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Synthesis and Characterization of Iron N-Confused Porphyrins: Structural Evidences of Agostic Interaction

Wan-Chin Chen and Chen-Hsiung Hung*

Department of Chemistry, National Changhua University of Education, Changhua 50058 Taiwan

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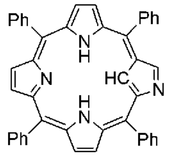
Agostic bonds are of interest in organometallic chemistry since they often lead to C−H activation.[1] The η^2 C−H interaction increases the acidity of the agostically bound proton so that deprotonation with a base frequently results.[2] Interestingly, the agostic bond was not widely considered as a possible intermediate in enzymatic hydrocarbon oxygenations until Collman and coworkers[3] recently demonstrated the inhibition of cyclohexane hydroxylation by H_2 or CH_4 in P-450 model complexes, and they suggested an agostic alternative to the P-450 rebound mechanism. Inspired by recent reports, we are aware of the intriguing tetraphenyl N-confused porphyrin (NCTPP, **1**), which has an inner core C−H bond from the inverted pyrrole ring. To understand the bonding interaction between a metal center and an inner core C−H, we have prepared and structurally characterized novel iron NCTPP complexes.



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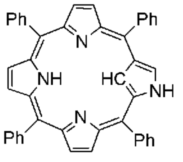

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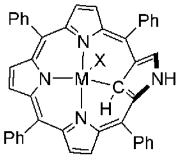

3: M = Fe, X = Br
4: M = Fe, X = SC_7H_7

The synthesis of NCTPP was first reported independently by the groups of Latos−Grazynski[4] and Furuta.[5] The optimization study performed by the Lindsey group[6] increased the yield to about 35%. NCTPP can exist in various tautomeric forms.[7] Theoretical calculations suggest that prearrangement with one inner hydrogen shifting to the outer peripheral nitrogen to give **2** is energetically feasible.[8] Most NCTPP complexes adopt a porphyrin type, four-coordinated planar core geometry, with a metal−carbon bond of about 2.0 Å.[9] The nonplanar geometry[10] with the inverted pyrrole tilted away from the porphyrin plane has been structurally characterized from the methylation of planar NCTPPNi(II) at the inner carbon of the inverted pyrrole. In addition, the NMR spectra of NCTPPCuCl and NCTPPZnCl suggest a tilted porphyrin core.[11]

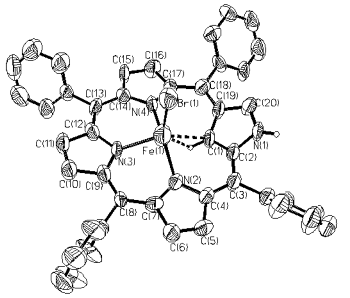

Figure 1. Molecular structure of Fe(NCTPP)Br (**3**). Important bond lengths (Å) and angles (deg): Fe(1)−C(1), 2.361(10); Fe(1)−N(2), 2.140(8); Fe(1)−N(3), 2.024(8); Fe(1)−N(4), 2.125(9); C(1)−C(2), 1.399(15); C(2)−N(1), 1.387(14); N(3)−Fe(1)−C(1), 143.3(4); N(3)−Fe(1)−Br(1), 107.0(3).

The anaerobic reaction of NCTPP and 5 equiv of $FeBr_2$ in a mixture of CH_3CN/THF and a few drops of lutidine gives an olive green solution. Heating at 65 °C for 2 h, followed by concentration and filtration affords green Fe^{II}(NCTPP)Br (yield 85%).[12] The absorption spectrum recorded in CH_2Cl_2 shows a Soret band and a broad Q-band at 461 and 744 nm, respectively. These spectral features resemble those of (2-NH-21CH_3CTPP)Ni^{II}Cl,[10] but are in marked contrast to those of the planar Ag^{III}(NCTPP) complex,[9] where the Soret band is observed at 447 nm and the Q-band appears with four peaks at 520, 554, 588, and 637 nm. The room-temperature effective magnetic moment obtained by Evan's method[13] in $CDCl_3$ gives $\mu_{\mathrm{eff}} = 4.85\ \mu_{\mathrm{B}}$. The value is close to the spin-only value ($\mu_{\mathrm{eff}} = 4.90\ \mu_{\mathrm{B}}$) for a high spin d^6 Fe(II) center with four unpaired electrons. Preliminary results show that Fe^{II}(NCTPP)Br can be oxidized to Fe^{III}(NCTPP)Br under aerobic conditions. The Soret band of the oxidized product blue shifts to give a split Soret at 348 and 414 nm, while the Q-band shifts to 564 and 882 nm.

X-ray single-crystal analysis gives direct information about the solid state conformation of Fe^{II}(NCTPP)Br (Figure 1). The relatively short distances of 1.399(15) and 1.391(14) for C(1)−C(2) and C(1)−C(19), respectively, show that an sp^2 hydridized geometry for C(1) is likely. In addition, the bond distances in the porphyrin core agree with the theoretical values for a prearranged tautomer form of NCTPP with a peripheral N−H and an inner core C−H.[8] The inverted pyrrole ring sharply bends

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* To whom correspondence should be addressed.

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[12] Fe(NCTPP)Br: absorption spectrum (CH_2Cl_2) [$\lambda_{\max}$, nm (log ϵ M^{-1} cm^{-1})]; 346(4.62), 461(5.00), 744(4.27). Anal. Calcd for $C_{44}H_{29}N_4BrFe\cdot 0.8CH_2Cl_2$: N, 6.85; C, 65.56; H, 3.77. Found: N, 6.73; C, 65.89; H, 3.70. $FeBrN_4C_{44}H_{29}$ Calcd mass 749, obsd 668 (M−H−Br, FAB). Crystallographic data for **3**: $C_{45}H_{31}BrCl_2FeN_4$, $T = 293$ K, MW = 834.40, monoclinic, space group $C2/c$, $a = 21.466(7)$, $b = 20.877$ (7), $c = 19.249$ (6) Å, $\beta = 114.897(4)°$, $V = 7843(4)$ Å^3, Z = 8, $D_c = 1.413$ Mg/m^{-3}, $\lambda = 0.71073$ Å, $\mu = 1.577$ mm^{-1}, $F(000) = 3392$. Data were collected on a Bruker Smart 1000 diffractometer for $1.43 < \theta < 20.82°$. The structure was solved by direct methods and refined by least-squares against F^2 to $R1 = 0.0744$ (w$R2 = 0.1002$) and $S_{\mathrm{goof}} = 0.843$.

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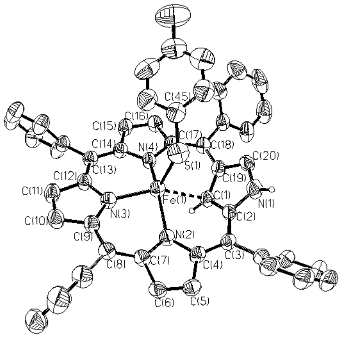

Figure 2. Molecular structure of Fe(NCTPP)(S−C_7H_7)(**4**). Important bond lengths (Å) and angles (deg): Fe(1)−C(1), 2.398(3); Fe(1)−N(2), 2.127(2); Fe(1)−N(3), 2.046(2); Fe(1)−N(4), 2.133(2); C(1)−C(2), 1.387(4); C(2)−N(1), 1.393(3); N(3)−Fe(1)−C(1), 142.85(10); N(3)−Fe(1)−S(1), 118.61(7).

from the porphyrin plane defined by N(2)N(3)N(4). The average Fe−N bond distance of 2.096(8) Å is within the limits (2.072(6)−2.096(4) Å) of high spin five coordinate iron(II) porphyrin complexes reported by Scheidt and Reed.[14] The Fe(1)···C(1) distance of 2.361 Å is much longer than the normal Fe−C bond distances found in the literature.[15] Meanwhile, the distance from Fe(1) to the inner core hydrogen is only 1.971 Å. As is found for five-coordinate iron porphyrins, the three regular pyrroles are slightly distorted, with mean deviation of 0.099 Å from the plane defined by 19 atoms on pyrrole rings and methine carbons. The iron atom sits 0.50 Å above the mean plane.

Subsequent reaction of complex **3** with sodium 4-methylbenzenethiolate under anaerobic condition gives Fe^{II}(NCTPP)(S−C_7H_7) (**4**, 78% yield).[16] The absorption spectrum of the thiolate complex mimics that of Fe^{II}(NCTPP)Br and suggests that the conformation and tautomer forms of **3** and **4** are alike. However, the solution magnetic moment obtained by Evan's method in $CDCl_3$ gives $\mu_{eff} = 2.77\ \mu_B$ and suggests an intermediate spin Fe(II) center.

The crystals of **4** were obtained from slow diffusion of hexanes into a THF/CH_2Cl_2 solution of **4**, Figure 2. The high quality data refine to give a solution with an *R* factor of 0.046, which allows for the direct assignment of hydrogens on the porphyrin core from the differential maps of electron density. Consequently, the peripheral N−H and the inner core C−H in **4** are assigned unambiguously. The overall structure demonstrates a nonplanar geometry with an inverted pyrrole ring tilted away from the porphyrin plane, as in **3**. In addition to the relatively short bond distances of C(1)−C(2) (1.387(4) Å) and C(1)−C(19) (1.408(4) Å), the bond angles of 106.2 (2)° for N(1)−C(2)−C(1) and 109.3(3)° for C(2)−N(1)−C(20) are consistent with the tautomer forms in **2** and **3**.[17] The thiolate ligand occupies the equatorial position with an Fe(1)−S(1)−C(45) angle of 106.33(11)°. The mean Fe−N distance of 2.102 Å in **4** is comparable to that of **3**, while the Fe(1)−C(1) distance of 2.398(3) Å is slightly longer than the 2.361(10) Å found in **3**.

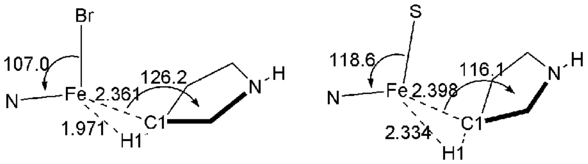

Figure 3. Important distances (Å) and angles (deg) around the iron coordination sphere in **3** (left) and **4** (right).

The comparisons of the iron coordination spheres (Figure 3) reveal significant structural differences between **3** and **4**. The Fe···C(1) distances are comparable in **3** and **4**. However, the Fe···H(1) distance of 1.971 Å in **3** is much shorter than the 2.334 Å found in **4**. Apparently, the flexible inverted pyrrole ring plays a role in attenuation of the Fe···H(1) distances. This point of view is supported by the much more acute angle between the inverted pyrrole ring and Fe in **4** (116.1°) than in **3** (126.2°). Moreover, the distance of 4.091 Å between Fe and peripheral nitrogen in **3** is longer than the 3.924 Å corresponding distance in **4**. Importantly, the solid-state geometry of C(1)−H(1)···Fe in **3** is within the bond distances of an agostic interaction between iron and pyrrolic C(1)−H(1) bond.[18] It is likely that the axial ligand may play a role in attenuating the strength of the agostic interaction. In our case, the reduced Lewis bascity of bromide creates a relatively electron-deficient iron center in **3** and results in the stronger three-center two-electron C(1)−H(1)···Fe interaction. Although it may not be as significant as the electronic effect, the solid-state packing would be another factor that can cause the interactions.[19] Noticeably, the larger angle of 118.6° for S(1)−Fe(1)−N(3) indicates that the axial ligand leans more toward the inverted pyrrole ring in **4**, which gives a more tetrahedral-like metal center in **4** rather than square-pyramidal, as found in five-coordinated iron porphyrin complexes. The much shorter distances of the Fe−N bonds trans to the inverted pyrrole rings in both **3** and **4** suggest stronger electron-donating ability of these pyrrolic nitrogens to the relatively electron deficient iron centers and further support the agostic interactions between metal and inner core C−H bond.[2]

The paramagnetism of both compounds makes quantitative measurement of the agostic interaction by NMR problematic. We are currently exploring the preparation of a nonplanar diamagnetic NCTPP complex for the direct observation of the potential agostic interaction. The studies on understanding the C−H activation during the formation of planar N-confused porphyrin metal complexes are also in progress.

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Supporting Information Available: Synthetic procedures and spectral data for **3** and **4**; X-ray crystallographic files of **3** and **4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Theorotical calculation in ref 8 shows that angles of N(1)−C(2)−C(1) and C(2)−N(1)−C(20) for **1** are 109.30 and 105.78°; meanwhile, the corresponding angles for **2** are 106.14 and 109.89°.

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