The synthesis of isostructural Mo²⁺ porphyrin and *N*-confused porphyrin complexes

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We have synthesized the first early transition metal *N*-confused porphyrin complex Mo(NCTPP)(pip)₂; this species is isostructural to its normal porphyrin analog Mo(TPP)(pip)₂ but exhibits significant electronic differences arising from the inversion of a single pyrrolic group.

Porphyrins and related complexes continue to be active foci of research owing to their biological relevance and their applications to materials such as catalysts and photonic arrays.[1] The porphyrin isomer *N*-confused porphyrin[2] (NCP) has been vigorously explored since the synthesis presented by Geier *et al.* allowed for the high yield production of this macrocycle.[3] NCP differs structurally from normal porphyrin in that it has a confused, or inverted, pyrrole ring which results in the placement of a nitrogen atom on the periphery of the ring and a carbon atom at an interior position. It has been shown that NCP often forms new, unique binding modes not observed in normal porphyrin due to the presence of this external nitrogen.[4] This structural change in NCP also leads to interesting properties not observed in normal porphyrin, such as tautomerization and abrogated aromaticity.[5] However, exploring the electronics of NCP metal complexes in relation to normal porphyrin metal complexes has been difficult due to the above structural differences. In this paper, we present the metallation of 5,10,15,20-tetraphenyl-*N*-confused porphyrin (H₂NCTPP) with a group VI metal using the activated molybdenum carbonyl *cis*-Mo(NHC₅H₁₀)₂(CO)₄ and its analagous porphyrin complex. The piperidine carbonyl reagent[6] allows the reactions to be performed in lower boiling solvents, such as toluene. In addition, unlike other reactions of NCP with metal carbonyls, the resulting Mo-TPP and Mo-NCTPP complexes are isostructural. This feature allows for an unusual look into the factors governing the electronics of NCP–metal complexes.

In our previous work, we have chosen to explore the use of metal carbonyl starting compounds in the metallation of NCP.[7] Carbonyl-based starting materials are very common in the realm of organometallic chemistry, and they were first used in porphyrin metallations by Buchler.[8] The strictly carbonyl-based methods are useful because they do not introduce additional coordinating species during the synthetic protocol. The use of transition metal carbonyls in the synthesis of metallated NCPs has been relatively limited (Fig. 1). Examples in the literature include the use of

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[Rh(CO)₂Cl]₂ for the synthesis of a bis-Rh(I) NCP complex, Mn₂(CO)₁₀ for the synthesis of the dimer [Mn(NCTPP)]₂, and of Re₂(CO)₁₀ leading to the formation of a *N*-fused tetraphenylporphyrin variant Re(NFTPP)(CO)₃.[7,9] In the case of [Mn(NCTPP)]₂ the lack of coordinating anions was essential to the isolation of the dimer complex which was shown to break apart in coordinating solvents such as pyridine. Comparing the above metallations with their normal porphyrin counterparts provides evidence of the structural differences that often result in the metallation of porphyrin analogs and isomers. Reactions of [Rh(CO)₂Cl]₂ or Re₂(CO)₁₀ with TPP generates a porphyrin with two metals bound to the interior, while the reaction of Mn₂(CO)₁₀ with TPP places the metal in the macrocycle in a square planar configuration. The differences in reactivity of the porphyrinoids result from the presence of a nitrogen at the periphery, and the lack of acidity of the internal C–H group.[10] The structural diversity observed in metallo-*N*-confused porphyrins often makes direct comparisons to their normal porphyrin analogs difficult.[7,11]

We are currently investigating the early transition metal chemistry of *N*-confused porphyrin, which remains largely unexplored. We examined the molybdenum chemistry *via* the reaction of an equimolar ratio of *cis*-Mo(NHC₅H₁₀)₂(CO)₄ with H₂NCTPP in refluxing toluene under anaerobic conditions. After three hours, the solution changes in colour from brown to green, and affords the species Mo(NCTPP)(pip)₂ (**1**). The absorption spectrum of this compound has a blue shifted Soret band at 420.5 nm with a shoulder at 481 nm and a Q band at 686 nm with a shoulder at 633 nm (Fig. 2). Upon cooling of the reaction solution, large single crystals form in the reaction flask. The structure of the product was elucidated by single crystal X-ray diffraction.† As seen in Fig. 3, the Mo atom lies in the core of the
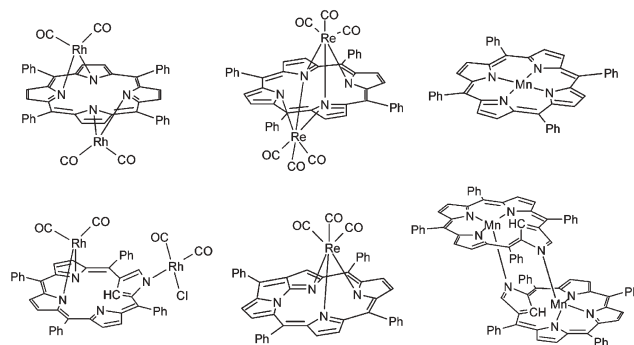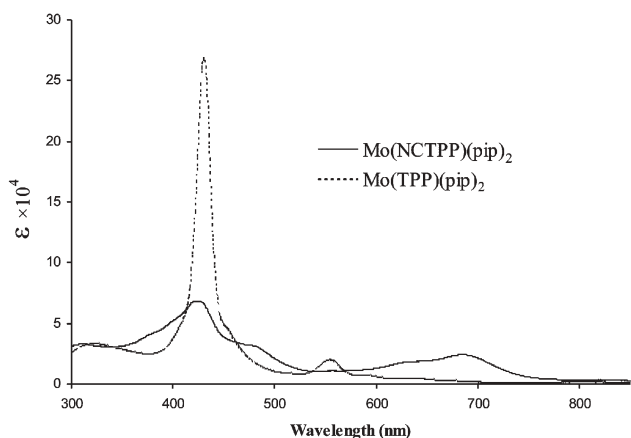

Fig. 1 Top: structures of metalloporphyrins using the carbonyl metallating reagents [Rh(CO)₂Cl]₂ (left), Re₂(CO)₁₀ (middle) and Mn₂(CO)₁₀ (right); bottom: structures of the *N*-confused porphyrin compounds using identical reaction conditions.

Fig. 2 Absorption spectra of MoNCTPP(pip)$_2$ **1** (—) and MoTPP(pip)$_2$ **2** (---). Both complexes were measured at 1.40×10^{-5} M in toluene.

porphyrin with two axial piperidines. The internal carbon atom is deprotonated and is coordinating the metal center in a manner similar to that observed in nickel and cobalt complexes of NCP.[2,7]

An identical reaction carried out with H$_2$TPP results in a colour change from reddish brown to dark brown and affords Mo(TPP)(pip)$_2$ (**2**). In the absorption spectrum, the Soret band red shifts to 429 nm, with a primary Q band appearing at 554 nm (Fig. 2). Crystallization also occurs upon cooling of the reaction mixture, and the structure can be elucidated by single crystal X-ray diffraction.† The normal porphyrin complex (Fig. 3) is structurally identical to that observed in compound **1**, with the exception of the pyrrolic inversion. All of the bond angles and lengths for the two complexes are within experimental error of each other with the largest deviation being the Mo–N(3) bond length to the axial piperidine molecule (**1**: 2.248(2) Å and **2**: 2.2620(17) Å). Since no other anions are present in either structure and upon inspection of the axial bond lengths, we can assign the metal oxidation state as +2. The axial Mo–N bond lengths are also similar to the lengths found in the molybdenum porphyrin pyridine complex (2.216 Å).[12]

While the two porphyrinoid complexes are structurally similar, the UV-visible spectra exhibit significant differences. First, the relative magnitude of the extinction coefficients of the Soret band and the Q bands is much larger in normal porphyrin than in

N-confused porphyrin. In normal porphyrin, the symmetry results in pseudoparity forbidden Q band transitions resulting from alternancy symmetry. In addition, the Soret band is enhanced in normal porphyrins because the transition dipoles reinforce, resulting in a larger oscillator strength. In *N*-confused porphyrin, the symmetry is broken and the effect of alternancy symmetry is significantly less, resulting in a ratio of Soret to Q band closer to unity. The second significant change to the spectrum upon inversion of a pyrrole ring is the red shift of the Q band absorption. This change results from the reduced HOMO–LUMO gap in *N*-confused porphyrin relative to normal porphyrin. In NCPs, the HOMO and HOMO-1 orbitals are destabilized and inverted, and combined with the lack of degeneracy in the LUMO and LUMO-1 orbitals, the transition energy is significantly lowered relative to normal porphyrin.[13] Interestingly, an opposite trend is observed in the shift of the Soret band *versus* the free base upon metallation. This indicates that the hypso/hyper classification of Gouterman does not readily apply to NCP metal complexes.[14]

The changes to the porphyrin electronic structure have a significant effect on the energy level of the d orbitals in transition metal NCP complexes. We recently presented a report on the high field EPR of Mn(NCTPP)(py)$_2$,[15] which exhibits a highly rhombic zfs in contrast to the axial systems found in normal porphyrins. It appears that the Mo complexes in this report are similarly affected; the magnetic susceptibility differs significantly between compounds **1** and **2**. For **2**, magnetic measurements showed a $\mu_{eff} = 2.79$, corresponding to a spin state of $S = 1$. This is similar to the $\mu_{eff} = 2.83$ for the Mo(TTP)(py)$_2$ complex, with a $S = 1$ state and also similar to the Mn(NCTPP)(py)$_2$ complex value with $\mu_{eff} = 2.83$.[7,12] However, **1** exhibits a magnetic susceptibility of $\mu_{eff} = 1.68$, much lower than **2**, Mo(TTP)py$_2$, and Mn(NCTPP)py$_2$.[7,12] Thus, the switching of two atoms in the porphyrin backbone has a demonstrable effect on the metal d orbital energy levels. This decrease in paramagnetism was also observed in the ^{1}H NMR spectra. In **1**, the pyrrole and phenyl protons exhibited paramagnetic shifts, but were shifted far less than those observed in complex **2**.

In conclusion, we have synthesized the first early transition metal *N*-confused porphyrin complex Mo(NCTPP)(pip)$_2$. Unlike most *N*-confused porphyrin metal complexes, this species is
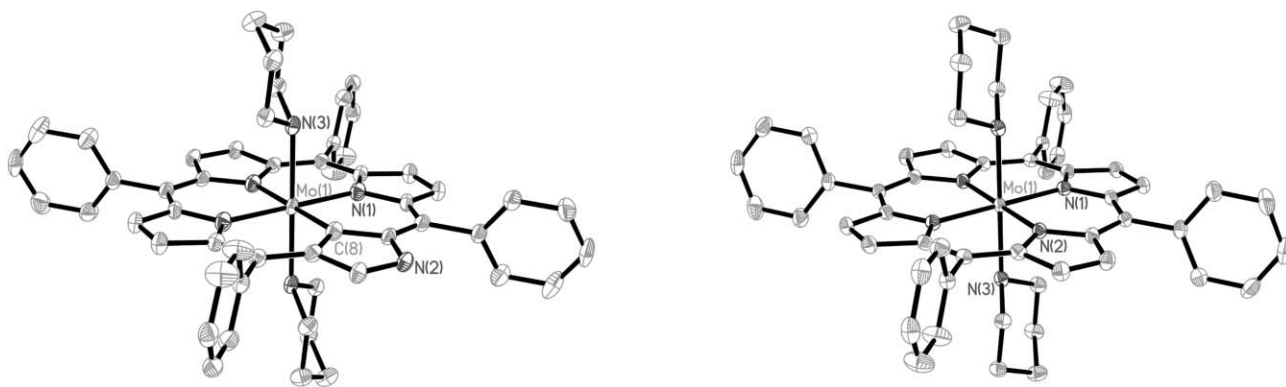

Fig. 3 Molecular structure of Mo(NCTPP)(pip)$_2$ (**1**, left) and Mo(TPP)(pip)$_2$ (**2**, right) with 50% thermal ellipsoids. Selected bond lengths (Å) for: **1**: Mo–N(1) 2.071(2), Mo–C(8) 2.0814(19), Mo–N(3) 2.248(2); **2**: Mo–N(1) 2.0726(16), Mo–N(2) 2.0826(16), Mo–N(3) 2.2620(17). Due to disorder of the nitrogen atom at the confused pyrrole ring and high symmetry of the crystal, one of eight possible orientations is shown for **1**.

isostructural to its normal porphyrin analog, $Mo(TPP)(pip)_2$ and allows for investigation of the electronic changes induced by inversion of a single pyrrolic ring. Changes can be readily observed in the π system *via* UV-visible spectroscopy, and in the metal d orbitals *via* magnetic susceptibility. We are continuing this work and will investigate the EPR spectroscopy of these compounds, which have the same d electron counts as our recently reported $Mn(NCTPP)(py)_2$ species.[15]

Notes and references

† Crystallographic summary for **1**: data was collected at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system. $MoC_{61}H_{58}N_6$ **1**; $M = 971.07$, black plate $0.20 \times 0.10 \times 0.03$ mm, triclinic, space group P-1, $Z = 1$ in a cell of dimensions $a = 9.8887(18)$, $b = 11.630(2)$, $c = 11.910(2)$ Å, $\alpha = 112.359(3)°$, $\beta = 94.035(3)°$, $\gamma = 103.615(3)°$, $V = 1211.5(4)$ Å^3, $D_c = 1.331$ Mg m^{-3}, μ(Mo-Kα) = 0.318 mm^{-1}, $F(000) = 508$, final R indices on 5580 independent reflections [$I > 2\sigma(I)$]: $R_1 = 0.0447$, $wR_2 = 0.1108$. Crystallographic summary for **2**: data was collected at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system. $MoC_{61}H_{58}N_6$ **2**; $M = 971.07$, black plate $0.26 \times 0.19 \times 0.04$ mm, triclinic, space group P-1, $Z = 1$ in a cell of dimensions $a = 9.9529(9)$, $b = 11.6864(10)$, $c = 11.9876(11)$ Å, $\alpha = 112.4130(10)°$, $\beta = 93.904(2)°$, $\gamma = 103.4010(10)°$, $V = 1234.77(19)$ Å^3, $D_c = 1.306$ Mg m^{-3}, μ(Mo-Kα) = 0.312 mm^{-1}, $F(000) = 508$, final R indices on 5671 independent reflections [$I > 2\sigma(I)$]: $R_1 = 0.0378$, $wR_2 = 0.0875$. CCDC 273837 and 273838. See http://dx.doi.org/10.1039/b508913a for crystallographic data in CIF or other electronic format.

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