Heptane Coordination to an Iron(II) Porphyrin

Daniel R. Evans,[†] Tatiana Drovetskaya,[†] Robert Bau,[†]
Christopher A. Reed,*[,†,‡] and Peter D. W. Boyd*[,§]

*Department of Chemistry, University of
Southern California, Los Angeles, California 90089-0744
Department of Chemistry
The University of Auckland, Private Bag 92019
Auckland 1, New Zealand*

One of the most interesting weak interactions of organo-transition metal chemistry is the coordination of an alkane to a metal center.[1] Formerly regarded as inert and non-nucleophilic, an sp^3 saturated C−H bond is now recognized to act as an electron pair donor in a three-center two-electron M−H−C bond, referred to as an agostic interaction.[2] These so-called σ-complexes[3] are obligatory intermediates in a number of important C−H activation reactions,[4] but the coordinate bond is sufficiently weak[1,5] that alkane complexes are not stable under ambient conditions unless they have the entropic advantage of being tethered to an adjacent, more strongly-bonded ligand. An alternative, noncovalent way of enhancing the stability of a weak interaction is to use clathrate or host/guest chemistry. Here, the tailored size and shape of a molecular cavity promotes intermolecular association. We now report to the operation of this concept in stabilizing the unexpected interaction of heptane with iron(II) in a crystalline porphyrin complex.[6] This is the first time that a free alkane complex has been stabilized at ambient temperatures for X-ray structural investigation. A new unsymmetrical bidentate mode of binding is proposed.

The double A-frame porphyrin H_2DAP (Figure 1) was prepared with the idea of excluding large ligands and large solvent molecules from binding to the axial coordination sites of its metal complexes. The strategy is an extension of that recently devised by Collman and co-workers.[7]

The iron(II) complex, Fe(DAP), was prepared by standard methods[8] and recrystallized from fluorobenzene via *n*-heptane diffusion to give crystals of Fe(DAP)·(*n*-heptane) suitable for X-ray crystallography.[9] The identity of the solvate molecule as heptane was established definitively by ^1H and ^{13}C NMR in toluene-d_8 solution.

Figure 2 shows a stereoview of Fe(DAP)·(*n*-heptane) and its symmetry expansion neighbor. The A-frame straps of the porphyrin lie off-center, consistent with structural compactness and the constraints of *o*-amidophenyl linkages. This exposes
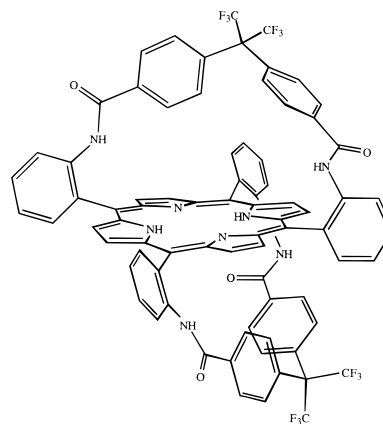

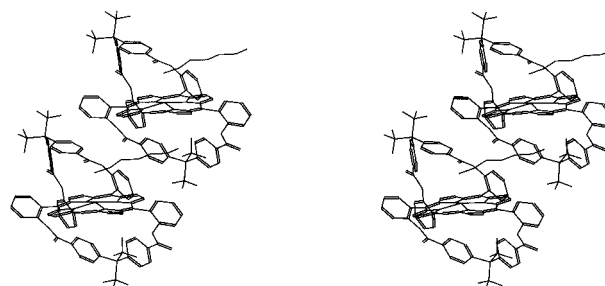**Figure 1.** The double A-frame porphyrin, H_2DAP.

Figure 2. Stereoview of a pair of Fe(DAP)·(*n*-heptane) molecules. Only one orientation of the disordered heptane molecule is shown.

the iron atoms to the ends of a heptane molecule which crystallizes in a cavity formed by two neighboring porphyrins.

Crystallographically, the *n*-heptane molecule has the appearance of *n*-octane with half occupancy of the terminal carbon atoms. This implies a positional disorder involving a one-atom displacement along the alkane chain. It has been successfully modeled with 50% occupancy of the two orientations shown in Figure 3.[10]

The coordination of the heptane molecule to iron is indicated primarily by the displacement of the iron atom from the mean plane of the four nitrogen atoms toward heptane. Refinement of the structure with an in-plane iron atom leads to a thermal ellipsoid for Fe that is unrealistically elongated in a direction normal to the heme plane. The disorder model required to treat this observation gives an out-of-plane displacement of 0.26 Å and Fe···C distances of 2.5 and 2.8 Å.[10] These values cannot be taken quantitatively but are consistent with a coordinative alkane/iron interaction. An out of plane displacement of iron is a universal criterion of five-coordination in iron porphyrin chemistry,[11] and metal-to-carbon distances in the range 2.5−3.0 Å are typical of moderate to weak agostic interactions.[12]

As expected for an X-ray structure with disorder, the H atoms of the coordinated methyl group cannot be located experimentally. Instead, we allow theory and conformational logic to

[†] University of Southern California.
[‡] E-mail: careed@usc.edu.
[§] The University of Auckland. E-mail: pdw.boyd@auckland.ac.nz.
(1) Hall, C.; Perutz, R. N. *Chem Rev.* **1996,** *96,* 3125−3146.
(2) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983,** *250,* 395−408.
(3) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 789−805.
(4) See for example Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995,** *28,* 154−162 and references therein.
(5) Yang, P.-F.; Yang, G. K. *J. Am. Chem. Soc.* **1992,** *114,* 6937−6938.
(6) Host/guest interactions bind alkanes in the vicinity of heme active sites in cytochrome P450 enzyme−substrate complexes[6a] and form lattice solvates in metalloporphyrins[6b] but there is presently no evidence for alkane interaction with an iron atom. (a) Raag, R.; Poulos, T. L. *Frontiers Biotransformations* **1992,** *7,* 1. (b) Byrn, M. P.; Strouse, C. E. *J. Am. Chem. Soc.* **1991,** *113,* 2501−2508.
(7) Collman, J. P.; Zhang, X., Herrman, P. C.; Uffelman, E. S.; Boitrel, B, Straumanis, A.; Brauman, J. I. *J. Am. Chem. Soc.* **1994,** *116,* 2681−2682.
(8) Wuenschell, G. E.; Tetreau, C.; Lavalette, D.; Reed, C. A. *J. Am. Chem. Soc.* **1992,** *114,* 3346−3355.
(9) Fe(II)DAP·heptane ($C_{78}H_{46}F_{12}$ Fe N_8O_4·C_7H_{16}), MW = 1543.3, dark red needle, orthorhombic, space group *Pna2₁*, *a* = 32.492(5) Å, *b* = 24.806(4) Å, *c* = 10.3330(10) Å, *V* = 8328(2) Å³, *Z* = 4, *R* = 0.086 [*I* > 2σ(*I*)], GOF = 0.880.
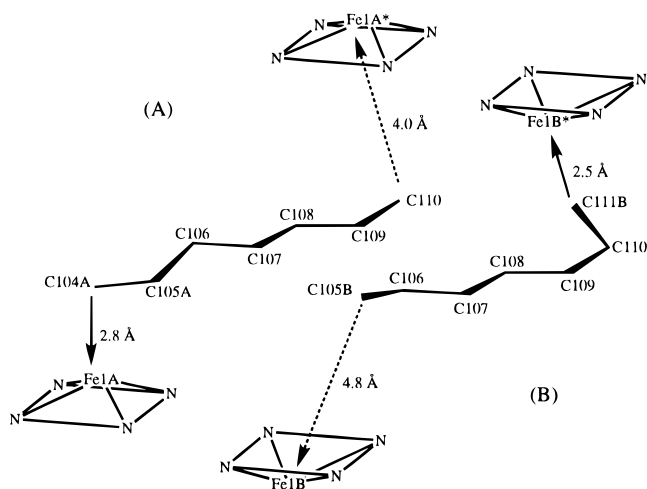
(10) The disordered heptane molecule was modeled as a superposition of two orientations (A and B) shifted one relative to another by one carbon atom along the chain. A partial occupancy of 0.5 was assigned to the terminal carbon atoms 104A and C111B/C105B as well as the carbon atom neighboring to the coordinated site A: C105A. The remainder of the chain (C106−C110) overlaps. The C−C bond distances in heptane were restrained to be equal at ca. 1.54 Å. The sp^3 C−C−C angles were restrained to be identical and adopted values of ca. 109−110°. The central Fe atom was resolved into two components, Fe1A and Fe1B, respectively, as shown in Figure 2. An alternative interpretation of the disorder, having the Fe atom displaced from the heme plane but remote from the heptane, is mathematically valid but chemically unrealistic.
(11) Scheidt, W. R. *The Porphyrins, Volume III;* Academic Press: New York, 1978; pp 463−511.
(12) Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehose, S. M. *Inorg. Chem.* **1985,** *24,* 1986−1992.

Figure 3. Representation of the disorder model for *n*-heptane binding to Fe in Fe(DAP)·(*n*-heptane).
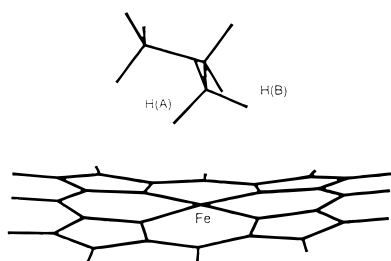

Figure 4. Calculated molecular geometry[14,15] for the Fe(porphine)−propane complex. Fe−N(av) = 1.953 Å; Fe−H(A) = 2.049 Å, Fe−H(B) = 2.619 Å, C−H(A) = 1.120 Å; C−H(B) = 1.106 Å, Fe−H(A)−C = 113.6°, Fe−H(B)−C = 82.1°.

guide us to their possible location. Density functional calculations[13] on Fe(porphine) complexes of methane, ethane, propane, and *n*-butane support an unsymmetrical bidentate structure.[14] The energetic minimum for propane is shown in Figure 4. For all four complexes, Fe···C distances are in the range 2.68−2.70 Å. The Fe−H distances are 2.01−2.13 Å and 2.62−2.65 Å for the close and more distant C−H bonds, respectively, and the corresponding Fe−H−C angles are 114−116° and 80−83°. The Fe···H−C "bonding pair" distances (d_{bp}), as defined by Crabtree *et al.*,[12] are 2.02 and 2.68 Å, respectively, in the propane complex. Subtracting 1.25 Å for the covalent radius of Fe gives bonding pair radii (r_{bp}) of 0.77 and 1.43 Å. Values of r_{bp} up to 1.60 Å have been observed in agostic interactions, and 1.79 Å is taken as the van der Waals nonbonding distance.[12] The calculated binding energies indicate weak interactions: 10.5, 14.1, 16.7, and 16.3 kcal mol^{-1} for CH_4, C_2H_6, C_3H_8, and C_4H_{10}, respectively. The increase with chain length correlates with increasing porphyrin contact. A less stable minimum for the

ethane complex having the uncoordinated methyl group approximately vertical to the porphine plane has a binding energy of 9.6 kcal mol^{-1}. This suggests a maximum of *ca.* 9 kcal mol^{-1} for the coordinate bond strength. Mulliken population analyses of charge distributions show the expected direction of charge donation from the alkane C−H framework to the iron porphine (0.23e for ethane and 0.40e for propane).

An unsymmetrical bidentate structure has also been proposed in computational approaches to the interaction of methane with rhodium,[15] but to date all experimental work has been interpreted in terms of a monodentate mode of coordination. It is possible that bidentate coordination has gone unnoticed because the H-atoms involved in agostic interactions are crystallographically either poorly defined or not located. Inferred positions of H atoms can be calculated using staggered conformations along the hydrocarbon backbone. However, since the coordinate bond energy can be greater than the ∼3 kcal preference for the staggered conformation of a terminal methyl group, there may be competition between the conformational and coordinative forces. At one end (C104A) of the heptane molecule in Fe(DAP)·(*n*-heptane), conformational analysis leads to unsymmetrical bidentate coordination with dimensions (Fe−H ca. 2.1, 2.7 Å; Fe−H−C ca. 120 and 80°, respectively) close to the coordinate mode derived from density functional theory. At the other end, however, it is obvious from the carbon backbone that the alkane does not adopt its lowest energy conformation; the C111B−C110 bond is *gauche* rather than *anti* with respect to the C109−C108 bond, and the dihedral angle of 27° between these bonds is intermediate between staggered and eclipsed ideals. Thus, it would be imprudent to predict the outcome of the coordinate versus conformational interplay at this end.

In summary, complexation of a free alkane has been ambiently stabilized for the first time by creating a binding cavity in the vicinity of a vacant coordination site. The computational evidence for an unsymmetrical bidentate coordination mode suggests that a renewed experimental effort should be directed toward accurately locating agostic hydrogen atoms.

Finally, it is tempting to draw a conceptual parallel between the solvation of the iron complex observed in the solid state and its solvation in the solution phase.[16] The organizational entropy of host/guest inclusion in the solid phase will be replaced by the high probability of complexation by ever-present solvent in the solution phase. In the context of vacant coordination sites that are sterically accessible to solvent molecules, this suggests that there is probably no such thing as a truly noncoordinating solvent.

Supporting Information Available: X-ray crystal structure determination and refinement, X-ray structure drawings, tables of crystal data, atomic coordinates, anisotropic thermal parameters, hydrogen coordinates, and bond distances and angles (13 pages). See any current masthead page for ordering and Internet access instructions.

JA970008H

(13) Density functional calculations were carried out using the Amsterdam Density Functional programs (ADF Version 2.01, Department of Theoretical Chemistry, Vrije Universiteit, Amsterdam; Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41−51. te Velde, G.; Baerends, E. J. *J. Comp. Phys.* **1992**, *99*, 84−98. Double-ζ basis sets were used for C (2s, 2p), H(1s), N(2s, 2p) augmented by a single 2d polarization function and a triple-ζ basis set for Fe (3s, 3p, 3d, 4s). The inner electron configurations were assigned to the core and were treated using the frozen core approximation.

(14) In each case a full geometry optimization of the iron(II) porphine-alkane complex was performed. Open shell calculations were carried out using a spin unrestricted model with a triplet ground state. The average experimental Fe−N distance of 1.98(2) Å indicates an intermediate $S = 1$ spin state and is incompatible with a high spin state. A calculation for the ethane complex with a singlet ground state was of higher energy. All optimizations were carried out using the local density approximation with the functional given by Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211.

(15) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1993**, *115*, 6883−6892; Margl, P.; Ziegler, T.; Blöchl, P. E. *J. Am. Chem. Soc.* **1995**, *117*, 12625−12634; Song, J.; Hall, M. B. *Organometallics* **1993**, *12*, 3118−3126.

(16) The complex is insufficiently soluble in noncompeting solvents for an exploration of solution phase interactions with alkanes. We have shown previously that more electron-rich solvents such as arenes can bind to metalloporphyrins, blurring the distinction between ligands and solvates: Xie, Z.; Bau, R.; Reed, C. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2433−2434.