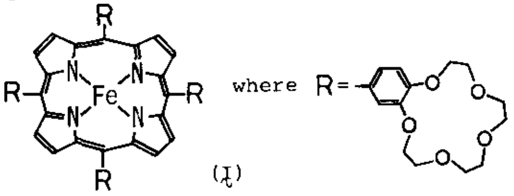
HETEROCYCLES, Vol 15, No 2, 1981

THE EFFECT OF SOLVENTS AND/OR ALKALI CATIONS ON ABSORPTION[†] SPECTRA OF IRON(III) CROWNED PORPHYRIN

Nagao Kobayashi and Tetsuo Osa*
Pharmaceutical Institute, Tohoku University,
Aobayama, Sendai 980, Japan

Abstract —— Iron(III) *meso*-tetraphenylporphyrin derivative with four crown ether moieties (1) was synthesized. It showed remarkable solubility in various solvents and spectral dependencies on solvents and/or alkali cations, attributed to the crown ether moieties in the structure.

One of the notable functions of the crown ether family is a cation binding ability. Its unusual solubility into various solvents has been utilized for many purposes.[1,2] In this report, preparation of a crown ring attached iron(III) porphyrin and the properties thereof will be reported. This work has been done from a view of clarifying following interests: 1) The incorporation of various alkali cations may be able to shift the redox potential of the central metal. 2) The enhanced solubility due to the crown ether moieties may subserve the spectral study of metal porphyrin in various solvent systems. 3) 1 may act as a catalyst for some reactions which may require simultaneous presence of both crown ether and porphyrin moieties.[3]



(1)

Compound 1 was prepared from pyrole and 4'-formylbenzo-15-crown-5[4] by refluxing in propionic acid for 30 minutes and subsequent iron insertion in $CHCl_3$-MeOH (50:50 v/v) mixture. The yield was 6%. Anal., Calcd for $C_{76}H_{84}N_4O_{20}Fe$: C;63.86, H;5.92, N;3.92. Found: C;63.55, H;6.10, N;3.74. IR(KBr disc), ν_{NH}=3400, ν_{CH_2}=2870 cm^{-1}. UV($CHCl_3$) ε_{422}=80000, ε_{512}=13300, ε_{652}=3900, ε_{693}=4000. PMR, δ($CDCl_3$) 3.50(48H,t), 3.72(16H,t), 7.2∿7.5(12H,m), 8.55(8H,d). 1 is well soluble in chloroform, pyridine, dimethylformamide, acetic acid, and soluble in acetone, benzene, methanol, dioxane,

---

[†] Dedicated to Professor Dr. Tetsuji Kametani on the occasion of his retirement.

acetonitrile, tetrahydrofuran, acetic acid-water (50:50 v/v), and slightly soluble in ethyl acetate, methanol-water (50:50 v/v).

Figure 1 shows the absorption spectra of **I** in acetic acid, chloroform, pyridine, and methanol together with that of iron(III)-*meso*-tetraphenylporphyrin (abbr;Fe(III) TPP) in chloroform as a reference. The spectra, particularly those in chlorofolm and acetic acid retain similarities in shape and intensity to those of ferric hemeproteins$^{5)}$ and are characteristics of ferric high-spin porphyrin compounds$^{6)}$. According to the extended Hückel calculations$^{7)}$, the bands labelled 1 and 2 are most likely to be charge-transfer transitions which arise from the promotions to iron $e_g(d_{xz},d_{yz})$ from the $a_{2u}'(\pi)$ and $b_{2u}(\pi)$ porphyrin orbitals. Bands 3 and 4 , respectively, seem to correspond to Q_α and Q_β transitions from the band positions, separation by 2000 cm^{-1}, and the intensity ratio between the two bands. Besides, a close accord to the spectra of Fe(III)TPP substantiates that the both compounds are in a similar electronic state, and therefore, that the crown ether moiety does not significantly affects the visivle absorption spectra of porphyrin nucleus in these solvents, unless alkali cations are incorporated. In pyridine, however, **I** exhibits the spectra which indicate an increase of low-spin form as expected from its strong ligand field (i.e., a bathochromic shift and a hypochromic effect in the Soret, and a hyperchromic effect in band 3 region). The spectra of **I** in methanol are difficult to be interpreted; The entire profile seems to be that of a ferric

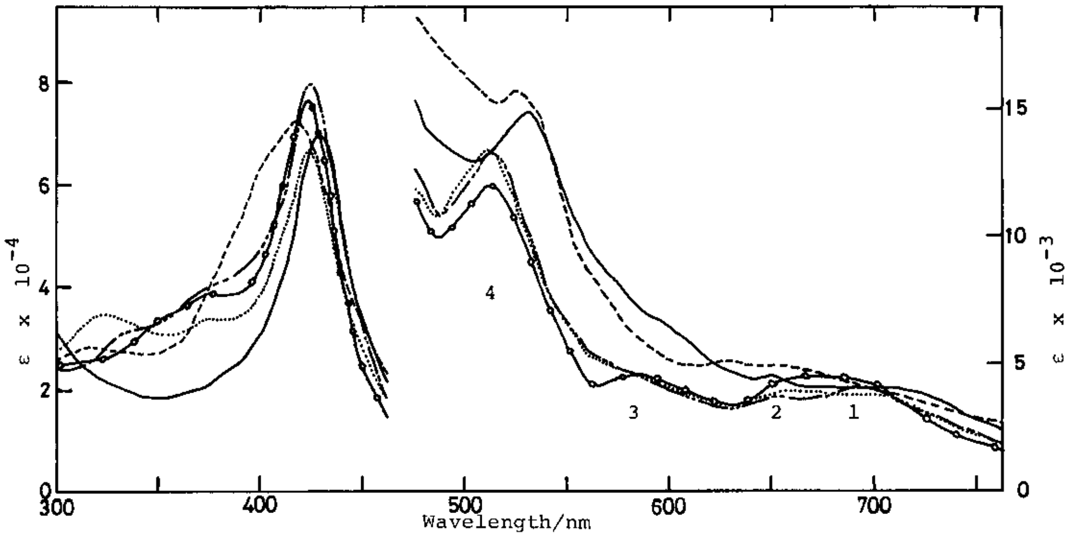


Figure 1. Absorption spectra of compound **I** in $CHCl_3$;—··—, CH_3COOH;··········, CH_3OH;-----, and pyridine;———, and Fe(III)TPP in $CHCl_3$;—o—. Concentration=*ca*.1 x 10^{-4}M. Path; 1 mm(300∿460), 10 mm(460∿760 nm)

high-spin porphyrin, but the Soret band seems to be composed of almost superinposed two bands nearly located, one of which at higher frequency site might possibly be a N band which is weak in usual case. Though we cannot definitely confine the cause of the anomalous feature of the spectra in methanol, the presence of the crown ether moieties may perhaps be responsible to some extent.

The absorption spectra of **1** in methanol in the presence of (a) KI, (b) NaI, and (c) KCN are shown in Figure 2 (Methanol was dared to use in order to heighten the solubility of the salts). The effect of K^+ and Na^+ is quite obvious. Though the visible region spectra are typical of a low-spin form (especially (a)), we could exemplify that these belong to those of high-spin form, and hence, that the origin of these phenomena exists at the crown moieties, through the following observations. 1) Addition of 18-crown-6 and 15-crown-5 to the system (a) or (b), respectively, returns the spectra to that in methanol (d). 2) Specrum (c) posesses a characteristic of low-spin form both in the Soret and visible regions so that if (a) and (b) actually belonged to low-spin state, they must exhibit curves classified into low-spin in the Soret band, too. We checked the effect of LiI, CsI and KCl both in methanol and in chloroform. The effect of LiI and CsI was small in both solvents as expected from their size.

Change in the iron redox potential is expected by incorporation of various alkali cations at various concentrations from one to four equivalents to **1**.

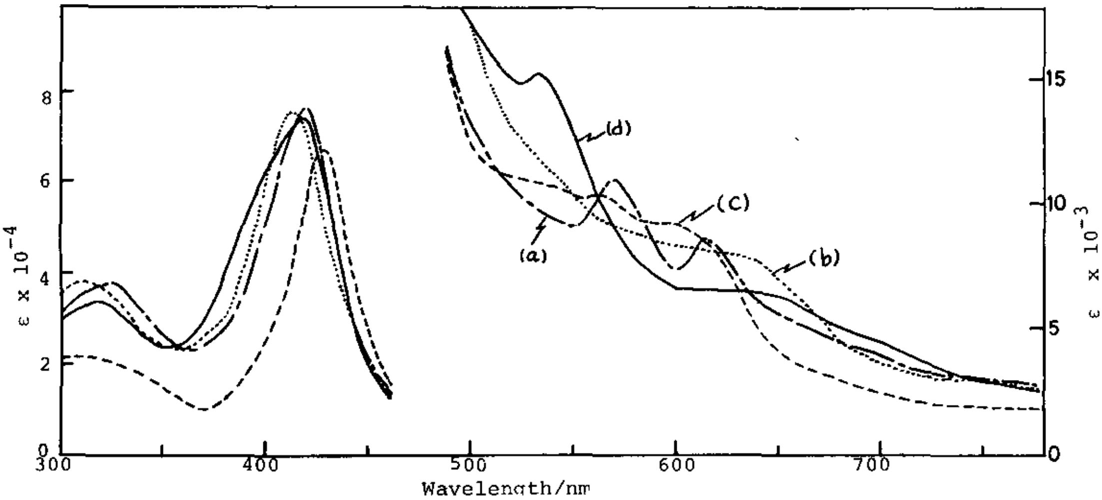


Figure 2. Absorption spectra of compound **1** in CH_3OH with a) KI;———, b) NaI; ··········, and c) KCN;-----. Concentration=*ca.*1 x 10^{-4}M. KI, NaI and KCN=5 x 10^{-3}M. Path; 1 mm(300∿460 nm), 10 mm(460∿780 nm).

However, just a subtle change was recognized in the redox potential for the addition of K^+, Na^+, Li^+ and Cs^+. One of the probable reason for the phenomenon seems to be in the fact that the iron in a ferric high-spin state locates out of porphyrin plane.

In conclution, enhanced solubility of porphyrin was attained by introduction of crown ether moieties. It was shown that the absorption spectra of porphyrin are influenced by the kind of solvent in an unexpected way and that, specifically in our case, alkali cation can affect the spectra because of the presence of crown ethers. The degree of influence decreases roughly in the order of $K^+ \geqq Na^+ > Li^+ \approx Cs^+$.

This research has been partially supported by a Grant-in-Aid for Scientific Research No. 479193 from the Ministry of Education, Science and Culture. We thank editorial board for their kind invitation to this special issue.

REFERENCES AND NOTE

1) C. J. Pederson, *J. Amer. Chem. Soc.*, 1967, **89**, 2495.
2) M. Hiraoka, "Kuraun Kagobutsu", Kodansha, 1978, chap.1 and refs. cited therein.
3) Such a system has not yet been reported. However, the electrochemical oxygen reduction in non-polar solvent in the presence of **1** and some simple inorganic salts might be one of possibilities.
4) R. Ungaro, B, El Haj and J. Smid, *J. Amer. Chem. Soc.*, 1976, **98**, 5198.
5) R. J. P. Williams, *Chem. Rev.*, 1956, **56**, 299.
6) K. M. Smith, "Porphyrins and Metalloporphyrins", Elsevier, New York, N. Y., 1975, p. 878.
7) M. Zerner, M. Gouterman and H. Kobayashi, *Theoret. Chim. Acta*, 1966, **6**, 363.

Received, 29th July, 1980