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HYDROXY IRON(III) SPECIES STABILIZED WITH BULKY PORPHYRINS

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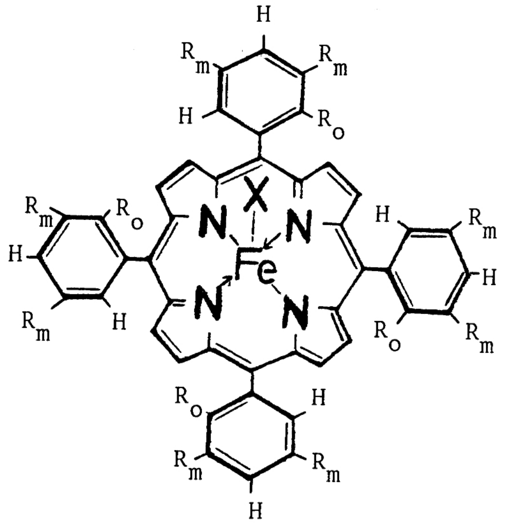
Stable hydroxy iron(III) complexes have been prepared in the use of bulky porphyrins, e.g., meso-tetrakis(3,5-di-t-butylphenyl)-porphyrin(Abbr. TBPP-H_2) and meso-tetrakis(3,5-di-t-butyl-2-nitrophenyl)porphyrin(TBNPP-H_2, 4 isomers). The stability of these complexes is rationalized as steric effect due to the t-butyl and/or nitro groups.

In recent years, several research groups1,2) have reported the formation of stable hydroxy iron(III) complexes by the use of the protected porphyrins such as meso-tetramesitylporphyrin or meso-tetrakis(2,4,6-trimethoxyphenyl)porphyrin. Our efforts, starting with the aim of developing the chemistry of new "bis pocket porphyrins",3) have also resulted in the isolation of stable hydroxy iron(III) porphyrins, Fe(TBNPP)(OH) (3-OH, see Fig. 1). By contrast, simple unprotected porphyrins, e.g., meso-tetraphenylporphyrin or octaethyl porphyrin, solely form the μ-oxo dimers based on the similar chemical treatments.4)



1-X R_o = H, R_m = t-butyl.
2-X R_o = H, R_m = CH_3.
3-X R_o = NO_2, R_m = t-butyl, 4 isomers.3)
(αααα, αααβ, ααββ, αβαβ.)
X = Cl, OH or $O_{1/2}$(OXO).

Fig. 1. The protected porphyrins.

Here we present the results of spectroscopic analyses of the products obtained for metathesis of chloroiron(III)porphyrins with aqueous sodium hydroxide for the protected porphyrins (1-3).5,6)

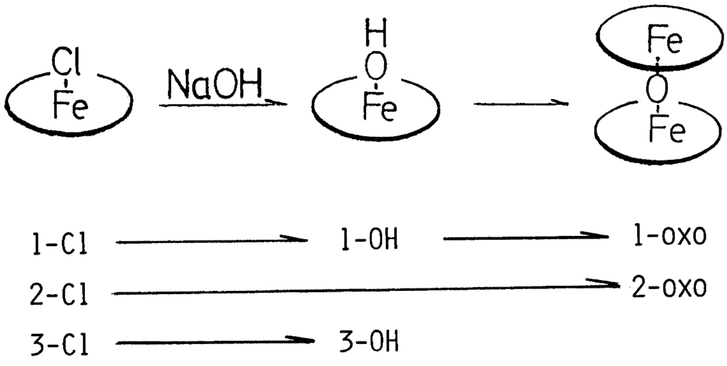
The treatment of chloro complex 2-Cl quantitatively gave μ-oxo dimer 2-OXO, while that of 1 afforded a mixture of hydroxy(1-OH) and oxo-bridged(1-OXO) compounds as shown in Scheme 1 and Table 1. The separation of 1-OH and 1-OXO was effected by Merck alumina 90 column chromatography (relative wieght of products: 1-OH/1-OXO = 5/1).7)

The purified complex 1-OH is stable in chloroform or toluene at room temperature (≈23 °C) for at least 6 d. At higher temperatures,

Table 1. Spectroscopic data of the products[a)]

Compounds	UV-Vis/nm					solvent	^{1}H-NMR/δ, in benzene-d_6 β-pyrrole	ortho	meta	para
1-OH	336	418	576	617		toluene	81.2		1.8 2.0	
1-oxo	321	411	576	616	648	toluene	13.9		1.3 1.7	
2-oxo		410	572	612	648	toluene	13.8	7.2	2.3 2.6	
3-OH-αααα	342	419	579			$CHCl_3$	78.4		1.6 1.9	8.5
3-OH-αααβ	338	417	579			$CHCl_3$	82.3		1.7	8.4
3-OH-ααββ	340	418	576			$CHCl_3$	79.9		1.7	8.3
3-OH-αβαβ		418	575			$CHCl_3$	79.5 82.5		1.7	8.1

a) Identification of the products was done in a similar way to that of Ref. 1.



Scheme 1.

however, 1-OH was gradually converted to 1-oxo. After 8 h reflux in chloroform (61 °C), only 1-oxo remained in the solution. The observed stability of 1-OH is in marked contrast to the fact that four complexes 3-OH are stable in chloroform under reflux for at least 8 h.[3)] Thus thermal stability of 1-OH is less secured than that of 3-OH.

In this way, we have demonstrated that steric bulk of 1 is just enough for the stabilization of hydroxy iron(III) species at room temperature, while that of 2 is insufficient. Furthermore it is certain that ortho substituted nitro groups of 3, giving rise to the great restrictions on the rotation about porphyrin-phenyl single bonds,[3)] afford the additional thermal stability to 3-OH.

References

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2) J. T. Groves, R. C. Haushalter, M. Nakamura, T. E. Nemo, and B. J. Evans, J. Am. Chem. Soc., 103, 2884 (1981).
3) T. K. Miyamoto, T. Hasegawa, S. Takagi, and Y. Sasaki, Chem. Lett., 1983, 1181.
4) J. W. Buchler, Porphyrins, 1, Chap. 10 (1981).
5) The porphyrin free bases, TBPP-H_2 and meso-tetrakis(3,5-dimethylphenyl)porphyrin (Abbr. TMPP-H_2), were prepared by the condensation of the corresponding substituted benzaldehydes with pyrrole. T. K. Miyamoto, unpublished results.
6) The direct conversion of the corresponding bromoiron(III)porphyrins to their hydroxy or μ-oxo complexes was also carried out by alumina column chromatography. The chloroform solution of the bromo complexes was passed through Merck alumina 90 column. The resulting effluent contained the hydroxy or oxo-bridged complexes. This method gave the similar results to metathesis.
7) The direct method according to Ref. 6 quantitatively gave the hydroxy complex 1-OH(solvent: toluene). Thus relative amount 1-OH/1-oxo depends upon reaction conditions.

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