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Cation and Anion Recognition of Crown Ether-armed Metalloporphyrin

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Metal complexes of 5-[3'-(12-crown-4)methoxy-carbonylphenyl]-15-phenylporphyrin (H₂-MCEPP) are synthesized as the hosts which have two receptor sites, the crown ether moiety being for cations and the porphyrin-metal site for the counter anions. Cation or anion recognition is highly dependent on the porphyrin-metal; that is, the zinc complex (Zn-MCEPP) recognizes anions preferentially and, on the contrary, the magnesium complex (Mg-MCEPP) recognizes cations more effectively.

Keywords: Metalloporphyrin, crown ether, cation recognition, anion sensing, ditopic host

INTRODUCTION

Porphyrins and metalloporphyrins can offer sophisticated sensors, since they are effectively monitored by NMR, UV-Vis and CD spectroscopy, electrochemistry, and fluorescence spectroscopy [1,2]. Indeed, they have been utilized in recognition of metal cations and anions. Anion sensing has been presented by the porphyrin host modified with cobaltocenium salt or *N*-phenylurea [3,4], and a calixarene-capped metalloporphyrin has been reported as

an unique ditopic receptor for iodide ion [5]. On the other hand, crown ethers and porphyrins have been combined to generate hosts which bind cations such as silver and sodium cations and they have been developed for recognition of ammonium and dipyridinium cations [6–10]. Research on crown ether-armed porphyrins as sensors or receptors, however, is limited to several reports and can play an important role in molecular devices and molecular recognition chemistry [11].

In our previous papers, we have described cation and/or anion recognition by crown ether-armed fluorophore hosts [12,13]. In a continuing study of molecular devices which recognize a cation and an anion, we would like to demonstrate a new type of crown ether-armed metalloporphyrin host recognizing a cation and an anion.

RESULTS AND DISCUSSION

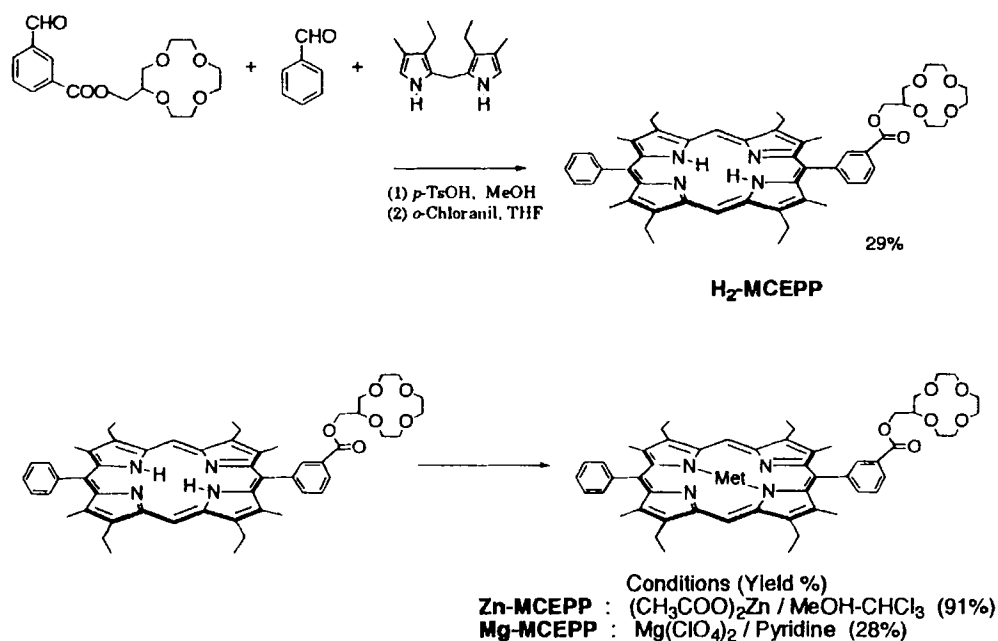
The porphyrin hosts were synthesized by the following reactions. The reaction of

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bis(3-ethyl-4-methyl-2-pyrrolyl)methane, 3-[(12-crown-4) methyloxycarbonyl]benzaldehyde, and benzaldehyde, followed by treatment of the formed porphyrinogen with *o*-chloranil gave 5-[3'-(12-crown-4)methyloxycarbonylphenyl]-15-phenylporphyrin (**H₂-MCEPP**) in 29% yield. The porphyrin **H₂-MCEPP** was purified with liquid chromatography and recrystallization (hexane-chloroform). Insertion of zinc or magnesium metal to the porphyrin ring was carried out with zinc acetate or magnesium perchlorate, according to the reported methods [1], to produce **Zn-MCEPP** or **Mg-MCEPP** in a good yield. The obtained porphyrin derivatives, particularly **H₂-MCEPP**, are so photosensitive as to decompose gradually under daylight. Therefore, their treatment was performed in the dark.

shows somewhat different ¹H-NMR spectra, indicating the crown ether moiety to be rather broadened and upfield-shifted, which suggests some interaction between the central magnesium metal and the crown ether side arm (Fig. 1). This interaction with the oxygen atom of the crown ether seems to be attributed to the hard character of the magnesium metal, compared to the zinc metal.

Addition of an equimolar amount of sodium perchlorate to a solution of **Zn-MCEPP** in deuteriochloroform changes the chemical shifts; that is, the crown ether moiety (δ 3.5~4.0) and the ester-methylene group (δ 4.4) are both broadened and upfield-shifted to δ 2.6~3.4, and the singlet meso protons are separated into two signals. The upfield-shift of the crown ether moiety is due to



SCHEME 1

The introduction of metal to the porphyrin ring causes a change in ¹H-NMR spectra. Although ¹H-NMR spectra of **Zn-MCEPP** are quite similar to those of **H₂-MCEPP**, **Mg-MCEPP**

the diamagnetic shielding of the porphyrin ring, which suggests that the crown ether moiety is stacked asymmetrically on the porphyrin ring through a sodium perchlorate bridge (Fig. 2).

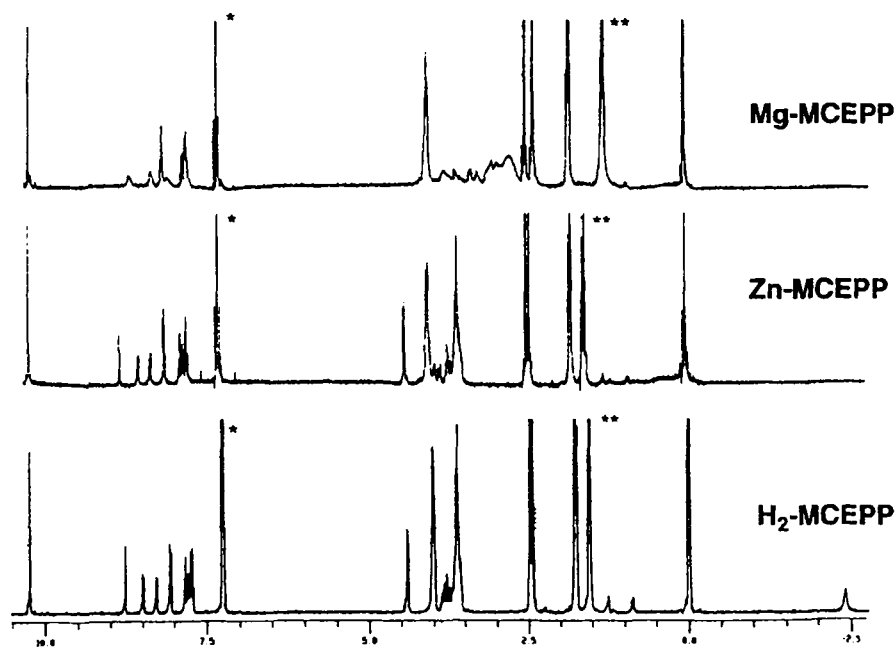


FIGURE 1 $^1\text{H-NMR}$ spectra of the MCEPP derivatives. Solvent, CDCl_3 ; *, contaminant of CDCl_3 ; **, water.

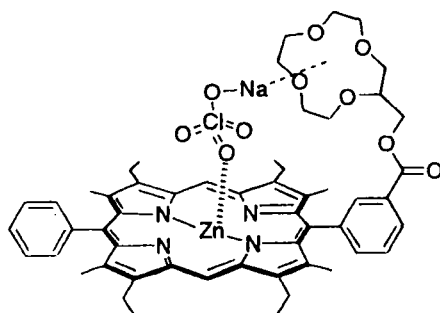


FIGURE 2 The coordinated complex between Zn-MCEPP and sodium perchlorate.

The complex ratio of Zn-MCEPP and sodium perchlorate was evaluated by the mole ratio method on the basis of the separation of the meso protons in $^1\text{H-NMR}$ spectra. The complex ratio is dependent on the solvent polarity; for example, in a 7:3 ratio of deuterioacetonitrile to deuteriochloroform, a 1:0.37 complex of Zn-MCEPP and sodium perchlorate is found. An incomplete ratio suggests partial aggregation of the porphyrin. With increase of the solvent polarity, the

complex ratio changes and is extrapolated to be a 1:1 ratio in deuterioacetonitrile, as shown in Figure 3. It should be added that Zn-MCEPP is poorly soluble in deuterioacetonitrile under $^1\text{H-NMR}$ conditions.

Addition of sodium perchlorate to an acetonitrile solution of the metal free porphyrin $\text{H}_2\text{-MCEPP}$ does not cause any change in absorbance and wavelength in the UV-Vis spectra. However, a very interesting change is observed upon addition of a guest salt such as sodium perchlorate, sodium thiocyanate, sodium iodide, calcium perchlorate, or calcium thiocyanate to a solution of Zn-MCEPP in acetonitrile. The change in absorbance depends highly on the kind of anion; that is, absorbance is substantially increased by perchlorate, decreased by thiocyanate, and not affected by iodide. A slight red-shift, other than the absorbance change, is noticed with thiocyanate. The association constant with each salt was evaluated from a standard plot based on the change in absorbance of the Soret band [14]. As was anticipated from the mole ratio method in the $^1\text{H-NMR}$ study,

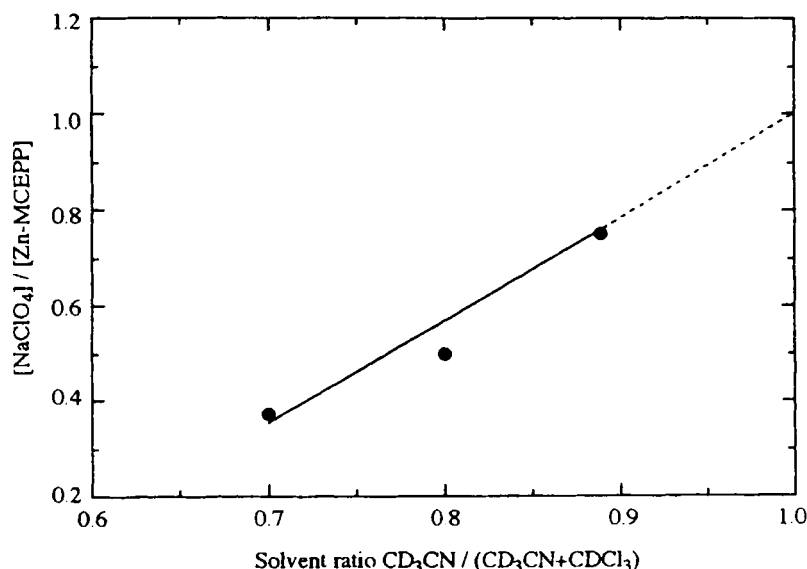


FIGURE 3 Solvent dependence of mole ratio for the complexation between Zn-MCEPP and sodium perchlorate.

Zn-MCEPP captures sodium perchlorate in a 1:1 ratio and its association constant is high, $\log K = 5.38$. Similarly, with calcium perchlorate or calcium thiocyanate, a 1:1 complex with high association constant is found. A 1:2 complex with sodium thiocyanate is found and this is supported by the slight, but appreciable, red-shift (3 nm), as shown in Table I. With sodium iodide, the change in absorbance is so small that the association constant cannot be evaluated. This is probably due to the weak capture of sodium iodide, which suggests that the spherical iodide does not construct the stable bridge drawn in Figure 2.

With **Mg-MCEPP**, although a slight red-shift is noticed in the binding of thiocyanate, the kind

of anion does not affect the change in absorbance, an increase in absorbance being caused by both thiocyanate and perchlorate. However, the kind of cation reflects profoundly on the association constant, sodium salts being fully recognized to give substantial association constants and calcium salts being recognized very poorly (Tab. II). The difference in association constant between sodium and calcium cations is seen to relate to the stacking of the central magnesium metal with the crown ether moiety. The sodium cation may break through the stacking because of the appreciable affinity with 12-crown-4, compared with the calcium cation.

The quenching of fluorescence in the complexation of **Zn-MCEPP** or **Mg-MCEPP** with

TABLE I Association constant ($\log K$) of **Zn-MCEPP**^a

Guest	$K(M^{-1})$	Host:Guest	$\Delta\lambda(\text{nm})^b$	Abs.Change ^c
NaClO ₄	5.38	1:1	0	+
NaSCN	6.46	1:2	3.0	-
NaI	-	-	0	~0
Ca(ClO ₄) ₂	4.63	1:1	0	+
Ca(SCN) ₂	5.00	1:1	1.0	-

^a In acetonitrile at 25°C. $[Zn-MCEPP] = 1.0 \times 10^{-5} M$.

^b Wavelength shift of the Soret band after the addition of guest.

^c Change in absorbance of the Soret band after the addition of guest.

TABLE II Association constant ($\log K$) of **Mg-MCEPP**^a

Guest	$K(M^{-1})$	Host:Guest	$\Delta\lambda(\text{nm})^b$	Abs.Change ^c
NaClO ₄	5.12	1:1	0	+
NaSCN	4.45	1:1	1.5	+
Ca(ClO ₄) ₂	-	-	0	+
Ca(SCN) ₂	-	-	1.0	+

^a In acetonitrile at 25°C. $[Mg-MCEPP] = 1.0 \times 10^{-5} M$.

^b Wavelength shift of the Soret band after the addition of guest.

^c Change in absorbance of the Soret band after the addition of guest.

salt is not clearly noticed. It is anticipated that the photoinduced electron transfer from the captured anion to the porphyrin is not able to occur because of the high energy of the highest occupied molecular orbital (HOMO) of the porphyrin.

CONCLUSIONS

Metalloporphyrins having a 12-crown-4 lariat ether are synthesized as ditopic hosts for alkali and alkaline earth metal salts. Their flexible structures are found to be suitable for cation or anion recognition, which is highly dependent on the porphyrin-metal. The zinc complex (**Zn-MCEPP**) recognizes anions, which can be monitored by the change in absorbance and, on the contrary, the magnesium complex (**Mg-MCEPP**) recognizes cations, which is reflected in the association constants. These interesting properties can be very useful for new types of molecular devices.

EXPERIMENTAL SECTION

The IR spectra were recorded on a JASCO A-100 spectrometer and samples were run as potassium bromide pellets. The UV-Visible spectra were recorded with a JASCO Ubest-50 spectrometer. The $^1\text{H-NMR}$ spectra were taken on a JEOL LA-400 (400 MHz) spectrometer for a solution in deuteriochloroform, unless otherwise noted. The chemical shifts are given in δ/ppm downfield from tetramethylsilane as the internal standard.

The preparative liquid chromatography was carried out by LC-908 (Japan Analytical Industry, Co., Ltd.) using JAI gel 1H (eluent, chloroform). Acetonitrile for spectroscopy is the highest quality from KOKUSAN Chemical Co. and was used without purification. The elemental analyses were measured with a Perkin Elmer 2400 II CHN Analyzer.

3-[(12-Crown-4)methyloxycarbonyl]benzaldehyde

3-Carboxybenzaldehyde (1.76 g, 11.7 mmol) was dissolved in toluene (80 ml) at 30°C. To the mixture, a toluene solution (20 ml) of 4-(*N,N*-dimethylamino)pyridine (0.26 g, 2.13 mmol) and successively a toluene solution (20 ml) of 2-hydroxymethyl-12-crown-4 (2.18 g, 10.6 mmol) were added slowly. After being stirred for 30 min, a toluene solution (20 ml) of *N,N'*-dicyclohexylcarbodiimide (3.25 g, 15.8 mmol) was added to the mixture and the mixture was stirred at room temperature for 2 h. A white precipitate was filtered off and the filtrate was evaporated under vacuo to leave a residue which was chromatographed on silica gel (eluent, chloroform/ethyl acetate = 3/1), giving 2.95 g (82%) of 3-[(12-crown-4)methyloxycarbonyl]benzaldehyde as a yellowish oil; IR 1720 (C=O) and 1100 (C—O) cm^{-1} ; $^1\text{H-NMR}$ δ 3.65–4.13 (m, 15H), 4.46 (m, 2H), 7.66 (dd, 1H, $J=7.6, 7.8$ Hz), 8.11 (d, 1H, $J=7.6$ Hz), 8.31 (d, 1H, $J=7.8$ Hz), 8.53 (s, 1H), and 10.09 (s, 1H).

The product was used for the next reaction without further purification.

5-[3'-(12-Crown-4)methyloxycarbonylphenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-phenylporphyrin (**H₂-MCEPP**)

To a methanol solution (85 ml) of bis(3-ethyl-4-methyl-2-pyrrolyl)methane [15] (1.64 g, 7.10 mmol), 3-[(12-crown-4)methyloxycarbonyl]benzaldehyde (1.20 g, 3.55 mmol) and benzaldehyde (0.38 g, 3.55 mmol) were added and the mixture was stirred for 15 min. The mixture was bubbled with Ar gas for 15 min, and *p*-toluenesulfonic acid (0.75 g, 4.36 mmol) was added. The mixture was stirred for 15 min in the dark and, moreover, stood at room temperature for 6 h and then at 0°C for 12 h. The reaction mixture was evaporated and the resulting residue was dissolved in THF (200 ml, dried over CaCl_2). *o*-Chloranil (2.23 g, 9.07 mmol) was added to the mixture and the

mixture was stirred at room temperature for 2 h. After evaporation of the solvent, the residue was dissolved in minimum amount of dichloromethane and precipitated by adding a solution of methanol and triethylamine (4/1). The precipitate was filtered, washed with cold methanol, and chromatographed on silica gel (eluent, chloroform/ethyl acetate = 3/1) to give 0.90 g (29%) of **H₂-MCEPP** as a violet powder. The crude porphyrin was moreover purified with liquid chromatography and by recrystallization (hexane-chloroform); mp 160.0°C (dec.); IR 3450 (NH), 1720 (C = O), 1250 (OC — O), and 1100 (C — O) cm⁻¹; ¹H-NMR δ-2.41 (br.s, 2H), 1.75–1.79 (m, 12H), 2.45 (s, 6H), 2.49 (s, 6H), 3.50–3.90 (m, 15H), 4.01 (q, 8H, J = 7.3 Hz), 4.43 (m, 2H), 7.74–7.86 (m, 4H), 8.07 (d, 2H, J = 6.3 Hz), 8.28 (d, 1H, J = 7.3 Hz), 8.49 (d, 1H, J = 7.8 Hz), 8.78 (s, 1H), and 10.24 (s, 2H); λ_{max} (CH₃CN)/nm, (log ε M⁻¹ cm⁻¹) 403 (5.64), 504 (4.53), 537 (3.98), 573 (4.11), and 625 (3.34).

Found: C, 74.70; H, 7.23; N, 6.40%. Calcd for C₅₄H₆₂N₄O₆: C, 75.15; H, 7.24; N, 6.49%.

5-[3'-(12-Crown-4)methyloxycarbonylphenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-phenylporphyrin zinc complex (Zn-MCEPP)

To a refluxing solution of **H₂-MCEPP** (0.40 g, 0.46 mmol) in chloroform (20 ml), a methanol solution (8.3 ml) saturated with zinc acetate was added and the mixture was refluxed for 2 h. The reaction mixture was cooled and evaporated, and the resulting residue was dissolved in chloroform. The mixture was washed with water and dried over anhydrous magnesium sulfate. After the solvent was removed, the crude product was recrystallized from hexane-chloroform to give 0.39 g (91%) of zinc complex as a violet powder; mp 245.0–246.0°C; IR 1720 (C = O) and 1240 (OC — O) cm⁻¹; ¹H-NMR δ 1.77 (t, 12H, J = 7.3 Hz), 2.41 (s, 6H), 2.46 (s, 6H), 3.40–3.80 (m, 15H), 4.00 (q, 8H, J = 7.3 Hz), 4.37 (m, 2H), 7.72–7.86 (m, 4H), 8.08 (d, 2H, J = 6.6 Hz), 8.30 (d, 1H, J = 8.0 Hz), 8.48 (d, 1H, J = 8.0 Hz), 8.78

(s, 1H), and 10.20 (s, 2H); λ_{max}(CH₃CN)/nm, (log ε M⁻¹ cm⁻¹) 413 (5.43), 543 (4.12), and 575 (3.62).

Found: C, 63.09; H, 6.03; N, 5.39%. Calcd for C₅₄H₆₀N₄O₆Zn · CHCl₃: C, 63.16; H, 5.88; N, 5.36%.

5-[3'-(12-Crown-4)methyloxycarbonylphenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-phenylporphyrin magnesium complex (Mg-MCEPP)

H₂-MCEPP (0.10 g, 0.12 mmol) and magnesium perchlorate (0.80 g, 3.58 mmol) were dissolved in dried pyridine (20 ml) and the reaction mixture was refluxed for 4 h, cooled, and evaporated. The residue was dissolved in ether and the mixture was washed with 0.1 N hydrochloric acid solution, aqueous solution saturated with sodium hydrogen carbonate, and brine. After dried over anhydrous magnesium sulfate, the mixture was evaporated and the crude product was recrystallized from hexane-chloroform to give 0.03 g (28%) of magnesium complex as a violet powder; mp 275.0–276.0°C; IR 1720 (C = O) and 1230 (OC — O) cm⁻¹; ¹H-NMR δ 1.74–1.80 (m, 12H), 2.32 (s, 6H), 2.46 (s, 6H), 2.67–3.65 (m, 17H), 3.98–4.02 (m, 8H), 7.70–7.80 (m, 4H), 8.00 (m, 1H), 8.05–8.15 (m, 2H), 8.20–8.30 (m, 1H), 8.60 (br.s, 1H), and 10.17 (s, 2H); λ_{max}(CH₃CN)/nm, (log ε M⁻¹ cm⁻¹) 415 (5.56), 550 (4.26), and 587 (3.61).

Found: C, 71.44; H, 7.12; N, 5.98%. Calcd for C₅₄H₆₀MgN₄O₆ · H₂O: C, 71.79; H, 6.92; N, 6.20%.

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- [14] A 1:1 complex follows to the equation, $C_H C_G / (A - A_H) = (\epsilon_{HG} - \epsilon_H)^{-1} \times C_G + (\epsilon_{HG} - \epsilon_H)^{-1} \times K^{-1}$ (where C_H and C_G mean the initial host concentration and the added guest concentration, respectively; A and A_H mean the measured absorbance and the initial host absorbance, respectively; ϵ_{HG} and ϵ_H mean the molar absorption coefficients of the complex and of the host, respectively). On the basis of a plot of C_G vs. $C_H C_G / (A - A_H)$, the association constant K is estimated from the slope divided by the intercept. Similarly, a 1:2 complex follows to the equation, $C_H C_G^2 / (A - A_H) = (\epsilon_{HG} - \epsilon_H)^{-1} \times C_G^2 + (\epsilon_{HG} - \epsilon_H)^{-1} \times K^{-1}$.
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