A Novel Stepwise Degradation of Porphyrins. Synthesis and Structural Characterization of meso-Tetraphenylchlorinato Nickel(II) and meso-Tetraphenylscecorhlinato Nickel(II)

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The search for novel photosensitizers for photodynamic therapy (PDT) as well as basic research interests has led to the synthesis of expanded porphyrins,2 porphyrin isomers,2,4,5 and porphyrins containing moieties other than pyrroles as building blocks. A current topic of interest in porphyrin chemistry is the study of nonplanar porphyrins6 for its relevance to the understanding of porphyrin-containing enzymes and light harvesting pigments.

We reported on the synthesis of scecorhlinato Ni 1, a metallochlorin-like pigment which was derived from meso-tetraphenylporphyrinate Ni by cleavage of one peripheral ββ'-double bond. We also described its conversion into the nonplanar homoporphyrin 2, in which one pyrrolic unit of a porphyrin is formally replaced by a oxazoline moiety (Scheme 1). Its X-ray crystal structure revealed that it was severely twisted (ruffled).6c

We now report the X-ray crystal structure of the Ni scecorhlin I and its stepwise decarbonylation. The structure of the resulting novel meso-tetraphenylchlorinato Ni 4 was confirmed by single-crystal X-ray crystallography. The crystal structures of 1 and 4 revealed that, surprisingly, both compounds also exist in significantly ruffled conformations comparable to that of 2.

In the course of our continuing work with the scecorhlin dialdehyde 1, we were able to grow crystals suitable for an X-ray crystal structure determination. This provided the ultimate proof of the proposed structure (Figure 1). It also showed that the plane of the metallescocorhlin, while retaining a square planar coordination sphere around the central metal, was severely twisted along an N--N axis resulting in a ruffled conformation of the porphyrin core (rms of the C18N4Ni mean plane, 0.465 Å). The conformation is very similar to that observed in 2 (rms of the C9N4Ni mean plane, 0.468 Å). This was unexpected since the intramolecular steric constraints imparted by the nonplanar six-membered ring in 2 are absent in 1. The conformation of 1 allows the carboxaldehyde moieties to be arranged parallel to each other, allowing for π-π-stacking interactions (average distance of the C=O bonds, 2.85 Å). However, this interaction should not be strong enough to distort the pigment into the observed extremes.

Scheme 1†  

Figure 1. Top view (hydrogen atoms omitted for clarity) and edge-on view (along a Ni--N axis, the hydrogen atoms and the meso-phenyl substituents have been omitted for clarity) of the X-ray crystal structures of 1, 2, 4 with Ni--N bond lengths. The Ni--N bond lengths for 4 have been determined by averaging the equivalent bond lengths of the two molecules present in the asymmetric unit.

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Supporting Information.  


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Aromatic aldehydes decarboxylate in the presence of (Ph₃P)_2RhCl. A solution of the dehydride 1 in benzolitrene when reacted with a stoichiometric excess of (Ph₃P)_2RhCl, under reflux for 45 min, produced, along with small amounts of starting material and side products, the monodecarboxylated pigment 3 in 10% and the bisdecarboxylated pigment 4 in 40% yield (Scheme 1). The structures of the blue-green pigments are supported by their spectroscopic and analytical data. Their UV-visible spectra indicate the presence of metallated chlorin-like systems ($\lambda_{max}$ [log ε] for 3: 448 [4.06], 630 [3.15], 678 [3.34]; $\lambda_{max}$ [log ε] for 4: 422 [4.33], 576 [3.28], 612 [3.58]). The stepwise loss of the carbonyl groups which served to extend the chromophore is also reflected in the hypsochromic shift of the Soret band of 1 ($\lambda_{max}$ [log ε] 466 [4.78]). This shift can also be taken as an indication for some reduction of the ruffling of the macrocycle. The HR mass spectra (EI) of the pigments (3: m/e calc for C₇₃H₃₉N₄O₉ 674.16168, found 674.16024; 4: m/e calc for C₇₃H₃₈N₄O 646.16675, found 646.16652) as well as elemental analysis corroborate the proposed composition. The 1H NMR spectra show $\delta$ 9.50 ppm; 5a $\delta$ 4.33, 5b $\delta$ 4.33, and 5c $\delta$ 4.33 ppm (ppm), and its isononconform replacement by a singlet at $\delta$ 9.80 ppm with an integration corresponding to 1H and 2H for 3 and 4, respectively. This diatropic shift for the $\alpha$-protons is comparable to those measured for $\beta$- and meso-protons of other 18-electron porphyrin systems, for instance, 5,15-diphenyl-porphyrin.

A single-crystal X-ray diffraction study was performed on 4. This unequivocally proved its assigned chlorophinato structure. One pyrrolic unit of the parent porphyrin has been degraded to an aldime linkage, without any other change in the connectivity of the macrocycle. Aldimine linkages in polypyrrolic macrocycles are known, albeit their establishment and position within the macrocycle. Aldimine linkages in polypyrrolic macrocycles (with the exception of the imine unit (Figure 1) analogous to precedents found in the solid-state structures of chlorinato Ni complexes. Unfortunately, the attempted acid-induced demetalation of pigments 3 and 4 led only to their decomposition; hence, no direct comparisons can be made with their free base analogues. Molecular modeling studies suggest that the free base of 4 is planar.

Synthesis of the parent chlorophin has been reported by Fritsch and co-workers.21,22 These compounds are the bacteriochlorin and isobacteriochlorin (meso-unsubstituted) analogues of chlorophin.4 In contrast to our facile preparation of 4, however, their total syntheses were very low yielding (<0.1% over several steps).

To conclude, we have shown that the stepwise decarboxylation of secocobilin 1 produces the new homoporphyrins 3 and 4. Thus, we have shown how to degrade one pyrrolic unit of the ultimate starting material meso-tetraphenylporphyrin in three steps (dihydroyxulation, diol cleavage, decarboxylation) to an aldime linkage. Although other porphyrin degradation pathways have been reported before, mainly involving cleavages at the meso-position,23,24 this degradation of the $\beta$-positions is novel to the field of porphyrin chemistry. Furthermore, the X-ray crystal structure determination of 1 and 4 revealed their severely central-metal induced ruffled conformations.

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Supporting Information Available: Procedures for the preparation of 3 and 4, experimental crystallographic details, positional and anisotropic thermal parameters for 1 and 4 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

(10) Selected analytical and spectroscopic data for 3: $^{1}H$ NMR (CDCl₃) 7.24 (s, 1H, C₆H₆-CO, 72), 492 (M⁻, 100), 646 (M⁻ - CO, 85), 597 (M⁻ - C₆H₅, 55), 568 (M⁻ - C₆H₄-CO, 72), 492 (M⁻ - 2C₆H₅-CO, 35). 4: mp > 310°C sublimation; 1H NMR (400 MHz, CDCl₃) $\delta$ 7.49 (t, J = 7.2, 1.1 Hz, 1H), 7.55-7.65 (m, 5H), 7.78 (d, J = 7.7 Hz, 2H), 7.86 (d, 6.1, 1.8 Hz, 2H), 8.15 (s, 1H, 8.20 (d, 4.8 Hz, 1H), 8.38 (d, 5.0 Hz, 1H), 9.80 (s, 1H), 9.85 (s, 1H); IR (film) 1657 (s, C=O), 1548 (m, C=C), 1439 (m); LR MS (EI) m/e (%) 674 (M⁺, 100), 646 (M⁺ - CO, 85), 597 (M⁺ - C₆H₅, 55), 568 (M⁺ - C₆H₄-CO, 72), 492 (M⁺ - 2C₆H₅-CO, 35). 4: mp > 310°C sublimation.
(20) MM2 force field, CAChe System, Oxford Molecular Systems, V.3.9, 1996.