Inorg. Chem. **2007**, *46*, 6239–6241

Inorganic Chemistry
Communication

Low-Coordinate Transition-Metal Complexes of a Carbon-Substituted Hemiporphyrazine

Anıl Çetin,[†] William S. Durfee,[‡] and Christopher J. Ziegler*,[†]

Department of Chemistry, University of Akron, Akron, Ohio 44304, and Department of Chemistry, Buffalo State College, Buffalo, New York 14222

Received June 6, 2007

The metallation of the core-modified phthalocyanine analogue dicarbahemiporphyrazine with manganese, iron, and cobalt results in the formation of low-coordinate metal(II) complexes. All three compounds are produced by the reaction of metal carbonyls with the free base macrocycle. As in many other carbaporphyrinoids, the internal C–H bonds remain intact upon metallation, resulting in the formation of two long-range agostic-type interactions. Each metal can thus be considered as a three-coordinate ion, where two inner isoindolene nitrogens and a single axial pyridine are bound to the metal. The manganese and cobalt complexes, Mn(dchp)py and Co(dchp)py, are nearly isostructural, but the iron complex, Fe(dchpH$_2$)py, exhibits a reduction at an iminic double bond upon metallation.

Transition-metal complexes with low coordination numbers continue to be challenging synthetic goals for chemists.[1] Such compounds have been used to model the chemistry of metal ions in biological systems, where the macromolecular superstructure regulates the coordination environment. Examples include models of the single copper electron-transfer site in fungal laccase[2] and small-molecule iron compounds for dinitrogen binding.[3] Porphyrins, while useful models for many biological systems, are typically not practical ligands for generating low-coordinate metal sites. Normal porphine is a tetradentate macrocycle, and additional ligands can coordinate in the two axial positions in the absence of steric bulk at the periphery of the ring. In this Communication, we present a porphyrinoid that can stabilize low-coordinate metal sites. An expanded porphyrinoid can be effectively converted into a bidentate ligand upon the replacement of two of the internal nitrogen positions with carbons.

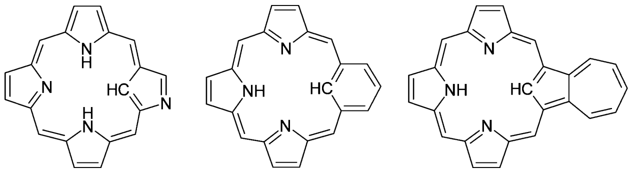


Figure 1. Structures of N-confused porphyrin (left), *m*-benziporphyrin (middle), and azuliporphyrin (right).

Recent developments in the syntheses of porphyrin isomers and analogues have resulted in macrocycles with carbon atoms at one or more core positions. Such rings include N-confused porphyrins,[4] benziporphyrins,[5] and azuliporphyrins (Figure 1).[6,7] These new macrocycles can be metalated with a variety of transition block elements.[8] Although in some cases the internal carbon is activated to form a direct M−C bond, often the C−H bond does not lose its proton and

---

* To whom correspondence should be addressed. E-mail: ziegler@uakron.edu.

[†] University of Akron.

[‡] Buffalo State College.

(1) (a) Panda, A.; Stender, A. F.; Wright, R. J.; Olmstead, M. M.; Klavins, P.; Power, P. P. *Inorg. Chem.* **2002**, *41*, 3909. (b) Nguyen, T.; Panda, A.; Olmstead, M. M.; Richards, A. F.; Stender, M.; Brynda, M.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 8545. (c) Smith, J. M.; Lachicotte, R. J.; Pittard, K. A.; Cundari, T. R.; Lukat-Rodgers, G.; Rodgers, K. R.; Holland, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 9222. (d) Holland, P. L.; Cundari, T. R.; Perez, L. L.; Eckert, N. A.; Lachicotte, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 14416. (e) Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *J. Am. Chem. Soc.* **2003**, *125*, 15752.

(2) (a) Palmer, A. E.; Randall, D. W.; Xu, F.; Solomon, E. I. *J. Am. Chem. Soc.* **1999**, *121*, 7138. (b) Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **1999**, *121*, 7270. (c) Palmer, A. E.; Szilagyi, R. K.; Cherry, J. R.; Jones, A.; Xu, F.; Solomon, E. I. *Inorg. Chem.* **2003**, *42*, 4006. (d) Randall, D. W.; George, S. D.; Holland, P. L.; Hedman, B.; Hodgson, K. O.; Tolman, W. B.; Solomon, E. I. *J. Am. Chem. Soc.* **2000**, *122*, 11632.

(3) (a) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385. (b) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 10782. (c) Smith, J. M.; Sadique, A. R.; Cundari, T. R.; Rodgers, K. R.; Lukat-Rodgers, G.; Lachicotte, R. J.; Flaschenriem, C. J.; Vela, J.; Holland, P. L. *J. Am. Chem. Soc.* **2006**, *128*, 757.

(4) (a) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767. (b) Chmielewski, P. J.; Latos-Grażyński, L.; Rachlewicz, K.; Glowiak, T. *Angew. Chem., Int. Ed.* **1994**, *33*, 779. (c) Geier, G. R., III; Haynes, D. M.; Lindsey, J. S. *Org. Lett.* **1999**, *1*, 1455.

(5) (a) Berlin, K.; Breitmaier, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1246. See also: Berlin, K.; Breitmaier, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 219. (b) Lash, T. D.; Chaney, S. T.; Richter, D. T. *J. Org. Chem.* **1998**, *63*, 9076. (c) Stępień, M.; Latos-Grażyński, L. *Chem.—Eur. J.* **2001**, *7* (23), 5113.

(6) (a) Lash, T. D.; Chaney, S. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 839. (b) Lash, T. D. *Chem. Commun.* **1998**, 1683.

(7) See also the following reviews: Lash, T. D. *Synlett* **1999**, *3*, 279. Furuta, H.; Maeda, H.; Osuka, A. *Chem. Commun.* **2002**, 1795. Stępień, M.; Latos-Grażyński, L. *Acc. Chem. Res.* **2005**, *38*, 88. Srinivasan, A.; Furuta, H. *Acc. Chem. Res.* **2005**, *38*, 10.

(8) (a) Harvey, J. D.; Ziegler, C. J. *Coord. Chem. Rev.* **2003**, *247*, 1. (b) Chmielewski, P. J.; Latos-Grażyński, L. *Coord. Chem. Rev.* **2005**, *249*, 2510. (c) Harvey, J. D.; Ziegler, C. J. *Inorg. Biochem.* **2006**, *100*, 869.

10.1021/ic7011099 CCC: $37.00

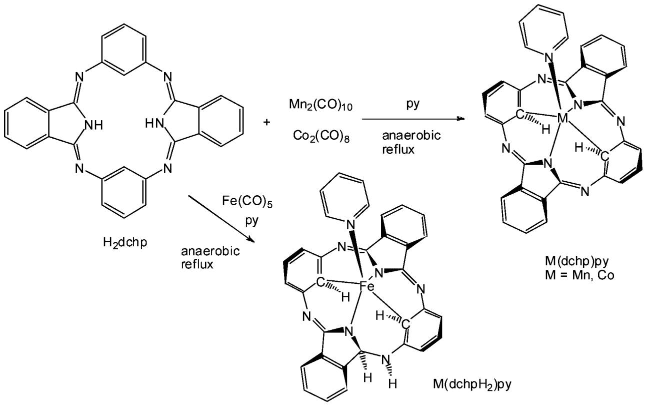
Figure 2. Diagrams of Mn(dchp)py (**1**, left), Co(dchp)py (**2**, middle), and Fe(dchpH_2)py (**3**, right) with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity except at the internal positions and on the reduced imine bond of Fe(dchpH_2)py.

instead forms a side-on "agostic"-type interaction.[8] This lack of C−H activation can promote the formation of lower-coordinate metal centers than are seen in normal porphyrins.

In the early 1950s, Linstead and co-workers synthesized the hemiporphyrazine family of macrocycles, expanded phthalocyanine analogues where one or two isoindolene units are replaced by pyridines.[9] These macrocycles are expanded antiaromatic tetradentate ligands, and metal ions typically are bound to these macrocycles in square-planar geometries similar to normal porphyrins and phthalocyanines.[10] Replacing the isoindolene units of phthalocyanine with one or two benzene rings leads to the formation of two carbaporphyrinoids: one is mononitrogen-deficient and the other is dinitrogen-deficient and can be considered as benziphthalocyanine and dicarbahemiporphyrazine (H_2dchp), respectively.[11] Although these two rings were first presented over half of a century ago, the coordination chemistry of these free bases remains largely unexplored. We recently presented a report on the copper(I) and silver(I) complexes of H_2dchp.[12] In both cases, the macrocycles retained one and two internal C−H bonds upon metallation, respectively.

As in many other carbaporphyrinoids, reaction of the free base H_2dchp with simple metal salts of manganese, iron, and cobalt does not produce the desired metal adducts. As in our work with N-confused porphyrins, we found that refluxing the macrocycles with metal carbonyls under an argon atmosphere resulted in the formation of the desired metalated products.[8] Scheme 1 shows the reactions of free base H_2dchp with dimanganese dodecacarbonyl, iron pentacarbonyl, and dicobalt octacarbonyl. The three reactions produced metalated products in 46, 31, and 69% yields, respectively.

Scheme 1



The reaction mixture of H_2dchp with either manganese or cobalt carbonyl in pyridine under reflux conditions in argon resulted in color changes to both solutions within minutes. Both reactions produced crystalline products upon diffusion with hexanes, and elucidation by single-crystal X-ray methods showed nearly identical structures for both products. Each complex has a formula of M(dchp)py, where a pyridine occupies the axial position in the resultant metalloporphyrinoid.[13,14] The macrocycle ring coordinates to the metal through the two internal nitrogen atoms, for a total of three nitrogens bound to each metal. The average equatorial distances are 2.091(3) and 1.982(3) Å for the manganese and cobalt species, respectively. The axial pyridine has slightly elongated bonds, with 2.140(2) Å for Mn(dchp)py, **1**, and 2.052(2) Å for Co(dchp)py, **2**. The internal C−H bonds of the benzene rings do not activate upon metal coordination and are found at a longer distance from the metals in both compounds. The M−C distances average 2.481(3) and 2.416(3) Å for the manganese and cobalt products, respectively. In these two compounds, the benzene rings are canted in the direction of the metal ion and thus prevent further ligand coordination. Over the past decade,

---

(9) Elvidge, J. A.; Linstead, R. P. *J. Chem. Soc.* **1952**, 5008.

(10) (a) Agostinelli, E.; Attanasio, D.; Collamati, I.; Fares, V. *Inorg. Chem.* **1984**, *23*, 1162. (b) Dirk, C. W.; Marks, T. J. *Inorg. Chem.* **1984**, *23*, 4325. (c) Fernández-Lázaro, F.; Torres, T.; Hauschel, B.; Hanack, M. *Chem. Rev.* **1998**, *98*, 563. (d) Farris, P. J.; Jacobs, J. T.; Okonczak, M. P.; Durfee, W. S.; Noll, B. C. *Acta Crystallogr.* **1999**, *C55*, 32.

(11) (a) Clark, P. F.; Elvidge, J. A.; Linstead, R. P. *J. Chem. Soc.* **1954**, 2490. (b) Elvidge, J. A.; Golden, J. H. *J. Chem. Soc.* **1957**, 700.

(12) Wu, R.; Çetin, A.; Durfee, W. S.; Ziegler, C. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 5670.

(13) Mn(dchp)py: yellow block, $C_{43}H_{31}N_9Mn_1$, $M_w = 728.71$, monoclinic, space group $P2(1)/n$, $a = 16.4993(15)$ Å, $b = 12.4912(11)$ Å, $c = 17.8396(17)$ Å, $\alpha = 90°$, $\beta = 110.685(2)°$, $\gamma = 90°$, $V = 3439.7(5)$ Å^3, $Z = 4$, $D_{calc} = 1.407$ g/cm^3, $T = 100(2)$ K. Final $R = 0.0633$ (GOF = 1.032) for 30 031 observed reflections with $I > 2\sigma(I)$, $R_w = 0.1665$ for 8276 reflections, all unique data.

single agostic-type C−H bonds have been frequently observed in the metal binding chemistry of the carbaporphyrinoids, including N-confused porphyrins and benziporphyrins. Interestingly, the H_2dchp ligand is the first example of a porphyrinoid that appears to regularly form two porphyrinic agostic bonds from separate subunits upon metal binding.

The reaction of the H_2dchp macrocycle with iron pentacarbonyl under the same conditions, however, resulted in metallation with a concomitant reduction of the ring.[15] As in the manganese and cobalt reactions, a low-coordinate geometry is formed in Fe(dchpH_2)py, **3**, with only three nitrogen atoms strongly coordinating to the metal ion. The equatorial Fe−N distances measure 1.9890(17) and 2.0216(16) Å, and the axial pyridine nitrogen is found at 2.0719(16) Å from the metal. The internal carbon sites lie at distances of 2.4091(19) and 2.4482(18) Å from the metal. The reduction of the ring occurs at one of the isoindolene Schiff base sites, such that both the α-carbon and *meso*-nitrogen are sp^3-hybridized, which is readily observed in the crystal structure. The N(5)−C(22) bond distance measures at 1.436(2) Å in contrast to the three remaining imine bonds, which range from 1.286(3) to 1.301(3) Å. In addition, the C(22) atom is clearly reduced and has a tetrahedral geometry, with bond angles ranging from 104.96(16)° to 114.52(17)°.

All three complexes have metals in the +2 oxidation state. Magnetic susceptibility experiments indicate that all have high-spin configurations, with spins of $^5/_2$, 2, and $^3/_2$ from μ_{eff} values of 6.11, 5.15, and 4.83 for the manganese, iron, and cobalt complexes, respectively. The axial M−N bond distances of compounds **1**−**3** are in good agreement with the spin-state assignment. In addition, all three compounds are reactive to atmospheric oxygen, resulting in demetallation of the macrocycles to afford the free bases. We are continuing to probe the electronic structure of compounds **1**−**3** by using spectroscopic, crystallographic, and theoretical methods.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society (to W.S.D.) and the NSF (Grant CHE-0616416). We acknowledge NSF Grant CHE-0116041, which was used to purchase the Bruker-Nonius diffractometer.

Supporting Information Available: Synthetic procedures, characterization, and the crystallographic data for manganese, iron, and cobalt complexes (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC7011099

---

(14) Co(dchp)py: yellow block, $C_{33}H_{21}N_7Co_1$, $M_w = 574.50$, monoclinic, space group $P2(1)/n$, $a = 16.6549(16)$ Å, $b = 12.5612(12)$ Å, $c = 17.5184(17)$ Å, $\alpha = 90°$, $\beta = 111.490(2)°$, $\gamma = 90°$, $V = 3410.2(6)$ Å^3, $Z = 4$, $D_{\mathrm{calc}} = 1.119$ g/cm^3, $T = 100(2)$ K. Final $R = 0.0521$ (GOF = 0.914) for 29 223 observed reflections with $I > 2\sigma(I)$, $R_w = 0.1255$ for 8016 reflections, all unique data.

(15) Fe(dchpH)py: yellow block, $C_{33}H_{23}N_7Fe_1$, $M_w = 573.43$, monoclinic, space group $C2/c$, $a = 31.610(5)$ Å, $b = 11.9896(18)$ Å, $c = 18.876(3)$ Å, $\alpha = 90°$, $\beta = 107.095(3)°$, $\gamma = 90°$, $V = 6838.0(18)$ Å^3, $Z = 8$, $D_{\mathrm{calc}} = 1.114$ g/cm^3, $T = 100(2)$ K. Final $R = 0.0485$ (GOF = 0.966) for 29 598 observed reflections with $I > 2\sigma(I)$, $R_w = 0.1162$ for 8215 reflections, all unique data.