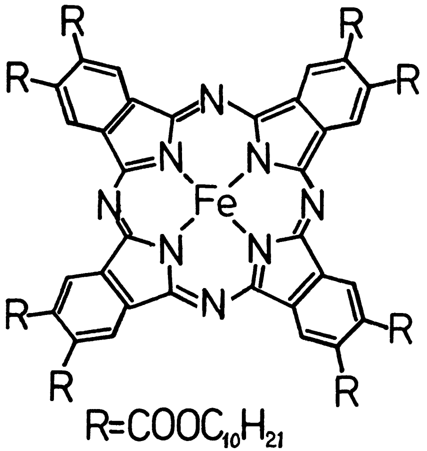
CHEMISTRY LETTERS, pp. 1633 - 1636, 1984.

ELECTROLYTE-INDUCED SPIN-STATE TRANSITION OF IRON IN IRON(III) PHTHALOCYANINE

Nagao KOBAYASHI,* Masami KOSHIYAMA,† Yoko ISHIKAWA,† Tetsuo OSA,*†
Hirofusa SHIRAI,†† and Nobumasa HOJO†††
Chemical Research Institute of Non-Aqueous Solutions, Tohoku University,
Katahira, Sendai 980
†Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980
††Department of Functional Polymer Science, Faculty of Textile Science and Technology,
Shinshu University, Ueda 386
†††Shinshu University, Asahi, Matsumoto 390

Magnetic susceptibility, magnetic circular dichroism(MCD), UV-visible absorption, and ESR spectroscopy have revealed that spin state of iron in 1,2,8,9,15,16,22,23-octadecyloxycarbonylphthalocyaninato-iron(III) dissolved in CH_2Cl_2 or $CHCl_3$ changes from high-spin to low-spin state by the addition of ca. 10 equiv. of tetrabutylammonium-chloride (Bu_4NCl) and/or -bromide(Bu_4NBr), (electrolytes).

In order to change spin state of metals in metalloporphyrins and phthalocyanines from, for example, high-spin to low-spin state, strong bases such as imidazoles and pyridines have generally been utilized for a long time.[1,2] In the case of normal iron(III) porphyrins, spin state of the iron transforms from high- to low-spin by the ligation of two molecules of these bases at the 5th and 6th coordination positions. Here, we present the first example of iron(III) phthalocyanine, **1**, in which the spin state of the iron changes by the addition of electrolytes as Bu_4NCl or Bu_4NBr.



R=$COOC_{10}H_{21}$

1

Complex **1** was obtained from 1,2,8,9,15,16,22,23-octacarboxy-chlorinated iron phthalocyanine[3] by esterification with decyl alcohol in anhydrous pyridine. In order to change **1**'s axial ligand from pyridine to Cl^-, crude **1** was first heated to constant weight in vacuo at 150 °C and then dissolved in distilled CH_2Cl_2 containing dry HCl gas. This solution was imposed on a silica gel column with absolute CH_2Cl_2. The first fraction was collected and brought to dryness. In the elemental analysis of thus obtained **1**, however, no halide (counter-anion) was detected.[4] It had an effective magnetic moment(μ_{eff}), determined by the use of Evans method,[5] of 5.9 and 5.8 Bohr magneton in CH_2Cl_2 and $CHCl_3$ at 35 °C, respectively. Also, **1** showed ESR signals at around g = 6 and 2 in CH_2Cl_2 at 7.5 K[6] which is a characteristic of high-spin iron(III) complexes. Thus, though the oxidation state of iron in iron phthalocyanines is generally **+II**,[3] the above values suggest that **1** is in a trivalent iron high-spin state in CH_2Cl_2 or $CHCl_3$.

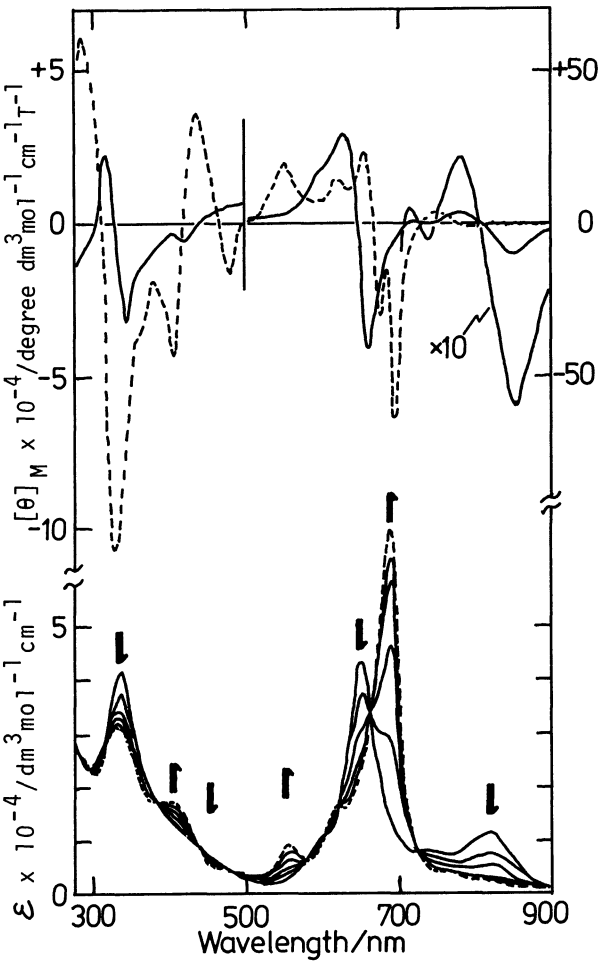


Fig. 1 Absorption spectral changes (bottom) observed on addition of Bu_4NCl to 1.75×10^{-5} M solution of **1** in CH_2Cl_2. $[Bu_4NCl]/[\mathbf{1}]$ (mol/mol): 0.0;0.35;0.70; 1.05;1.40;5.0; and 10.0 (dotted line). MCD (top) spectra of **1** in the absence (solid line) and presence (dotted line) of $[Bu_4NCl]/M = 1.75 \times 10^{-4}$. Magnetic field/T = 1.1.

Absorption and MCD spectra of 1 can also be interpreted as an iron(III) high-spin state complex (Fig.1). Namely, as we reported in detail for 2,9,16,23-tetradecyloxycarbonylphthalocyaninatoiron(III) (2),$^{7)}$ the redmost band at 817 nm can be assigned to the $a_{1u}(\pi)$ to $e_g(d\pi)$ charge-transfer(CT) transitions.$^{8,9)}$

Figure 1 includes also the spectral changes which take place when Bu_4NCl is added to 1. In the absence of Bu_4NCl, 1 exhibits peaks at 817(ε=11800), 738(7900), 650(43700), and 337(41800) nm. When Bu_4NCl is added, this spectrum changes dramatically with a set of isosbestic points at 723, 662, 617, 604, 578, 472, 433, 383, and ca. 295 nm, and for $[Bu_4NCl]/[1]$ = ca. 10, saturation occurs with new peaks at 690(ε=69000), 617(16800), 552(9700), 410 (17300), and 329(31200) nm. As shown minutely for the reaction of 2 and imidazole,$^{7)}$ this change appears to correspond to from the high-spin to low-spin transition of 1. Accompanying this change in electronic absorption spectrum, on the other hand, the strength of the Soret MCD is greatly intensified. This phenomenon is also consistent with that observed from iron(III) high-spin to low-spin state transition in iron porphyrins.$^{10)}$ The datum of the magnetic susceptibility also lends support to this conclusion. That is, the above final solution gave μ_{eff} of 2.1 Bohr magneton at 35 °C,$^{11)}$ exemplary for low-spin iron(III) complexes ($2.1<\mu_{eff}<2.8$).$^{1)}$ Similar behavior was observed by the use of Bu_4NBr. In this case also, the condition that $[Bu_4NBr]/[1]$ = ca. 10 was required to attain spin state transition. When this condition was satisfied, the μ_{eff} of the solution became 2.5 Bohr magneton.$^{11)}$ Spectral changes were, however, not complete when Bu_4NClO_4 was employed.

It has been pointed out, in the electrochemistry of metal porphyrins and phthalocyanines, that there is some interaction between metals and electrolytes.$^{12)}$ For example, redox potentials of these complexes vary depending on the concentration of electrolytes. However, in no case has been found such a drastic influence to produce spin-state transition. As one of the causes for this phenomenon, we can propose a very weak interaction between iron in 1 and axial ligand in the absence of extraneous electrolytes.$^{13)}$ As summarized in Table 1, 1 reacts with strong bases to form its

Table 1. Complex formation constants of **1** and bases to form its mono-(K_1) and subsequently di-base(K_2) complexes in CH_2Cl_2 at ca. 20 °C *a)*

Base	K_1/M	K_2/M
Imidazole	$\geq 10^7$	81
1-Methylimidazole	$\geq 10^7$	68
4-Dimethylaminopyridine	$\geq 10^6$	145
4-Aminopyridine	$\geq 10^6$	-

a) Estimated in a manner reported previously.[7)]

mono- and subsequently di-base complexes with formation constants of $\geq 10^6$ (K_1s) and 68-145 $dm^3\ mol^{-1}$ (K_2s), respectively. Then, based on the results of NMR study of high-spin iron(III) porphyrins, XFeP (X = Cl^-, Br^-, and I^-), which showed that the greater the extent of dissociation of X the larger the K_1/K_2 ratio becomes,[14)] it is concluded that Fe-X bond in **1** is very weak. There is another fact which may support the weak Fe-X interaction in **1**. Namely, it is known that tetrabenzoporphinatoiron(III) is, in many respects, a compound situating between normal iron(III) porphyrins and iron(III) phthalocyanines.[15)] And, Fe-Cl^- interaction decreases markedly on going from meso-tetraphenylporphinatoiron(III) chloride to tetrabenzoporphinatoiron(III) chloride. Since, as mentioned above, no counter-anion could be detected in the combustion analysis of **1**, it is difficult to measure the strength of its Fe-X interaction. However, the above fact "suggests" that Fe-X bond in **1** is very weak, if present at all. Under such condition, the access of electrolyte molecule to iron, i.e. the coordination of extraneous ligand(s) to iron would become easier, thereby facilitating the spin-state change.

Thus **1** is the first example which shows spin-state transition by the addition of electrolytes in the metalloporphyrin and metallophthalocyanine family.

We thank Dr. Muneteru Kozuka, Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, for his courtesy in measuring ESR spectra. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, No. 59750698.

References

1) M. Gouterman, "Optical Spectra and Electronic Structure of Porphyrins and Related Rings," in "The Porphyrins," ed by D. Dolphin, Academic Press, New York, London (1979), Vol. 3, p. 1; E. Antonini and M. Brunori, "Hemoglobin and Myoglobin in their Reactions with Ligands," North-Holland, Amsterdam (1971), p. 40.

2) A. B. P. Lever, Adv. Inorg. Chem. Radiochem., 7, 27 (1965).

3) D. R. Boston and J. C. Bailar, Jr., Inorg. Chem., 11, 1578 (1972); H. Shirai, A. Maruyama, J. Takano, K. Kobayashi, N. Hojo, and K. Urushido, Makromol. Chem., 181, 565 (1980).

4) No counter-anion has been detected for hitherto reported iron(III) phthalocyanines (see Ref. 7). **1** gave satisfactory elemental analyses for C, H, and N, and IR data.

5) D. F. Evans, J. Chem. Soc., 1959, 2003.

6) For heretofore reported iron(III) high-spin phthalocyanines including **1**, ESR signals at g ca. 5-6 can be detected only at temperatures lower than ca. 15 K, and their intensities increase with decreasing temperature.[7)]

7) N. Kobayashi, M. Koshiyama, K. Funayama, T. Osa, H. Shirai, and K. Hanabusa, J.

Chem. Soc., Chem. Commun., 1983, 913, 915; N. Kobayashi, H. Shirai, and N. Hojo, J. Chem. Soc., Dalton Trans., in the press.

8) D. W. Smith and R. J. P. Williams, Struct. Bonding (Berlin), 7, 1 (1970); T. Yamamoto, T. Nozawa, N. Kobayashi, and M. Hatano, Bull. Chem. Soc. Jpn., 55, 3059 (1982), and references 13-19 therein.

9) L. K. Lee, N. H. Sabelli, and P. R. LeBreton, J. Phys. Chem., 86, 3926 (1982).

10) L. Vickery, T. Nozawa, and K. Sauer, J. Am. Chem. Soc., 98, 343, 351 (1976); N. Kobayashi, T. Nozawa, and M. Hatano, Biochim. Biophys. Acta, 427, 652 (1976); 493, 340 (1977).

11) Definate ESR spectrum could not be obtained from this solution even at 7.5 K. The absorption spectrum at [Bu$_4$NCl]/[**1**]=[Bu$_4$NBr]/[**1**] = ca. 10 was obviously different from that of iron(II) low-spin state complex of **1** which was obtained by electrochemically reducing the solution at -0.4 V vs. SCE (reduction of iron (iron(III) to iron(II)) in **1** occurs at ca. +0.2 V vs. SCE in CH$_2$Cl$_2$ containing ca. 0.2 mol/dm^3 of [Bu$_4$NCl] or [Bu$_4$NBr]). That is, as typically shown for **2**,7) the Soret and main Q band peaks of iron(II) low-spin species of **1** appear, respectively, at longer and shorter wavelength side than those of the iron(III) low-spin state complex. Details will be described in a full length paper.

12) D. G. Davis, "Electrochemistry of Porphyrins," in "The Porphyrins," ed by D. Dolphin, Academic Press, New York, London (1979), Vol. 5, Chap. 4; K. M. Kadish, "The Electrochemistry of Iron Porphyrins in Nonaqueous Media," in "Iron Porphyrins, Part II," ed by A. B. P. Lever and H. B. Gray, Addison-Wesley, London (1983), p. 161.

13) Axial ligand may be solvent molecule itself.

14) Comments in the following paper; F. A. Walker, M. Lo, and M. T. Lee, J. Am. Chem. Soc., 98, 5552 (1976).

15) N. Kobayashi, M. Koshiyama, and T. Osa, Chem. Lett., 1983, 163; Inorg. Chem., submitted for publication.

(Received June 12, 1984)