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Incorporation of some Transition Metal Ions into Polyvalent Porphyrin, Tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)porphyrin

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Abstract

Incorporations of some transition metal ions into polyvalent porphyrin, tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)porphyrin (H_2T^tBHPP, 1) were investigated by the usual synthetic methods. Iron(III), cobalt(II) and copper(II) ions were easily incorporated into H_2T^tBHPP to give the corresponding metalloporphyrins. However, manganese porphyrin was not prepared by the reaction of Mn(II) ion with H_2T^tBHPP, but the oxidation product of H_2T^tBHPP, 5,15-di-(3,5-di-tert-butyl-4-hydroxyphenyl)-10,20-di-(3,5-di-tert-butyl-4-quinomethene)porpho-10,20-dimethene (2), was almost quantitatively prepared. The difference of the reaction mode was discussed on the basis of the ionic radii of each of the metal ions.

Introduction

Recently, polyvalent porphyrin, tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)porphyrin (H_2T^tBHPP, 1) and its complexes with metals such as Zn(II) and Fe(III) have been extensively studied [1–8]. In particular, Fe(III)T^tBHPP is thought to be a good model for horseradish peroxidase (HRP) [1]. HRP reacts with hydrogen peroxide or peracids to produce a two-electron oxidized species which is currently considered to be a Fe(IV)–porphyrin π-cation radical species [9], *i.e.* iron is in the Fe(IV) state and the porphyrin is a π-cation radical [9, 10]. A similar radical intermediate is thought to be formed from H_2T^tBHPP which has the advantage of the steric protection afforded by the tert-butyl groups.

In order to obtain other model compounds of HRP, we have examined the reactions of H_2T^tBHPP with some transition metal ions and found that Cu(II) and Co(II) ions as well as Fe(III) ion are easily incorporated into H_2T^tBHPP to give the corresponding metalloporphyrins. However, Mn(II) ion was not incorporated into H_2T^tBHPP, but oxidized H_2T^tBHPP to give the quinone, 5,15-di-(3,5-di-tert-butyl-4-hydroxyphenyl)-10,20-di-(3,5-di-tert-butyl-4-quinomethene)porpho-10,20-dimethene (2), quantitatively. These results are reported in this paper.

Experimental

Materials

H_2T^tBHPP was prepared by the condensation reaction between pyrrole and 3,5-di-tert-butyl-4-hydroxybenzaldehyde in propionic acid and was purified by column chromatography on silica gel with 1:1 benzene-cyclohexane as eluent [7]. $CoCl_2$, $Cu(CH_3COO)_2$, $FeCl_2 \cdot 4H_2O$ and $MnCl_2 \cdot 2H_2O$ were obtained from Wako Pure Chemical Ind. Ltd. and used without further purification. *N,N*-dimethylformamide (DMF) was distilled under reduced pressure and stored over freshly activated 4 Å molecular sieves under argon gas. Chloroform ($CHCl_3$) was distilled and passed through a neutral alumina column (Woelm) prior to use. Other solvents were distilled prior to use.

Physical Measurements

Visible absorption spectra were recorded at room temperature on a Union Giken SM-401 spectrophotometer. Infrared (IR) spectra were recorded on a JASCO IRA-1 infrared spectrophotometer. The proton magnetic resonance (^1H NMR) were recorded on a JEOL JNM-FX-100 spectrometer in deuteriochloroform ($CDCl_3$) solution with tetramethylsilan (TMS) as an internal standard.

Preparation of Metalloporphyrins (3)

Co(II)T^tBHPP

H_2T^tBHPP (1 g, 0.89 mmol) was dissolved in 200 ml of DMF and the solution was refluxed. $CoCl_2$ (0.25 g, 1.93 mmol) was added to this refluxed solution and the reaction mixture was refluxed for a further 15 min. Then, the solvent was removed by a rotary evaporator. The residues were dissolved in $CHCl_3$ and the $CHCl_3$ solution was loaded on a neutral alumina column (Woelm, activity I) and eluted by $CHCl_3$. The reddish-purple eluate was collected and the solvent was evaporated to dryness. Co(II)T^tBHPP was crystallized from $CHCl_3$–MeOH. Yield: 1.06 g (98.9% based on porphyrin). *Anal.* Calc. for $C_{76}H_{92}N_4O_4Co \cdot CH_3OH$: C, 76.03; H, 7.95; N, 4.61. Found: C, 75.91; H, 7.89; N, 5.17%.

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Cu(II)T^{t}BHPP

To H_2T^tBHPP (0.51 g, 0.45 mmol) in 150 ml of boiling $CHCl_3$ was added a saturated solution of $Cu(CH_3COO)_2$ in 15 ml of methanol. The reaction mixture was further refluxed for 1 h, and then the reaction solution was evaporated to dryness. The residues dissolved in $CHCl_3$ were loaded on a neutral alumina column (Woelm, activity IV) and eluted by $CHCl_3$. The reddish eluent was collected and concentrated by a rotary evaporator. MeOH was added to the concentrated solution to give crystals. The fine crystals were filtered and air-dried. Yield: 0.539 g (100% based on porphyrin). *Anal.* Calc. for $C_{76}H_{92}N_4O_4Cu$: C, 76.76; H, 7.80; N, 4.71. Found: C, 75.98; H, 7.64; N, 4.76%.

Fe(III)T^{t}BHPP·Cl

H_2T^tBHPP (0.535 g, 0.475 mmol) and $FeCl_2 \cdot 4H_2O$ (0.288 g, 1.4 mmol) were dissolved in 200 ml of DMF and the reaction mixture was refluxed for 5 h. The completion of the reaction was checked spectrophotometrically. The reaction solution was evaporated to dryness by a rotary evaporator and then the residues dissolved in $CHCl_3$ were stirred with 1 ml of conc. HCl overnight. The solution was evaporated to dryness by a rotary evaporator. The solid was dissolved in $CHCl_3$ and chromatographed on a dry neutral alumina column (Woelm, activity I) using $CHCl_3$ as an eluent agent. The first fraction was H_2T^tBHPP and the second fraction was the Fe complex. Fe(III)T^{t}BHPP·Cl was crystallized from $CHCl_3$–hexane. Yield: 0.570 g (98.5% based on porphyrin). *Anal.* Calc. for $C_{76}H_{92}N_4O_4FeCl$: C, 75.01; H, 7.62; N, 4.60. Found: C, 75.88; H, 7.62; N, 4.81%.

Preparation of 5,15-Di-(3,5-di-tert-butyl-4-hydroxyphenyl)-10,20-di-(3,5-di-tert-butyl-4-quinomethene)porpho-10,20-dimethene, the quinone (2), from the Reaction of H_2T^tBHPP with Mn(II) Ion

H_2T^tBHPP (0.944 g, 0.84 mmol) was dissolved in 200 ml of DMF and the solution was refluxed. $MnCl_2 \cdot 2H_2O$ (0.644 g, 4.1 mmol) was added to this refluxing solution and the reaction mixture was refluxed for 15 min. After completion of the reaction, the reaction solution was evaporated to dryness by a rotary evaporator. The residues dissolved in a minimum amount of $CHCl_3$ were placed on a column packed with a dry neutral alumina (Woelm, activity I) and chromatographed with $CHCl_3$ as eluent. The first eluate, a reddish fraction, was the unreacted porphyrin and the second purple eluate was collected and concentrated to dryness. The solid was crystallized from $CHCl_3$–MeOH to give greenish crystals. Their spectroscopic data were identical with those of the quinone (2) [1, 5, 7]: ^{1}H NMR ($CDCl_3$): δ 1.35 (s, m-^{t}Bu), 6.71 (s, p-OH), 7.40 (s, o-H), 8.92 ppm (s, pyrrole H). IR ($CHCl_3$): 3700 and 3520 (OH), 1600–1610 cm^{-1} (carbonyl C=O). Visible ($CHCl_3$): 522 nm (log ϵ = 5.09). Yield: 0.899 g (95.2% based on porphyrin).

Results and Discussion

The reactions leading to metal complexes of H_2T^tBHPP were carried out in an analogous manner to that previously used for metal complexes of *meso*-tetraphenylporphyrin (H_2TPP) [11]. Simple modifications were made to get the metalloporphyrins of H_2T^tBHPP as described in 'Experimental'.

Co(II) and Cu(II) ions were almost quantitatively incorporated into H_2T^tBHPP to give the corresponding metalloporphyrins. When Fe(II) ion was used, at the first step of the reaction Fe(II)T^{t}BHPP was formed, but it was too unstable to be immediately oxidized to the Fe(III) complex by oxygen. The visible spectral data for these metal complexes of H_2T^tBHPP (Table I) show that these metalloporphyrins are the normal type [12]. On metalation, the 4 absorption bands in the visible spectrum of H_2T^tBHPP (λmax (nm): 526, 566, 605 and 660) are altered to give a spectrum showing 2 bands in the visible region; the Soret band is retained. The two visible bands are labeled α and β. Typical visible spectrum of Cu(II)T^{t}BHPP is shown in Fig. 1.

TABLE I. Visible Spectral Data for the Metalloporphyrins in DMSO

Metalloporphyrins	λ_{max} (nm) (log ϵ)		
	Soret	β	α
Co(II)T^{t}BHPP	425 (5.13)	542 (4.18)	578 (3.70)
Cu(II)T^{t}BHPP	427 (5.53)	550 (4.28)	590 (3.96)
Fe(III)T^{t}BHPP Cl	427 (5.04)	545 (4.31)	578 (4.04)

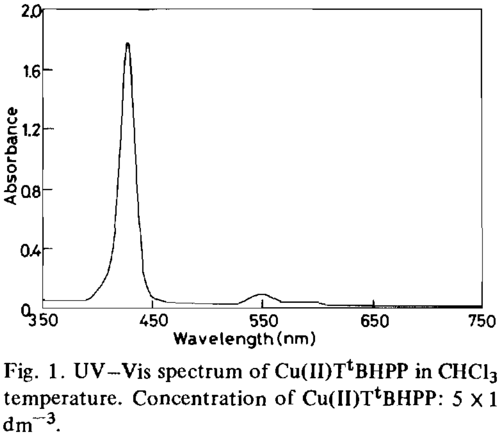
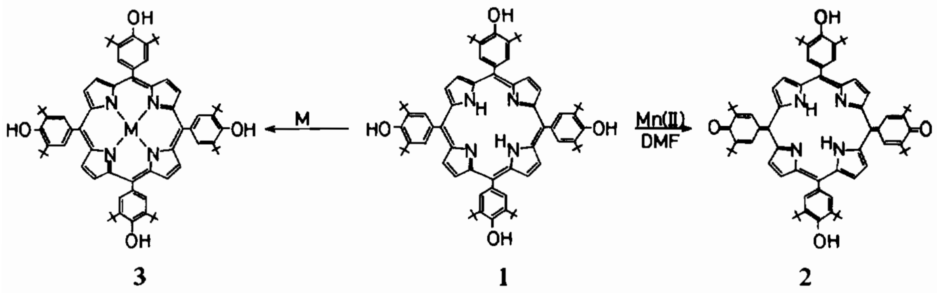


Fig. 1. UV–Vis spectrum of Cu(II)T^{t}BHPP in $CHCl_3$ at room temperature. Concentration of Cu(II)T^{t}BHPP: 5 × 10^{-6} mol dm^{-3}.



M = Cu(II), Co(II), Fe(III)

Scheme 1.

TABLE II. Incorporation of Metal Ions into H_2T^tBHPP and Their Ionic Radii

Metal ions	Ionic radii (Å)[a]	Metal incorporation
Cu(II)	0.72	yes
Fe(II)	0.83	yes
Mn(II)	0.91	no
Co(II)	0.82	yes
Zn(II)	0.69	yes[b]

[a]Ref. 13. [b]Ref. 1.

On the other hand, when Mn(II) ion was used, the oxidation product of H_2T^tBHPP, the quinone (2), was almost quantitatively prepared instead of Mn(II)T^tBHPP. Since the yield of the quinone (2) was 95.2% in the manganese system and 50.1% in the superoxide oxidation [7], respectively, it indicated that Mn(II) ion is a suitable reagent for preparing the quinone (2) at the high yield.

The fact that a different reaction product, the quinone (2), was obtained by the reaction of Mn(II) ion and H_2T^tBHPP may be explained on the basis of the size of the ionic radii of metal ions used (Table II) [13]. Since the Cu(II) ion has the smallest ionic radius, it is easily incorporated into H_2T^tBHPP. Fe(II) and Co(II) ions are also incorporated into H_2T^tBHPP, because both ions have moderate ionic radii. In the case of the Fe(II) incorporation, the Fe(II) ion is usually incorporated into the porphyrin ring, but the incorporated Fe(II) ion is too unstable to be oxidized to Fe(III) [12]. Therefore, in this reaction Fe(III)T^tBHPP is finally prepared by the reaction of Fe(II) ion with H_2T^tBHPP. Co(II) ion is hardly oxidized by O_2 to Co(III) ion which has a high reduction potential (1.842 eV) [14] and then it is incorporated into H_2T^tBHPP to give Co(II)T^tBHPP. On the other hand, since the high-spin Mn(II) ion is too big to fit into the porphyrin N_4-cavity which is thought to be 64 Å as best-fit for the hole [15], Mn(II) ion was not incorporated into H_2T^tBHPP. Perhaps, Mn(II) ion is oxidized by O_2 to the Mn(III) ion which has a high reduction potential (1.51 eV) [14], and then the Mn(III) ion formed may oxidize H_2T^tBHPP to give the quinone (2) instead of being incorporated into H_2T^tBHPP. That is, the redox reaction between Mn(III) ion and H_2T^tBHPP precedes the metal incorporation reaction. The reactions mentioned above are summarized in Scheme 1.

In conclusion, this work describes the formation of the new metal complexes of polyvalent porphyrin, H_2T^tBHPP such as Co(II) and Cu(II) as well as Fe(III). Further, it is indicated that Mn(II) ion is a suitable reagent for preparing the quinone form (2) of H_2T^tBHPP at the high yield.

References

1 T. G. Traylor, K. B. Nolan and R. Hildreth, *J. Am. Chem. Soc., 105,* 6149 (1983).
2 T. G. Traylor, K. Nolan, R. Hildreth and T. A. Evans, *Heterocycles, 21,* 249 (1984).
3 T. A. Evans, G. S. Srivasta, D. T. Sawyer and T. G. Traylor, *Inorg. Chem., 24,* 4773 (1985).
4 K. B. Nolan, *J. Chem. Soc., Chem. Commun.,* 760 (1986).
5 L. R. Milgrom, *Tetrahedron, 39,* 3895 (1983).
6 L. R. Milgrom, *J. Chem. Soc., Perkin Trans. I,* 2535 (1983).
7 T. Ozawa and A. Hanaki, *Inorg. Chim. Acta, 108,* L11 (1985).
8 T. Ozawa and A. Hanaki, *Polyhedron, 5,* 1881 (1986).
9 D. Dolphine, R. H. Felton, D. C. Borg and J. Fajer, *J. Am. Chem. Soc., 92,* 743 (1970).
10 J. T. Groves, R. C. Haushalter, M. Nakamura, T. E. Nemo and B. J. Evans, *J. Am. Chem. Soc., 103,* 2884 (1981).
11 J.-H. Fuhrop and K. M. Smith, in K. M. Smith (ed.), 'Porphyrins and Metalloporphyrins', Elsevier, Amsterdam, 1975, p. 757.
12 J. W. Buchler, in K. M. Smith (ed.), 'Porphyrins and Metalloporphyrins', Elsevier, Amsterdam, 1975, p. 157.
13 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 3rd edn., Wiley, New York, 1972, p. 52.
14 W. M. Latimer, 'Oxidation Potentials', 2nd edn., Prentice-Hall, Englewood Cliffs, N.J., 1952.
15 J. L. Howard, in K. M. Smith (ed.), 'Porphyrins and Metalloporphyrins', Elsevier, Amsterdam, 1975, p. 317.