3360 © 1985 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 58, 3360—3364 (1985) [Vol. 58, No. 11

Optical Absorption and Conductimetric Studies on Ionic Dissociation of Metallotetraphenylporphyrins in Ethanol Solutions

Mikio Hoshino,* Shunzo Katayama, and Kiyoko Yamamoto
The Institute of Physical and Chemical Research, Wako, Saitama 351-01

(Received June 17, 1985)

Optical absorption spectra of chloro[tetraphenylporphyrinato(2-)]metals, $M^{III}Cl(tpp)$ (M=Mn, Fe, Co, and In), and diacetato[tetraphenylporphyrinato(2-)]tin(IV), $Sn^{IV}(CH_3COO)_2(tpp)$, in ethanol and benzene solutions were measured. A marked difference in the absorption spectra between the ethanol and benzene solutions was observed for $Mn^{III}Cl(tpp)$, $Fe^{III}Cl(tpp)$, and $Co^{III}Cl(tpp)$, while a small difference for $In^{III}Cl(tpp)$ and $Sn^{IV}(CH_3COO)_2(tpp)$. The electric conductivity measurements demonstrated that $M^{III}Cl(tpp)$ (M=Mn, Fe, Co, and In) undergoes ionic dissociation in ethanol, whereas $Sn^{IV}(CH_3COO)_2(tpp)$ does not. Solvent effects on the optical absorption spectra observed for ethanol and benzene solutions of the metallotetraphenylporphyrins are discussed on the basis of (1) the ionic dissociation revealed from the conductivity measurements and (2) charge-transfer (from porphyrin ligand to the central metal) character of the electronic absorption bands.

Synthetic metalloporphyrins have received much attention because of their importance as a model compound of natural metalloporphyrins that dominate electron-transport phenomena occurring in life.[1,2] Furthermore, the chemical and physical properties of these porphyrins strikingly depend on the nature of the central metal. For these reasons, studies of synthetic metalloporphyrins have been carried out by many researchers in diversed fields.[3-6]

Recently, the study of solar energy conversion and storage has been increasingly important subject of photochemistry.[7-9] Since metalloporphyrins efficiently absorb visible light from the sun, the photochemistry of them has been subjected to numerous studies, in particular, on electron transfer reactions between the excited states of porphyrins and electron-acceptor molecules.[10-16]

Despite of the importance of metalloporphyrins as mentioned above, conductivity measurements of them in solutions have not yet been carried out. The conductivity measurements have been proved of great use for the study of the ionic dissociation of solute molecules in solutions.

In the present study we have measured optical absorption spectra and conductivity of metalloporphyrins in ethanol and benzene solutions. The metalloporphyrins used are chloro[tetraphenylporphyrinato(2-)]metals, $M^{III}Cl(tpp)$ (M=Mn, Fe, Co, and In), and diacetato[tetraphenylporphyrinato(2-)]-tin(IV). The optical absorption spectra of the former three porphyrins in ethanol solutions were found to differ markedly from those in benzene solutions. On the other hand, the spectra of the latter two porphyrins showed slight difference between the ethanol and benzene solutions. We consider that this result is interpreted in terms of either (1) ligation of an ethanol molecule in the vacant axial position of metalloporphyrins or (2) ionic dissociation of metalloporphyrins. The conductivity measurements give a clear solution for this problem. On the basis of the optical absorption spectroscopic and conductivity measurements, the dissolved states of these metalloporphyrins are discussed in detail.

Experimental

Chloro[tetraphenylporphyrinato(2-)]metals, $M^{III}Cl(tpp)$ (M=Mn, Fe, Co, and In), and diacetate[tetraphenylporphyrinato(2-)]tin(IV) (these are abbreviated, respectively, as $Mn^{III}Cl(tpp)$, $Fe^{III}Cl(tpp)$, $Co^{III}Cl(tpp)$, $In^{III}Cl(tpp)$, and $Sn^{IV}(CH_3COO)_2(tpp)$ hereafter), were synthesized and purified according to the literature.[17-20] Reagent grade ethanol and benzene were fractionally distilled after being dried over molecular sieves to remove traces of water: conductivity of dry ethanol was obtained to be 2×10^{-8} S cm^{-1} and that of dry benzene, 1.0×10^{-9} S cm^{-1} at 25 °C.

Optical absorption spectra were recorded on a Hitachi 330 spectrophotometer.

The electric conductivity of solutions was measured at 1000 Hz by the conductance-linear-bridge method as described in the previous paper.[21] The resistance readings of the linear-bridge were calibrated by substitution method with a precision decade resistance box (Dekastat RS-624 from Electro Scientific Industries: the accuracy is ±0.005%). A conductivity cell which is specially designed for solutions of low conductivity was used throughout this study. The cell constant was determined to be 0.1348 cm^{-1} with the use of standard potassium chloride solutions. The experimental error of the conductivity measurements was less than 0.1%. All the measurements were carried out at 25.00±0.01 °C by using a water bath equipped with a thermostat.

The thermodynamic ion-association constants, K_A, for the reactions

$$Cl^- + [M^{III}(tpp)]^+ \rightleftarrows M^{III}Cl(tpp)$$
$$\text{(M: Mn, Fe, Co, and In)}$$

and

$$[Sn^{IV}(CH_3COO)(tpp)]^+ + CH_3COO^- \rightleftarrows Sn^{IV}(CH_3COO)_2(tpp) \quad (1)$$

can be calculated from the conductivity data on the basis of the Fuoss-Hsia conductance theory.[22-24] The revised

Fuoss-Hsia equation for the molar conductivity, Λ, of an associated symmetrical electrolyte is given by

$$\Lambda = \Lambda^{\infty} - S \cdot c^{1/2} \cdot \gamma^{1/2} + E \cdot c \cdot \gamma \log(c \cdot \gamma) + J_1 \cdot c \cdot \gamma - J_2{}^{3/2}(c \cdot \gamma)^{3/2} - K_A \cdot c \cdot \gamma \cdot f_{\pm}^2 \cdot \Lambda \tag{2}$$

with

$$K_A = (1-\gamma)/c \cdot \gamma^2 \cdot f_{\pm}^2 \tag{3}$$

where Λ^{∞} is the limiting molar conductivity; c, the molar concentration; γ, the degree of dissociation; S, the Onsager limiting slope; $f_{\pm}$, the mean ionic activity coefficient, and E, J_1, and J_2 are the theoretical coefficients, respectively. The coefficients, J_1 and J_2, are formulated as a function of the mean distance (a) of closest approach of positive and negative ions. These coefficients were used for the evaluation of a.

The mean activity coefficient $f_{\pm}$, was estimated by means of Debye-Hückel equation:

$$\log f_{\pm} = -A|z_+ z_-|\sqrt{I}/(1+B \cdot a \cdot \sqrt{I}) \tag{4}$$

where z_+ and z_- are the charge numbers of the positive and negative ions, respectively, I is the ionic strength, and A and B are the theoretical coefficients. The values of permitivity and viscosity of ethanol used in the present calculation were taken from literature.[25] A set of Λ^{∞}, K_A, and a values was obtained in such a way that the theoretical equation gives the best fit to the conductivity data obtained experimentally. All the calculations were performed on a FACOM computer using a FORTRAN program (JCCOND) which was kindly supplied from Professor J. C. Justice in Universitè de Paris.

Results and Discussion

Optical Absorption Spectra. Figure 1 shows the optical absorption spectra of $Mn^{III}Cl(tpp)$ in benzene and ethanol solutions at room temperature. The spectrum observed in ethanol is found to differ considerably from that in benzene. When the solvent is changed from benzene to ethanol, the absorption bands located around 1.3 and 2.7×10^4 cm^{-1} are red-shifted and those around 1.7 and 2.1×10^4 cm^{-1}, to the contrary, are blue-shifted. The solvent effects on the optical absorption spectra are closely related to the nature of each electronic band.

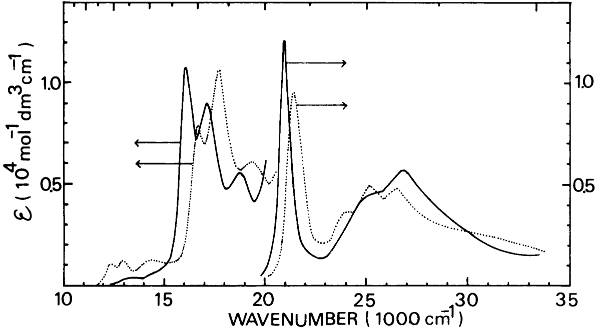

Fig. 1. Optical absorption spectra of $Mn^{III}Cl(tpp)$ in benzene (——) and in ethanol (----) solution.

The theoretical calculation has been carried out in order to elucidate the significant difference in the optical absorption spectra between manganese(III) porphyrin and usual metalloporphyrin such as zinc(II) porphyrin.[26–27] For manganese(III) porphyrin, d levels of the central manganese atom are very close to the porphyrin π levels, resulting in strong mixing of the d and π levels. As a consequence of the strong mixing, porphyrin has a number of charge-transfer bands in the UV-visible region of the absorption spectrum.[28] On the other hand, d levels of zinc(II) porphyrin are too low to make a strong mixing with the porphyrin π levels.

The location of the electronic bands having charge-transfer character in the spectra of manganese porphyrin is known to vary depending on the nature of the axial ligands as well as the negative ion in the axial position.[27] Boucher[28] has studied the absorption spectra of manganese(III) protoporphyrin IX dimethyl ester complexes in coordinating and non-coordinating solvents. The spectra observed in benzene solutions are characteristically different for each of the halide ion complexes of the manganese(III) porphyrin. However, the spectra observed in methanol solutions are independent of the axial halide ions. These results are well interpreted in terms of the ionic dissociation of the manganese(III) porphyrin in methanol solutions:[28]

$$\textbf{[Mn}^{\textbf{III}}\textbf{X porphyrin] (X: halogen atom)} \longrightarrow \textbf{X}^- + \textbf{[Mn}^{\textbf{III}}\textbf{ porphyrin]}^+$$

No ionic dissociation is observed for the benzene solutions.

The above discussion is also acceptable for the interpretation of the absorption spectra of $Mn^{III}Cl(tpp)$: $Mn^{III}Cl(tpp)$ undergoes ionic dissociation in ethanol, while it does not in benzene. The previous studies on one-electron reduction induced by γ-rays at 77 K have strongly suggested that $Mn^{III}Cl(tpp)$ in ethanol dissociated into Cl^- and $[Mn^{III}(tpp)]^+$.[29] Furthermore, the conductivity measurements, as will be described later, confirmed the ionic dissociation of $Mn^{III}Cl(tpp)$ in ethanol solutions.

Figure 2 shows the optical absorption spectra of $Fe^{III}Cl(tpp)$ in benzene and ethanol solutions. The spectrum observed in ethanol differs markedly from that in benzene. In comparison with the spectrum measured in benzene, four major features are recognized for the spectrum in ethanol: (1) The 1.5×10^4 cm^{-1} band loses its intensity without shift, (2) The 1.95×10^4 cm^{-1} band is red-shifted, (3) The 2.4×10^4 cm^{-1} band is slightly blue-shifted, and (4) The 2.7×10^4 cm^{-1} band is largely blue-shifted.

The situation of the metal d levels and porphyrin π levels in iron(III) porphyrins is very similar to that in manganese(III) porphyrins.[27] Thus, we can expect

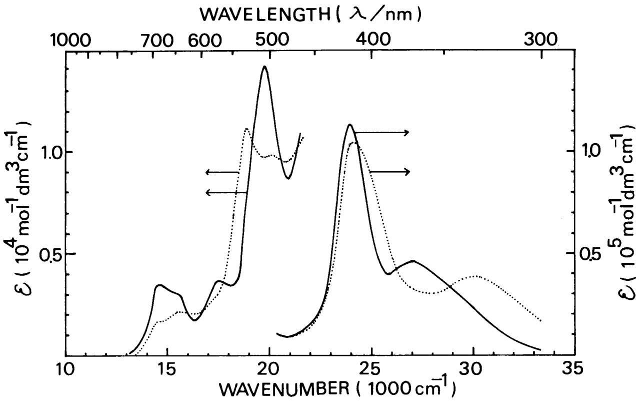

Fig. 2. Optical absorption spectra of Fe^{III}Cl(tpp) in benzene (——) and in ethanol (----) solution.

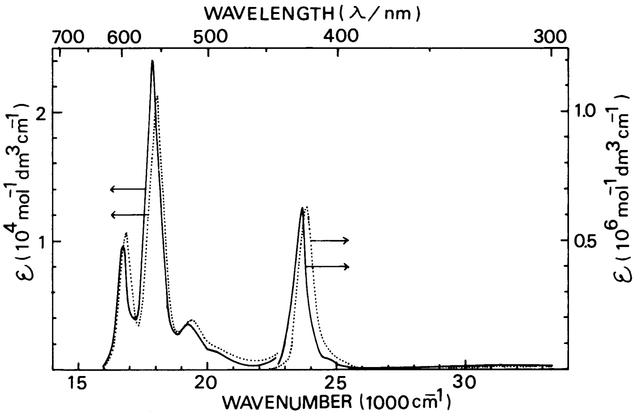

Fig. 3. Optical absorption spectra of In^{III}Cl(tpp) in benzene (——) and in ethanol (----) solution.

that the electronic bands of Fe^{III}Cl(tpp) have a charge-transfer character as in the case of Mn^{III}Cl(tpp).[27] In fact, the theoretical calculation involving the configuration interaction between the porphyrin π states and the charge-transfer (from porphyrin to iron(III)) states gives a consistent interpretation for the optical absorption spectra of Fe^{III}Cl(tpp).[30] Since the charge-transfer character of the electronic bands depends on the d levels of the central metal and the porphyrin π levels, the absorption spectrum of Fe^{III}Cl(tpp) is regarded to vary by the coordinating nature of the solvents. Therefore, the absorption spectrum of Fe^{III}Cl(tpp) as well as Mn^{III}Cl(tpp) observed in non-coordinating solvent, benzene, is considered to differ from that in coordinating solvent, ethanol.

A significant change in the absorption spectra of Fe^{III}Cl(tpp) between ethanol and benzene solutions suggests that ionic dissociation of Fe^{III}Cl(tpp) occurs in ethanol solutions.

The absorption spectra of Co^{III}Cl(tpp) in benzene and ethanol solutions exhibit two distinct features: (1) the Soret (*ca.* 2.3×10^4 cm^{-1}) and Q (*ca.* 1.8×10^4 cm^{-1}) bands in an ethanol solution become narrower than those in a benzene solution and (2) although the peak maximum of the Soret band observed for an ethanol solution is remarkably red-shifted by *ca.* 1.1×10^4 cm^{-1}, the Q band is slightly blued-shifted by *ca.* 0.2×10^4 cm^{-1} in comparison with each band observed for a benzene solution.

The absorption spectrum in the ethanol solution is in good agreement with that observed for the six-coordinated Co^{III}(tpp).[31] Therefore, the species in the ethanol solution is presumed to be Co^{III}Cl(tpp)-(C_2H_5OH) or [Co^{III}(tpp)(C_2H_5OH)$_2$]$^+$ in which ethanol molecule(s) are located in the axial position(s). The spectrum observed for the benzene solution is ascribed to the five-coordinated species, Co^{III}Cl(tpp).[32]

It is suggested that cobalt porphyrins have a number of charge-transfer transitions as in the case of nickel porphyrins.[27] A significant difference in the spectra between ethanol and benzene solutions is interpreted by assuming that the absorption bands, in particular the Soret band, have a charge-transfer character.

As to the ionic dissociation of Co^{III}Cl(tpp), paper electrophoresis study has revealed that Co^{III}Cl(tpp) in ethanol is dissociated as[32]

$$\mathrm{Co^{III}Cl(tpp)} + 2\mathrm{C_2H_5OH} \longrightarrow \mathrm{Cl^-} + [\mathrm{Co^{III}(tpp)(C_2H_5OH)_2}]^+$$

Here, C_2H_5OH molecules in [Co^{III}(tpp)(C_2H_5OH)$_2$]$^+$ are assumed to be located in the axial positions. The ionic dissociation of Co^{III}Cl(tpp) in ethanol was also suggested on the basis of the optical and ESR studies of one-electron reduced species of Co^{III}Cl(tpp) produced by γ-radiolysis of the ethanol solution at 77 K.[29]

Figure 3 shows the optical absorption spectra of In^{III}Cl(tpp) in benzene and ethanol solutions. The spectra differ remarkably from those of Mn^{III}Cl(tpp), Fe^{III}Cl(tpp), and Co^{III}Cl(tpp) but are very similar to those of usual metallotetraphenylporphyrins such as tetraphenylporphyrinato(2-)zinc(II). This fact suggests that the absorption bands scarcely have a charge-transfer character. In fact, only small difference in the spectra between ethanol and benzene solutions is observed. Both the Q and Soret bands are found to be slightly blue-shifted on going from benzene to ethanol solutions as shown in Fig. 3. This result may be interpreted in terms of general solvent effects on the optical absorption bands.

There have been no reports on the ionic dissociation of In^{III}Cl(tpp) in ethanol solutions. However, we assumed the dissociation of In^{III}Cl(tpp) in ethanol solutions in order to elucidate the electron-transfer reaction from the photoexcited triplet state of In^{III}Cl(tpp) to methylviologen.[16] The electiric conductivity measurements, as will be shown later, confirmed the ionic dissociation:

$$\mathrm{In^{III}Cl(tpp)} + 2\mathrm{C_2H_5OH} \longrightarrow \mathrm{Cl^-} + [\mathrm{In^{III}(tpp)(C_2H_5OH)_2}]^+$$

Table 1. Molar conductivities Λ of $Mn^{III}Cl(tpp)$, $Fe^{III}Cl(tpp)$, $Co^{III}Cl(tpp)$, $In^{III}Cl(tpp)$, and $Sn^{IV}(CH_3COO)_2(tpp)$ in ethanol solutions at 25 °C

$Mn^{III}Cl(tpp)$		$Fe^{III}Cl(tpp)$		$Co^{III}Cl(tpp)$		$In^{III}Cl(tpp)$		$Sn^{IV}(CH_3COO)_2(tpp)$	
10^4c mol dm^{-3}	Λ S cm^2 mol^{-1}	10^4c mol dm^{-3}	Λ S cm^2 mol^{-1}	10^4c mol dm^{-3}	Λ S cm^2 mol^{-1}	10^4c mol dm^{-3}	Λ S cm^2 mol^{-1}	10^4c mol dm^{-3}	Λ S cm^2 mol^{-1}
1.995	30.91	0.80	28.81	1.601	29.76	0.5472	29.39	4.097	3.10
2.993	30.55	1.00	28.64	2.002	29.52	0.7290	29.13	8.193	3.02
4.989	29.97	1.20	28.50	3.203	28.93	0.9113	28.89	10.241	3.00
6.984	29.52	1.60	28.23	4.984	28.21	1.0935	28.69	16.386	2.98
9.977	28.96	2.00	28.00	8.007	27.26	1.4580	28.30	20.483	2.80
14.058	28.35			10.008	26.71	1.8230	27.96		
20.082	27.64			20.017	24.64				

Table 2. Limiting molar conductivities Λ^∞, ion-association constants K_A, and ion-size parameter a, of $Mn^{III}Cl(tpp)$, $Fe^{III}Cl(tpp)$, $Co^{III}Cl(tpp)$, and $In^{III}Cl(tpp)$ in ethanol solutions at 25 °C

	Λ^∞ S cm^2 mol^{-1}	K_A dm^3 mol^{-1}	a_{J_2} nm
$Mn^{III}Cl(tpp)$	32.75±0.02	18±2	1.24±0.4
$Fe^{III}Cl(tpp)$	30.10±0.01	94±1	1.14±0.1
$Co^{III}Cl(tpp)$	31.64±0.01	82±2	1.42±0.2
$In^{III}Cl(tpp)$	30.71±0.01	282±4	1.14±0.1

where C_2H_5OH molecules in $[In^{III}(tpp)(C_2H_5OH)_2]^+$ are assumed to occupy the axial positions.

The optical absorption spectra of $Sn^{IV}(CH_3COO)_2(tpp)$ in benzene and ethanol solutions are very similar to those of $In^{III}Cl(tpp)$. The peak maxima observed for a benzene solution are located at 1.66×10^4, 1.78×10^4, and 1.93×10^4 cm^{-1} in the Q band region and at 2.34×10^4 cm^{-1} in the Soret band region. When the solution is changed from benzene to ethanol, the Q band peaks are slightly blue-shifted by *ca.* 0.1×10^4 cm^{-1} and the Soret band peak, by *ca.* 0.3×10^4 cm^{-1}. No significant differences in the spectra between the two solutions are observed, indicating that the charge-transfer character in the optical absorption is very weak. The small blue shift of the Q and Soret band observed in ethanol solutions is regarded as being due to the general solvent effects similar to the case of $In^{III}Cl(tpp)$.

Electric Conductivity Measurements. The molar conductivities, Λ, for $Mn^{III}Cl(tpp)$, $Fe^{III}Cl(tpp)$, $Co^{III}Cl(tpp)$, $In^{III}Cl(tpp)$, and $Sn^{IV}(CH_3COO)_2(tpp)$ in ethanol solutions at 25 °C are summarized in Table 1. The Λ values of the former four porphyrins are obtained to be 24—31 S cm^2 mol^{-1} in their concentration range 5×10^{-5}—2×10^{-3} mol dm^{-3}. However, the Λ value of $Sn^{IV}(CH_3COO)_2(tpp)$ is extremely small in comparison with those of the former four porphyrins. Taking account of the limiting molar conductivity of acetate ion in ethanol ($\lambda_-^\infty=17.9$ S cm^2 mol^{-1}),[33] we conclude that $Sn^{IV}(CH_3COO)_2(tpp)$ is hardly dissociated in ethanol solutions.

In Table 2 are listed the values of Λ^∞, K_A, and a determined for $Mn^{III}Cl(tpp)$, $Fe^{III}Cl(tpp)$, $Co^{III}Cl(tpp)$, and $In^{III}Cl(tpp)$ in ethanol solutions at 25 °C. The values of Λ^∞ are calculated to be 30—33 S cm^2 mol^{-1}. Since λ_-^∞ of Cl^- in ethanol is reported to be 24.3 S cm^2 mol^{-1},[34] the limiting molar conductivities of $[M^{III}(tpp)]^+$ ions (λ_+^∞) are determined to be 8.45, 5.80, 7.34, and 6.41 S cm^2 mol^{-1} for M=Mn, Fe, Co, and In, respectively. The fact that $[M^{III}(tpp)]^+$ gives the λ_+^∞ values smaller than the λ_-^∞ value of Cl^- is ascribed to the ion size in solutions: $[M^{III}(tpp)]^+$ has a larger size than Cl^-.

The K_A values obtained for the four metallotetraphenylporphyrins are found to decrease in the sequence $In^{III}Cl(tpp) \gg Fe^{III}Cl(tpp) \cong Co^{III}Cl(tpp) > Mn^{III}Cl(tpp)$. By using K_A values, we can calculate the degree of ionic dissociation, γ, from the equation 3. When $c=10^{-4}$ mol dm^{-3}, the values of γ are obtained to be 0.998, 0.992, 0.993, and 0.970 for $Mn^{III}Cl(tpp)$, $Fe^{III}Cl(tpp)$, $Co^{III}Cl(tpp)$, and $In^{III}Cl(tpp)$ in ethanol solutions, respectively. Since the absorption spectroscopic measurements in the present study were carried out in the concentration range 10^{-5}—10^{-4} mol dm^{-3}, the major species (>90%) in the ethanol solutions of $M^{III}Cl(tpp)$ (M=Mn, Fe, Co, and In) are ascribed to $[M^{III}(tpp)]^+$ produced by the ionic dissociation of $M^{III}Cl(tpp)$. Presumably, $[M^{III}(tpp)]^+$ in ethanol solution has two axial ethanol molecules to be formulated as $[M^{III}(tpp)(C_2H_5OH)_2]^+$.

The mean distance (a_{J_2}) of the closest approach of $[M^{III}(tpp)]^+$ and Cl^- is calculated from J_2 to be 1.1—1.4 nm. These values of the distance are found to be in good agreement with those estimated from the Stokes' law.[38] In comparison with the distance (0.22—0.24 nm) between the central metal and Cl atom in $M^{III}Cl(tpp)$,[18,35—37] the distance of the closest approach in ethanol solution is very large. It is likely that the solvent sphere around Cl^- and the axial ethanol molecules in $[M^{III}(tpp)(C_2H_5OH)_2]^+$ afford the large value of the distance of the closest approach.

Conclusion

The optical absorption spectra of $M^{III}Cl(tpp)$ (M=Mn, Fe, and Co) in ethanol solutions markedly differ from those in benzene solutions, whereas the spectra of $In^{III}Cl(tpp)$ and $Sn^{IV}(CH_3COO)_2(tpp)$ in ethanol solutions are rather similar to those in benzene solutions. The electric conductivity measurements carried out for the ethanol solutions revealed that $M^{III}Cl(tpp)$ (M=Mn, Fe, Co, and In) undergo ionic dissociation, while $Sn^{IV}(CH_3COO)_2(tpp)$ does not. A marked difference in the absorption spectra between the ethanol and benzene solutions of $M^{III}Cl(tpp)$ (M=Mn, Fe, and Co) is concluded to be caused not only from the ionic dissociation but also from the charge-transfer character of the absorption bands. This conclusion is further supported by the facts that (1) $In^{III}Cl(tpp)$ undergoes ionic dissociation in ethanol without giving rise to substantial difference in the absorption spectra between ethanol and benzene solutions and (2) the absorption spectra of $In^{III}Cl(tpp)$ in ethanol and benzene solutions are very similar to those of $Sn^{IV}(CH_3COO)_2(tpp)$ which is demonstrated to be nondissociative in an ethanol solution.

We thank Professor Reita Tamamushi of Fukushima University for critical reading of the manuscript.

References

1) D. Ostefeld and M. Tsutsui, *Accounts Chem. Res.*, **7**, 52 (1974).

2) D. Dolphin and R. H. Felton, *Accounts Chem. Res.*, **7**, 26 (1974).

3) W. C. Lin, "The Porphyrins," ed by D. Dolphin, Academic Press, New York (1978), Vol. IV, Chap. 7.

4) J. Fajer and M. S. Davis, "The Porphyrins," ed by D. Dolphin, Academic Press, New York (1978), Vol. IV, Chap. 4.

5) A. Wolberg and J. Mansassen, *J. Am. Chem. Soc.*, **92**, 2982 (1970).

6) M. Gouterman, R. A. Mathies, and B. E. Smith, *J. Chem. Phys.*, **52**, 3795 (1979).

7) A. B. P. Lever, B. S. Ramaswamy, and S. Licoccia, *J. Photochem.*, **19**, 173 (1982).

8) J. R. Bolton, "Solar Power and Fuels," Academic Press, New York (1977).

9) G. Sprintschnik, H. W. Sprintshnik, P. P. Kirsh, and D. G. Whitten, *J. Am. Chem. Soc.*, **99**, 4974 (1979).

10) J. Kiwi, and M. Gratzel, *J. Am. Chem. Soc.*, **101**, 7214 (1979).

11) I. Okura, and N. K. Thuan, *J. Chem. Soc., Faraday Trans. 1*, **76**, 2209 (1980).

12) T. Matsuo, K. Ito, and K. Takama, *Chem. Lett.*, **1980**, 1009.

13) D. Holten, M. W. Windsor, W. W. Parson, and M. Gouterman, *Photochem. Photobiol.*, **28**, 951 (1978).

14) T. L. Netzel, M. A. Bergkamp, and C. K. Chang, *J. Photochem.*, **17**, 451 (1981).

15) M. Migita, T. Okada, N. Mataga, S. Nishitani, N. Kurata, Y. Sakata, and S. Misumi, *Chem. Phys. Lett.*, **84**, 263 (1981).

16) M. Hoshino, H. Seki, and H. Shizuka, *J. Phys. Chem.*, **89**, 470 (1985).

17) G. D. Dorough, J. R. Miller, and F. M. Huennekens, *J. Am. Chem. Soc.*, **73**, 4315 (1951).

18) T. Sakurai, K. Yamamoto, H. Naito, and N. Nakamoto, *Bull. Chem. Soc. Jpn.*, **49**, 3042 (1976).

19) A. D. Alder, F. R. Long, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).

20) M. Bhatti, W. Bhatti, and E. Mast *Nucl. Chem. Lett.*, **8**, 133 (1972).

21) S. Katayama, *Bull. Chem. Soc. Jpn.*, **46**, 106 (1973).

22) R. M. Fuoss and K. L. Hsia, *Proc. Natl. Acad. Sci. U. S.*, **57**, 1550 (1966).

23) K. L. Hsia and R. M. Fuoss, *J. Am. Chem. Soc.*, **90**, 3055 (1968).

24) R. Fernandez-Prini, *Trans. Faraday Soc.*, **65**, 3311 (1969).

25) G. J. Janz and R. P. T. Tomkins, "Nonaqueous Electrolyte Handbook," Academic Press, New York and London (1972), Vol. I, p. 94.

26) a) M. Zerner and M. Gouterman, *Theoret. Chim. Acta*, **4**, 44 (1966); b) M. Zerner, M. Gouterman, and H. Kobayashi, *Theoret. Chim. Acta*, **6**, 363 (1966); c) M. Gouterman, L. K. Hanson, G. E. Khalil, W. L. Leenstra, and J. W. Buchler, *J. Chem. Phys.*, **62**, 2343 (1975).

27) L. J. Boucher, *Coord. Chem. Rev.*, **7**, 289 (1972).

28) L. J. Boucher, *J. Am. Chem. Soc.*, **90**, 6640 (1968).

29) M. Hoshino, S. Konishi, and M. Imamura, *Bull. Chem. Soc. Jpn.*, **57**, 1713 (1984).

30) H. Kobayashi, T. Higuchi, Y. Kaizu, H. Osada, and M. Aoki, *Bull, Chem. Soc. Jpn.*, **48**, 3137 (1975).

31) K. Yamamoto and S. Tonomura, *Sci. Papers Inst. Phys. Chem. Res.*, **58**, 122 (1964).

32) K. Yamamoto, *Sci. Papers Inst. Phys. Chem. Res.*, **71**, 111 (1977).

33) "Landolt-Börnstein Tablellen," Springer-Verlag, II Band, 7 Teil, Electrische Eigenschaften II (1960), p. 622.

34) D. Dobos, "Electrochemical Data," Elsevier Sci. Pub. Co.: Amsterdam-Oxford-New York (1975).

35) A. Tulinsky and B. M. L. Chen, *J. Am. Chem. Soc.*, **99**, 3647 (1977).

36) R. G. Ball, K. M. Lee, A. G. Marshall, and J. Trotter, *Inorg. Chem.*, **19**, 1463 (1980).

37) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Am. Chem. Soc.*, **89**, 1992 (1967).

38) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths: London (1959), p. 43.