CYCLOTRIPHOSPHAZENE LINKED TETRAPHENYLPORPHYRINS

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Abstract - Condensation of the functionalised cyclophosphazene aldehyde, $N_3P_3(OC_6H_5)_5(m\text{-}OC_6H_4\text{-}CHO)$(3) with pyrrole affords the tetraphenylporphyrin (4) containing the cyclophosphazene unit. This has been characterised by spectroscopic and analytical methods. Kinetics of metallation(Cu^{2+}, Zn^{2+}) of (4) indicate slower rates of insertion relative to normal tetraphenylporphyrins. The esr spectrum indicates an axial symmetry for the Cu^{2+} derivative (6).

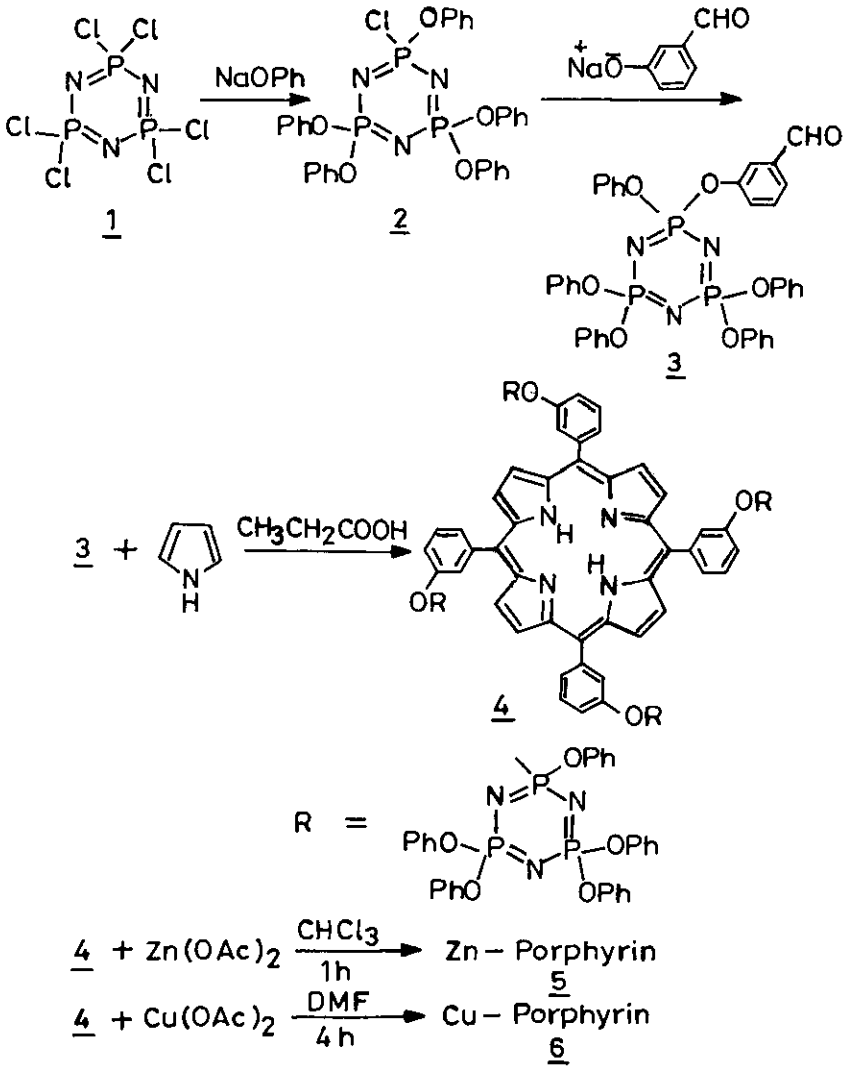
INTRODUCTION

Porphyrin systems are involved in several biologically important functional units.[1] In order to understand the correlation between the structure of the porphyrin with its function and reactivity several new types of synthetic porphyrins have been synthesized and studied in recent years.[2] The structural diversity of the model systems can be achieved by substitution at the periphery as well as in the core of the porphyrin. Thus, for example, a number of recent reports indicate modification of the porphyrin periphery by the introduction of diverse groups such as crown ethers,[3] peptides[4] and amide linkages.[5] The core modification is achieved by replacement of the pyrrole unit by thiophene and furan rings.[6] Another recent interest has been to incorporate the porphyrins in long chain macromolecules to enhance their structural and functional versatility.[7] In this account we wish to report the first example to our knowledge where an

inorganic heterocycle, a cyclotriphosphazene has been substituted in the periphery of a porphyrin system. Apart from increasing the structural diversity this opens the possibility of the synthesis of porphyrin containing polyphosphazenes.

RESULTS AND DISCUSSION

The synthetic strategy involved is to make a phosphazene precursor that can be condensed to a porphyrin by reaction with pyrrole (Scheme 1). A suitable precursor would be one that contains a single reactive functionality.



Scheme 1

We have chosen monochloropentaphenoxycyclotriphosphazene, $N_3P_3(OPh)_5Cl$ (2) as our starting material because of its stability and ease of preparation.[8] This was reacted with m-hydroxybenzaldehyde to obtain the desired functionalised aldehyde containing phosphazene precursor, $N_3P_3(OPh)_5(m\text{-}OC_6H_4\text{-}CHO)$ (3). Condensation of 3 with pyrrole using standard synthetic procedures affords a purple brown powder which was purified by chromatography to obtain a dark purple fluorescing solid (4) in 5% yield. The electronic spectrum (Figure 1) of this product (4) shows a typical

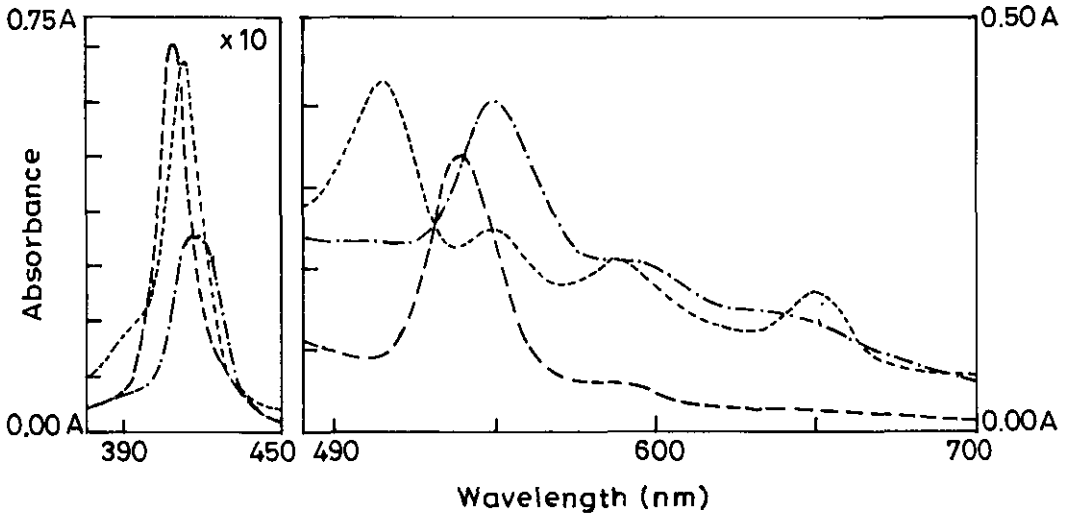


Figure 1. Electronic spectrum of phosphazene porphyrin (4) (--------) Zn-porphyrin (5) (— — — —) and Cu-porphyrin (6) (—·—·—·—)

etio type absorption containing both the Q-bands and the intense soret band showing unambiguously the formation of a porphyrin. Addition of a drop of dilute trifluroacetic acid in CH_2Cl_2 to a solution of (4) generated the dication of (4) as indicated by its absorption spectrum, 651 nm, 596sh nm and 437 nm (soret).[9] The proton nmr of this free base porphyrin shows a sharp singlet at 8.9 ppm due to β-pyrrole protons and a complex multiplet at 7.5 ppm due to phenyl protons. The phosphorus nmr is very similar to the phosphazene precursor and shows a sharp singlet suggesting that the original cyclotriphosphazene unit is retained intact in the final product. The apparent isochrony of chemical shifts and their values are

similar to those observed for related derivatives.[10]

The metal insertion kinetics has been carried out using optical absorption methods by monitoring the decrease in the absorption at 515 nm band of free base porphyrin as a function of time in 1:1. $CHCl_3$:CH_3OH solvent mixture (Figure 2). The pseudo first order rate constant (k_1) for the

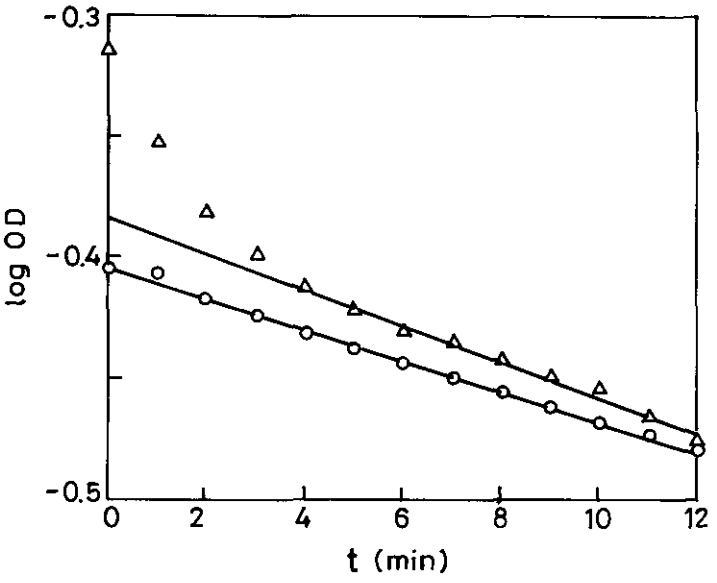


Figure 2. A plot of change in absorbance with time for Cu^{2+} (Δ) and Zn^{2+} (o) insertion in 1:1 $CHCl_3$: Methanol.

incorporation of Zn^{2+} and Cu^{2+} are $2.45x10^{-4}$ and $2.85x10^{-4}$ s^{-1} respectively. These rate constants are approximately 100 fold slower than those obtained for the normal tetraphenylporphyrin derivates of the same metal ions.[12] Two reasons can account for this observation. First, it is possible that the slower reaction rates are due to a decreased basicity of the porphyrin ring. The porphyrin ring basicity depends on the peripheral substituents. Presence of electron withdrawing groups is known to reduce the ring basicity.[13] Cyclophosphazenes have been found to be electron withdrawing on many organic functional groups. Thus, cyclophosphazenes containing vinyl monomers have been found to be polymerised less easily because of a decrease of electron density in the polymerisable olefin

functionality.[14] Thus, the observed slower rate of metallation of the porphyrin (4) is in keeping with the electron withdrawing nature of the cyclophosphazene substituent. Secondly, the presence of bulky substituents is known to deform the geometry of the porphyrin rendering it less reactive, thereby decreasing the rate. Such steric effects are well documented.[15]

Both the Cu^{2+} and Zn^{2+} derivatives show two banded electronic spectrum (Figure 1) characteristic of a metalloporphyrin. It is well known that the 4-banded Q-band region optical spectrum of a free base porphyrin will reduce to a 2-banded spectrum upon insertion of the metal ion due to a change in symmetry from D_2h to D_4h.[16] The phosphorus nmr of the metallo derivatives also show a single line spectrum indicating the retention of the cyclophosphazene unit. The esr spectrum at 77 K of the copper derivative shows an axial symmetry ($g_{\parallel}$ = 2.165, $g_{\perp}$ = 2.Ø46) with metal hyperfine and nitrogen superhyperfine structures typical of copper porphyrins.[17]

EXPERIMENTAL

The solvents were purified by standard procedures. Pyrrole, phenol and m-hydroxybenzaldehyde were obtained from Aldrich and were used as such. ^1H Nmr and ^{31}P nmr spectra were recorded on a Jeol-FX-9Ø operating at 9Ø MHz and 36.43 MHz, respectively using TMS (internal) and 85% H_3PO_4 (external) as standards. Esr spectra were recorded on a Varian E-1Ø9 at 77 K. Melting points reported are uncorrected. For the metallation kinetics the following concentrations were used. Porphyrin (4) ($8.44x1Ø^{-5}$ M); metal acetates ($9x1Ø^{-5}$ M).

Preparation of 2-chloro-2,4,4,6,6-pentaphenoxycyclotriphosphazene, $N_3P_3(OPh)_5Cl$ (2)

Compound (2) was prepared by a modification of the procedure reported earlier.[8] A solution of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (1) (3.35g,

9.64 mmol) in acetone (60 ml) was added dropwise over a 30 min period to a stirred solution of sodium phenoxide (5.60 g, 48.20 mmol) in acetone (150 ml) kept at 10 °C. The reaction mixture was allowed to come to room temperature (25 °C) and was stirred for 21 h. Acetone was removed under vacuum to afford a semisolid. This was extracted with ether (300 ml). The ether layer was washed with 0.1 N NaOH (2x50 ml), water (2x50 ml), dried ($CaCl_2$) and stripped off the solvent in vacuo to afford an oil. This was dissolved in a minimum amount of ether (5 ml) and a few drops of n-hexane were added. Compound (2) crystallised at room temperature by slow evaporation (3.96 g, 63.9%). mp 67 °C (lit.[8] 67-68 °C); ^{31}P nmr (chloroform-d) δ : 8.32 ($\underline{P}(OPh)_2$), 23.20 ($\underline{P}(Cl)(OPh)$); J, 83.7 Hz.

$N_3P_3(OPh)_5(m\text{-}OC_6H_4\text{-}CHO)$ (3)

m-Hydroxybenzaldehyde (1.22 g, 10 mmol) was dissolved in dry acetonitrile (50 ml) and added to a suspension of sodium hydride (0.24 g, 10 mmol) in the same solvent (30 ml) at 25 °C. The reaction mixture was heated to 50 °C and tetra-n-butylammonium bromide (30 mg) was added. This mixture was allowed to cool to 25 °C and was added dropwise to a solution of $N_3P_3(OPh)_5Cl$ (2) (3.78 g, 6 mmol) in dry acetonitrile (100 ml) at 25 °C. The reaction mixture was stirred at the same temperature for 50 h and heated under reflux for 15 h. After allowing it to come to 25 °C the mixture was filtered and the filtrate was stripped off the solvent in vacuo affording an oil (2.05 g, 47.8%) which was tlc pure (benzene:n-hexane, 1:1). Anal. Calcd for $C_{37}H_{30}N_3O_7P_3$: C, 61.59; H, 4.19; N, 5.82. Found: C, 61.42; H, 4.31; N, 5.67. ^{31}P Nmr (chloroform-d) δ : 4.68 (s); ^{1}H nmr (chloroform-d) : 9.76 (s, C$\underline{H}$O), 7.50 (m, aromatic).

Phosphazeneporphyrin (4)

The phosphazenealdehyde (3) (2.80 g, 3.88 mmol) and pyrrole (0.26 g, 3.88 mmol) were added together to boiling propionic acid (400 ml) and the reaction mixture was heated under reflux for 1 h. The reaction mixture was

cooled overnight to 25 °C and the solvent was removed in vacuo to afford a semisolid. This was chromatographed thrice over silica gel (60-120 mesh) using benzene as the eluant. A single pink fraction was collected. Removal of solvent afforded residue which was recrystallised from chloroform : n-hexane (1:1) to give (4) (0.15 g, 5%). mp > 200°C. Anal. Calcd for $C_{168}H_{130}N_{16}O_{24}P_{12}Cl_{12}$ (includes 4 solvent molecules of chloroform): C, 56.76; H, 3.69; N, 6.30. Found: C, 56.72; H, 3.77; N, 6.44. ^{31}P Nmr (chloroform-d) δ : 7.06 (s); ^{1}H nmr (chloroform-d) δ : 8.9 (s, β-pyrrole protons), 7.5 (m, aromatic). Electronic spectrum: λ_{max} (nm) (log ε) in chloroform: 650 (3.09), 588 (3.18), 549 (3.25), 515 (3.48) (Q-bands), 419 (4.68) (soret).

Metallo derivatives

The metallo derivatives (5) (Zn^{2+}) and (6) (Cu^{2+}) were prepared using standard methods using metal acetates.[16] ^{31}P Nmr (5): (chloroform-d) δ : 10.74 (s); (6) : 10.67 (s). Electronic spectrum: λ_{max} (nm) (log ε) in chloroform, (5): 549 (3.78), 590 (3.58) (Q-bands), 422 (5.10) (soret); (6): 539 (3.86) (Q-band), 416 (4.81) (soret).

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