt of cobalt(III) octaethylporphyrin **1** was obtained by using tetrahydrofuran as the solvent. This could easily be converted to bis(aqua) adduct **2** by recrystallization from benzene–dichloromethane saturated with water. The tetrafluoroborate salt of octaethylporphyrinatocobalt(III) was obtained by the same method as that for tetraphenylporphyrin derivative **9**. Bis(amine) adducts **4**, **5**, **15**, **16**, **17**, **18**, and **19** were prepared by recrystallization from benzene containing each amine in excess. The bis(pyridine) adduct of chloride salt **18** was easily converted into mono(pyridine) adduct **19** by recrystallization from benzene–chloroform. However, the bis(pyridine) adduct of perchlorate salt **15** could not be converted into mono(pyridine) adduct. These two types of pyridine adducts were confirmed by elemental analysis and ^{1}H NMR spectra.

Molecular Weights. For cobalt(III) complexes of porphyrin, no aggregation phenomena have been reported.[17)] However, the molecular weight measurements in chloroform indicate that two of the complexes, **8** and **9**, tend to aggregate as the concentration is increased. For example, Fig. 1 shows the concentration dependence of molecular weight for **9** and **3**. At low concentrations around 0.01 mol dm^{-3}, both the complexes assume monomeric molecular weights. However, as the concentration is increased, the molecular weight of **9** is gradually increased. As high concentrations around 0.05 mol dm^{-3}, complex **9** is almost dimeric; in polar solvents such as methanol all of the tervalent complexes are monomeric at these high concentrations. As will be described below, ^{1}H NMR spectra of complexes **8** and **9** show no significant changes when the concentration is increased from 0.01 to 0.05 mol dm^{-3}. The observed molecular weights indicate that the complexes are not ionized in these solvents. When the anions are coordinated, the solute species are considered to be of nonelectrolyte; otherwise, they should be of ion pair or ion-pair aggregate.

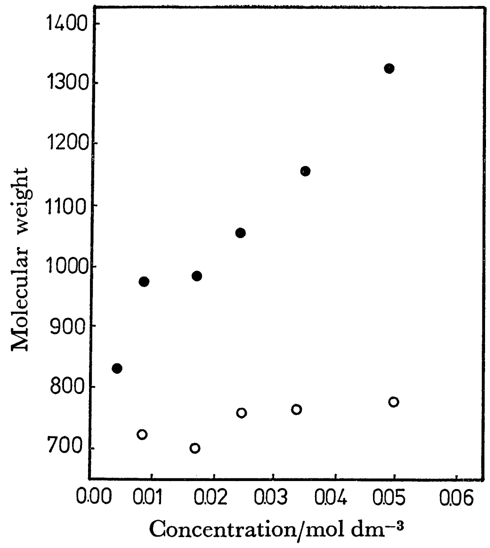


Fig. 1. Concentration dependency of the molecular weight in chloroform.
●: [Co^{III}(TPP)(H$_2$O)$_2$]BF$_4$, ○: [Co^{III}(OEP)(H$_2$O)$_2$]BF$_4$.

In the case of tetraphenylporphyrin derivatives **8** and **9** where higher molecular weights were observed, the aggregation mode of ion pair is not considered to be the stacking of porphyrin planes *via* a sort of the π-π interaction,[17)] because such stacking is more difficult to be realized in the case of tetraphenylporphyrin derivatives because of the large steric hindrance of phenyl groups; this is contrary to the present situation. The most probable picture for the aggregation seems to be that in which the ion-pairs are bound through hydrogen bonding between the aqua ligands and the perchlorate (or tetrafluoroborate) anions as is realized in crystals.[16)] Such hydrogen bonding seems to be more favorable in the case of tetraphenylporphyrin derivatives than in the case of octaethylporphyrin derivatives owing to the electron-withdrawing character of the former.

Absorption Spectra. Absorption spectral data are summarized in Table 1. Absorption spectra of the tervalent cobalt complexes except the amine complexes are highly dependent on properties of solvents.[15)] Halides and pseudohalides **10**—**14** showed Soret bands at about 400—407 nm in nonpolar solvents such as dichloromethane. Addition of polar solvents such as methanol gave shifts toward longer wavelengths. In methanol the spectra of these complexes are very similar to one another. This can be explained in terms of the coordination of polar solvent molecules to form [Co^{III}(TPP)(solvent)$_2$]$^+$ species. On the other hand, BF$_4$ and ClO$_4$ salts **8** and **9** showed Soret bands at 426 nm in dichloromethane which are close to those in methanol (425 nm). This result indicates that, in dichloromethane, the cobalt atoms of BF$_4$ and ClO$_4$ salts are coordinated by water molecules as the fifth and sixth axial ligands.[16)] In methanol these water molecules seem to be replaced with solvent molecules as suggested by the ^{1}H NMR and the cyclic voltammetry studies described below. The six-coordinated species [Co^{III}(TPP)(H$_2$O)$_2$]$^+$ or [Co^{III}(TPP)(solvent)$_2$]$^+$

Table 1. Absorption spectra of tervalent cobalt porphyrins

Compound	Solvent	λ_{max}/nm(log ε)		
1	CH_2Cl_2	378(4.82),	524(8.35),	557(3.86)
2	CH_2Cl_2	375(4.82),	524(3.85),	556(3.86)
	CH_3OH	409(4.98),	525(3.99),	559(3.99)
	py	418(5.09),	530(4.00),	562(3.98)
3	CH_2Cl_2	377(4.82),	524(3.35),	557(3.86)
4	CH_2Cl_2	418(5.09),	530(4.00),	562(3.98)
5	CH_2Cl_2	424(5.11),	536(4.01),	556(4.47)
6	CH_2Cl_2	393(5.30),	520(4.01),	556(4.47)
7	CH_2Cl_2	396(5.40),	522(4.03),	558(4.50)
8	CH_2Cl_2	426(4.98),	536(3.84)	
	CH_3OH	425(4.99),	539(3.88)	
9	CH_2Cl_2	426(4.99),	540(3.83)	
	CH_3OH	426(4.99),	539(3.89)	
10	CH_2Cl_2	407(5.01),	528(3.92)	
	CH_3OH	426(4.99),	540(3.88)	
11	CH_2Cl_2	405(4.99),	549(3.53)	
	CH_3OH	426(4.99),	542(3.90)	
12	CH_2Cl_2	404(5.00),	545(3.80)	
	CH_3OH	426(4.99),	543(3.99)	
13	CH_2Cl_2	400(5.00),	550(3.74)	
	CH_3OH	426(4.99),	542(3.98)	
14	CH_2Cl_2	403(4.99),	550(3.99)	
	CH_3OH	426(4.99),	550(3.89)	
15	CH_2Cl_2	434(5.01),	550(3.91),	584(3.41)
16	CH_2Cl_2	433(5.14),	545(3.99),	578(3.65)
17	CH_2Cl_2	434(5.13),	550(3.99),	585(3.66)
18	CH_2Cl_2	434(5.12),	550(3.99),	580(3.65)
19	CH_2Cl_2	437(5.00),	552(3.96),	588(3.60)
20	CH_2Cl_2	408(5.20),	526(4.00)	
21	CH_2Cl_2	407(5.21),	522(3.99)	

can be expected to have a cationic character, if the solvent molecule is allowed to dissociate easily due to weak solvation. Neither the bis(amine) adducts nor the mono(amine) adduct was much influenced by solvent polarity. This result indicates that there exists tight coordination of the amine molecules to the cobalt atom, which is consistent with results from ^{1}H NMR spectra.

^{1}H NMR Spectra. ^{1}H NMR data are summarized in Table 2. In nonpolar solvents such as dichloromethane and chloroform these tervalent cobalt complexes except the amine adducts and organocobalt complexes show very broad and shifted signals. Figure 2 illustrates the ^{1}H NMR spectra of **8**—**14** in chloroform at room temperature. The signals of the phenyl and β-pyrrole protons are significantly broad and shifted compared with those for usual diamagnetic spectrum. This phenomenon is qualitatively the same as that reported by Yamamoto *et al.* in the case of chloride salt **12**.[14k)] It is noteworthy that the signals of the pyrrole β-protons for complexes **8** and **9** are very much shifted toward higher magnetic fields.[18)] The magnetic moments of complexes **8** and **9** in chloroform at room temperature (31 °C) showed smaller paramagnetism (about 0.7 BM) than the one for a chloride salt (1.66 BM) previously reported.[14k)] Such large upfield shifts of pyrrole β-protons and small paramagnetism, as compared with those of the chloride salt, suggest that the mechanisms of the spin delocalization on the porphyrin plane are somewhat different from each other. The difference in the mechanism of spin delocalization between the group of ClO_4 and BF_4 salts and the group of Cl, Br, I, and N_3 salts may result from the different coordination modes. Sakurai *et al.*[14h,l)] reported that the cobalt atom in the chloride salt is coordinated by the chlorine atom as the fifth ligand. In perchlorate salt **8**, on the other hand, the cobalt atom is coordinated by two water molecules as described above.[16)]

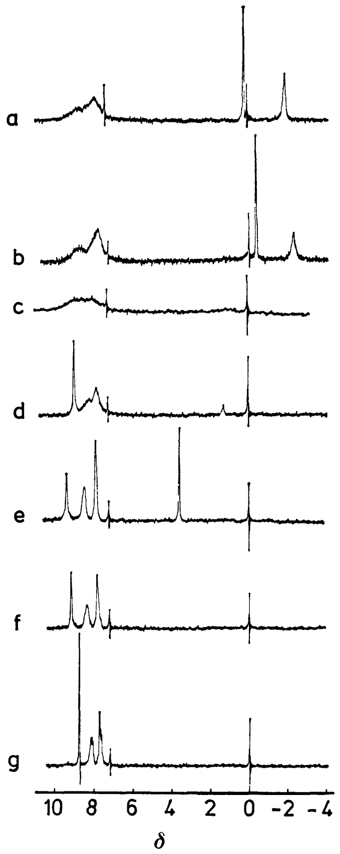


Fig. 2. ^{1}H NMR spectra in chloroform at 31.5 °C. (a): $[Co^{III}(TPP)(H_2O)_2]BF_4$, (b): $[Co^{III}(TPP)(H_2O)_2]ClO_4$, (c): $[Co^{III}(TPP)(H_2O)Cl]$, (d): $[Co^{III}(TPP)(H_2O)Br]$, (e): $[Co^{III}(TPP)(H_2O)I]$, (f): $[Co^{III}(TPP)(H_2O)N_3]$, (g): $[Co^{III}(TPP)(H_2O)SCN]$.

In polar solvents these complexes showed usual diamagnetic ^{1}H NMR spectra. The addition of amines such as pyridine gave also diamagnetic spectra which were very similar to those of bis(amine) adducts. For example, bis(tetrahydrofuran) adduct **1** showed only one broad signal at about 2 ppm in chloroform, but an addition of pyridine in twice the equivalent gave a spectrum indicating the existence of the bis(pyridine) adduct and free tetrahydrofuran.[15)] The ^{1}H NMR spectra of amine adducts **4**, **5**, and **15**—**20** indicate a coordination of these amine molecules to the cobalt atom. In particular, it is noteworthy that both bis(pyridine) adduct **19** and mono(pyridine) adduct **20** can be isolated in the case of chloride salt,

Table 2. ^{1}H NMR data of tervalent cobalt porphyrins (δ values)[a]

	Solvent	*meso*	α-CH_2	β-CH_3	Others
1	CD_2Cl_2	Very broad signal at about 2			
	CD_2Cl_2+py	10.10(s, 4H),	4.04(q, 16H),	1.80(t, 24H)	3.56(m, 8H, THF), 1.68(m, 8H, THF) 5.66(t, 2H, γ-H of py), 4.50(t, 4H, β-H of py), 0.00(d, 4H, α-H of py)
2	CD_2Cl_2	Very broad signal at about 2			
	Acetone-d_6	9.10(s, 4H),	5.44(q, 16H),	1.81(t, 24H)	
	Methanol-d_4	10.78(s, 4H),	4.40(q, 16H),	2.04(t, 24H)	
	DMSO-d_6	10.41(s, 4H),	4.15(q, 16H),	1.77(t, 24H)	
3		Very broad signal at about 2			
4	CD_2Cl_2	10.06(s, 4H),	4.04(t, 16H),	1.80(t, 24H)	5.66(t, 2H, γ-H of py), 4.48(t, 4H, β-H of py), 0.00(d, 2H, α-H of py)
5	CD_2Cl_2	9.67(s, 4H),	5.88(q, 16H),	1.72(t, 24H)	3.88(m, 2H, 5-H of 2-MeIm), 1.26(m, 2H, NH), −1.04(t, 2H, 4-H of 2-MeIm), −2.76(s, 6H, 2-CH_3)
6	CD_2Cl_2	10.03(s, 4H),	4.13(q, 16H),	1.99(t, 24H)	1.09(m, 4H, $OC\underline{H}_2$-), 0.06(t, 6H, $OCH_2C\underline{H}_3$), −4.80(t, 1H, -$CH_2C\underline{H}$), −6.40(bd, 2H, -$C\underline{H}_2CH$)
7	CD_2Cl_2	10.34(s, 4H),	3.83(q, 16H),	1.88(t, 24H)	3.20(t, 1H, $C\underline{H}O$), −4.28(d, 2H, $C\underline{H}_2$)
		Pyrrole β	Phenyl		
8	$CDCl_3$	−2.2(br, 8H),	8(br, 20H)		
9	$CDCl_3$	−2.1(br, 8H),	8(br, 20H)		
	Acetone-d_6	9.18(s, 8H),	8.20(m, 8H), 7.80(m, 12H)		
10	$CDCl_3$	9.36(br, 8H),	8.44(br), 7.84(br)		
11	$CDCl_3$	10.0(br),	9.28(br), 8.76(br)		
12	$CDCl_3$	9.0(br),	8.8(br), 7.7(br)		
13	$CDCl_3$	8.8(br),	8.14(br), 7.72(br)		
14	$CDCl_3$	9.22(br),	8.38(br), 7.86(br)		
15	$CDCl_3$	9.13(s, 8H),	7.8(m, 20H)		6.21(t, 2H, γ-H of py) 5.06(t, 4H, β-H of py) 0.90(d, 4H, α-H of py)
16	$CDCl_3$	9.28(s, 8H),	7.9(m, 20H)		5.56(d, β-H of 4-CNpy) 1.20(d, 4H, α-H of 4-CNpy)
17	$CDCl_3$	9.02(s, 8H),	7.7(m, 20H)		4.84(d, 4H, β-H of 4-Mepy) 1.26(s, 6H, 4-CH_3) 0.66(d, 4H, α-H of 4-Mepy)
18	$CDCl_3$	9.13(s, 8H),	7.8(m, 20H)		6.21(t, 2H, γ-H of py) 5.06(t, 4H, β-H of py) 0.90(d, 4H, α-H of py)
19	$CDCl_3$	9.00(s, 8H),	8.8(m, 8H), 7.7(m, 12H)		5.82(t, 1H, γ-H of py) 4.84(t, 2H, β-H of py) 0.84(d, 2H, α-H of py)
20	$CDCl_3$	9.39(s, 8H),	8.04(m, 8H), 7.60(m, 12H)		1.44(m, 4H, -$OC\underline{H}_2$), 0.45(t, 6H, $OCH_2C\underline{H}_3$) −2.22(t, 1H, $CH_2C\underline{H}$) −4.06(d, 2H, $C\underline{H}_2CH$)
21	$CDCl_3$	8.82(s, 8H),	8.04(m, 8H), 7.60(m, 12H)		3.81(t, 1H, $C\underline{H}O$) −3.72(d, 2H, $C\underline{H}_2$)

a) Abbrebiations used: s, singlet; d, doublet; t, triplet; q, qualtet; m, multiplet; br, broad.

although mono(pyridine) adduct can not be isolated in the case of perchlorate salt. Moreover, the ^{1}H NMR spectrum of 2-methylimidazole adduct **5** showed tight coordination of such a sterically-hindered axial base.

Cyclic Voltammetry. The electrochemical behavior of cobalt porphyrin complexes has actively been investigated.[19,20] These studies usually dealt with cobalt(II) porphyrins and disclosed two distinct redox couples for the metal redox processes, Co(III)/Co(II) and Co(II)/Co(I). Addition of various types of amines to such systems was found to bring about shifts of the redox potentials for Co(III)/Co(II) to more negative values, the shift getting greater as the basicity of the amine is increased. The redox couple Co(II)/Co(I), on the other hand, was almost insensitive. However, there have been no reports on redox process of Co(III) porphyrins in which anions are present either as axial ligands or as counter ions. Study of such process seems to be of importance for estimation of the influence by such anions on the electrophilicity of cobalt atoms. There have been some reports on the effect of anions in the supporting electrolyte on the redox couple Co(III)/Co(II) associated with cobalt(II) porphyrins,[20a] but no study on such factors can give any direct information and we have no assurance that the anion is coordinated during the oxidation process.

Table 3 summarizes the half wave potentials ($E_{1/2}$) of tervalent cobalt porphyrins. One of the most outstanding features is that in dichloromethane these tervalent cobalt porphyrins have Co(III)/Co(II) redox couples varing in their combination significantly with counter anions or axial ligands and that accordingly, they can be categorized into three groups: Group (i) complexes have $\mathrm{BF_4^-}$ or $\mathrm{ClO_4^-}$ as the counter anion and have the most positive redox values similar to that of the bivalent complex $\mathrm{Co^{II}(TPP)}$. Group (ii) includes salts of $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{SCN^-}$, and $\mathrm{N_3^-}$ and have less positive redox potentials by about 0.4 V which varies slightly with the kind of counter anions. These values reveal that there is no exchange of the axially coordinated anion with the perchlorate ion of the supporting electrolyte TBAP; otherwise, the redox values for these complexes would be close to that of the perchlorate salt. Group (iii) complexes have various amines as axial ligands and have the lowest redox potentials.

The difference between the redox potentials of Groups (i) and (ii) may be explained in terms of different modes of coordination. As previously discussed, two water molecules are coordinated axially in $[\mathrm{Co^{III}(TPP)(H_2O)_2]ClO_4}$ and the same is expected to be true with the tetrafluoroborate salt and its corresponding OEP derivatives. The fact that the values for both Group (i) complexes and the bivalent complex are quite similar to one another, indicates that coordination of the axial water molecules is very weak and that it has little influence on the redox potentials in dichloromethane. On the other hand, the chloride anion, and probably other halide and pseudohalide anions, too, coordinate to the cobalt atom directly as the fifth ligand, and the increasing covalency of such axial ligands seems to lower the redox potential of the Co(III)/Co(II) couple.

It is interesting to compare the Co(III)/Co(II) potentials of Co(III) porphyrins with those of $\mathrm{Co^{II}(TPP)}$ with various supporting electrolytes, reported by Truxillo and Davis.[20a] Thus, the redox values for $[\mathrm{Co^{III}(TPP)(H_2O)_2]X}$ (X=$\mathrm{ClO_4}$, $\mathrm{BF_4}$) and $[\mathrm{Co^{III}(TPP)(H_2O)Y}]$ (Y=Br, Cl) are +0.72, +0.72, +0.38, and +0.27, respectively. The redox values for the Co(III)/Co(II) couple of $\mathrm{Co^{II}(TPP)}$ are reported to be +0.75, +0.94, +0.29, and +0.74 volt for electrolytes TBAP, TBAF, TBAB, and TBAC, respectively. Slightly lower values of the cobalt(III) porphyrin

TABLE 3. HALF-WAVE POTENTIALS FOR BI- AND TERVALENT COBALT PORPHYRINS

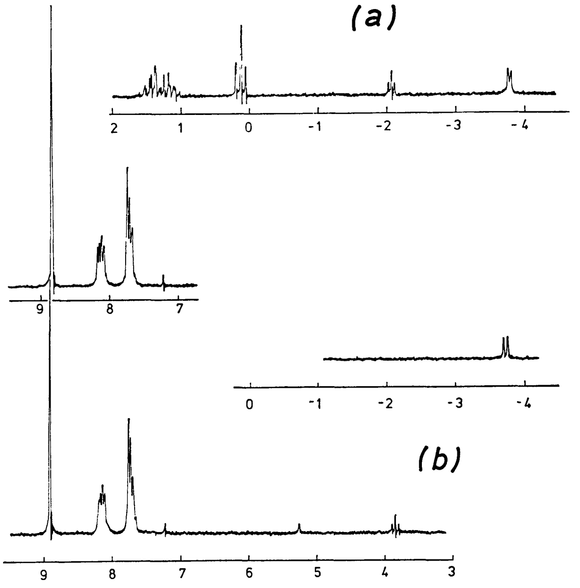
Compound	Solvent	V *vs.* SCE	
		Co(III)/Co(II)	Co(II)/Co(I)
$\mathrm{Co^{II}(TPP)}$	$\mathrm{CH_2Cl_2}$	+0.71	−0.93
$[\mathrm{Co^{III}(TPP)(H_2O)_2]BF_4}$		+0.72	−1.14
$[\mathrm{Co^{III}(TPP)(H_2O)_2]ClO_4}$		+0.72	−1.05
$[\mathrm{Co^{III}(TPP)(H_2O)Br}]$		+0.35	−1.03
$[\mathrm{Co^{III}(TPP)(H_2O)Cl}]$		+0.27	−1.12
$[\mathrm{Co^{III}(TPP)(H_2O)SCN}]$		+0.26	−0.94
$[\mathrm{Co^{III}(TPP)(H_2O)I}]$		+0.23	−0.91
$[\mathrm{Co^{III}(TPP)(H_2O)N_3}]$		+0.18	−0.89
$[\mathrm{Co^{III}(TPP)(4\text{-}CNpy)_2]ClO_4}$		+0.15	−0.98
$[\mathrm{Co^{III}(TPP)(py)_2]ClO_4}$		−0.05	−1.14
$[\mathrm{Co^{III}(TPP)(4\text{-}Mepy)_2]ClO_4}$		−0.11	−1.04
$[\mathrm{Co^{III}(TPP)(imd)_2]ClO_4}$		−0.31	−1.02
$[\mathrm{Co^{III}(TPP)(H_2O)_2]BF_4}$	$\mathrm{CH_2Cl_2\text{-}EtOH}$	+0.31	−0.85
$[\mathrm{Co^{III}(TPP)(H_2O)_2]ClO_4}$		+0.32	−0.95
$[\mathrm{Co^{III}(TPP)(H_2O)Br}]$		+0.27	−0.96
$[\mathrm{Co^{III}(TPP)(H_2O)Cl}]$		+0.28	−0.99
$[\mathrm{Co^{III}(TPP)(H_2O)N_3}]$		+0.29	−0.99

perchlorate and tetrafluoroborate than those of Co(II) porphyrin in TBAP and TBAF can reasonably be explained in terms of the presence of axially coordinated water molecules which have a weak electron-donating character. On the other hand, the much higher potential of the Co(II) porphyrin in the presence of TBAC than that of [Co^{III}(TPP)(H_2O)Cl] indicates that the chloride ion in the supporting electrolyte coordinate neither to Co(II) porphyrin nor to Co(III) formed by the oxidation of Co(II) porphyrin during the time of voltage cyclings.

In dichloromethane–ethanol solution the tervalent cobalt complexes studies showed almost the same redox potentials with one another, referring presumably to [Co^{III}(TPP)(EtOH)$_2$]$^+$ (0.27—0.33 V), in conformity with the replacement of the axial anion by the solvent molecules as has just been concluded from the absorption spectra.

In the case of Group (iii) porphyrins, the redox potentials are still lower and dependent predominantly on the nature of axial ligands, which is consistent with the results in the case of bivalent cobalt porphyrins with various amines, reported by Walker *et al.*[20e)] The ^{1}H NMR spectra of these complexes in chloroform indicate a tight coordination of two amine molecules. Large irreversibility for the bis(amine) adduct, compared with that for other tervalent complexes, suggests a considerable dissociation of the axial amines in the reduced state. In fact, it is well known that bivalent cobalt complexes prefer five-coordination to six-coordination.[22)]

Reaction with Ethyl Vinyl Ether. We previously reported[15)] that perchlorate salts **1** and **2**, and **8** react with ethyl vinyl ether to afford organocobalt(III) complexes **6** and **20**, respectively. Other halides and pseudohalides also gave similar reaction products in ethanol solution although their yields are low. This result indicates that the solvent-coordinated species (B) has sufficient electrophilicity toward ethyl vinyl ether to form organocobalt complex (D) probably *via* π-complex (C). The obtained 2,2-diethoxyethylcobalt(III) complexes **6** and **20** could easily be converted to formylmethylcobalt(III) complexes **7** and **21**, respectively. These organocobalt complexes have been well characterized by elemental analysis and spectroscopic measurements, in particular ^{1}H NMR spectra. Figure 3 shows the ^{1}H NMR spectra of **20** and **21**. The presence of 2,2-diethoxyethyl and formylmethyl groups bonded to the central metal ion can reasonably be confirmed by the high field shift of the protons in the groups due to the large diamagnetic ring-current effect of porphyrin ring. Assignments of the protons are listed in Table 2.



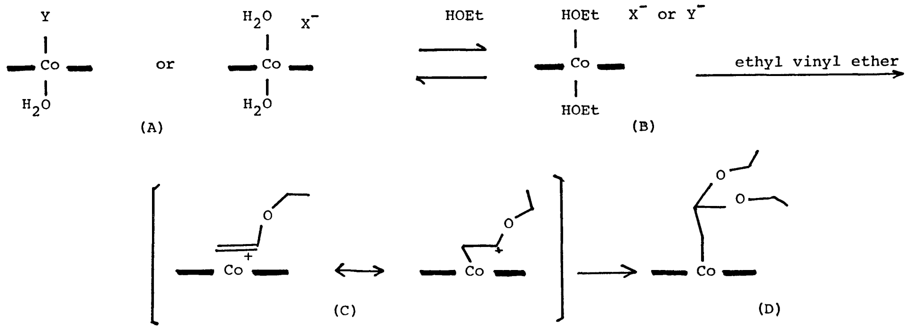
δ

Fig. 3. ^{1}H NMR spectra of (a) [Co^{III}(TPP)$CH_2CH(OC_2H_5)_2$] and (b) [Co^{III}(TPP)CH_2CHO] in chloroform.

This synthetic method for organocobalt(III) complexes of porphyrins is very convenient for the model study of vitamin B_{12}, because it is very simple and gives high yields, compared with the reaction of Co(I) species with organo halides.

On the other hand, bis(amine) adducts or mono(amine) adduct reacted with ethyl vinyl ether to give only reduced bivalent cobalt porphyrins. These results indicate that the strong electrophilic property of central cobalt(III) ion in the amine adducts is cancelled by the strong ligation of amine molecules and that only the electron transfer from ethyl vinyl ether to cobalt ion occurs.

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.



Scheme 1.

References

1) P. G. Lenhart and D. C. Hodgkin, *Nature (London)*, **192**, 937 (1961).

2) Reviews; G. N. Schrauzer, *Acc. Chem. Rec.*, **97** (1968); G. Costa, *Coord. Chem. Rev.*, **8**, 63 (1972); A. Biggetto, G. Costa, G. Mestroni, G. Pelliger, A. Puxeddu, E. Reisenhofer, L. Stefani, and G. Tauzher, *Inorg. Chim. Acta Rev.*, **4**, 41 (1970); D. Dodd and M. D. Johnson, *Organomet. Chem. Rev.*, **52**, 1 (1973); G. N. Schrauzer, *Angew. Chem.*, **88**, 465 (1976).

3) E. Ochiai, K. M. Long, C. R. Sperati, and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 3201 (1969).

4) K. Farmery and D. H. Busch, *Inorg. Chem.*, **11**, 2901 (1972).

5) C. Y. Mok and J. E. Endicott, *J. Am. Chem. Soc.*, **99**, 1276 (1972); **100**, 123 (1978).

6) J. H. Esperson and A. H. Martin, *J. Am. Chem. Soc.*, **99**, 5953 (1977).

7) W. P. Schaefer, R. Walizman, and B. T. Huie, *J. Am. Chem. Soc.*, **100**, 5063 (1978).

8) H. Elroi and D. J. Meyerstein, *J. Am. Chem. Soc.*, **100**, 5540 (1978).

9) Y. Murakami and Y. Aoyama, *Bull. Chem. Soc. Jpn.*, **49**, 683 (1976); Y. Murakami, Y. Aoyama, and K. Tokunaga, *J. Am. Chem. Soc.*, **102**, 6736 (1980).

10) H. Ogoshi, J. Sestune, T. Omura, and Z. Yoshida, *J. Am. Chem. Soc.*, **97**, 6461 (1975); H. Ogoshi, J. Sestune, Z. Yoshida, *J. Chem. Soc., Chem. Commun.*, **1975**, 572.

11) H. Ogoshi, J. Sestune, and Z. Yoshida, *J. Organomet. Chem.*, **159**, 317 (1978).

12) R. B. Silverman and D. Dolphin, *J. Am. Chem. Soc.*, **95**, 1686 (1973); **96**, 7094 (1974); **98**, 4626 (1976).

13) H. Ogoshi, J. Sestune, Y. Nanbo, and Z. Yoshida, *J. Organomet. Chem.*, **159**, 329 (1978).

14) a) A. W. Johnson and I. K. Kay, *J. Chem. Soc.*, **1960**, 2979; b) J. W. Buchler, G. Eikelmann, L. Puppe, K. Rohbock, H. H. Schneege, and D. Weck, *Ann. Chem.*, **745**, 135 (1971); c) R. Bonnett and M. J. Dimsdale, *J. Chem. Soc., Perkin Trans. 1*, **1972**, 2540; d) N. Datta-Gupta and T. J. Bardos, *J. Pharm. Sci.*, **57**, 3000 (1968); e) W. R. Scheidt, J. A. Cunningham, and J. L. Hoard, *J. Am. Chem. Soc.*, **95**, 8289 (1978); f) D. A. Clarke, D. Dolphin, R. Grigg, A. W. Johnson, and H. A. Pinnock, *J. Chem. Soc., C*, **1968**, 881; g) J. A. Kaduk and W. R. Scheidt, *Inorg. Chem.*, **13**, 1875 (1974); h) T. Sakurai, K. Yamamoto, H. Naito, and N. Nakamoto, *Bull. Chem. Soc. Jpn.*, **49**, 3042 (1976); i) T. Sakurai, K. Yamamoto, N. Seino, and M. Katsuta, *Acta Crystallogr., Sect. B*, **31**, 2514 (1975); k) K. Yamamoto, J. Uzawa, and T. Chijimatsu, *Chem. Lett.*, **1979**, 89.

15) H. Sugimoto, M. Nagano, Z. Yoshida, and H. Ogoshi, *Chem. Lett.*, **1980**, 521.

16) H. Masuda, T. Taga, K. Osaki, H. Sugimoto, and M. Mori, *Bull. Chem. Soc. Jpn.*, in press.

17) "The Porphyrins," ed by D. Dolphin ,Vol. V, Chap. 7.

18) "The Porphyrins," ed by D. Dolphin, Vol. IV, Chap. 2.

19) "The Porphyrins," ed by D. Dolphin, Vol. V, Chap. 3.

20) a) L. A. Truxillo and D. G. Davis, *Anal. Chem.*, **47**, 2260 (1975); b) A. Giraudeau, H. J. Carrot, J. Jordan, I. Ezhar, and M. Gross, *J. Am. Chem. Soc.*, **101**, 3857 (1979); c) K. M. Kadish, L. A. Bottomley, and D. Beroiz, *Inorg. Chem.*, **17**, 1124 (1978); d) A. Wolbery and J. Manassen, *J. Am. Chem. Soc.*, **92**, 2982 (1970); e) F. A. Walker, D. Beroiz, and K. M. Kadish, *J. Am. Chem. Soc.*, **98**, 3484 (1976); f) M. J. Carter, D. P. Rillema, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974).

21) D. P. Rillema, J. F. Endicott, and E. Papaconstantniu, *Inorg. Chem.*, **10**, 1739 (1971); P. A. Rock, *ibid.*, **7**, 837 (1968).

22) F. A. Walker, *J. Am. Chem. Soc.*, **92**, 4235 (1970).