

Halogeno-Coordinated Iron Corroles

Liliya Simkhovich and Zeev Gross*

Department of Chemistry and Institute of Catalysis Science and Technology,
Technion - Israel Institute of Technology, Haifa 32000, Israel

Received July 2, 2004

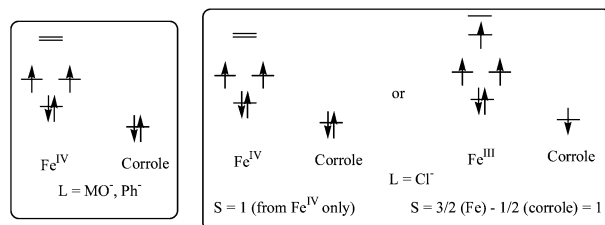
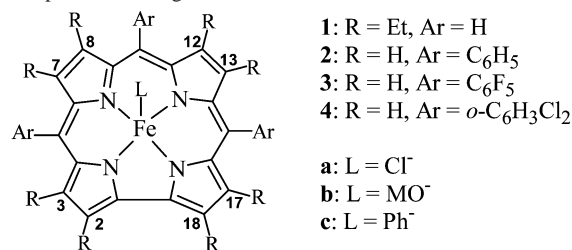
The first full assignment of ^1H NMR chemical shifts for iron corroles and the first synthesis of a series of (halogeno)iron corroles reveal very large effects of the axial ligands on the corresponding spectra, which apparently reflect differences in the relative importance of metal-to-corrole and corrole-to-metal π -donation. These findings pave the way for a thorough analysis of the electronic structures of such complexes.

The involvement of high-valent metalloporphyrins as reaction intermediates in the various processes that are catalyzed by heme enzymes continues to serve as a main inspiration for research into synthetic porphyrins and porphyrin analogues.¹ Most issues regarding structural and electronic factors that affect spin and oxidation states in iron porphyrins are well resolved to date,² but this is not the situation for iron corroles, which were recently found to catalyze quite a variety of reactions.^{2,3} The main shortcomings that hamper the latter research are the limited number of well-characterized complexes and the vague assignments of ^1H NMR resonances therein.⁴ The quite extensive debate about the proper definition of the electronic state [iron(IV) corrole vs iron(III) corrole radical] in complexes with the general formula of $\text{Fe}(\text{cor})(\text{Cl})$ clearly suffers from the fact that the four magnetically different β -pyrrole substituents ($\text{R} = \text{H}$ or alkyl in Chart 1) were never assigned by NMR analysis, as well as the lack of any information about complexes with other halogeno ligands.^{2–5}

* To whom correspondence should be addressed. E-mail: chr10zg@technion.technion.ac.il.

- (1) (a) Watanabe, Y. *Curr. Opin. Chem. Biol.* **2002**, *6*, 208. (b) Fujii, H. *Coord. Chem. Rev.* **2002**, *226*, 51.
 (2) Walker, F. A. *Inorg. Chem.* **2003**, *42*, 4526.
 (3) (a) Gross, Z.; Simkhovich, L.; Galili, N. *Chem. Commun.* **1999**, 599. (b) Gross, Z.; Golubkov, G.; Simkhovich, L. *Angew. Chem., Int. Ed.* **2000**, *39*, 4045. (c) Golubkov, G.; Bendix, J.; Gray, H. B.; Mahammed, A.; Goldberg, I.; DiBilio, A. J.; Gross, Z. *Angew. Chem., Int. Ed.* **2001**, *40*, 2132. (d) Simkhovich, L.; Gross, Z. *Tetrahedron Lett.* **2001**, *42*, 8089.
 (4) (a) Simkhovich, L.; Goldberg, I.; Gross, Z. *Inorg. Chem.* **2002**, *41*, 5433. (b) Vogel, E.; Will, S.; Schulze Tilling, A.; Neumann, L.; Lex, J.; Bill, E.; Trautwein, A. X.; Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 731.
 (5) Steene, E.; Wondimagegn, T.; Ghosh, A. *J. Phys. Chem. B* **2001**, *105*, 11406; *J. Phys. Chem. B* **2002**, *106*, 5312.

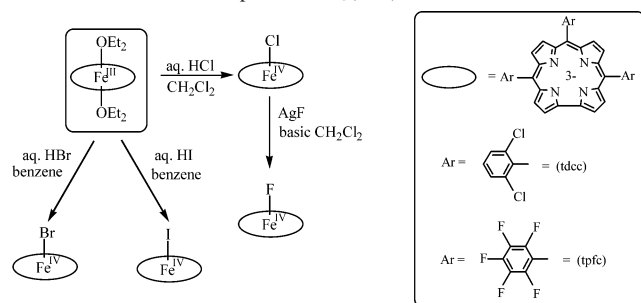
Chart 1. Formal Drawing of Previously Reported Five-Coordinate Iron Corroles and the Two Electronic Configurations that Are Consistent with Experimental Magnetic Data^a



^a M in b is another iron corrole, i.e., a (cor)Fe–O–Fe(cor) complex).

We now report the preparation of a series of five-coordinated (halogeno)iron complexes of 5,10,15-tris(pentafluorophenyl)corrole and 5,10,15-tris(2,6-dichlorophenyl)corrole, $\text{H}_3(\text{tpfc})$ and $\text{H}_3(\text{tdcc})$, respectively.⁶ The two particular corroles were chosen for three reasons: (a) they are much more stable than all other corroles,⁷ (b) they are the only ones whose metal complexes were used as catalysts, and (c) they complement each other in terms of spectroscopic sensing of the *meso*-aryl groups by ^{19}F and ^1H NMR spectroscopies, respectively. Full assignment of all ^1H NMR resonances was achieved via selective deuteration of $\text{H}_3(\text{tpfc})$ and $\text{H}_3(\text{tdcc})$. The results revealed two very large effects of axial ligands on the ^1H NMR spectra of the iron complexes: variations in chemical shift that were most pronounced for β -pyrrole protons and differences in broadness of resonances that were most distinctive for *meso*-aryl protons. These phenomena seem more consistent with iron(IV) corrole

- (6) (a) Gross, Z.; Galili, N.; Saltsman, I. *Angew. Chem., Int. Ed.* **1999**, *38*, 1427. (b) Gryko, D. T.; Koszarna, B. *Org. Biomol. Chem.* **2003**, *1*, 350.
 (7) Geier, G. R., III; Chick, J. F. B.; Callinan, J. B.; Reid, C. G.; Auguscinski, W. P. *J. Org. Chem.* **2004**, *69*, 4159.

Scheme 1. Synthetic Pathways for Preparation of the New Five-Coordinate Iron Complexes of $H_3(\text{tdcc})$ 

formulation than the alternative iron(III) corrole radical description.

The syntheses of the new five-coordinated iron corroles relied on the previously described complexes shown in Scheme 1. This includes all synthetic details for preparation and full spectroscopic characterization of $H_3(\text{tpfc})$ and $H_3(\text{tdcc})$ ⁶ and their six-coordinated iron(III) and the (chloro)-iron(IV) complexes.⁸ The chloro- and bromo-coordinated complexes **3-Cl**, **3-Br**, **4-Cl**, and **4-Br** were prepared from the corresponding (bis-ether)iron(III) corroles via treatment with the appropriate mineral acid (HCl, HBr) in aerobic solutions. To obtain $\text{Fe}(\text{tdcc})\text{I}$, the red-brown $\text{Fe}(\text{tdcc})(\text{OEt}_2)_2$ was dissolved in benzene and washed extensively with aqueous HI. The last (halogeno)iron complex of $H_3(\text{tdcc})-\text{Fe}(\text{tdcc})\text{F}$ was obtained by heating of a dry and acid-free dichloromethane solution of $\text{Fe}(\text{tdcc})\text{Cl}$ with an excess of AgF. The yields of all of the reactions described herein were in the range of 90–95% for pure crystalline or powder materials. All halogeno-coordinated iron complexes of $H_3(\text{tdcc})$ (**4-F**, **4-Cl**, **4-Br**, **4-I**) were stable, but the fluoro- and iodo-coordinated iron complexes of $H_3(\text{tpfc})$ (**3-F** and **3-I**) that were obtained in analogy to **4-F** and **4-I** decomposed quite rapidly in solution.

The first step of the investigations was to assign observed chemical shifts in the ^1H NMR spectra of the paramagnetic complexes to specific hydrogen atoms. This task became feasible as a result of the recent demonstration of selective deuteration of corroles and the full NMR assignment of triarylcorroles and their diamagnetic complexes.⁹ The approach is illustrated in Figure 1, which shows the ^1H NMR spectra of natural-abundance and partially deuterated corrole, together with those of the corresponding natural-abundance and partially deuterated (chloro)iron(IV) complexes. The analysis of Figure 1b revealed that about 50% of H3, 50% of H2, and 20% of H8 of the free base corrole were replaced by deuterium in this particular case, a comparison between the spectra in Figure 1c and d exposed a decrease in the intensities of the resonances at 3.4, -8.6, and -34.4 ppm, which was confirmed by complementary information obtained from the ^2H NMR spectra of the same complex.

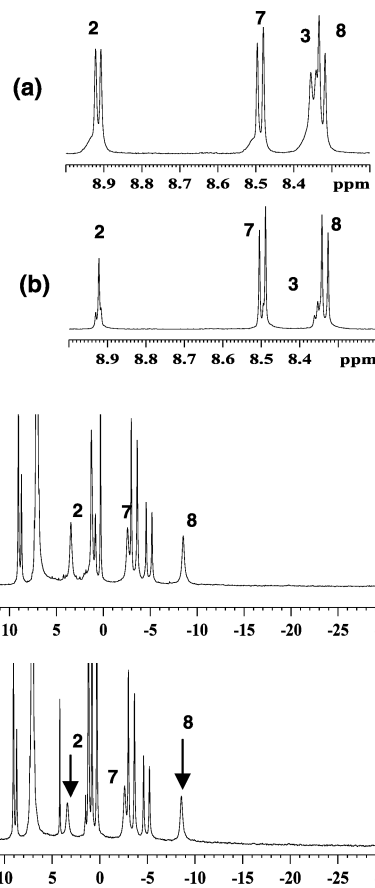


Figure 1. ^1H NMR spectra of (a) natural-abundance $H_3(\text{tdcc})$, (b) partially deuterated $H_3(\text{tdcc})$, (c) natural-abundance $\text{Fe}(\text{tdcc})\text{Cl}$, and (d) partially deuterated $\text{Fe}(\text{tdcc})\text{Cl}$ prepared from the sample whose spectrum is shown in b. Measurements were performed in (a,b) CDCl_3 and (c,d) C_6D_6 at 293 K.

Similar procedures were carried out for the other complexes, allowing for a complete assignment of the resonances for all complexes. Whenever the assignment was ambiguous, the procedures were repeated with batches of corroles that differed in the extent of deuteration: the shorter the reaction time of the corroles with trifluoroacetic acid-*d*, the more the initial selectivity of deuteration of $\text{C}3 \geq \text{C}2 > \text{C}8 > \text{C}7$ is reflected in the outcome.^{9a} Finally, the assignment of aryl resonances relies on the 2-fold symmetry that enforces one unique and two identical aryls, reflected in 1:2 sets of ^1H and ^{19}F NMR resonances for *para*-H and *meta*-H in $\text{Fe}(\text{tdcc})\text{X}$ and for *ortho*-F, *meta*-F, and *para*-F in the $\text{Fe}(\text{tpfc})\text{X}$ complexes.

The chemical shifts and assignments that are shown in Figure 2 and summarized in Figure 3 reveal very large effects of the coordinated halide ions on the spectra of the (halogeno)iron(IV) complexes. Another aspect that is also apparent from Figure 2 is the large effect of the axial ligands on the line widths, from very broad resonances in $\text{Fe}(\text{tdcc})\text{F}$ to very sharp in $\text{Fe}(\text{tdcc})\text{I}$. This is further illustrated in Figure 4, which serves to demonstrate that the resonances of $\text{Fe}(\text{tdcc})\text{I}$ are narrow enough that the small *J* coupling constants of its aryl hydrogen atoms can be resolved.

Importantly, both phenomena are reminiscent of similar effects of axial ligands on the spectra of manganese(III) and iron(III) porphyrins,¹⁰ clearly indicating that there is no need

(8) (a) Simkhovich, L.; Galili, N.; Saltsman, I.; Goldberg, I.; Gross, Z. *Inorg. Chem.* **2000**, *39*, 2704. (b) Simkhovich, L.; Mahammed, A.; Goldberg, I.; Gross, Z. *Chem. Eur. J.* **2001**, 1041.

(9) (a) Gross, Z.; Mahammed, A. *J. Porphyrins Phthalocyanines* **2002**, *6*, 553. (b) Balazs, Y. S.; Saltsman, I.; Mahammed, A.; Tkachenko, E.; Golubkov, G.; Levine, J.; Gross, Z. *Magn. Reson. Chem.* **2004**, *42*, 624–635.

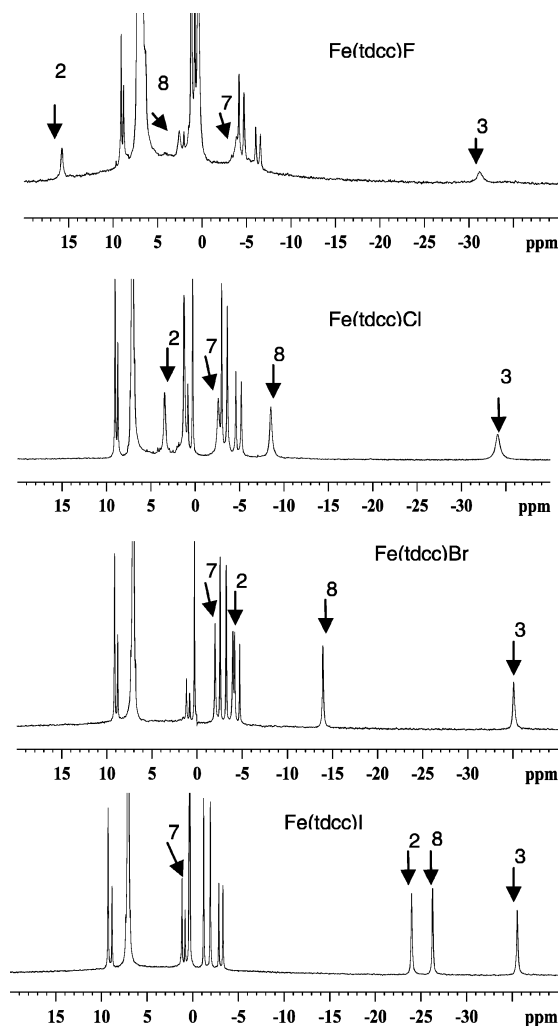


Figure 2. Full ^1H NMR spectra of $\text{Fe}(\text{tdcc})\text{F}$, $\text{Fe}(\text{tdcc})\text{Cl}$, $\text{Fe}(\text{tdcc})\text{Br}$, and $\text{Fe}(\text{tdcc})\text{I}$ (293 K, benzene- d_6), also showing the assignment of the β -pyrrole hydrogen atoms.

to invoke oxidized corrole to explain the results. Rather, ligand-dependent changes in the relative importance of the direction of π -donation, corrole-to-metal vs metal-to-corrole, might well be responsible for the quite pronounced differences. Some evidence for this hypothesis is the increasing difference between the chemical shifts of H2 and H3 upon moving from $\text{Fe}(\text{tdcc})\text{I}$ to $\text{Fe}(\text{tdcc})\text{F}$. Metal-to-corrole π -donation might be expected to be more important in the latter complex, and published calculations on the π -accepting LUMO orbitals of closed-shell corroles disclose a large difference in the coefficients on C2 and C3.¹¹ Unfortunately,

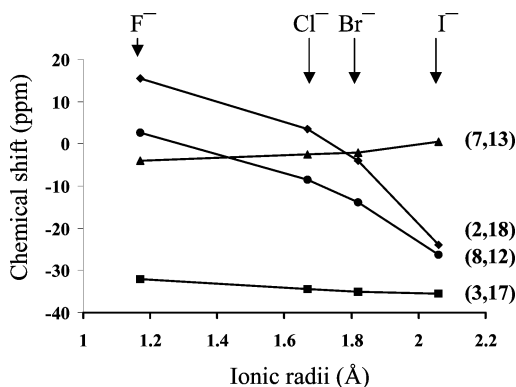


Figure 3. Chemical shifts of β -pyrrole hydrogen atoms in (halogeno)iron complexes of $\text{H}_3(\text{tdcc})$, plotted arbitrarily as a function of the ionic radii of the halides.

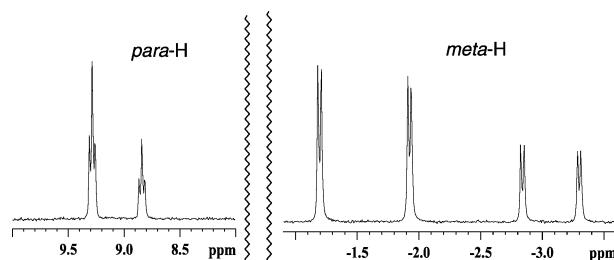


Figure 4. Partial ^1H NMR spectrum of $\text{Fe}(\text{tdcc})\text{I}$, focusing on the unusually sharp resonances of the hydrogen atoms of *meso*-aryl rings.

it is not currently possible to analyze corrole-to-metal π -donation because there are no reported calculations on the filled corrole orbitals that are of proper symmetry (lower in energy than the highest occupied ones that are of improper symmetry) to interact with the singly occupied d_π metal orbitals.

The synthesis of a full series of (halogeno)iron corroles and the assignment of all chemical shifts in the corresponding ^1H NMR spectra enable an in-depth analysis of the electronic structures of such complexes. We have already obtained X-ray-quality crystals of **3-Br**, **4-Br**, and **4-Cl** that, together with various new spectroscopic data (including about less electron-poor corroles), will be used for that purpose in forthcoming publications.

Acknowledgment. This research was supported by the Israel Science Foundation under Grant 368/00 (Z.G.). A postdoctoral fellowship for L.S. from the Institute of Catalysis Science and Technology is acknowledged as well.

IC0491332

(10) (a) La Mar, G. N.; Walker, F. A. *J. Am. Chem. Soc.* **1975**, *97*, 5103. (b) Wojaczynski, J.; Latos-Grazynski, L.; Chmielewski, P. J.; Van Calcar, P.; Balch, A. L. *Inorg. Chem.* **1999**, *38*, 3040. (c) Behere, D. V.; Birdy, R.; Mirta, S. *Inorg. Chem.* **1982**, *21*, 386.

(11) (a) Bendix, J.; Dmochowski, I. J.; Gray, H. B.; Mahammed, A.; Simkhovich, L.; Gross, Z. *Angew. Chem., Int. Ed.* **2000**, *39*, 4048. (b) Ghosh, A.; Taylor, P. R. *Curr. Opin. Chem. Biol.* **2003**, *7*, 113.