Isolation and Characterization of the Principal Kinetic Product in the Preparation of a Sterically Hindered Tetra-arylporphyrin: *X*-Ray Structure of a Bis(dipyrromethene) Complex of Zinc, $Zn^{II}(C_{22}H_{13}Cl_4N_2)_2 \cdot$ toluene

Craig L. Hill* and Michael M. Williamson

Department of Chemistry, Emory University, Atlanta, Georgia 30322, U.S.A.

The principal kinetic product in the Rothemund template synthesis of sterically hindered tetra-arylporphyrins is not the metalloporphyrin complex but the bis(dipyrromethene) complex; the latter has been isolated from a typical porphyrin preparation, that of tetrakis(2,6-dichlorophenyl)porphyrin, and characterized by u.v.–visible, i.r., and n.m.r. spectroscopy, and *X*-ray crystallography.

In the last few years hindered tetra-arylporphyrin complexes have become the principal species used not only to model the chemical and physical properties of cytochrome P-450 and other heme enzymes but also to investigate catalytic oxygen transfer and other biomimetic oxidations by synthetic metalloporphyrins.[1] Hindered tetra-arylporphyrin complexes are resistant to dimerization and various bimolecular decomposition processes, and are often more stable to intramolecular oxidative decomposition than the unhindered analogues such as the tetraphenylporphyrin (TPP) complexes. Unfortunately the yields of the hindered derivatives are far lower than for TPP using either the propionic acid-based[2] or the Rothemund zinc template-based[3] condensation processes.[1] We have examined the latter condensation methodology to ascertain the factors that limit the yields of the desired porphyrins.

The Rothemund template condensation with zinc salts leads in one case to a dipyrromethene complex of reasonable tractability. In a typical preparation, pyrrole (28 mmol), 2,6-dichlorobenzaldehyde (28 mmol), and $Zn(OAc)_2$ (10 mmol) in collidine (25 g) were refluxed for 3 h. After removal of the collidine *in vacuo*, the resulting black tarry mixture was treated with toluene (200 ml), and 0.25 g (3.7% yield) of the desired porphyrin complex tetrakis(2,6-dichlorophenyl)-porphinatozinc(II) (**1**) was separated by filtration. The electronic spectrum indicated that the supernatant liquid contained up to a 40% yield of another product, bis[(*meso*-2,6-dichlorophenyl)-5-(*o,o*′-dichlorobenzyl)dipyrromethene]-zinc(II) (**2**). The yields of (**1**) and (**2**) in the Rothemund template condensation appear to be relatively unaffected by the presence of air during the reaction despite the sensitivity of both the pyrrole and the 2,6-dichlorobenzaldehyde to O_2. The major kinetic product (**2**) can be purified by chromatography (neutral activity grade I alumina with toluene as eluant). Recrystallization from toluene afforded fluorescent green-yellow crystals ($\lambda_{max.}$ 504 nm; ε 1.80×10^5 $dm^3\,mol^{-1}\,cm^{-1}$). The i.r. spectrum of (**2**) shows a large number of bands including those typical of dipyrromethene derivatives[4] and no carbonyl stretch; the ^1H n.m.r. spectrum (360 MHz) confirms the presence of the (*meso*-2,6-dichlorophenyl)-5-(*o,o*′-dichlorobenzyl)dipyrromethene moiety. A crystal of (**2**) was analysed by *X*-ray crystallography.

Crystal data: $Zn^{II}(C_{22}H_{13}Cl_4N_2)_2 \cdot C_6H_5CH_3$, $M = 1051.84$, triclinic, space group $P\bar{1}$; $a = 10.5324(45)$, $b = 15.3938(61)$, $c = 16.2235(44)$ Å, $\alpha = 70.012(26)$, $\beta = 76.472(30)$, $\gamma =$

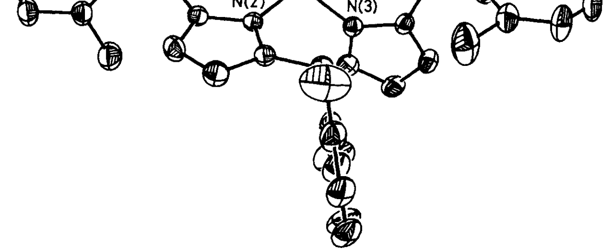

Figure 1. ORTEP[5] plot of (**2**). The thermal ellipsoids are drawn at the 30% probability level.

84.278(34)°, $U = 2402.78(1.60)$ Å^3, $D_c = 1.45$, $D_m = 1.42(2)$ g/cm^3; $Z = 2$; 5124 unique reflections with $F_o > 2.5\sigma(F_o)$ were measured using Mo-K_α radiation on a Syntex P2$_1$ diffractometer. The structure was solved by the heavy atom method and refined by least squares to a final R factor of 0.0683. An ORTEP[5] plot of (**2**) (Figure 1) confirms the presence of the monobenzyl substituted dipyrromethene moieties. The Zn–N distances range from 1.958(4) [Zn–N(3)] to 1.984(5) Å [Zn–N(4), and the N–Zn–N angles range from 94.5(2) [N(3)–Zn(4)–N(4)] to 123.9(2)° [N(1)–Zn–N(3)] to define and idealized geometry approaching C_{2v} for the ZnN$_4$ co-ordination polyhedron.†

In (**2**), the principal kinetic product of the template condensation, the dipyrromethene ligands are in the same oxidation state as that of the pyrrole and the 2,6-dichlorobenzaldehyde reactants, and 6 electrons (6 H) more reduced than the metalloporphyrin (**1**). Several methods convert (**2**) into (**1**) to some extent. The best found thus far involves allylic bromination (4 equiv. of *N*-bromosuccinimide, CCl$_4$) followed by refluxing for 6 h in collidine; a 26% yield of (**1**) is produced.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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