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Formation of Molecular Complexes of Water-Soluble Porphyrin with Cation-18-Crown-6 Complexes

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The formation of molecular complexes of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphine (H_2tspp) with cation-18-crown-6 (M(18C6)) has been studied spectrophotometrically at I=0.1 mol dm^{-3} (MX and MX_2, M: Na^+, K^+, Cs^+, NH_4^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, X: NO_3^-, Cl^-, Br^-, I^-, SCN^-), and pH 7.0 (*N,N′*-bis(2-sulfonatoethyl)piperazine: PIPES buffer, 2.0×10^{-3} mol dm^{-3}). The absorption spectrum of H_2tspp considerably changed in the presence of both cation and 18-crown-6, but not in the absence of either of them. The formation constants (log K) of the molecular complexes (M(18C6)·H_2tspp) were found to be 2.17±0.05, 2.31±0.03, 2.45±0.03, 2.58±0.02, 1.94±0.03, 2.07±0.02, and 2.12±0.02 for Na^+, K^+, Cs^+, NH_4^+, Ca^{2+}, Sr^{2+}, and Ba^{2+}, respectively at 25.0±0.5 °C and I=0 mol dm^{-3}. Thermodynamic parameters ΔH/(kJ mol^{-1}) and ΔS/(J K^{-1} mol^{-1}) are −19.9, −25.0; −33.0, −66.0; −29.3, −50.8; −48.5, −113.7; −21.9, −34.2 and −32.5, −68.0 for Na^+, K^+, Cs^+, NH_4^+, Sr^{2+}, and Ba^{2+}. The enthalpy changes are linearly correlated to the entropy changes. The equilibrium studies show that charge transfer between M(18C6) and porphyrin π-system is a driving force for the formation of the molecular complex (M(18C6)·H_2tspp) as well as hydrophobic interaction.

The interaction of porphyrins or metalloporphyrins with aromatic ligands such as methyl viologen,1) 1,10-phenanthrolines,2) anthraquinones,3) or DNA4,5) has been the subject of a number of investigations. The basis for these studies in part is related to the observation that porphyrins can serve as photocatalysts6) for photoproduction of H_2 and O_2 in water and photosensitizer for destruction of tumor cells7) (i.e., phototeraphy). The thermodynamic, optical, and physicochemical evidences have suggested the formation of molecular complex by π-π interaction between aromatic donors or acceptors and porphyrin plane. Shelnutt has demonstrated that charge-transfer interaction is a binding force for complexation of metal uroporphyrins with 1,10-phenanthrolines on the basis of the results of resonance Raman differential spectroscopy.2) Kano et al., concluded that a van der Waals interaction is the predominant binding force and hydrophobic interaction assists the stabilization of the molecular complexes in the reaction of anionic porphyrin with anionic aromatics.3)

In this studies we describe the formation of molecular complex of 5,10,15,20-tetrakis(4-sulfonatophenyl)-porphine (H_2tspp) with cation-18-crown-6 (M(18C6)), where M is Na^+, K^+, Cs^+, NH_4^+, Ca^{2+}, Sr^{2+}, and Ba^{2+}. 18-Crown-6, of course, does not have π-system. The thermodynamic studies suggest that the formation of the molecular complex ((M(18C6)·H_2tspp)) results from charge transfer between cation-18-crown-6 and π-system of porphyrin as well as hydrophobic interaction of ethylene group of 18-crown-6 with porphyrin. The desolvation of both cation and 18-crown-6 caused by formation of cation-18-crown-6 enables hydrophobic interaction of porphyrin with cation-18-crown-6 and the positive charge in M(18C6) stabilizes the molecular complex.

Experimental

18-Crown-6 (Tokyo Kasei Co. Ltd., Japan) was dried in vacuo at room temperature for 3 days. The inorganic compounds were analytical reagent grade. Porphyrin (H_2tspp) was synthesized and its sodium salt was purified as described previously.8) The purity was checked by thin-layer chromatography and NMR spectroscopy. Concentrations of calcium(II), strontium(II), and barium(II) in the stock solutions were determined complexometrically. Other stock solutions were prepared by weighing the reagents. Water redistilled in the presence of permanganate was used for all solutions.

The formation constant of the molecular complex was determined spectrophotometrically at pH 7.0 (*N,N′*-bis(2-sulfonatoethyl)piperazine: PIPES buffer) and at given temperatures (20, 25, 30, and 35 °C). Ionic strength was adjusted to 0.1 mol dm^{-1} by cation salts of which molecular complex was studied. Sample solution was prepared by addition of 1 cm^3 H_2tspp (5×10^{-5} mol dm^{-3}) to a solution containing 18C6, PIPES buffer (2.0×10^{-3} mol cm^{-3}) and cation in a 25 cm^3 flask, followed by addition of water to the mark. The solution was kept in a thermostated bath for about 30 min. The absorption spectra were recorded by a Hitachi 323 UV-VIS spectrophotomerter in a 1 cm cell with a thermostated water jacket.

Results

Formation of Molecular Complex of H_2tspp with M(18C6). Absorption spectrum of H_2tspp changed considerably in the presence of both 18-crown-6 and cation as shown in Fig. 1(a), but not in the absence of either of them. The absorption maximum at 413 nm decreased with increasing of 18-crown-6. The isosbestic points were 388 and 420 nm. Similar absorption spectra of porphyrins were also observed in the reaction of H_2tspp with 1,10-phenanthroline9) and that of 5,10,15,20-tetrakis(4-*N*-methylpyridyl)porphine (H_2tmpyp) with DNA5) at soret bands.

Under the present experimental conditions (pH 7.0) porphyrin is free base form, because the protonation constants of H_2tspp to form H_3tspp and H_4tspp are $10^{4.99}$ and $10^{4.76}$, respectively (charges on porphyrin are omitted for the simplicity).10) The formation of the molecular complex decreased at pH lower than 5.

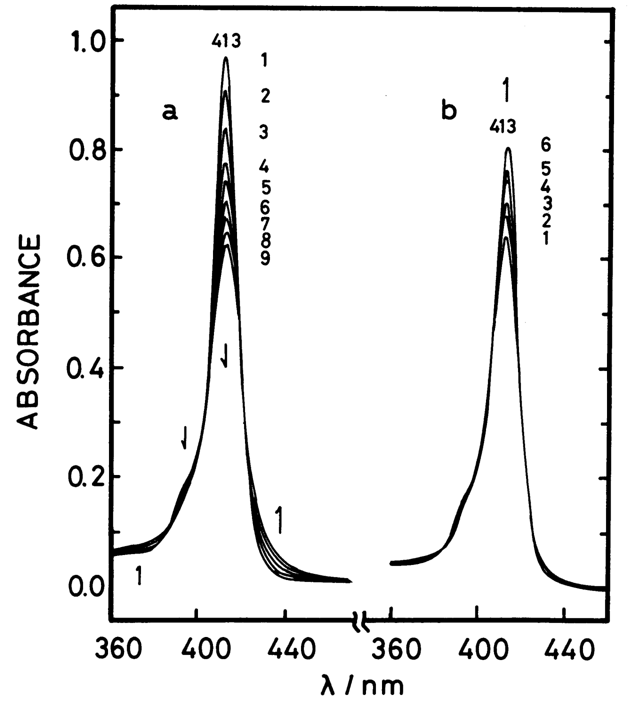


Fig. 1. (a), Absorption spectra of H_2tspp (2.11×10^{-6} mol dm^{-3}) with increasing of 18-crown-6 ((1), 0.000; (2), 1.09×10^{-3}; (3), 2.18×10^{-3}; (4), 3.63×10^{-3}; (5), 5.44×10^{-3}; (6), 7.25×10^{-3}; (7), 1.09×10^{-2}; (8), 1.45×10^{-2}; (9), 1.81×10^{-2}, (unit= mol dm^{-3}) in the presence of K^+ (0.1 mol dm^{-3}) at pH 7.0, and (b) the spectral change of H_2tspp (1.99×10^{-6} mol dm^{-3}) with increasing of ethanol ((1), 0; (2), 2; (3), 4; (4), 6; (5), 8; (6), 10% (v/v)) in the presence of 18-crown-6 (1.97×10^{-2} mol dm^{-3}) and Ba^{2+} (3.47×10^{-2} mol dm^{-3}) at pH 7.0.

Cation (M) reacts with 18-crown-6 (A) to form cation-18-crown-6 (MA) as

$$\mathrm{M}+\mathrm{A} \overset{K_{\mathrm{MA}}}{\rightleftharpoons} \mathrm{MA}, \tag{1}$$

and the equilibrium constant is defined by

$$K_{\mathrm{MA}}=[\mathrm{MA}][\mathrm{M}]^{-1}[\mathrm{A}]^{-1}. \tag{2}$$

Thus the reaction of H_2tspp with 18-crown-6 in the presence of cation may be given by

$$\mathrm{MA}+\mathrm{H_2tspp} \overset{K}{\rightleftharpoons} \mathrm{MA\cdot H_2tspp}, \tag{3}$$

and the equilibrium constant is written by

$$K=[\mathrm{MA\cdot H_2tspp}][\mathrm{MA}]^{-1}[\mathrm{H_2tspp}]^{-1} \tag{4}$$

From the Eqs. 2 and 4 we obtain Eqs. 5—7:

$$K=[\mathrm{MA\cdot H_2tspp}][\mathrm{H_2tspp}]^{-1} \\ ([\mathrm{MA}]+[\mathrm{A}])^{-1}(1+K_{\mathrm{MA}}{}^{-1}[\mathrm{M}]^{-1}) \tag{5}$$

and

$$K=[\mathrm{MA\cdot H_2tspp}][\mathrm{H_2tspp}]^{-1}[\mathrm{A'}]^{-1}\alpha_{\mathrm{MA}} \tag{6}$$

$$=\alpha_{\mathrm{MA}}K', \tag{7}$$

where A′ and α_{MA} denote the total concentration of 18-crown-6 unbound to H_2tspp and side-reaction coefficient of MA, respectively, and they are defined as follows:

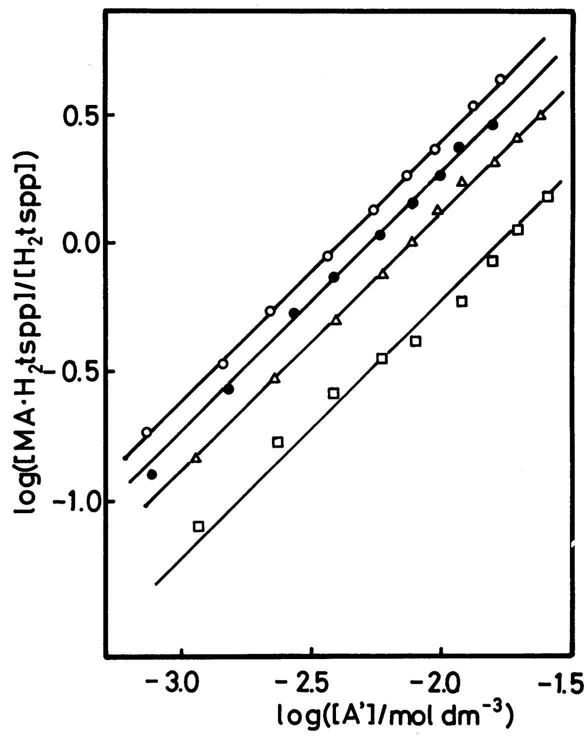


Fig. 2. Plot of log([MA·H_2tspp]/[H_2tspp]) vs. log([A′]/mol dm^{-3}) in the reaction of H_2tspp with NH_4^+ (○), K^+ (●), Ba^{2+} (△), and Na^+ (□) at 25 °C and I=0.1 mol dm^{-3}, where [A′] is the concentration of 18-crown-6 unbound to H_2tspp. $C_{\mathrm{H_2tspp}}=2.00\times10^{-6}$ mol dm^{-3}, and pH 7.0.

$$[\mathrm{A'}]=[\mathrm{MA}]+[\mathrm{A}] \tag{8}$$

and

$$\alpha_{\mathrm{MA}}=1+K_{\mathrm{MA}}{}^{-1}[\mathrm{M}]^{-1} \tag{9}$$

Conditional formation constant (K') of the molecular complex can be rearranged in logarithmic form from Eqs. 6 and 7 as follows:

$$\log K'=\log([\mathrm{MA\cdot H_2tspp}]/[\mathrm{H_2tspp}])-\log[\mathrm{A'}]. \tag{10}$$

The first term in right-hand side of Eq. 10 was determined from the absorbances in the various concentrations of 18-crown-6, and is plotted against logarithmic concentration of 18-crown-6 in Fig. 2. The plot gives a straight line with a slope of unity and shows that one molecule of MA reacts with an H_2tspp. Thus the formation constants of molecular complexes (K) were calculated from Eqs. 7 and 9, where the logarithmic values of K_{MA} in Eq. 9 were taken from literatures:[11] 0.84, 2.03, 1.01, 1.23, 1.8, 2.71, and 3.83 for Na^+, K^+, Cs^+, NH_4^+, Ca^{2+}, Sr^{2+}, and Ba^{2+}, respectively at I=0.1 mol dm^{-3} and at 25 °C. Table 1 summarizes the formation constants of molecular complexes.

Dependence of the Formation Constant on the Temperature. The formation constants of the molecular complexes for Na^+, K^+, Cs^+, NH_4^+, Ba^{2+}, and Sr^{2+}

Table 1. Formation Constants of Molecular Complexes of $MA \cdot H_2tspp$ at $I=0.1$ mol dm^{-3} and at 25 °C (A=18-crown-6)

Cation salt	log *K*	Cation salt	log *K*
	mol^{-1}dm^3		mol^{-1}dm^3
KNO_3	2.31±0.03	NH_4NO_3	2.58±0.02
KCl	2.28±0.03	CsCl	2.45±0.05
KBr	2.40±0.06	$Ca(NO_3)_2$	1.94±0.03
KI	2.32±0.05	$Sr(NO_3)_2$	2.07±0.02
KSCN	2.37±0.04	$Ba(NO_3)_2$	2.12±0.02
$NaNO_3$	2.17±0.05		

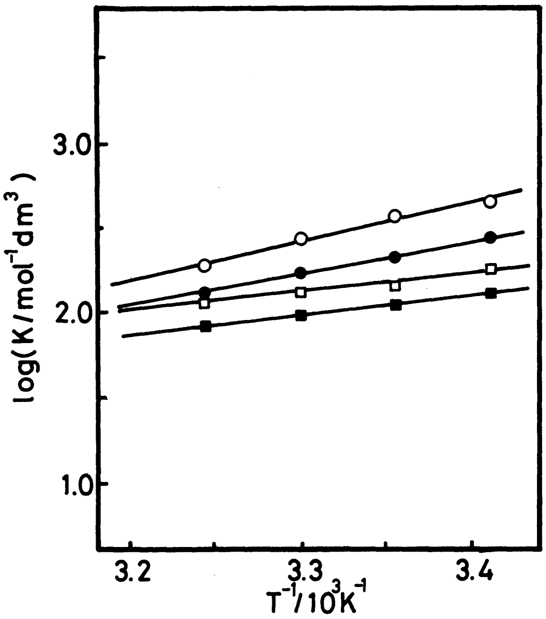


Fig. 3. Temperature dependence of the formation constant of molecular complex between H_2tspp and cations of NH_4^+ (○), K^+ (●), Na^+ (□), and Sr^{2+} (■) at $I=0.1$ mol dm^{-3}. $C_{H_2tspp}=2.00 \times 10^{-6}$ mol dm^{-3}, and pH 7.0.

were determined at temperatures of 20, 25, 30, and 35 °C. The thermodynamic parameters of enthalpy change (ΔH) and entropy change (ΔS) were calculated from van't Hoff plots of $R\ln K$ vs. T^{-1} and ΔG vs. T, respectively (Fig. 3). The thermodynamic parameters of the formation of the molecular complexes ($MA \cdot H_2tspp$) are listed in Table 2.

Dependence of the Formation of the Molecular Complex on Ethanol. Addition of ethanol to a solution containing Ba^{2+}, 18-crown-6, and H_2tspp increased the absorbance at 413 nm. At high concentration of ethanol the absorption spectrum is the same as that of H_2tspp in the absence of cation and 18C6 (Fig. 1(b)). The spectral change indicates the dissociation of the molecular complex by addition of ethanol. Since the increase of ethanol decreases dielectric constant of the aqueous solution, the interaction between M(18C6) and H_2tspp does not arise from ion-pair formation. If the molecular complex is ion pair, the formation of the molecular complex may become easier with the decrease of dielectric constant.

Table. 2. Thermodynamic Parameters in the Formation of Molecular Complexes of $MA \cdot H_2tspp$ (A=18-crown-6)

Cation	$-\Delta G$[a)]	$-\Delta H$	ΔS
	kJ mol^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}
Na^+	12.4	19.9	−25.0
K^+	13.2	33.0	−66.0
Cs^+	14.0	29.3	−50.8
NH_4^+	14.7	48.5	−113.7
Sr^{2+}	11.8	21.9	−34.2
Ba^{2+}	12.1	32.5	−68.0

a) Value at 25 °C.

Discussion

The formation constant of molecular complex is independent of anionic species (Table 1). This shows that anion is not involved in the formation of molecular complex. The formation constants increase in the following order: $Na^+ < K^+ < Cs^+ < NH_4^+$ for univalent and $Ca^{2+} < Sr^{2+} < Ba^{2+}$ for bivalent cations. Comparison of the formation constants of the molecular complexes with those of cation-18-crown-6 shows that the formation of molecular complex is not so affected for different cations as the formation of cation-18-crown-6. Cation size and cavity radius of 18-crown-6 are factors affecting the stability of cation-18-crown-6.[11,12)] On the other hand, the molecular complex formation is a weak interaction between porphyrin plane and crown ether complex, and is not so much influenced by the cation size and cavity size of 18-crown-6. As shown in Table 1, the formation constants for bivalent cations are smaller than those for univalent cations. This is the opposite situation compared with the formation of crown ether complex. Since porphyrins trend to associate with organic ligands such as 1,10-phenanthrolines,[2)] anthraquinones,[3)] and DNA,[4,5)] porphyrin plane may be hydrophobic. Thus the large hydration in cation-18-crown-6 may make difficult the interaction between cation-18-crown-6 with porphyrin plane. The hydration free energies ($-\Delta G_h$/(kJ mol^{-1})) are 411.3, 338, 297, 1593, 1447, and 1318 for Na^+, K^+, Cs^+, Ca^{2+}, Sr^{2+}, and Ba^{2+}, respectively.[13)] The hydration free energies imply the following relative order for the stabilities of the molecular complexes: $Cs^+ > K >^+ > Na^+ > Ba^{2+} > Sr^{2+} > Ca^{2+}$. The hydration enthalpies of

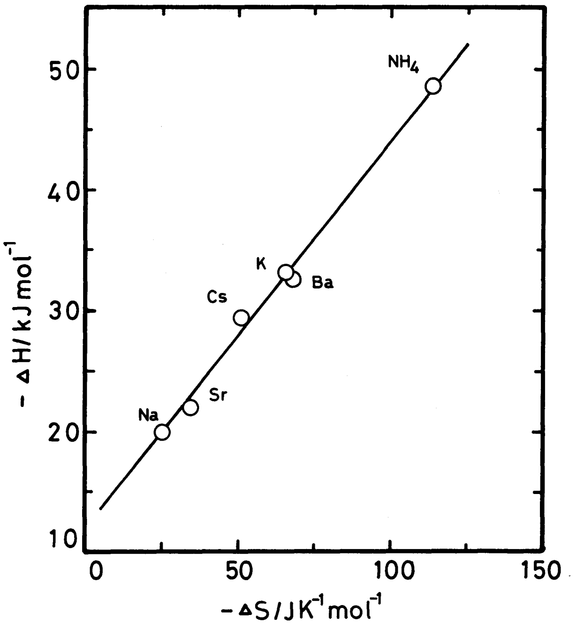
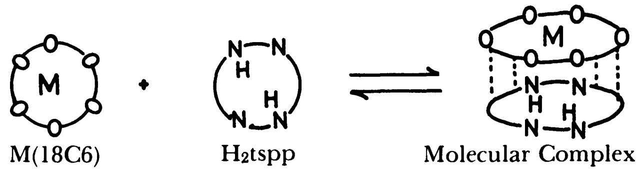


Fig. 4. Plot of $-\Delta H/(\mathrm{kJ\,mol^{-1}})$ vs. $-\Delta S/(\mathrm{J\,K^{-1}\,mol^{-1}})$ for the formation of the molecular complexes of MA·H_2tspp (M=Na^+, K^+, Cs^+, Sr^{2+}, Ba^{2+}, and NH_4^+).

cations also suggest the same order for the formation of the molecular complexes, because the hydration enthalpy is much higher than the hydration entropy.[13] The observed formation constants of the molecular complexes decrease with the order as expected above. This is a reason why the molecular complex of bivalent cation-18-crown-6 is unstabler than that of univalent cation-18C6. Other contribution of cation in the formation of molecular complex is charge-transfer interaction between cation-18-crown-6 and porphyrin π-system.

In Fig. 4, the enthalpy change is plotted against the entropy change in the formation of the molecular complex. The plots give a good straight line. The correlation was generally observed for the charge-transfer complexes such as iodine-aromatic ligands.[14] The enthalpy change is compensated with the entropy change and shows Barcley-Buttler rule. The large contribution of enthalpy change indicates the charge-transfer interaction between cation of M(18C6) and porphyrin π-system. Hydrophobic interaction also contributes to the molecular complex formation. Crown ether does not interact with porphyrin in the absence of cation. Coordination of cation to crown ether releases water molecules from both crown ether and metal ion. The desolvation from 18-crown-6 may increase the hydrophobicity of 18C6, and water around M(18C6) may be structured. In fact the negative entropy change was observed in the reaction of cation with 18-crown-6.[11] The negative enthalpy change in the formation of the molecular complex suggests that water may be structured between cation-18-crown-6 and porphyrin plane. The positive charge in 18-crown-6 complex stabilizes the molecular complex by the charge transfer through porphyrin π-system.

A possible reaction scheme in the formation of molecular complex is given in Scheme 1, in which cation-18-crown-6 may be parallel to porphyrin plane like "crowned porphyrin."[15] The present studies show, for the first time, the formation of molecular complex of porphyrin with non-aromatic ligands.



Scheme 1.

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