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Dimeric and monomeric forms of manganese N-confused porphyrin

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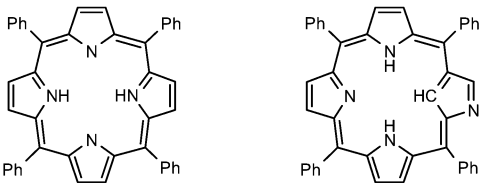
The synthesis and structural characterization of a manganese adduct of N-confused tetraphenylporphyrin (NCTPP) is presented; in the absence of coordinating ligands this complex forms a novel dimer structure and demonstrates a potential manganese agostic interaction with the interior pyrrolic CH as seen in other first row transition metal NCTPP compounds.

N-confused porphyrin, also known as inverted porphyrin or 2-aza-21 carbaporphyrin, is a biologically relevant ligand of increasing interest to inorganic chemists.[1] Investigations continue into the metallation of this macrocycle since there is not yet a complete understanding of how transition and main group elements coordinate to the central pore of N-confused porphyrins. A number of factors can potentially affect coordination, including the tautomeric form of the macrocycle, the degree of planarity, and the acidity (or lack thereof) of the internal pyrrolic carbon.[2] To date, at least seven binding modes of N-confused porphyrin have been reported, and more are theorized to exist. Recent reports have examined metallation of this macrocycle with the transition metals iron, zinc, copper, and nickel.[3] We decided to investigate the metallation of 5,10,15,20 tetraphenyl-N-confused porphyrin freebase (H_2NCTPP, Fig. 1) with manganese to further probe the structures of first row transition metal complexes of this porphyrin isomer. As in iron and zinc N-confused porphyrins, the internal carbon is not deprotonated and the confused pyrrole ring is tilted away from the metal. In addition, we have structurally characterized a new coordination mode for N-confused porphyrin that was recently suggested to exist by Furuta in his characterization of the zinc complexes of this macrocycle. In this report, we present the metallation of N-confused porphyrin with manganese and the structures of both the dimeric form and pyridine complex.

We prepared H_2NCTPP freebase by using an improved synthesis described by Lindsey and coworkers, which can be employed to generate gram scale quantities of the macrocycle.[4] Freebase NCTPP can be readily metallated with manganese by using the metal carbonyl method.[5] Under strict anaerobic conditions, a solution of H_2NCTPP (260 mg, 0.42 mmol) in toluene (20 mL) was refluxed in the presence of a slight manganese mole excess of $Mn_2(CO)_{10}$ (86 mg, 0.22 mmol). The color of the solution changed to bright green soon after heating and the reaction was completed within four hours. The UV-visible spectrum of the initial metallation product, species **1**, in this reaction is shown in Fig. 2. Species **1** has a distinctly different spectrum from that of the freebase precursor. The Soret band at 413 nm is broad and has a low extinction coefficient of 5.16 × 10^4 M^{-1} cm^{-1}. In addition, a Q band at 683 nm with a shoulder at 625 nm is observed. Positive ion electrospray MS of a THF/$CHCl_3$ solution of this product showed the presence of Mn(NCTPP) as the initial product of this reaction. This Mn(NCTPP) species is extremely air sensitive, rapidly demetallating to the freebase upon exposure to atmospheric dioxygen. A green product was isolated upon recrystallization from toluene/heptane in 73% yield.



H_2TPP (A)

H_2NCTPP (B)

Fig. 1 The structures of freebase tetraphenylporphyrin (H_2TPP, A) and the internally protonated freebase N-confused tetraphenylporphyrin (H_2NCTPP, B).

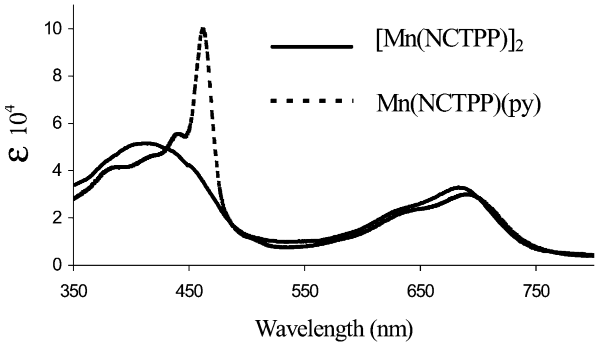


Fig. 2 UV-visible spectrum in toluene of the initial metallation product $[Mn(NCTPP)]_2$ **1** (solid line) and Mn(NCTPP)(py) **2** (dashed line).

Crystals of **1** were isolated from hot toluene, and elucidation of the structure from single crystal X-ray diffraction revealed that this complex forms a dimer in the solid state.† Furuta proposed that such a structure exists for Zn(NCTPP) in non-coordinating environments, but only characterized this species by NMR. Other N-confused porphyrin dimers have been reported, but these involve organometallic bonds to the phenyl rings, as found in the Pd dimer, or bridging units, as observed in Furuta's Zn_4 complex.[6,3] As can be seen in Fig. 3, species **1** is a self-coordinated manganese N-confused porphyrin, where the external nitrogen of one macrocycle is ligated to the axial position in the second. The unit cell contains a dimer of dimer molecules. The proton on the interior carbon is still present, and the confused pyrrole ring is tilted away from the metal. The resultant deformation of the macrocycle ring is significant: the confused pyrroles are at an average angle of 44.0° from the plane of the three internal nitrogen atoms and four of the phenyl

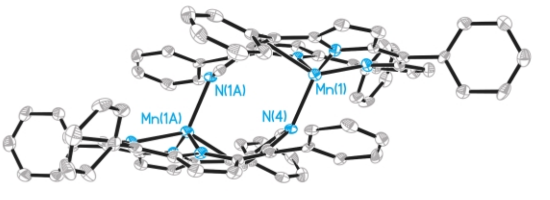


Fig. 3 The structure of $[Mn(NCTPP)]_2$ (**1**) with 50% thermal ellipsoids. Selected bond lengths (Å) for **1**: Mn(1)–C(17), 2.407(6); Mn(1)–N(1), 2.179(4); Mn(1)–N(2), 2.104(4); Mn(1)–N(3), 2.195(4); Mn(1)–N(4), 2.223(4). The same atom assignments are used as in Fig. 4 where they are clearly labelled. Hydrogen atoms have been omitted for clarity.

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rings per dimer are nearly coplanar (average angle 34.0°) with the porphine ring. Within the two dimers, the manganese atoms are an average of 5.06 Å apart and the porphine rings are 4.32 Å away from each other, using the planes of the inner pyrrolic nitrogens.

Upon exposure to pyridine, the spectrum of **1** changes significantly as shown in Fig. 2, indicating possible axial coordination. The soret band is twice as intense and red shifted from 413 nm to 462 nm. However, the Q bands show very little change exhibiting a band at 691 nm with a shoulder at 630 nm. Large single crystals of a pyridine adduct of manganese N-confused porphyrin were grown from pyridine/heptane and isolated in quantitative yield. The structure of the resulting complex was then elucidated by X-ray crystallography.

The structure of **2**, shown in Fig. 4, shows important similarities to the recently elucidated structures of the zinc and iron N-confused porphyrin derivatives.[3] As in these two compounds, the interior pyrrolic carbon is not deprotonated in the manganese derivative and it appears that this specific geometry is a general trend for many of the first row transition metal N-confused porphyrin structures. As a result, the confused pyrrole ring is tilted out of the plane of the macrocyle by an angle of 30.8° relative to the plane of the three interior nitrogens. This is similar to that found in the monomeric zinc complex, which has an angle of 29.2°. Alternatively, this tilt can be described by examining the angle of the Mn–C bond relative to the plane of the confused pyrrole ring; the angle in the Mn complex is 142° compared to 126° and 116° observed in the two iron complexes.

Based on the lack of anions in the structures, we can readily assign the oxidation state of the metal as the Mn(II) ion. Mn(I) ions are not typically observed in porphyrinic macrocycles, and the reduction of Mn(TPP) is more negative than −700 mV *vs.* SCE.[7] Thus, the exterior pyrrolic nitrogen is clearly deprotonated in **2**, as seen in Furuta's zinc complex. The manganese–pyrrolic nitrogen bond distances in **2** show identical trends to those observed in the previously reported monomeric iron and zinc N-confused porphyrin compounds.[3] In both **1** and **2**, the bond lengths to the nitrogens adjacent to the confused pyrrole ring are longer than the bond lengths to the opposite pyrrolic nitrogen. The decrease in distance to this nitrogen results in part from the steric interactions with the confused pyrrole ring. In addition, the distance between the manganese and the internal carbon is 2.407(6) Å and 2.357(5) Å for **1** and **2** respectively, which is once again in the range of that observed in iron and zinc N-confused porphyrins. The close proximity of the CH group to the manganese metal center in both complexes suggests the possibility of an agostic interaction;[8] however due to the paramagnetic nature of the Mn(II) ion we cannot directly probe this communication *via* ^{1}H NMR in either compound.

The environments about the metal centers in **1** and **2** are asymmetric 5-coordinate geometries including interactions from the confused pyrrolic carbon. As in normal 5-coordinate manganese porphyrins, the metal extends above the macrocycle, rising above the plane of the three internal nitrogens by 0.757 Å in **1** and 0.509 Å in **2**. The axial pyridine in **2** was found to be disordered with two primary orientations. One orientation of the axial pyridine is roughly orthogonal to the plane of the macrocycle, while the second is tilted slightly toward the meso carbon directly adjacent to the external nitrogen of the confused pyrrole. The angle of this tilted pyridine ring is at 108° to the plane of the three internal nitrogens. Similar differences in tilting angles are observed between the two isolated iron N-confused porphyrin structures presented by Hung and co-workers.[3]

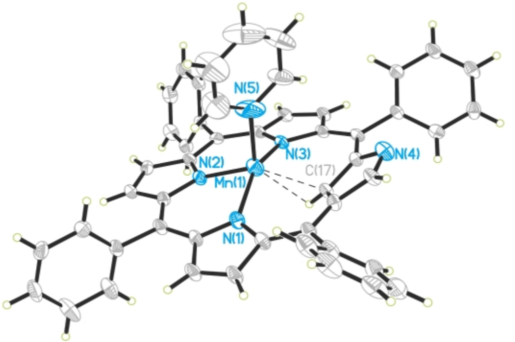

Fig. 4 The structure of Mn(NCTPP)(py) (**2**) with 50% thermal ellipsoids. For clarity, only the orthogonal orientation of the disordered pyridine is shown. Selected bond lengths (Å) for **2**: Mn(1)–C(17), 2.357(5); Mn(1)–N(1), 2.169(4); Mn(1)–N(2), 2.091(4); Mn(1)–N(3), 2.154(4); Mn(1)–N(5), 2.190(8).

The transition metal chemistry of N-confused porphyrin is of continued interest, and progress in this field is accumulating rapidly. In the absence of coordinating ligands, manganese N-confused porphyrins form a dimeric structure. As shown above, we have found that the manganese complexes of this novel macrocycle demonstrate many of the same structural characteristics observed in the iron and zinc derivatives. Our future work will probe the chemistry of both of these manganese derivatives. At present, we are continuing our characterization of this complex, including investigating by spectroscopy such as EPR.[9,10]

Notes and references

† *Crystallographic summary* for **1**: data were collected at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system. $Mn_2C_{91.5}H_{60}N_4$ **1**: M = 1381.54, green plate 0.2 × 0.2 × 0.02 mm, triclinic, space group $P1$, $Z = 2$ in a cell of dimensions a = 9.477(2), b = 15.165(4), c = 22.935(5) Å, a = 100.162(5), β = 94.140(4), γ = 95.555(4)°, V = 3215.8(13) Å^3, D_c = 1.433 Mg m^{-3}, μ(Mo-Kα) = 0.454 mm^{-1}, $F(000)$ = 1436, final R indices on 12452 independent reflections [$I > 2\sigma(I)$]: R_1 = 0.0716, wR_2 = 0.1764.

Crystallographic summary for **2**: data were collected at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system. $MnC_{48.5}H_{38.5}N_{6.5}$ **2**: M = 767.30, green-black plate 0.2 × 0.2 × 0.04 mm, triclinic, space group $P1$, $Z = 2$ in a cell of dimensions a = 12.931(3), b = 13.497(3), c = 14.928(3) Å, α = 73.783(3), β = 69.248(3), γ = 66.975(3)°, V = 2212.1(8) Å^3, D_c = 1.152 Mg m^{-3}, μ(Mo-Kα) = 0.337 mm^{-1}, $F(000)$ = 800, final R indices on 7755 independent reflections [$I > 2\sigma(I)$]: R_1 = 0.0822, wR_2 = 0.2265.

CCDC reference numbers 188828 and 186796. See http://www.rsc.org/suppdata/cc/b2/b205345d/ for crystallographic data in .cif or other electronic format.

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