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Metal Oxidation Promoted C–H Activation in Manganese Complexes of N-Confused Porphyrin

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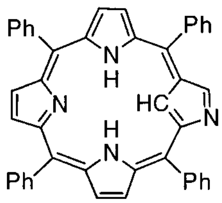
The N-confused porphyrin complex Mn^{II}(NCHPP)Br exhibits a nonplanar porphyrin ring with an inner core C–H on the inverted pyrrole ring. The aerobic metal oxidation promotes the dissociation of an inner-core proton on the inverted pyrrole ring and changes the N-confused porphyrin conformation to a planar porphyrin ring to form Mn^{III}(NCPP)Br. The conjugate systems and metal oxidation states are confirmed by crystal structures as well as spectroscopic data. The reverse reaction can be achieved by treating the Mn^{III}(NCPP)Br with *p*-toluenesulfonhydrazide.



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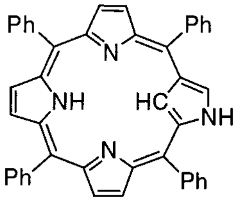

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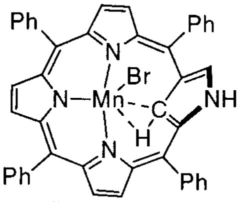
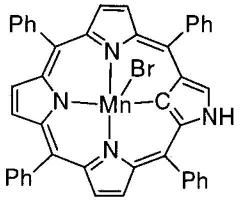


Mn^{II}(NCHPP)Br, 3



Mn^{III}(NCPP)Br, 4

N-Confused porphyrin (NCP), first isolated in 1994 independently by Furuta[1] and Latos-Grazynski,[2] has an inverted pyrrole ring jointed to the porphyrinic conjugated system with a β-carbon. A recent review[3] by Latos-Grazynski demonstrated that N-confused porphyrin exhibits unusual physical properties as well as coordination chemistry. According to the theoretical calculations,[4] N-confused porphyrin can exist in different tautomeric forms. The free base NCP adopts the most stable tautomeric form, **1**, with an inner C−H and two trans-positioned inner core NHs in CH_2Cl_2. There was not much information available for the alternations between different tautomeric forms until recently Furuta and co-workers[5] observed through NMR spectroscopy in DMF that NCP adopts the tautomeric form **2**. This is also the case in the solid-state structure as well.[5] In terms of the metal complexes, the Ag(III) complex[6] of NCP adopts tautomeric form **1** with a 3− charged deprotonated NCP ring system. Other N-confused porphyrin complexes[7] adopt the higher energy tautomeric form **2** with one peripheral N−H and a 2− charged NCP core. Interestingly, there is still little discussion on the processes of the C−H activation during metalation in both tautomeric forms.

C−H activation is one of the most topical research areas in chemistry. In addition to applications on catalysis, the biological systems rely on the C−H activation to carry out further enzymatic hydroxylation.[8] Several models have been proposed to elucidate the mechanism of enzymatic C−H activation.[9,10] The unusual porphyrin core geometry of N-confused porphyrin with an inner core carbon atom makes it an ideal compound for the study of C−H activation within a large conjugated ring system. Recently, we have isolated two five-coordinated N-confused porphyrin iron complexes[11] which exhibit nonplanar NCP core geometry with a tilted inverted pyrrole ring. The relatively short distances between iron and inner core C−H suggest that an agostic interaction

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(1) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767.

(2) Chmielewski, P. J.; Latos-Grazynski, L.; Rachlewiwicz, K.; Glowiak, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779.

(3) Latos-Grazynski, L. In *Core Modified Heteroanalogues of Porphyrins*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 2.

(4) Ghosh, A.; Wondimagegn, T.; Nilsen, H. J. *J. Phys. Chem. B* **1998**, *102*, 10459.

(5) Furuta, H.; Ishizuka, T.; Osuka, A.; Dejima, H.; Nakagawa, H.; Ishikawa, Y. *J. Am. Chem. Soc.* **2001**, *123*, 6207.

(6) Furuta, H.; Ogawa, T.; Uwatoko, Y.; Araki, K. *Inorg. Chem.* **1999**, *38*, 2676.

(7) Chmielewski, P. J.; Latos-Grazynski, L.; Glowiak, T. *J. Am. Chem. Soc.* **1996**, *118*, 5690.

(8) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411.

(9) Basch, H.; Musaev, D. G.; Mogi, K.; Morokuma, K. *J. Phys. Chem. A* **2001**, *105*, 3615.

(10) Collman, J. P.; Chien, A. S.; Eberspacher, T. A.; Brauman, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 425.

(11) Chen, W.-C.; Hung, C.-H. *Inorg. Chem.* **2001**, *40*, 5070.

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between the iron and inverted pyrrolic C−H bond is likely. The axial ligand dependent core geometries are controlled by the basicity of ligands consistent with having an agostic interaction.[12] Still, little information is available for the mechanism of conformational change from a nonplanar NCP core to a planar NCP geometry in NCP metal complexes. In this paper we report that in the Mn(II) oxidation state, the NCP adopted the tilted geometry similar to the iron complexes; however, the inverted pyrrolic C−H bond can be activated when Mn(II) is oxidized to Mn(III) to form a planar NCP manganese complex.

When the free base NCP was treated with $MnBr_2$ in the mixed solvent of 2:1 CH_3CN/THF in the presence of a few drops of lutidine under anaerobic conditions, Mn^{II}(NCHPP)Br (**3**)[13] was isolated in 82% yield. The electronic spectrum of **3** in CH_2Cl_2 gives a Soret type absorption band at 462 nm while the Q bands are located at 715 and 782 nm. The pattern of the electronic spectrum is distinct from the free base NCP but resembles other nonplanar N-confused porphyrin complexes such as methylated (NCP)Ni[7] and Fe(NCP)Br.[11] The similar electronic spectra suggest that these compounds exhibit identical ring conformations. Mn^{II}(NCHPP)Br has a magnetic moment of 5.50 μ_B at room temperature from the SQUID magnetic susceptibility measurement. The plot of $1/\chi$ vs T is linear between 5 and 300 K. The room temperature magnetic moment suggested a high-spin Mn(II) ($s = {}^5/_2$) state in **3**. The ESR spectrum of the Mn^{II}(NCHPP)Br in toluene glass at 6.8 K gives an $s = {}^5/_2$ Mn(II) type high-spin axial spectrum with $g_\perp$ at 5.65 and $g_\parallel$ at 2.01.

X-ray single-crystal analysis confirms the solid-state conformation of Mn^{II}(NCHPP)Br. As shown in Figure 1, the N-confused porphyrin ring adopts a nonplanar geometry with inverted pyrrole ring tilted away from the mean plane defined by the tripyrrole unit. The comparison of the bond distances and bond angles in the porphyrin ring with the theoretical values[14] agrees that the porphyrin core in the Mn^{II}(NCHPP)Br adopts the higher energy resonance form as in **2**. The distance of 2.437(7) Å between Mn and inner core carbon in the inverted pyrrolic ring is much longer than the normal Mn−C bond.[15] The Mn atom sits 0.77 Å atop the mean porphyrin plane, resembling other five-coordinated porphyrin complexes. Finally, the Mn−Br bond distance of 2.491 Å is almost identical to 2.490 Å in the five-coordinated Mn(TPP)Br.[16]

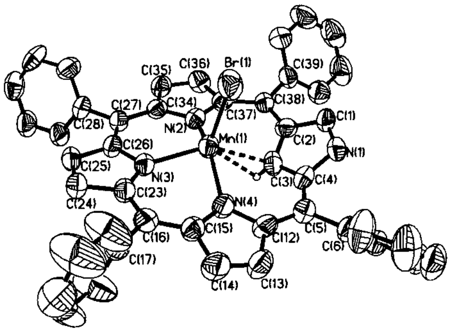

Figure 1. Molecular structure of Mn^{II}(NCHPP)Br (**3**). Important bond lengths (Å) and angles (deg): Mn(1)−C(3) 2.437(7); Mn(1)−N(2) 2.164(5); Mn(1)−N(3) 2.085(4); Mn(1)−N(4) 2.151(5); C(3)−C(4) 1.383(9); C(4)−N(1) 1.377(7); N(3)−Mn(1)−C(3) 140.9(2); N(3)−Mn(1)−Br(1) 115.58(13).

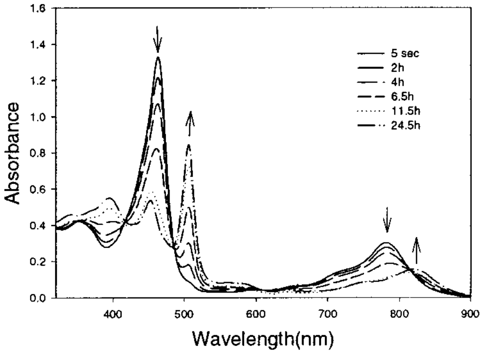

Figure 2. The time trace of absorption spectra for the oxidation reaction of Mn^{II}(NCHPP)Br in the presence of O_2.

Mn^{II}(NCHPP)Br is stable in the solid state as well as in solution under anaerobic conditions. Interestingly, the electronic spectrum changed immediately when **3** was exposed to air. A time trace of the electronic spectra is shown in Figure 2. The intensity of the Soret band at 462 nm for Mn^{II}(NCHPP)Br decreases and is accompanied by an increase in a Soret type peak at 507 nm. The final product, after 24 h, gives the electronic spectrum with the Soret band at 507 nm and the Q band at 754 and 825 nm. The isolated product gives an effective magnetic moment of 4.87 μ_B at room temperature from SQUID and suggests a one-electron oxidation of the Mn^{II}(NCHPP)Br to give Mn^{III}(NCPP)Br (**4**).[17] **4** is stable in the solid state as well as in solution under aerobic conditions. No further variation was observed when the absorption spectra were traced under aerobic conditions for 72 h.

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(12) The distance between iron and inner core C−H hydrogen in Fe(NCTPP)Br is 1.971 Å while in Fe(NCTPP)(S−C_7H_7) the corresponding bond distance increases to 2.334 Å.

(13) Mn^{II}(NCHPP)Br: absorption spectrum (CH_2Cl_2) [λ_{max}, nm (log ϵ, M^{-1} cm^{-1})] 352 (4.69), 462 (5.14), 782 (4.41), 715 (4.06), 598 (3.54), 656 (3.7). Anal. Calcd for $C_{44}H_{29}N_4BrMn{\cdot}0.8CH_2Cl_2$: N, 6.86; C, 65.90; H, 3.78. Found: N, 6.74; C, 65.88; H, 4.04. $MnBrN_4C_{44}H_{29}$: calcd mass 748.582, obsd 667 (M − H − Br, FAB). Crystallographic data for **3**: $C_{45.50}H_{30}BrCl_3MnN_4$, $T = 295(2)$ K, MW = 875.93, monoclinic, space group $P2/c$, a =13.2250(11) Å, b = 13.8871(11) Å, c = 22.5276(18) Å, $\alpha = 90°$, $\beta = 92.651(2)°$, $\gamma = 90°$, $V = 4132.9(6)$ Å^3, $Z = 4$, $D_c = 1.408$ Mg/m^{-3}, $\lambda = 0.71073$ Å, $\mu = 1.517$ mm^{-1}, $F(000) = 1776$. Data were collected on a Bruker Smart 1000 diffractometer for $1.54° < \theta < 27.57°$. The structure was solved by direct methods and refined by least-squares against F^2 to R1 = 0.0545 (wR2 = 0.1051) and $S_{GOF} = 1.136$.

(14) Szterenberg, L.; Latos-Grazynski, L. *Inorg. Chem.* **1997**, *36*, 6287.

(15) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 2117.

(16) Turner, P.; Gunter, M. J.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1998**, *51*, 835.

(17) Mn^{III}(NCPP)Br: absorption spectrum (CH_2Cl_2) [λ_{max}, nm (log ϵ, M^{-1} cm^{-1})] 340 (4.39), 394 (4.46), 454 (4.31), 507 (4.70), 583 (3.64), 754 (3.66), 825 (3.91). Anal. Calcd for $MnBrN_4C_{44}H_{28}{\cdot}0.5THF{\cdot}0.1CH_2Cl_2$: N, 7.07; C, 69.90; H, 4.10. Found: N, 7.27; C, 69.87; H, 4.26. $MnBrN_4C_{44}H_{28}$: calcd mass 747.574, obsd 667 (M − Br, FAB). Crystallographic data for **4**: $C_{44}H_{28}BrMnN_4$, $T = 293(2)$ K, MW = 747.55, monoclinic, space group $P2_1/n$, a = 10.2386(6) Å, b = 15.8204(9) Å, c = 20.9468(13) Å, $\alpha = 90°$, $\beta = 90.000(1)°$, $\gamma = 90°$, $V = 3392.9(3)$ Å^3, $Z = 4$, $D_c = 1.463$ Mg/m^{-3}, $\lambda = 0.71073$ Å, $\mu = 1.606$ mm^{-1}, $F(000) = 1520$. Data were collected on a Bruker Smart 1000 diffractometer for $1.61° < \theta < 27.54°$. The structure was solved by direct methods and refined by least-squares against F^2 to R1 = 0.0753 (wR2 = 0.1734) and $S_{GOF} = 0.732$.

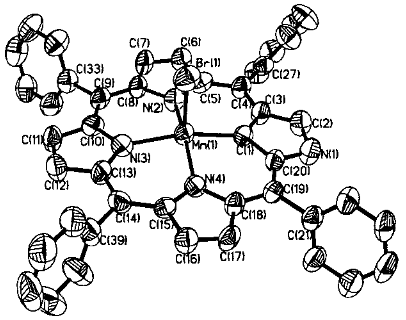
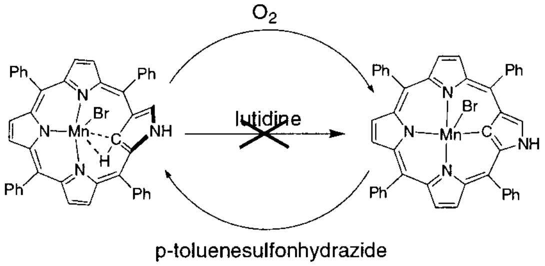


Figure 3. Molecular structure of Mn^{III}(NCPP)Br (**4**). Important bond lengths (Å) and angles (deg): Mn(1)−C(1) 2.020(6); Mn(1)−N(2) 2.026(5); Mn(1)−N(3) 2.049(5); Mn(1)−N(4) 2.044(5); C(1)−C(20) 1.390(8); C(20)−N(1) 1.403(7); N(3)−Mn(1)−C(1) 162.5(2); N(3)−Mn(1)−Br(1) 97.10(15).

The crystal structure of the oxidative product **4** (Figure 3) clearly demonstrates that the conformation of the N-confused porphyrin ring changes from a nonplanar geometry in the Mn^{II}(NCHPP)Br to a planar conformation in Mn^{III}(NCPP)Br. The comparable bond distances and bond angles around the porphyrin cores suggest that **3** and **4** are under the same resonance forms and the planar porphyrin ring with a short (2.020(6) Å) Mn−C bond in **4** is generated from the activation of the inner core C−H bond in **3**. The averaged Mn−N bond distance of 2.040 Å, which is shorter than the corresponding distance of 2.133 Å for Mn^{II}(NCHPP)Br, is consistent with a metal oxidation of Mn(II) to Mn(III). A possible mechanism of the conformation change would be that the aerobic oxidation of the Mn(II) metal center in the nonplanar N-confused porphyrin core gives a more electron deficient Mn(III) center and promotes a direct electrophilic addition[18] of Mn(II), acting as a Lewis acid, into an acidic C−H bond. Alternatively, metal oxidation would increase the acidity of the C−H bond through a stronger agostic interaction[19] and the electron pair on the carbon would coordinate to the metal center after the proton dissociation.

The reaction of Mn^{II}(NCHPP)Br with bases such as lutidine failed to deprotonate the inner core C−H on the inverted pyrrole ring consistent with a metal oxidation promoted C−H activation. To confirm the product as well as to establish a possible catalytic cycle, we have treated the oxidized Mn^{III}(NCPP)Br with reductants (Scheme 1). When Mn^{III}(NCPP)Br was treated with sodium borohydride in THF, the distinctive Soret band for Mn^{III} NCP at 507 nm disappeared accompanied by an increased Soret band at 457 nm. The fine structure of the Q band with λ_{max} at 722 nm, however, is distinctively different from Mn^{II}(NCHPP)-Br. The preliminary crystal structure demonstrates an elimination of bromide to give a Mn^{II} NCP product with a THF as axial ligand and a planar 2− charged NCP core. Interestingly, the *p*-toluenesulfonhydrazide reacts slowly with Mn^{III}(NCPP)Br to give the final product with an electronic spectrum identical to that of the Mn^{II}(NCHPP)Br.

Scheme 1



These studies for the first time shed light on the C−H activation processes of N-confused porphyrin complexes. They also suggest that N-confused porphyrin complexes have the potential of being used as catalysts, where there is a redox active metal coupled to a redox-tautomeric chelating ligand. The detailed mechanisms and ligand effect of the C−H activation in the systems of iron and manganese N-confused porphyrins are currently under intense study.

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Supporting Information Available: Experimental procedures, UV−vis, EPR, and SQUID data, and X-ray crystallographic data for**3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Taylor, R. *Electrophilic Aromatic Substitution*; John Wiley & Sons: New York, 1990; Chapter 5.

(19) Vigalok, A.; Uzan, O.; Shimon, L. J. W.; Ben-David, Y.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 12539.