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Synthesis and Characterization of Copper(II) 5,10,15,20-Tetrakis(2,6-dipivalamidophenyl)porphyrinate: A Bis-Picket-Fence Porphyrin

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The synthesis and characterization of a new series of cofacial porphyrins is described. 5,10,15,20-tetrakis(2,6-diaminophenyl)porphyrin (**1**) can be synthesized from 2,6-diaminobenzaldehyde and pyrrole or by the reduction of 5,10,15,20-tetrakis(2,6-dinitrophenyl)porphyrin. Compound **1** was condensed with pivaloyl chloride to yield 5,10,15,20-tetrakis(2,6-dipivalamidophenyl)porphyrin (**2**), which can be metalated to form copper(II) 5,10,15,20-tetrakis(2,6-dipivalamidophenyl)porphyrinate (**3**). The EPR spectrum of **3** indicates the pivolyl groups prevent porphyrin aggregation and the coordination of pyridine by the metal center.

Introduction

Synthetic metalloporphyrins are employed to investigate the active-site structure and reactivity of various metalloproteins.[1] The success of these investigations often depend upon the unique steric properties of the synthetic porphyrin employed. Steric control at the metal site has been facilitated by the use of capped, single- and double-strapped, bis-pocket, and picket-fence type porphyrins.[1] Substituent groups can govern several aspects of metalloporphyrin chemistry, including site isolation of the metal ion. This is accomplished by preventing porphyrin dimerization and by controlling metal coordination with a Lewis base. However, in certain cases, the polarity and hydrogen-bonding properties of the porphyrin substituent stabilize the coordination of an axial ligand, such as dioxygen, by the metal ion.[1]

We report the synthesis of 5,10,15,20-tetrakis(2,6-diaminophenyl)porphyrin (**1**) (Figure 1). It was expected that **1** can be used as a starting point for the synthesis of a variety of cofacially hindered porphyrins. The successful synthesis of 5,10,15,20-tetrakis(2,6-dipivalamidophenyl)porphyrin, bis-picket-fence porphyrin **2**, which incorporates a high degree of steric protection on both porphyrin faces, demonstrates the potential versatility of **1**. The structure and reactivity of **2** was of interest because the pivolyl groups might prevent significant deformation of the porphyrin ring. However, the observation that **2** can be readily metalated by copper(II) to form **3** was unexpected.

Experimental Section

General Data. All starting materials were purchased from Aldrich or Alfa. Solvents were purified according to standard procedure[2] and stored over molecular sieves. Vibrational spectra were obtained on an IBM Instruments FT-85 infrared spectrometer, NMR spectra were collected on a Brüker AM-300 instrument, and UV–visible spectra were recorded on an IBM Instruments 9400 spectrometer. EPR spectra were collected on a Brüker EPR spectrometer equipped with a liquid-N_2 finger Dewar located at the MIT Spectrometry Laboratory. Fast-atom-bombardment (FAB) mass spectra were obtained as a service at the MIT Mass Spectrometry Laboratory. Elemental analyses were performed by Schwarzkopf.

Several different methods are available for porphyrin synthesis. The UV–visible spectrum of the reaction mixture indicates the Lindsay method[3] yields trace quantities of the porphyrin from either 2,6-dinitro or 2,6-diaminobenzaldehyde, while the Rothemund method[4] does not yield any detectable porphyrin from these aldehydes.

5,10,15,20-Tetrakis(2,6-diaminophenyl)porphyrin (1). Method A.[5] Pyrrole (6.0 mL, 0.077 mol) in 20 mL of toluene was added dropwise over 0.5 h to a refluxing solution containing 2,6-dinitrobenzaldehyde, (15 g, 0.077 mol) dissolved in 280 mL of 2:1 dry glacial acetic acid/trifluoroacetic acid. The resulting dark solution was refluxed for 0.5 h after addition of the pyrrole was complete. Then, 200 mL of $CHCl_3$ was added to the cooled (35 °C) reaction mixture, and the solution was filtered. After the mixture was refluxed 0.5 h with *p*-chloranil, the resulting crude product can be purified with a silica gel column eluted with methylene chloride. Each fraction was observed by TLC and UV–visible spectroscopy to identify the sparingly soluble 5,10,15,20-tetrakis(2,6-dinitrophenyl)porphyrin. UV–visible spectrum (CH_2Cl_2): 420, 515, 575, 612 nm.

5,10,15,20-Tetrakis(2,6-dinitrophenyl)porphyrin was reduced by dissolving it in 800 mL of concentrated HCl and adding 50 g of $SnCl_2$. The solution was refluxed for 1.0 h and titrated in an ice bath with concentrated NH_4OH until strongly basic. The warm solution was extracted with five 200-mL portions of $CHCl_3$. The combined organic fraction was dried over $MgSO_4$ and rotoevaporated to dryness. The impure 5,10,15,20-tetrakis(2,6-diaminophenyl)porphyrin was washed by $CHCl_3$ on a 5 × 20 cm silica gel column to remove less polar impurities. The top band was removed with acetone, dried over $MgSO_4$, and recrystallized from chloroform/methanol. The UV–visible spectrum indicated the absence of the chlorin. Th FAB mass spectrum in a nitrophenyl octyl ether matrix exhibits the expected ($P + 1$) pseudoparent ion (*m*/*e* (relative intensity)): 735 (49.7), 736 (100.0), 737 (58.3), 738 (50.0). Yield based on starting pyrrole: 0.106 g, 0.75%.

Method B. 2,6-Dinitrobenzaldehyde[6] (5 g, 0.025 mol) was added to a solution containing 140 g (0.92 mol) of ferrous sulfate, 0.75 mL of concentrated HCl, and 260 mL of distilled H_2O in a flask equipped with a mechanical stirrer. The solution was heated at 90 °C for 10 min, and 25 mL of concentrated NH_4OH was added, followed by the addition of five 10-mL aliquots of concentrated NH_4OH every 2 min. The solution was immediately filtered, cooled in an ice bath, extracted with anhydrous Et_2O, and dried with $MgSO_4$ and the solvent removed. The remaining solid was dried in vacuo in the dark for 3–6 h. The resulting ivory-colored crystals of the air- and water-sensitive 2,6-diaminobenzaldehyde were 97% pure by ^1H NMR. Mp: 88–90 °C. The yield ranges between 69–75%. The minor 2,6-dinitrobenzaldehyde impurity does not interfere with subsequent steps of the porphyrin synthesis. Condensation of 2,6-diaminobenzaldehyde and pyrrole was accomplished under the conditions outlined in method A. The ^1H and ^{13}C NMR and UV–visible spectra were identical with those of **1** synthesized by method A. Yield of **1** based on starting aldehyde is 0.5%.

5,10,15,20-Tetrakis(2,6-Dipivalamidophenyl)porphyrin (2). Purified **1** (1.31×10^{-4} M) was dissolved in $CHCl_3$ containing an excess of pi-

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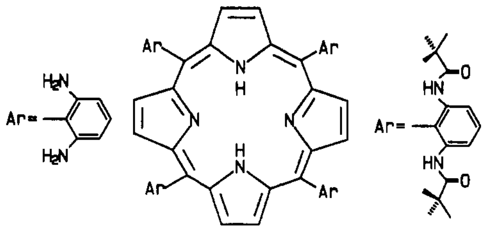

Compound (1) Compound (2)

Figure 1. Diagram of 5,10,15,20-tetrakis(2,6-diaminophenyl)- (**1**) and 5,10,15,20-tetrakis(2,6-dipivalamidophenyl)porphyrin (**2**).

valoyl chloride and stirred for 3.0 h at 25 °C and the solvent removed. Impure 5,10,15,20-tetrakis(2,6-dipivalamidophenyl)porphyrin was recrystallized from 20 mL of benzene in an Erlenmeyer flask. The flask was placed in a closed jar containing anhydrous MeOH at 5 °C for 1-2 weeks. The resulting benzene/methanol solution was reduced in volume by one-third by evaporation and placed in a freezer at −15 °C. After 3 days, the solution was filtered to yield crystals of pure 5,10,15,20-tetrakis(2,6-dipivalamidophenyl)porphyrin. Yield: 0.18 g (1.3×10^{-4} M), 0.7% based on starting 2,6-dinitrobenzaldehyde. UV-visible ($CHCl_3$) spectroscopy indicated that no chlorin was present. ^{13}C NMR (acetone-d_6): 176, 140, 135, 133, 131, 124, 122, 118, 39, 23 ppm. No starting materials were observed in the ^1H or ^{13}C NMR spectra. Elemental analysis was consistent for the porphyrin cocrystallized with two benzene molecules. Anal. Calcd. for $C_{84}H_{102}N_{12}O_8 \cdot 2C_6H_6$: C, 73.71; H, 7.35; N, 10.74; O, 8.20. Found: C, 73.61; H, 7.31; N, 10.94; O, 8.14 (by difference).

Copper(II) 5,10,15,20-Tetrakis(2,6-dipivalamidophenyl)porphyrinate (3). Anhydrous $AgClO_4$[7] (0.0500 g, 2.417×10^{-4} mol) and anhydrous $CuBr_2$ (0.1077 g, 4.823×10^{-4} mol) were dissolved separately in a minimum of dry dimethylformamide, DMF, in an inert-atmosphere box. The two solutions were mixed, and AgBr(s) was filtered off after 15 min. Anhydrous Et_2O was added to the mother liquor to precipitate $[Cu(DMF)_6](ClO_4)_2$, which was dried in vacuo in the dark for 12 h. *Caution*! All perchlorates were handled with protective gloves behind a $^1/_2$-in. plexiglass shield, and any waste solutions containing them were washed down the drain. The following operations were conducted under a dry, inert gas.

Anhydrous $[Cu(DMF)_6](ClO_4)_2$ (0.0108 g, 1.184×10^{-5} mol) and 5,10,15,20-tetrakis(2,6-dipivalamidophenyl)porphyrin (0.0015 g, 1.066 $\times 10^{-5}$ mol) were added to 10 mL of dry DMF and the solution refluxed for 1 h when the UV-visible spectrum indicated no remaining free base. The solvent volume was reduced under low pressure to 1-2 mL and dry pentane added to precipitate copper(II) 5,10,15,20-tetrakis(2,6-dipivalamidophenyl)porphyrinate. ^{252}Cf plasma-desorption time-of-flight mass spectrometry of the product exhibited the presence of a parent ion peak at *m*/*e* 1469, which is consistent with $C_{84}H_{100}N_{12}O_8Cu$, the copper bis-picket-fence porphyrinate.[9]

Results and Discussion

The successful synthesis of 5,10,15,20-tetrakis(2,6-diaminophenyl)porphyrin (**1**) by method A or B provides a starting point for a new class of cofacially modified tetraphenyl porphyrins. By analogy to $\alpha,\alpha,\alpha,\alpha$-5,10,15,20-tetrakis(aminophenyl)porphyrin (**4**), in the 5,10,15,20-tetrakis(2,6-diaminophenyl)porphyrin (**1**), the amino groups are expected to allow for the formation of a variety of new cofacial porphyrins in high yield. The purity and structure of the free-base porphyrins **1** and **2** were characterized by elemental analysis, mass spectroscopy, UV-visible spectra, and ^1H and ^{13}C NMR spectra.

The visible spectral data for the porphyrins are listed in Table I. Each porphyrin exhibits a characteristic Soret band near 420 nm. The cofacial porphyrins have a broadened Soret band which is characteristic of ortho-substituted tetraphenylporphyrins.[9] The blue-shift of the Soret band for the bis-picket-fence porphyrin suggests that the excited state is destabilized relative to the ground state. This destabilization could result from (i) a change in the dipolar interaction of the amide groups, (ii) the bulky substituents altering the angle between the plane of the phenyl and porphyrin rings, or (iii) the substituents on each porphyrin face of the bis-picket-fence porphyrin altering the degree of porphyrin plane deformation.[10]

Table I. Electronic Absorption Spectral Data[a]

4	1	5	2	3	Cu^{II}TPP
653	650	641	645	615	611
591	585	587	590	571	574
550	545	544	545	538	538
516	512	512	510	497	497
422	420	420	405	422	446

[a] All spectra were run in $CHCl_3$, excepting w3 run in acetone. All wavelengths in nanometers (±2 nm). Key: **1**, 5,10,10,15,20-tetrakis-(2,6-diaminophenyl)porphyrin; **2**, 5,10,15,20-tetrakis(2,6-dipivalamidophenyl)porphyrin; **3**, copper(II) 5,10,15,20-tetrakis(2,6-dipivalamidophenyl)porphyrinate; **4**, $\alpha,\alpha,\alpha,\alpha$-5,10,15,20-tetrakis(2-aminophenyl)porphyrin; **5**, $\alpha,\alpha,\alpha,\alpha$-5,10,15,20-tetrakis(2-pivalamidophenyl)porphyrin; TPP, tetraphenylporphyrin.

Table II. ^1H NMR Chemical Shifts[a]

	4	5	1	2
pyrrole	−2.5 bs (2)	−2.45 bs (2)	−2.5 bs (2)	−2.5 bs (2)
$-NH_2$	3.6 s (8)		3.5 s (16)	
tert-butyl		0.05 s (36)		0.05 s (72)
phenyl	6.8–7.8 m (16)	7.1–8.1 m (16)	7.4–7.8 m (12)	7.6–7.8 m (12)
pyrrole β H	9.0 s (8)	8.90 s (8)	9.00 s (8)	9.18 s (8)
amide N-H		8.65 s (4)		8.85 s (8)

[a] Compound numbers in boldface correspond to those stated in the text. In $CDCl_3$; δ is given in ppm from TMS. Intensities in parentheses: s, singlet; bs, broad singlet; m, multiplet.

Table II indicates that the ^1H spectra of **1** and **2** are consistent with the corresponding $\alpha,\alpha,\alpha,\alpha$-5,10,15,20-tetrakis(2-aminophenyl)- and $\alpha,\alpha,\alpha,\alpha$-5,10,15,20-tetrakis(2-pivalamidophenyl)porphyrins, **4** and **5**, respectively.[1,11] The *tert*-butyl group for both the picket-fence **5** and the bis-picket-fence **2** porphyrins is a singlet at 30 °C (300 MHz) indicative of rapid rotation of the methyl groups. The ^{13}C NMR spectrum of the bis-picket-fence porphyrin is consistent with the assignments of picket-fence porphyrin.[11]

Porphyrin metallation in aprotic solvents such as DMF has been shown to be first order in both the porphyrin free-base and metal ion concentration.[7] The metal ion incorportion by porphyrins in DMF solvent is believed to involve a mechanism in which solvent dissociation from the metal ion is a rate-determining factor.[7] It is thought that porphyrin deformation becomes an important part in the rate-limiting step when the rate of metalation becomes rapid. Turay and Hambright[12] report the rate constant for the formation of copper(II) picket-fence porphyrin is approximately 2 orders of magnitude slower than the formation of copper(II) tetraphenyl porphyrin, Cu^{II}TPP, using anhydrous $Cu(ClO_4)_2$ in DMF at 25 °C. Since the rate of complexation of copper(II) by the para-substituted analogue of picket-fence porphyrin, $H_2T(p-((CH_3)_3CONH)PP$, is more than twice as fast as H_2TPP, the pivolyl substituents in the ortho-substituted porphyrin exhibit a steric effect that is responsible for the reduction in the rate of metallation. This steric effect is thought to influence the rate of solvent dissociation from the metal ion and both the rate and equilibrium position of porphyrin ring deformation. It is proposed[12] that the sterically congested face of the picket-fence porphyrin prevents metalation and restricts the porphyrin to a geometry that is relatively unfavorable for metal ion incorporation. These observations suggest that alternative mechanisms exist for the metalation of sterically congested porphyrins.

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(10) A blue-shift in the UV-visible spectrum indicates a relatively stabilized ground state or destabilized excited state. However, no blue-shift is observed for picket-fence porphyrin **4** relative to its aminoporphyrin precursor **5**. It is expected that in the ground state the bis-picket-fence porphyrin is more constrained to a planar geometry than H_2TPP or picket-fence porphyrin. Evidently, the blue-shift observed in compounds **2** and **3** is the result of a highly destabilized excited state due to steric constraints.

(11) The ^1H and ^{13}C NMR and UV-visible spectra for compounds **4** and **5** were measured in our laboratory and compare favorably with those in ref 1a.

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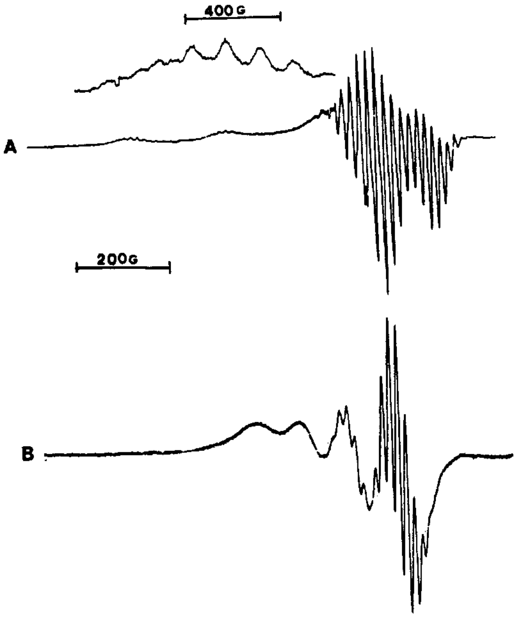

Figure 2. EPR spectra of copper(II) 5,10,15,20-tetrakis(2,6-dipivalamidophenyl)porphyrinate (3) in 1:1 toluene/CH$_2$Cl$_2$: (A) at 77 K; (B) at 300 K.

Despite the steric bulk of the four pivolyl groups on each face of the porphyrin, the metallation of 2 by anhydrous Cu(ClO$_4$)$_2$ in DMF occurs at a rate greater than 7.6×10^2 M^{-1} s^{-1} at 60 °C. This rate is significantly more rapid than the rate of 8.4×10^{-1} M^{-1} s^{-1} associated with H$_2$TPP under identical reaction conditions.[13] Clearly, the assumption that the pivolyl groups prevent the incorporation of copper ion into the porphyrin must be revised. The rapid rate of metallation of the bis-picket-fence porphyrin suggests that either the porphyrin ring can assume a conformation which is very favorable for metal ion complexation or a new pathway for metalation is available.[14]

The formation of copper(II) 5,10,15,20-tetrakis(2,6-dipivalamidophenyl)porphyrinate (3) is demonstrated by its visible (Table I) and EPR spectra. It is interesting to note that the Soret band of 3 also exhibits a blue-shift relative to copper(II) picket-fence porphyrinate[11] and Cu^{II}-TPP. The EPR spectrum of 3 (Figure 2) indicates that both the g values [g(iso) = 2.193, $g(z)$ = 2.075, $g(x,y)$ = 2.122)] and A values ($\times 10^4$ cm^{-1}) [(A(iso)Cu) = 88, ($A(z)$Cu) = 183, ($A(x,y)$Cu) = 38, (A(iso)N) = 15, ($A(z)$N) = 13, ($A(x,y)$N) = 16][15] are similar to those of copper(II) porphyrinates.[16] The degree of resolution of the nitrogen superhyperfine structure in the EPR spectrum of copper(II) porphyrinates is indicative of the extent of porphyrin aggregation.[16] The 17-line hyperfine splitting pattern observed in the $g(x,y)$ region of the EPR spectrum at 77 K indicates that 3 does not aggregate in solution. Previous investigators have shown that the coordination of a Lewis base such as pyridine to the copper(II) ion is reflected by a marked increase in the g factor and a decrease in the nitrogen superhyperfine coupling constant.[16] Since the g factor and A-values remain virtually unchanged in 1:1 toluene/CH$_2$Cl$_2$ and pyridine solvent, it is clear that the pivolyl groups prevent the coordination of pyridine by the copper(II) ion. Collman reports the formation of Fe$^{II}\alpha,\alpha,\alpha,\alpha$-T($o$-((CH$_3$)$_3$CONH)PP(L)$_2$ (L = 1-methylimidazole), although this species is disfavored compared to the 1:1 base/metal adduct.[1a] In solution, the steric interaction of the pivolyl substituents on the sterically congested face of picket-fence porphyrin can be diminished by the deformation of the porphyrin plane. In this configuration, the deformed metalloporphyrin can bind two molecules of solvent at the metal center. In the case of the cofacially substituted sterically hindered bis-picket-fence metalloporphyrin 3, preferential distortion of the porphyrin plane to relieve the steric interaction of the pivolyl groups on one porphyrin face will increase steric interaction on the opposite face. For this reason, it is not surprising that 3 is unable to coordinate a base such as pyridine to the copper ion even at 77 K.

Note Added in Proof. An alternative synthesis of tetrakis(2,6-dinitrophenyl)porphyrin has been reported: Quintana, C. A.; Assink, R. A.; Shelnutt, J. A. *Inorg. Chem.* **1989**, *28*, 3421.

Acknowledgment. We are grateful for the ^{252}Cf plasma-desorption time-of-flight mass spectrum kindly performed by the Rockefeller University Mass Spectrometry Laboratory. The valuable insight regarding the visible spectra of porphyrins provided by Professor Mauzerall (Rockefeller U.) is appreciated.

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(14) An alternative pathway for metalation could involve the participation of the carbonyl oxygen lone pairs found on the pivolyl group(s). In the case of the picket-fence porphyrin the conformation of the porphyrin plane might make this pathway less favorable.

(15) [Cu(por)] = 1×10^{-4} M in 1:1 toluene/CH$_2$Cl$_2$ or pyridine. Isotropic X-band EPR measurements were at 298 K; anisotropic measurements were at 77 K. Modulation amplitude is 5 G.

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Synthesis and Reactivity of a Nickel(II) Complex with a Macrocycle Containing a Peripheral Hydroxyl Group

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The neutral nickel(II) complex of an anionic macrocyclic ligand, (6,14-diacetyl-10-hydroxy-7,13-dimethyl-1,4,8,11-tetraazacyclopentadeca-4,6,12,14-tetraenato)nickel(II) ([Ni(Ac$_2$Me$_2$(OH)[15]tetraenato-κ^4N)]), is formed by a template reaction involving the closure of [3,3′-(ethylenebis(iminomethylidene))bis(2,4-pentanedionato)]nickel(II) with 1,3-diamino-2-propanol. The uncoordinated hydroxyl group on the macrocyclic ligand reacts smoothly with acylating agents. Previous reports have indicated that hydroxyl groups on the carbon framework of transition-metal complexes exhibit low reactivity toward electrophilic reagents. The differences in behavior are discussed.

Introduction

With the continued expansion of chelate chemistry and organometallic chemistry into such areas as inclusion chemistry and bioinorganic chemistry it has become increasingly routine to conduct organic chemical reactions on both coordinated and free functional moieties within the metal complexes. This focuses attention on the relative reactivities of functional groups in the presence and absence of the metal ion of the chelate. An abnormal absence of reactivity toward electrophiles has been reported for uncoordinated alcoholic OH groups in a number of chelate complexes. We report here the synthesis and characterization of a nickel(II) complex of a macrocyclic ligand having an appended

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