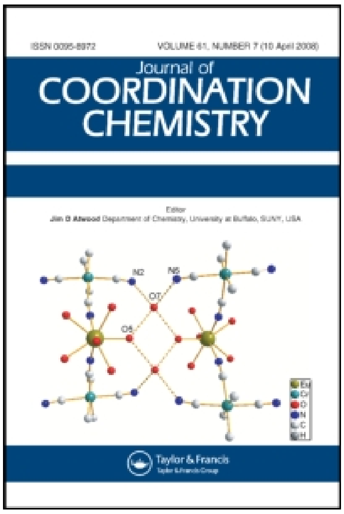

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A NEW METHOD OF PREPARATION OF IRON(II) PORPHYRIN COMPLEXES — ISOLATION AND CHARACTERIZATION OF *BIS*(*N*-BUTYLAMINE) IRON(II) PORPHYRIN

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A NEW METHOD OF PREPARATION OF IRON(II) PORPHYRIN COMPLEXES – ISOLATION AND CHARACTERIZATION OF *BIS*(*N*-BUTYLAMINE) IRON(II) PORPHYRIN

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$Fe(II)T(p\text{-}X)PP(NH_2Bu^n)_2$ ($X = H, Cl, CH_3, OCH_3$, TPP = dianion of *meso*-tetraphenylporphyrin) complexes have been prepared by the reduction of Fe(III) porphrins with *n*-butylamine in antiformin/dichloromethane in air, and by sodium borohydride reduction. The complexes were characterized by electronic and IR spectra and elemental analysis.

KEYWORDS: iron(II), porphyrin, *n*-butylamine, synthesis

INTRODUCTION

Iron porphyrins have been subject to numerous studies.[1] Since iron(II) porphyrin complexes are generally quite unstable, in order to prepare these complexes, strict anaerobic techniques and pure dry reagents are required[2,3] to prevent the formation of the u-oxo dimer $[Fe(Por)]_2O$ (where Por = dianion of a porphyrin). Much attention has focussed on complexes containing axial ligands such as pyridine, imidazole, phosphine, *etc.* Reduction of Fe(III) to Fe(II) has been carried out using sodium borohydride, chromium(II) acetylacetonate, zinc amalgam, *etc.* Although aliphatic amines can reduce Fe(III) complexes to Fe(II),[4–6] no aliphatic amine adducts of iron(II) porphyrins have been isolated and characterized. Known compounds of metalloporphyrin complex with axial aliphatic amine ligands are still very few, and involve only the alkylamine complexes of rhodium,[7] osmium,[8] and ruthenium.[9]

Herein, we report the isolation and characterization of iron(II) porphyrins with *n*-butylamine as the sole axial ligand. These complexes serve as the first examples of iron(II) porphyrins isolated in air and in a solvent containing water. They are relevant to some of the astonishing varieties of biochemical processes[10a] in which

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amines participate. For example, amines and their derivatives can undergo a variety of transformations with cytochrome P-450.[10b]

EXPERIMENTAL

Synthesis of $Fe(II)T(p\text{-}X)PP(NH_2Bu^n)_2$

$H_2T(p\text{-}X)PP$ and FeT(p-X)PPCl were prepared and purified according to literature procedures.[11] FeTPPCl (200 mg) was dissolved in dichloromethane (100 cm^3)/*n*-butylamine (5 cm^3) mixed solution and then 10 cm^3 of antiformin (sodium hypochlorite solution) was added to the solution. The colour of the solution immediately turned red. After stirring for *ca* 3 minutes, the CH_2Cl_2 layer was washed with distilled water to remove antiformin, dried over sodium sulfate and evaporated to dryness. The complex was purified by column chromatography on alumina by eluting with CH_2Cl_2/*n*-NH_2Bu (10:1). The first fraction of the eluate was collected and evaporated the complex was obtained as red crystals which were collected and dried under vacuum (yield: 84%). Anal.: calcd. for $C_{52}H_{46}N_6Fe$: C, 76.66; H, 6.14; N, 10.32%. Found: C, 76.24; H, 6.29; N, 10.01%.

Another common method for preparation of iron(II) porphyrins was used to prepare $FeTPP(NH_2Bu^n)_2$. Under a nitrogen atmosphere, FeTPPCl (200 mg) was reduced by sodium borohydride (100 mg) in dichloromethane (100 cm^3)/methanol (40 cm^3) containing 5 cm^3 of *n*-butylamine. After stirring for *ca* 3 hours at 30–40°C, the product was isolated by distilling off the solvent. Electronic and IR spectra of the product were identical to those of the complex obtained with the procedures mentioned above. The other complexes, $Fe(II)T(p\text{-}X)PP(NH_2Bu^n)_2$ (X = Cl, CH_3, OCH_3), were prepared by both methods described previously.

RESULTS AND DISCUSSION

Electronic spectra of $Fe(II)T(p\text{-}X)PP(NH_2Bu^n)_2$ show that the iron has oxidation state + 2. The soret and β bands of these comlexes are red-shifted compared with those of Fe(III) porphyrins (FeTPPCl, λ_{max}: 416 and 510 nm).[12] Electronic spectra of $Fe(II)T(p\text{-}X)PP(NH_2Bu^n)_2$ show a normal iron(II) porphrin pattern as Buchler and Gouterman defined,[13] which is quite similar to the spectra of *bis*(pyridine),[2] and *bis*(hydrazine)[14] adducts of iron(II) porphyrins.

The coordination of *n*-butylamine with the Fe(II) porphyrins is confirmed by the IR spectra. All complexes exhibit two sharp bands at 3320 and 3266 cm^{-1}, which can readily be assigned to the ν_{N-H} stretching vibration of axially ligated

Table 1 Electronic spectroscrpic data for $Fe(II)T(p\text{-}X)PP\ (NH_2Bu^n)_2$

p-X	λ_{max} (nm) (in $CH_2Cl + NH_2Bu^n$)		
	soret	β	α
p-H	424	529	561
p-Cl	424	529	561
p-CH_3	425	530	562
p-OCH_3	425	530	562

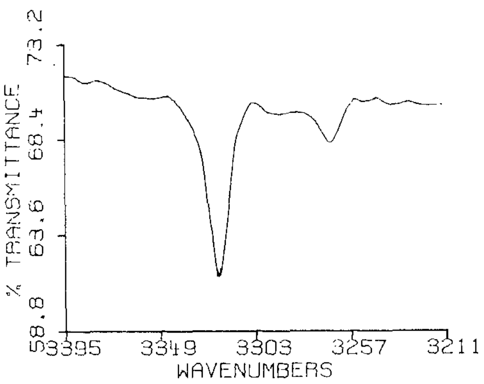

Figure 1 N-H region of the IR spectrum of Fe(II)TPP(NH_2Bu^n)$_2$.

n-butylamine. The ν_{N-H} frequencies of Fe(II)T(p-X)PP(NH_2Bu^n)$_2$ are *ca* 50 cm^{-1} lower than in free *n*-butylamine (ν_{N-H} 3373 and 3289 cm^{-1}).[15] Obviously, this is because the Fe(II) ion interacts with *n*-butylamine and weakens the *n*-butylamine N-H bond.[16]

In solution, in the presence of *n*-butylamine, FeT(p-X)PP(NH_2Bu^n)$_2$ complexes are very stable even in the presence of antiformin, while without *n*-butylamine they are very sensitive to air. We presume that antiformin may oxidize Fe(III) porphyrin to an unstable Fe(IV) porphyrin, which is reduced to Fe(II) by *n*-butylamine. This is supported by the fact that after the addition of antiformin to a solution of Fe(III) porphyrin, the electronic spectrum of the solution is different to those of iron(III) and iron(II) porphyrins, and gradually changes to that of [Fe(Por)]$_2$O. This agrees with the fast reduction of Fe(III) porphyrin by *n*-butylamine.

$$\mathrm{Fe^{III}(Por)} \xrightarrow{\text{antiformin}} \mathrm{Fe^{IV}(Por)} \xrightarrow{\text{amine}} \mathrm{Fe^{II}(Por)}$$

Scheme 1

The importance of this work lies in the potential use of the complexes as good precursors to alkylimido iron porphyrins. According to work on ruthenium and osmium porphyrins,[8,17] oxidative deprotonation of the complexes possibly serves as a successful route to the corresponding high-valent alkylimido complexes. Such studies are currently underway.

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