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# A NEW METHOD OF PREPARATION OF IRON(II) PORPHYRIN COMPLEXES—ISOLATION AND CHARACTERIZATION OF AMINE COMPLEXES OF FERROUS PORPHYRIN

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**Abstract**—The six-coordinate complexes  $[Fe^{II}(TPP)(NHR_2)_2]$  (TPP = meso-tetraphenylporphyrinate, NHR<sub>2</sub> = NH<sub>2</sub>CH<sub>2</sub>Ph, NHMe<sub>2</sub>) have been prepared by the reduction of Fe<sup>III</sup> porphyrin with amines in sodium hypochlorite solution in air as well as by the sodium borohydride reduction method. The complexes were characterized by UV-vis and IR spectroscopies and elemental analysis. Copyright © 1996 Elsevier Science Ltd

Iron porphyrins have been the subjects of numerous studies.<sup>1</sup> Iron(II) porphyrin complexes are generally quite unstable. In order to prevent the formation of the  $\mu$ -oxo dimer  $[Fe(P)]_2O$  (where P = dianion of a porphyrin), the restricted anaerobic technique and pure dry reagents are required for preparation.<sup>2-4</sup> Due to the difficulties in synthesizing iron(II) porphyrins, only a few types of iron(II) porphyrin compounds have been prepared. The main ligands reported are pyridine, imidazole and phosphine. To our knowledge, no aliphatic amine adducts of iron(II) porphyrins have been isolated and well characterized. The known compounds of metallaporphyrin with axial aliphatic amine ligands are still very few, all of which involve the alkyl amines of rhodium,<sup>6</sup> osmium<sup>6</sup> and

ruthenium<sup>7</sup> metal centres. Herein we report the isolation and characterization of iron(II) porphyrins with benzylamine and dimethylamine as the sole axial ligands, which seems to provide the first example of the isolation of iron(II) porphyrin complexes in a solution containing water without the protection of an inert gas. This work is relevant to some of the astonishing variety of biochemical processes<sup>8a</sup> in which amines can participate. For example, amines and their derivatives are known carcinogens.<sup>8b</sup> They are know to enhance the mixedfunction oxidase system in liver microsomes.<sup>9</sup>

#### **EXPERIMENTAL**

 $[Fe^{11}(TPP)(NH_2CH)_2Ph)_2]$  (1),  $H_2TPP$  and FeTPPC1 were prepared according to literature procedures.<sup>10</sup> FeTPPC1 (200 mg) was dissolved in tetrahydrofuran (100 cm<sup>3</sup>)/benzylamine (5 cm<sup>3</sup>) mixed solution and then sodium hypochlorite solution (10 cm<sup>3</sup>) was added to the solution. The colour

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of the solution turned to red at once. After the reaction mixture was stirred for *ca* 3 min, the THF layer was washed with distilled water three times to remove sodium hypochlorite, and then dried over sodium sulfate. The resulting red solution was evaporated to dryness. The residue was redissolved in trichloromethane  $(3 \text{ cm}^3)$ /benzylamine  $(1 \text{ cm}^3)$  and chromatographied on alumina using dichloromethane/benzylamine (10:1) as the eluent. The leading red band was collected and concentrated to *ca* 3 cm<sup>3</sup>, n-heptane was then added to precipitate the product. The complex was obtained as red violet crystals which were collected and dried *in vacuo* (yield: 87%).

[Fe<sup>II</sup>(TPP)(NHMe<sub>2</sub>)<sub>2</sub>] (2) was prepared similarly to 1, except FeTPPC1 was dissolved in a THF (100 cm<sup>3</sup>)/dimethylamine solution (10 cm<sup>3</sup>) mixture. The eluent was dimethylamine solution in dichloromethane (obtained by vigorously stirring dichloromethane/dimethylamine solution (15:1) for 20 min). The product was obtained as red crystals (yield: 84%).

A common method for preparing  $Fe^{II}$  porphyrin was also carried out to prepare 1 and 2. In dried solvent in Schlenk tubes under a nitrogen atmosphere, FeTPPC1 was reduced by sodium borohydride in trichloromethane/methanol solution containing amine at 50°C. After being stirred for *ca* 4 h the product was isolated by distilling off the solvent. The UV-vis and IR spectra of the products obtained with this method were identical to those of the complexes obtained with procedures mentioned above.

The formulation of complexes 1 and 2 was initially based on their elemental analysis. 1: Found: C, 78.6; H, 5.5; N, 9.2. Calc. for  $C_{68}H_{46}N_6Fe: C, 78.9; H, 5.2; N, 9.5\%$ . 2: Found C, 76.2; H, 5.2; N, 11.4. Calc. for  $C_{48}H_{42}N_6Fe:$  C, 76.0; H, 5.5; N, 11.1%. Such formulation is consistent with the fact that the known typical compounds of iron(II) porphyrin are six-coordinate.

#### **RESULTS AND DISCUSSION**

The coordination of amine with the Fe<sup>II</sup> porphyrin moiety was confirmed by the IR spectra of complexes 1 and 2. Both the complexes exhibited sharp bands in the region  $3420-3316 \text{ cm}^{-1}$  (1: 3324,  $3316 \text{ cm}^{-1}$ ; 2:  $3298 \text{ cm}^{-1}$ ), which were assigned to the  $v_{N-H}$  stretching vibration of axially ligated amines.

The UV-vis spectra of complexes 1 ( $\lambda_{max} = 424$ , 529, 561 nm) and 2 ( $\lambda_{max} = 421$ , 532, 564 nm) also suggest that the iron in the complexes has the oxidation state of +2. The UV spectra of complexes 1

and 2 show normal iron(II) porphyrin spectra, which are quite similar to the spectra of bis  $(pyridine)^2$  and bis(hydrazine) complexes.<sup>11</sup>.

In solution in the presence of amine (PhCH<sub>2</sub>NH<sub>2</sub> or Me<sub>2</sub>NH) complexes 1 and 2 are very stable, even in the presence of the strong oxidant sodium hypochlorite. However, without amine, they are very sensitive to the air. We presume that sodium hypochlorite oxidizes Fe<sup>III</sup> porphyrin to Fe<sup>IV</sup> porphyrin and the very unstable Fe<sup>IV</sup> porphyrin is then reduced to Fe<sup>II</sup> porphyrin by amine. This is supported by the fact that after the addition of sodium hypochlorite to the solution of Fe<sup>III</sup> porphyrin, the UV-vis spectra of the resulting solution was neither the same as that of Fe<sup>III</sup> nor Fe<sup>II</sup> porphyrin and it gradually changed to the spectrum of [Fe(P)]<sub>2</sub>O. This presumption also agrees with the rapid rate of reduction of the Fe<sup>III</sup> porphyrin by amines.

The importance of this work also lies in the potential use of the complexes as good precursors to alkylimido iron porphyrins. According to the experience with ruthenium and osmium porphyrins,<sup>7,12</sup> oxidative deprotonation of the complexes possibly serves as a route to the corresponding high-valent alkylimido complexes. Such studies are currently being undertaken.

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