Contracted Porphyrinoids

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Norcorrole: Observation of the Smallest Porphyrin Variant with a N_4 Core**

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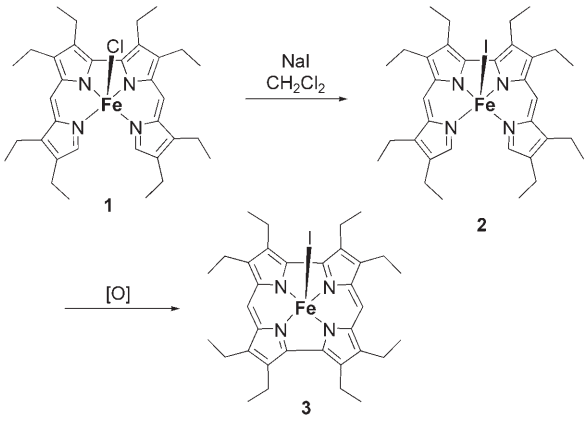
Dedicated to Prof. Emanuel Vogel on the occasion of his 80th birthday

Porphyrin variants with expanded, contracted, or heteroatom-substituted cavities have been a growing area of highly interdisciplinary research over the last decade.[1] A plethora of structural variants of the biogenic macrocycle porphyrin has been prepared and has attracted significant attention due to the manifold potential application of such functional macrocycles, particularly for expanded systems.[2] In addition, porphyrinoids with contracted cavities, and in particular metal chelates of those, show remarkable metric and electronic features.[3] Due to the increasing ring strain upon contraction of the core, however, only corrole[4] and a small number of other macrocycles[5,6] from this subgroup have been studied in more detail.

Conceptually, the further development of this field by the excision of a second *meso*-methine unit would lead to the norcorrole system. However, the preparation of this particularly strained porphyrin variant with alledged antiaromatic 16π-character has not been realized so far. The direct approach, by cyclocondensation of 2,2′-bipyrrole and 5,5′-diformylbipyrrole derivatives, leads to an unstrained dimeric cyclooctapyrrole[7] or—with varied substitution—to higher cyclo[*n*]phyrins[8] rather than to the strained norcorroles. A DFT analysis on the electronic structure and the question of general stability of norcorrole has recently been reported.[9] From this analysis it was derived that norcorrole displays polyenic rather than antiaromatic character. In addition, the ring strain of metal chelates of norcorroles was predicted to promote a convex conformation of the macrocycle. The remaining *meso*-methine positions of metalated norcorroles are computed to be prone to reduction and nucleophilic attack, so that the stabilization of the compounds upon loss of cyclic conjugation appears feasible. We now report here on evidence for such a highly reactive metalated norcorrole and for its predicted reactivity.

During our studies on iron bilin analogues we observed that the iodido complex of an iron 2,2′-bidipyrrin (**2**), formed by ligand exchange from the chlorido derivative **1** (Scheme 1),[10] is not as stable in air as **1** or the respective bromido derivative. Instead, **2** slowly decays over 24 h in solution quite unselectively to a number of different intractable products. By using inert conditions and freshly sublimed $FeCl_3$, this oxidative transformation can be directed in such a way that the ^{1}H NMR spectrum of the reaction mixture after 30 min indicates the presence of only one major paramagnetic compound in solution (Scheme 1, and trace B in Figure 1).



Scheme 1. Formation of iron norcorrole **3**.

This spectrum is markedly different from that of the starting material **2**. The reduced number of resonance lines between $\delta = 95$ and 10 ppm is particularly indicative of an increase in symmetry for the new paramagnetic compound **3**. Only four signals are detected at low field with a relative intensity of 2:2:1:4. The smallest one is also the broadest of

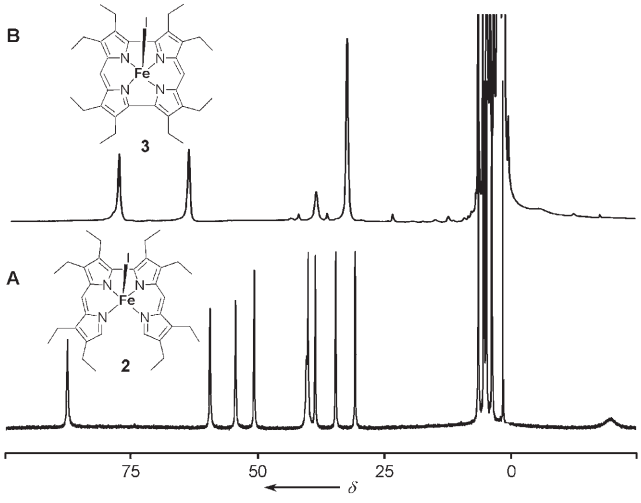


Figure 1. ^{1}H NMR spectra (300 MHz, CD_2Cl_2) of **2** (trace A) and the putative norcorrole **3** (trace B).

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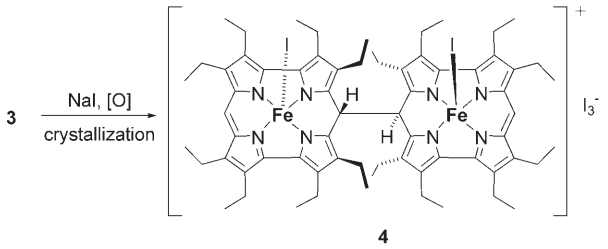
the group, and the intensity of 4 for the signal at $\delta = 32$ ppm points towards a superposition of two incidentally isochronic nuclei. In addition, the signal for the terminal hydrogen atoms of the starting complex **2** at $\delta = -20$ ppm has vanished in the product mixture, indicating the loss of these hydrogen atoms in the product. The region between $\delta = 0$ and 10 ppm houses several small, broadened peaks of unknown origin in addition to a dominant singlet at $\delta = 2.2$ ppm that was assigned to the methyl group protons of the ethyl substituents of the new compound **3**. MALDI-TOF mass spectrometry of the reaction mixture revealed an intense signal at *m*/*z* 689, which could be identified by a high-resolution measurement as the $[\mathbf{2}-2\,H]^+$ signal. Further data could not be obtained since **3** tends to decompose very quickly in solution, and all attempts to isolate or crystallize the species failed. Symmetry and molecular mass of the species, however, indicate the presence of an iron complex of deprotonated norcorrole (H_2nc), [(nc)FeI] (**3**).

Although in most instances the decomposition of **3** in solution proceeded unselectively and resulted in a significant number of unassigned species, one attempt to isolate at least one of the decomposition products of **3** was finally successful. As shown in Scheme 2, the crystallization of **3** in the presence of excess NaI from an aerated dichloromethane/*n*-hexane mixture yielded a small amount of crystalline material **4**, which was investigated by single-crystal X-ray crystallography.

The molecular structure of the new porphyrinoid compound **4** is depicted in Figure 2, and the observed connectivity of the ligand framework confirms the NMR finding of a norcorrole. Evidently, a dimerization had occurred during the crystallization process. The dimeric compound **4** shows two macrocycles devoid of cyclic conjugation which are weakly connected via the *meso*-methine groups (C1–C1′ 1.62 Å). This distance is quite long for a C–C single bond, but resembles earlier findings on other sterically enforced and strained organic compounds such as bis(triarylmethane)s.[11] The presence of one equivalent of a triiodide anion per dimeric norcorrole in the crystal indicates a mixed-valence nature of the dinuclear complex **4**. Due to the high crystallographic symmetry, however, the different monomeric norcorrole subunits cannot be distinguished from the crystallographic analysis.

The second intriguing feature of the molecular structure of **4** is the bowl-like conformation of the macrocycle and the large doming of the iron ion, which resides 0.521 Å above the mean squares plane of the four nitrogen atoms. The observed Fe–N distances are rather short (1.843 and 1.873 Å), and an iodido axial ligand is bound to the iron atom (2.620 Å). The



4

Scheme 2. Formation of the dimeric norcorrole **4**.

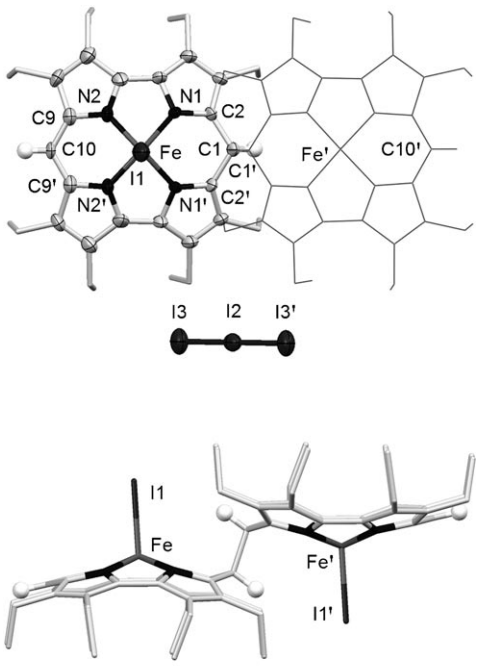


Figure 2. Molecular structure of **4** in the solid state. Top: View along the Fe–I1 axes, with numbering scheme and triiodide counterion; thermal ellipsoids are set at 50% probability. Bottom: side view of the monocation. Only selected hydrogen atoms are shown. Selected bond lengths [Å] and angles [°]: Fe–N1 1.873(10), Fe–N2 1.843(10), Fe–I1 2.620(3), C1–C1′ 1.62(4), C1–C2 1.513(16), C9–C10 1.416(16), I2–I3 2.9097(19); N1-Fe-N1′ 90.2(6), N1-Fe-N2 81.3(4), N1-Fe-N2′ 147.4(5), N1-Fe-I1 108.0(4), N2-Fe-N2′ 89.1(6), N2-Fe-I1 104.6(4), C2-C1-C1′ 108.0(13), C2-C1-C2′ 114.8(15), C9-C10-C9′ 119.4(16).

different hybridization of the *meso*-methine carbon atoms C1 and C10 is clearly apparent from the C1–C2 and C9–C10 bond lengths of 1.513 and 1.416 Å, respectively. The angles at these *meso* positions also follow the expected trends and show no sign of a particularly stressed system. It appears plausible to assume that most of the intramolecular strain is taken up by the nonplanar, bowl-shape conformation of the macrocycle, and that this conformation again is supported by metal coordination. Owing to the mixed-valence nature of **4**, however, the bonding details of the iron ion are median values and cannot be interpreted in terms of oxidation state and/or spin state. The compound decomposes upon dissolution in all common solvents, so that the question of electronic structure still remains open at this point.

The comparison of the physical data obtained on the first norcorrole species **3** and **4** with the results from the above-mentioned DFT analysis allows additional insight into the compound. For metal chelates of an intact norcorrole ligand such as [(nc)FeI] (**3**), the calculations have predicted ionization energies similar to those of metal porphyrins, but a value twice as high for the electron affinity. The LUMO and LUMO+1 display very large coefficients at the *meso*-methine carbon atoms, whereas practically no electron density is present at these positions from the HOMO to the HOMO–5. The *meso* positions thus seem to be particularly prone to reduction and to nucleophilic attack as observed for the reaction **3**→**4**. Additional calculations on a chloridoiron

complex of a reduced norcorrole ligand, the hydronorcorrole, yielded a molecular geometry very similar to the one observed for the monomeric subunits of complex **4**. Specifically, short C2-C1-C2′ and long C9-C10-C9′ bonds of 1.407 and 1.514 Å, and short pyrrole–pyrrole bonds of 1.419 Å have been reported, as compared to 1.416, 1.513, and 1.420 Å, respectively, observed for **4**. As discussed above the mixed-valence nature of **4** influences mainly the observed median metrics of the FeN_4I coordination unit. Theory and experiment therefore show the largest divergence for these data with calculated (observed) Fe–N bond lengths of 1.896 (1.843) and 1.901 (1.873) Å, and with a doming displacement of the iron atom of 0.590 (0.521) Å.

In summary we have presented first physical data of a derivative of norcorrole, the much sought-after smallest porphyrin variant with a N_4 core, and could demonstrate that iron norcorroles exist and tend to dimerize spontaneously. This finding now marks a new frontier in the field of porphyrin variants, and we now return the ball to the theoreticians to gain useful hints from additional calculations on spectroscopic data and on the question of how to stabilize such species with a borderline stability sufficiently for detailed investigations.

Experimental Section

Preparation of **3** and **4**: The chlorido complex **1** (18 mg, 0.028 mmol) and NaI (10 mg, 0.066 mmol) in dry dichloromethane (20 mL) were treated with freshly sublimed $FeCl_3$ and stirred under inert conditions at ambient temperature for 30 min. The mixture was then filtered and the solvent was removed in vacuo to leave a dark, greenish mass that was immediately analyzed by ^{1}H NMR spectroscopy and mass spectrometry.

^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta = 77.4$ (br. s, 4H), 63.6 (br. s, 4H), 41.8 (br. s, 2H), 32.2 (br. s, 8H), 2.3 ppm (br. s, 24H); HRMS: calcd for $C_{34}H_{42}N_4FeI$: *m/z* 689.1804, found: 689.1807.

The material was redissolved in dichloromethane, layered with *n*-hexane and kept at −20 °C for crystallization. Single crystals of **4** formed in small amounts and were used for the X-ray diffraction study. CCDC-680549 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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