

## Iron(III) and Iron(IV) Corroles: Synthesis, Spectroscopy, Structures, and No Indications for Corrole Radicals

Liliya Simkhovich,<sup>†</sup> Israel Goldberg,<sup>\*†</sup> and Zeev Gross<sup>\*†</sup>

Department of Chemistry and Institute of Catalysis Science and Technology, Technion-Israel Institute of Technology, Haifa 32000, Israel, and School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel

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A delicate control of reaction conditions allows the isolation of several distinctively different iron complexes of tris(pentafluorophenyl)- and tris(2,6-dichlorophenyl)corrole. As long as coordinating ligands are present, the iron(III) complexes are stable in solution. Otherwise they are aerobically oxidized to either mononuclear chloroiron(IV) or dinuclear ( $\mu$ -oxo)iron(IV) complexes, in acidic and basic solutions, respectively (the latter holds only for tris(pentafluorophenyl)corrole). When treated with NaNO<sub>2</sub>, the mononuclear chloroiron(IV) corroles are efficiently converted into diamagnetic iron nitrosyl complexes. The low- and intermediate-spin iron(III), iron nitrosyl, and chloroiron(IV) corroles were fully characterized by a combination of spectroscopic methods and X-ray crystallography. There was no indication for an open-shell corrole in any of the complexes.

## Introduction

Synthetic iron porphyrins are extensively investigated because of their relevance to heme-containing proteins and enzymes.<sup>1</sup> In sharp contrast, iron complexes of corroles (Scheme 1)—the one carbon atom short analogues of porphyrins, which are also related to the metal-chelating macrocycle in Vitamin B<sub>12</sub> (a corrin)—are much less known. In addition, there is no general consensus about the electronic structures of iron corroles. The early spectroscopic investigations (mainly by NMR) by Licocchia and Paolesse led the authors to the conclusion that the product obtained from insertion of iron into H<sub>3</sub>(omc) is a simple low-spin iron(III) complex and that the ligand field of corroles is stronger than that of porphyrins.<sup>2,3</sup> But the studies of Vogel and co-workers with iron complexes of H<sub>3</sub>(oec) revealed that the air-stable oxidation state is actually higher than iron(III).<sup>4</sup> These authors have fully characterized mononuclear Fe(oec)Cl and dinuclear (oec)Fe—O—Fe(oec) by various spectroscopic meth-

ods and X-ray crystallography. All the acquired information supported a low-spin iron(IV) oxidation state for Fe(oec)Cl, and the diamagnetism of (oec)Fe—O—Fe(oec) was analyzed as resulting from strong antiferromagnetic coupling between the two d<sup>4</sup> irons. Stabilization of the iron(III) oxidation state was possible in the presence of pyridine, but surprisingly, only the pentacoordinated Fe(oec)(py) was isolated. This is unique to corroles: analogous porphyrin complexes cannot be isolated because of the very small dissociation constants of hexacoordinated bis(amine)iron(III) porphyrins.<sup>5</sup> Still, in a recent reexamination of Fe(omc)Cl and Fe(dmhec)Cl, Licocchia et al claimed that the *formally* iron(IV) corroles should be formulated as iron(III) corrole radicals.<sup>6</sup> Their conclusion is based on NMR spectroscopy, relying on the very low field chemical shifts of the *meso*-protons therein. The explanation provided by the authors with regard to the

\* To whom correspondence should be addressed. E-mail: chr10zg@tx.technion.ac.il (Z.G.).

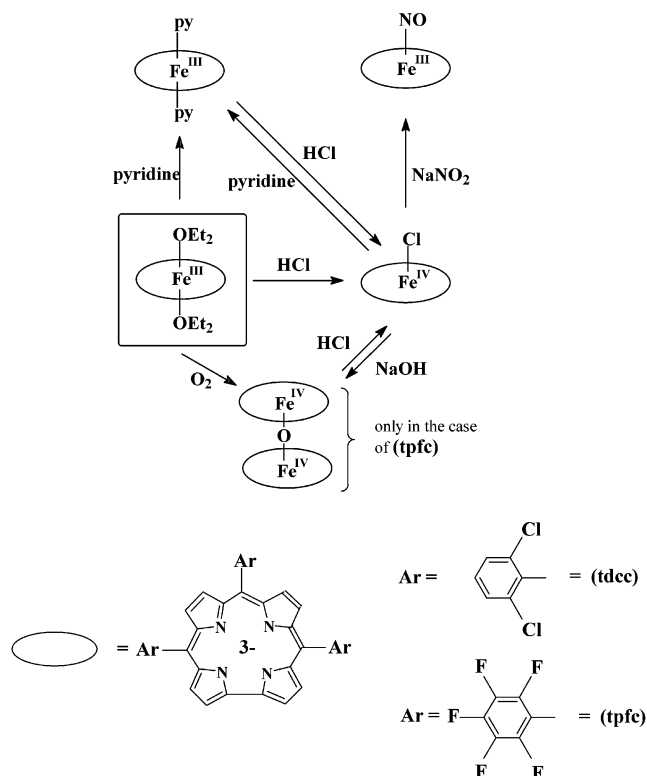
<sup>†</sup> Technion-Israel Institute of Technology.

<sup>‡</sup> Tel Aviv University.

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(2) Abbreviations: oec, omc, dmhec, tpfc, and tdcc, trianions of octaethylcorrole, octamethylcorrole, 7,13-dimethyl-2,3,8, 12,17,18-hexaethylcorrole, 5,10,15-tris(pentafluorophenyl)corrole, and 5,10,15-tris(2,6-dichlorophenyl)corrole; tpp, tmp, and oep, dianions of *meso*-tetraphenylporphyrin, *meso*-tetramesitylporphyrin, and octaethylporphyrin. (3) Licocchia, S.; Paci, M.; Paolesse, R.; Boschi, T. *J. Chem. Soc., Dalton Trans.* **1991**, 461. (4) (a) Vogel, E.; Will, S.; Tilling, A. S.; Neumann, L.; Lex, J.; Bill, E.; Trautwein, A. X.; Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 731. (b) Caemelbecke, E. V.; Will, S.; Autret, M.; Adamian, V. A.; Lex, J.; Gisselbrecht, J.-P.; Gross, M.; Vogel, E.; Kadish, K. M. *Inorg. Chem.* **1996**, *35*, 184. (5) Nasset, M. J. M.; Shokhirev, N. V.; Enemark, P. D.; Jacobson, S. E.; Walker, F. A. *Inorg. Chem.* **1996**, *35*, 5188. (6) Cai, S.; Walker, F. A.; Licocchia, S. *Inorg. Chem.* **2000**, *39*, 3466.

Scheme 1



conflicting evidence from Mossbauer spectroscopy and magnetic susceptibility ( $S = 1$ ) in favor of low-spin iron(IV) is that the complexes are composed of an intermediate-spin iron(III) ion ( $S = 3/2$ ) that is strongly coupled in an antiferromagnetic fashion with the unpaired electron on the corrole, i.e.,  $S_{\text{total}} = 3/2 (\text{Fe}) - 1/2 (\text{corrole radical}) = 1$ . The NMR spectrum of the bis(pyridine)iron corrole (obtained by adding excess pyridine to  $\text{Fe}(\text{omc})\text{Cl}$ ) was analyzed as reflecting a low-spin iron(III) coupled to the corrole radical in a ferromagnetic fashion, despite the fact that both the EPR spectrum and the magnetic moment were only consistent with a low-spin iron(III) coordinated by a closed-shell corrole.

Our interest in corrole chemistry started with the facile synthesis of tris(pentafluorophenyl)corrole,  $\text{H}_3(\text{tpfc})$  in Scheme 1, and the demonstration that its metal complexes are potent catalysts for a variety of reactions.<sup>7</sup> The substitution pattern in  $\text{H}_3(\text{tpfc})$ —only electron-withdrawing substituents—suggests that it should be much more oxidation resistant than all previously reported corroles, i.e., much more innocent in terms of metal vs macrocycle oxidation. In addition, the presence of  $\beta$ -pyrrole hydrogens in  $\text{H}_3(\text{tpfc})$  is a large advantage for relatively straightforward interpretation of the  $^1\text{H}$  NMR spectra of its paramagnetic complexes. Additional information can be obtained by sensing the *meso*- $\text{C}_6\text{F}_5$  substituents via  $^{19}\text{F}$  NMR spectroscopy. In parallel with many other metal corroles,<sup>8</sup> we have prepared the iron complexes of  $\text{H}_3(\text{tpfc})$  in various oxidation states and with different axial ligands.<sup>8a,9a</sup> These syntheses and the X-ray crystal structures

of the mono- and dinuclear iron(IV) corroles are described in these publications, and we have also demonstrated that the catalytic activity of iron(III) and iron(IV) is very different.<sup>9b</sup> We now report a detailed analysis of the electronic structures of several iron complexes of  $\text{H}_3(\text{tpfc})$  and  $\text{H}_3(\text{tdcc})$ , based on spectroscopic methods and X-ray crystallography. The results reveal no indications for oxidized corrole in any of the complexes, with isolated low-spin and intermediate-spin iron(III) in the bis(pyridine) and bis(ether) complexes, respectively. Quite strong iron to metal back-donation is apparent in the  $\text{Fe}(\text{NO})$  corroles, and the closed-shell corroles support an iron(IV) oxidation state in the  $\text{Fe}(\text{cor})\text{Cl}$  complexes.

## Experimental Section

**Physical Methods.** The  $^1\text{H}$  NMR spectra were recorded on a Bruker AM 200 and Bruker AM 400, operating at 200 and 400 MHz, respectively. Chemical shifts are reported in ppm relative to residual hydrogens in the deuterated chloroform:  $\delta = 7.24$ . An HP 8452A diode array spectrophotometer was used to record the electronic spectra. The EPR spectra were recorded on a Bruker EMX 220 digital X-band radiospectrometer equipped with a Bruker ER 4121VT temperature control system operating within the temperature range of 100–700 K. Spectra processing and parameter calculations were performed using WIN-EPR software. Mass spectroscopy was performed on a TSQ 70 Finnigan with isobutane as carrier gas, and IR spectra were recorded as KBr pellets of a FT-IR Bruker Vector 22.

**Synthetic Methods.** The synthetic details for the preparation and full spectroscopic characterization of  $\text{H}_3(\text{tpfc})$  and its iron complexes are provided in previous publications.<sup>7a,b,9a</sup> X-ray-quality crystals of  $\text{Fe}(\text{tpfc})(\text{NO})$  were obtained via recrystallization from a mixture of benzene and *n*-heptane.

**$\text{H}_3(\text{tdcc})$ .** A total of 1.32 g (7.5 mmol) of solid 2,6-dichlorobenzaldehyde was put in a 50 mL flask that was heated on a hot plate (about 75–80 °C) to melt the substrate. To the same flask was added at once 1.05 mL (15 mmol) of pure pyrrole. After being stirred for 10 min, the mixture was cooled to RT (room temperature) and the resulting brown solid was dissolved in  $\text{CH}_2\text{Cl}_2$ . A 0.75 g amount of DDQ was added to the solution, and the mixture was stirred for 1 h at RT. Purification of  $\text{H}_3(\text{tdcc})$  was performed on a chromatographic column with silica gel (20:5 *n*-hexane/ $\text{CH}_2\text{Cl}_2$ ). A 70 mg amount (3.8% yield) of pure  $\text{H}_3(\text{tdcc})$  was obtained. UV-vis ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{max}}$ , nm) (relative  $\epsilon$ ): 415 (1.00), 570 (0.32), 609 (0.24).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz,  $\delta$  in ppm,  $J$  in Hz): 8.91 (d,  $J = 4.17$ , 2H,  $\beta$ -pyrrole H), 8.48 (d,  $J = 4.8$ , 2H,  $\beta$ -pyrrole H), 8.33 (m, 4H,  $\beta$ -pyrrole H), 7.73–7.63 (m, 9H, *meso*-Ph H).

**Insertion of Iron into  $\text{H}_3(\text{tdcc})$ , for the Synthesis of  $\text{Fe}(\text{tdcc})(\text{OEt}_2)_2$ ,  $\text{Fe}(\text{tdcc})(\text{py})_2$ ,  $\text{Fe}(\text{tdcc})\text{Cl}$ , and  $\text{Fe}(\text{tdcc})(\text{NO})$ .** All iron corroles were obtained by the previously published procedure for

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Table 1. Crystal and Experimental Data

	Fe(tpfc)(py) <sub>2</sub> <sup>a</sup>	Fe(tpfc)(NO) <sup>a</sup>	Fe(tdcc)(NO)
empirical formula	2C <sub>47</sub> H <sub>18</sub> F <sub>15</sub> FeN <sub>6</sub> ·3/2C <sub>7</sub> H <sub>16</sub>	C <sub>37</sub> H <sub>8</sub> F <sub>15</sub> FeN <sub>5</sub> O·C <sub>7</sub> H <sub>16</sub>	C <sub>37</sub> H <sub>17</sub> Cl <sub>6</sub> FeN <sub>5</sub> O·2C <sub>6</sub> H <sub>6</sub>
fw	2165.34	979.53	972.32
cryst system	triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	14.0800(5)	7.0690(1)	38.6430(13)
<i>b</i> /Å	16.6300(5)	20.0240(7)	14.5000(3)
<i>c</i> /Å	20.9740(8)	27.8390(9)	15.8420(5)
$\alpha$ /deg	101.32(2)	92.089(1)	90.00
$\beta$ /deg	103.88(2)	90.149(2)	100.889(1)
$\gamma$ /deg	93.24(2)	93.555(2)	90.00
<i>V</i> /Å <sup>3</sup>	4647.0(3)	3930.4(2)	8716.8(4)
<i>Z</i>	2	4	8
<i>T</i> /K	115	110	115
<i>D</i> <sub>c</sub> /g·cm <sup>-3</sup>	1.548	1.655	1.482
2 $\theta$ range/deg	4–50	3.5–55	4–51
no. of unique reflens	16 319	16 762	7696
no. of reflens with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	9766	10 966	5630
no. of refined params	1369	1146	562
R1 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.068	0.067	0.063
R1 (all data)	0.133	0.116	0.092
wR2 (all data)	0.193	0.203	0.174
$\Delta\rho$ ] <sub>max</sub> /e·Å <sup>-3</sup>	0.64	0.88	0.96

<sup>a</sup> There are two crystallographically independent corrole species in the asymmetric unit of these structures.

inserting iron into H<sub>3</sub>(tpfc),<sup>9a</sup> i.e., heating of dry DMF or pyridine solution of H<sub>3</sub>(tdcc) under N<sub>2</sub> in the presence of about 20 equiv of FeCl<sub>2</sub>. The products that were obtained directly after metal insertion are Fe(tdcc)(OEt<sub>2</sub>)<sub>2</sub> (after purification of the complex via chromatography on silica gel with diethyl ether) or Fe(tdcc)(py)<sub>2</sub> (via recrystallization of Fe(tdcc)(OEt<sub>2</sub>)<sub>2</sub> from a mixture of benzene and *n*-heptane in the presence of pyridine). To obtain Fe(tdcc)Cl, the red-brown Fe(tdcc)(OEt<sub>2</sub>)<sub>2</sub> was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed extensively by aqueous HCl. Pure Fe(tdcc)Cl (brown color) was obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane. The yields of all the reactions described herein were in the range of 90–95% for pure crystalline materials. The last Fe(III) complex, Fe(tdcc)(NO), was obtained from the iron(IV) chloride as discussed in our previous publication.<sup>9a</sup> Final purification by recrystallization from benzene and *n*-heptane afforded highly crystalline Fe(tdcc)(NO) in about 50% yield. X-ray-quality crystals of Fe(tdcc)(NO) were obtained via recrystallization from a mixture of benzene and *n*-heptane.

**Fe(tdcc)(OEt<sub>2</sub>)<sub>2</sub>.** UV–vis (diethyl ether;  $\lambda_{\text{max}}$ , nm) (relative  $\epsilon$ ): 408 (1.00), 550 (0.26), 730 (0.05). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz,  $\delta$  in ppm): 47.7, 32.7, –61.8, –135.4 (8H,  $\beta$ -pyrrole H), 10.49 and 9.23 (9H, *meso*-Ph H).

**Fe(tdcc)(py)<sub>2</sub>.** UV–vis (C<sub>6</sub>H<sub>6</sub>,  $\lambda_{\text{max}}$ , nm) (relative  $\epsilon$ ): 414 (1.00), 550 (0.27), 752 (0.07). <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>, 200 MHz,  $\delta$  in ppm): 3.5, –34.7, –49.3, –121.3 (8H,  $\beta$ -pyrrole H), 8.9 and 9.23 (9H, *meso*-Ph H). MS (–DCI) [*m/z* (%): 785.1 (100) [M<sup>+</sup> – 2py].

**Fe(tdcc)Cl.** UV–vis (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{\text{max}}$ , nm) (relative  $\epsilon$ ): 368 (0.92), 394 (1.00). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz,  $\delta$  in ppm): 10.0 (s, *para*-H of *meso*-Ph, 2H), 9.7 (s, *para*-H of *meso*-Ph, 1H), 6.6 (s, 2H,  $\beta$ -pyrrole), –2.9 (s, 2H, *meta*-H of *meso*-Ph), –3.3 (s, 2H, *meta*-H of *meso*-Ph), –3.8 (s, 2H,  $\beta$ -pyrrole), –4.3 (s, 1H, *meta*-H of *meso*-Ph), –4.8 (s, 1H, *meta*-H of *meso*-Ph), –8.9 (s, 2H,  $\beta$ -pyrrole), –37.5 (s, 2H,  $\beta$ -pyrrole). MS (+DCI) [*m/z* (%): 821.9 (5) [MH]<sup>+</sup>, 784.9 (100) [MH<sup>+</sup> – Cl]. MS (–DCI) [*m/z* (%): 820.0 (20) [M]<sup>+</sup>, 785.1 (100) [M<sup>+</sup> – Cl].

**Fe(tdcc)(NO).** UV–vis (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{\text{max}}$ , nm) (10<sup>–4</sup> $\epsilon$ ): 378 (7.82), 538 (1.16). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$  in ppm, *J* in Hz):  $\delta$  = 7.98 (d, *J* = 4.65, 2H,  $\beta$ -pyrrole H), 7.57 (d, *J* = 4.88, 2H,  $\beta$ -pyrrole H), 7.58–7.42 (m, 9H, *meso*-Ph H), 7.26 (d, *J* = 4.87, 2H,  $\beta$ -pyrrole H), 7.20 (d, *J* = 4.86, 2H,  $\beta$ -pyrrole H). MS (+DCI) [*m/z* (%):

814.9 (30) [MH]<sup>+</sup>, 784.6 (100) [MH<sup>+</sup> – (NO)]. MS (–DCI) [*m/z* (%): 815.1 (10) [M]<sup>+</sup>, 785.1 (100) [M<sup>+</sup> – (NO)]. IR (KBr):  $\nu$  = 1783 cm<sup>–1</sup> (NO).

**Crystallography.** The diffraction measurements were carried out on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.7107 Å). The crystalline samples of the analyzed compounds were covered with a thin layer of light oil and cooled to 110–115 K to minimize solvent escape, structural disorder, and thermal motion effects and increase the precision of the results. The crystal and experimental data for Fe(tpfc)(py)<sub>2</sub>, Fe(tpfc)(NO), and Fe(tdcc)(NO) are summarized in Table 1. These structures were solved by direct methods (SIR-92)<sup>10</sup> and refined by full-matrix least-squares on *F*<sup>2</sup> (SHELXL-97).<sup>11</sup> All non-hydrogen atoms were refined anisotropically. The hydrogens were located in idealized positions (the methyls being treated as rigid groups) and were refined using a riding model with fixed thermal parameters [*U*<sub>ij</sub> = 1.2*U*<sub>ij</sub>(equiv) for the atom to which they are bonded]. The three compounds crystallized with uncoordinated solvent, which is disordered in the crystal lattice even at the low temperature. Partial rotational disorder characterizes also some of the pentafluorophenyl and dichlorophenyl rings of the corrole molecules (as it is demonstrated in particular by excessively large thermal displacement parameters of the corresponding halogen and carbon atoms), affecting to some extent the quality of the crystals (high mosaicity) and diffraction data (high percentage of weak reflections) and, thus, the precision of the crystallographic determination.

## Results and Discussion

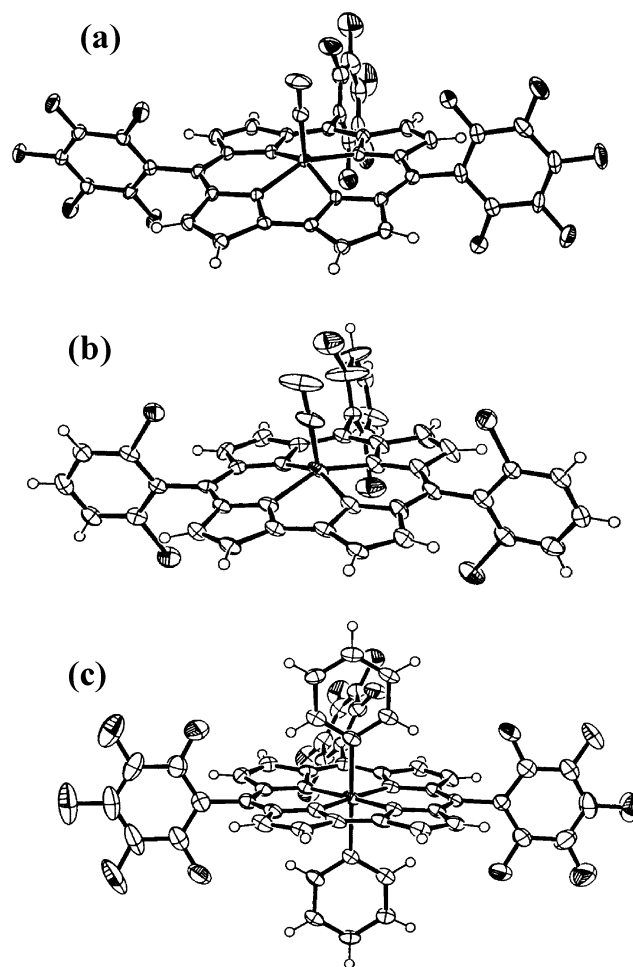
**Synthesis.** The procedures for insertion of iron into H<sub>3</sub>(tpfc) and the electrochemistry of the complexes were fully described in one of our previous publication.<sup>9a</sup> In general, metalation of H<sub>3</sub>(tpfc) proceeds readily in hot DMF with FeCl<sub>2</sub> as the metal source. The oxidation state of the isolated

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iron corrole is determined by the workup procedure. Elution of the crude reaction mixture with solutions that contain either diethyl ether or pyridine results in the red iron(III) complexes,  $\text{Fe}(\text{tpfc})(\text{OEt}_2)_2$  and  $\text{Fe}(\text{tpfc})(\text{py})_2$ , respectively. When no coordinating ligands are added (the DMF is also completely removed), an extensive extraction with either aqueous HCl or NaOH solutions allows the quantitative isolation of the iron(IV) complexes,  $\text{Fe}(\text{tpfc})\text{Cl}$  and  $[\text{Fe}(\text{tpfc})]_2\text{O}$ , respectively. An additional *formally* iron(III) complex of  $\text{H}_3(\text{tpfc})$  was  $\text{Fe}(\text{tpfc})(\text{NO})$ , which was obtained by treating  $\text{Fe}(\text{tpfc})\text{Cl}$  with  $\text{NaNO}_2$ . Some of the complexes can be converted into each other by simple means, as illustrated in Scheme 1. In addition to the above methodologies,  $[\text{Fe}(\text{tpfc})]_2\text{O}$  can also be obtained via the crystallization of  $\text{Fe}(\text{tpfc})(\text{OEt}_2)_2$  from aerobic mixtures of benzene and *n*-heptane in the absence of diethyl ether. In the presence of excess pyridine,  $\text{Fe}(\text{tpfc})\text{Cl}$  was not stable and was auto-reduced to  $\text{Fe}(\text{tpfc})(\text{py})_2$ . Except for  $\text{Fe}(\text{tpfc})(\text{OEt}_2)_2$ , X-ray-quality crystals were obtained for all complexes. In our first publication about corroles, we also reported the novel tris-(2,6-dichlorophenyl)corrole,  $\text{H}_3(\text{tdcc})$ ,<sup>7a</sup> whose large *ortho*-phenyl substituents may serve as to avoid the formation of  $\mu$ -oxo bis metallic corroles. Insertion of iron into  $\text{H}_3(\text{tdcc})$  was performed exactly by the same methodology as in the case of  $\text{H}_3(\text{tpfc})$ . The new  $\text{Fe}(\text{tdcc})(\text{OEt}_2)_2$ ,  $\text{Fe}(\text{tdcc})(\text{py})_2$ ,  $\text{Fe}(\text{tdcc})\text{Cl}$ , and  $\text{Fe}(\text{tdcc})(\text{NO})$  complexes were prepared and characterized by spectroscopy, as well as by X-ray crystallography for the nitrosyl complex. As anticipated, a complex analogous to  $[\text{Fe}(\text{tpfc})]_2\text{O}$  is not formed with this corrole.

**Crystallography.** The structures of the iron(IV) complexes,  $\text{Fe}(\text{tpfc})\text{Cl}$  and  $[\text{Fe}(\text{tpfc})]_2\text{O}$ , were described in two separate publications.<sup>8a,9a</sup> The previously reported structure of  $\text{Fe}(\text{tpfc})(\text{py})_2$  was obtained with a large R factor, and we have now succeeded in growing better crystals from a different crystallization environment.<sup>9a</sup> In addition, we have obtained X-ray-quality crystals of the two nitrosyl complexes,  $\text{Fe}(\text{tpfc})(\text{NO})$  and  $\text{Fe}(\text{tdcc})(\text{NO})$ . The three new structures are depicted in Figure 1, and selected structural parameters of all iron triarylcorrole complexes that were isolated so far are summarized in Table 2. The structure of  $\text{Fe}(\text{tpfc})(\text{py})_2$  consists of a quite planar macrocycle with the metal ion located perfectly in the center. The Fe–N(pyrrole) bond lengths (1.862–1.906 Å) are comparable to that in  $\text{Co}(\text{tpfc})(\text{py})_2$  (1.873–1.900 Å) and significantly shorter than in  $\text{Cr}(\text{tpfc})(\text{py})_2$  (1.926–1.952 Å).<sup>12</sup> As there cannot be any doubt that  $\text{Co}(\text{tpfc})(\text{py})_2$  contains a closed-shell corrole (it is a perfectly diamagnetic low-spin cobalt(III) complex);<sup>12a</sup> the same conclusion is most likely for  $\text{Fe}(\text{tpfc})(\text{py})_2$ . The significantly longer Fe–N(pyridine) bond lengths in the iron corrole (2.022–2.042 Å) relative to the analogous cobalt complex (1.994 Å) is reasonable, considering the different ligand field stabilization energies of low-spin  $d^5$  and  $d^6$  metal ions. Another expectation for low-spin iron(III) complexes that is fulfilled in  $\text{Fe}(\text{tpfc})(\text{py})_2$  is the mutual arrangement



**Figure 1.** X-ray structures of (a)  $\text{Fe}(\text{tpfc})(\text{NO})$ , (b)  $\text{Fe}(\text{tdcc})(\text{NO})$ , and (c)  $\text{Fe}(\text{tpfc})(\text{py})_2$ . In (a) and (b), for clarity only, the mean Cl positions of the rotationally disordered central aryl ring are displayed.

of the coordinated pyridine molecules. The twist angles in the two independent species are only 2.3 and 4.2°; i.e., they are almost perfectly parallel to each other as expected for an electronic configuration of  $(d_{xy})^2(d_{xz}, d_{yz})^3$ .<sup>13</sup> The corrole macrocycle is essentially flat. The largest deviation from the mean plane defined by all the corrole atoms is only 0.14 Å, and the twist angles between adjacent pyrrole rings are within 2–9°.

A different comparison is with the nitrosyl complexes, whose structural parameters are perfectly consistent with authentic ferric ions coordinated to nitric oxide. The Fe–NO bonds in both  $\text{Fe}(\text{tpfc})(\text{NO})$  and  $\text{Fe}(\text{tdcc})(\text{NO})$  are practically linear (the three independent Fe–N–O bond angles are within 172–178°), as expected for  $\{\text{FeNO}\}^6$  complexes.<sup>14</sup> The five-coordinate metal ion deviates, by 0.45–0.46 Å, from the corrole plane toward the axial ligand,

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**Table 2.** Selected Parameters for All Structurally Characterized Iron Complexes of Triarylcorroles

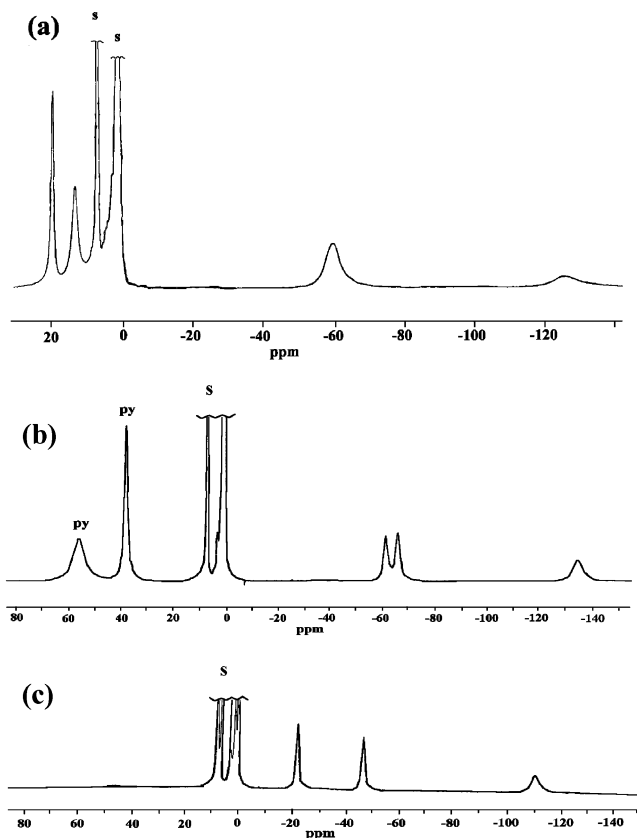
complex	Fe(tpfc)Cl	[Fe(tpfc)] <sub>2</sub> O	Fe(tpfc)(py) <sub>2</sub> <sup>a</sup>	Fe(tpfc)(NO) <sup>a</sup>	Fe(tdcc)(NO)
Fe–N(corrole) bond length range/Å	1.880–1.922	1.884–1.923, 1.888–1.929	1.862–1.906	1.893–1.926	1.898–1.922
Fe–axial ligand dists/Å	2.238(2)	1.709(4), 1.726(4)	2.022, 2.042(4)	1.639, 1.648(4)	1.641(4)
Fe out-of-plane displacement/Å <sup>b</sup>	0.367(1)	0.421(1), 0.426(1)	0.010, 0.015(1)	0.465, 0.464(1)	0.452(2)
C <sub>6</sub> F <sub>5</sub> -corrole angles/deg	70.8, 64.0, 60.6	66.3, 79.0, 78.4, 59.0, 73.1, 68.5	79.9, 66.3, 85.6, 80.6, 61.7, 72.0	64.7, 84.5, 81.3, 78.1, 86.2, 77.3	87.8, 82.3, 83.0
Fe–NO angle/deg				177.3(4), 178.0(4)	172.3(4)
NO bond length/Å				1.164(4), 1.166(4)	1.169(5)
NO stretching freq/cm <sup>-1</sup>				1790	1783

<sup>a</sup> There are two crystallographically independent corrole species in the asymmetric unit of these structures. <sup>b</sup> Plane defined by the four inner N atoms. <sup>c</sup> The aryl rings in these compounds exhibit in most cases large-amplitude wagging rotational motion, or partial orientational disorder, about the C–C bonds through which they are bonded to the main corrole framework. The listed dihedral angles between these substituents and the central corrole ring relate to the average position of the aryl groups.

assuming a square-pyramidal coordination environment and imparting to the complexes a domed conformation. This involves also a consistent deviation of the pyrrole N atoms (toward Fe) from the mean plane of the 19-membered all-carbon corrole ring, 0.09–0.16 Å in Fe(tpfc)(NO) and 0.04–0.14 Å in Fe(tdcc)(NO). The latter values reflect also on the slightly more ruffled corrole structure in Fe(tpfc)(NO) than in Fe(tdcc)(NO), as may be appreciated by the maximal deviations of the individual atoms from the mean corrole plane (0.18 and 0.23 Å vs 0.13 Å) and twist angle range between adjacent pyrrole rings along the macrocycle (1–16° vs 3–8°). The new nitrosyl complexes are also quite ideal {FeNO}<sup>6</sup> complexes. As expected for this diamagnetic electronic state, their NMR spectra are sharp and the Fe–NO units are linear (Table 2). In addition, the NO stretching frequencies of Fe(tpfc)(NO), Fe(tdcc)(NO), and Fe(eoc)(NO) (1790, 1783, and 1767 cm<sup>-1</sup>, respectively) display a trend of increasing  $\pi$ -donation ability by these corroles.<sup>14c</sup> These values may be compared to that of corresponding porphyrin complexes, which are in the range of 1862–1937 cm<sup>-1</sup>. Another indication for the significantly stronger  $\pi$ -donation into the Fe(NO) moiety by corroles is the longer N–O bonds therein, 1.169(5)–1.164(4) Å vs 1.144(3)–1.112(4) Å in porphyrins.<sup>14</sup>

One feature of tetraarylporphyrin radicals is that the angles between the aryls and the porphyrin are usually significantly smaller than in closed-shell complexes.<sup>15</sup> For example, the dihedral angles between the phenyl rings and the oxidized porphyrin in [Fe(tp<sup>•+</sup>)Cl]<sup>+</sup> are as low as 43.7, 48.8, 39.5, and 46.2°. An inspection of Table 2 reveals that in the nitrosyl complexes, where the observed data rule out corrole oxidation, the aryl substituents are aligned in a roughly perpendicular manner with respect to the corrole macrocycle. The corresponding dihedral angles between the mean planes of the aryl and the corrole residues vary from 65 to 88°. As the angles in the other complexes (Fe(tpfc)Cl, [Fe(tpfc)]<sub>2</sub>O, Fe(tpfc)(py)<sub>2</sub>) are also within the same range, we conclude that by crystallographic criteria there is no indication for an open-shell corrole in any of the complexes.

**Spectroscopy.** The most informative <sup>1</sup>H NMR resonances are those of the  $\beta$ -pyrroles, as the extensive work with iron porphyrins revealed the following rules with regard to their positioning: at very low field for high-spin iron(III) ( $S =$



**Figure 2.** <sup>1</sup>H NMR spectra of (a) Fe(tpfc)(OEt<sub>2</sub>)<sub>2</sub> (25 °C, benzene-*d*<sub>6</sub>), (b) Fe(tpfc)(py)<sub>2</sub> (25 °C, benzene-*d*<sub>6</sub>), and (c) Fe(tpfc)(py)<sub>2</sub> (25 °C, pyridine-*d*<sub>5</sub>). (s and py stand for coordinated pyridine and solvent impurities, respectively.)

5/2), at very high field for low-spin iron(III) ( $S = 1/2$ ), and medium-high to medium-low fields for intermediate- and mixed-spin iron(III) ( $S = 3/2$  or  $S = 5/2 + S = 1/2$ ).<sup>16</sup> The spectrum of the bis(ether) corrole [Fe(tpfc)(OEt<sub>2</sub>)<sub>2</sub>] (Figure 2a) displays two resonances at low field and two at high field (19.7, 13.4, –60.0, –126.0), consistent with an intermediate-spin iron(III) complex. In contrast, all four resonances of the bis(pyridine) corrole [Fe(tpfc)(py)<sub>2</sub>] (3.2, –61.1, –65.8, –134.6 ppm) are located at high field as expected for a low-spin iron(III) complex.<sup>17</sup> This is further

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(17) The <sup>1</sup>H NMR measurements, performed in benzene only, indicate two signals at high field and four at low field (Figure 2b), but when pyridine-*d*<sub>5</sub> was utilized as a solvent, the two resonances at high field were absent. The same phenomenon was obtained for the iron(III) complex of H<sub>3</sub>(tdcc).

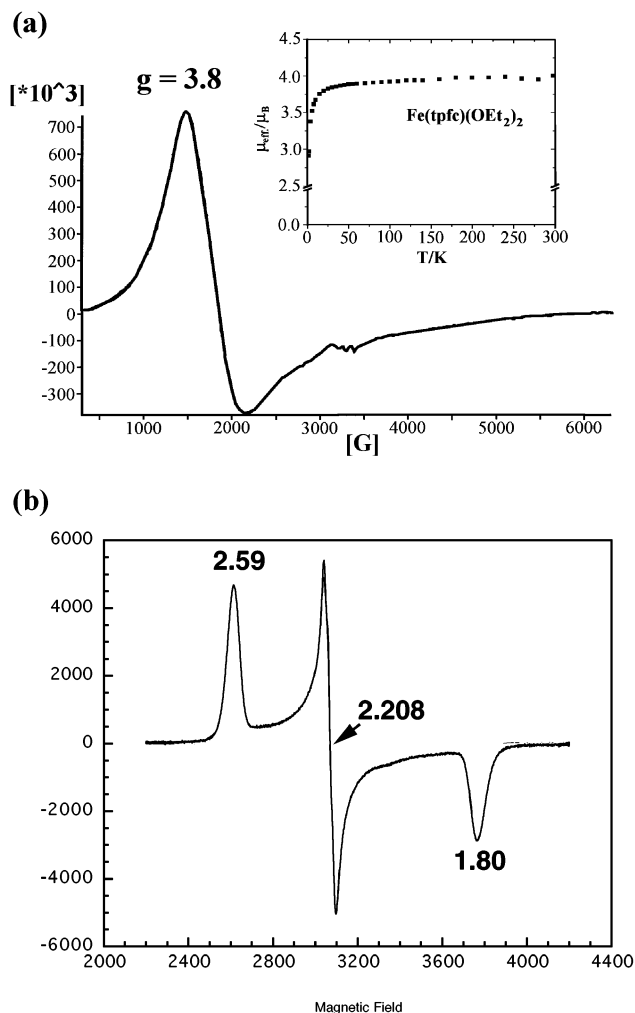
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**Table 3.** Paramagnetic  $^1\text{H}$  NMR Shifts for High-Valent Iron Corroles and Porphyrins (in ppm)

complex	<i>para</i> -H	<i>meta</i> -H	$\Delta(p-m)$	<i>pyrrole</i> H	ref
$\text{Fe}^{\text{III}}(\text{tpp}^{\bullet+})(\text{ClO}_4)_2$	-13.2	35.0	47.2	31.1	19
$\text{Fe}^{\text{III}}(\text{tpp}^{\bullet+})(\text{Cl})(\text{ClO}_4)_2$	29.5	-12.4	34.9	66.1	20, 21
$\text{Fe}^{\text{III}}(\text{tpp}^{\bullet+})(\text{Cl})(\text{SbCl}_6)$	35.0	-12.3	37.6	68.8	19
$\text{Fe}^{\text{III}}(\text{tpp}^{\bullet+})(\text{imidazole})_2$	-22.1	30.4	52.5	-40.1	22
$\text{Fe}^{\text{IV}}(\text{tdcc})\text{Cl}$	10.0, 9.7	-2.9, -3.3, -4.3, -4.8	<15	6.6, -3.8, -8.9, -37.5	this work
$\text{Fe}^{\text{IV}}(\text{tpfc})\text{Cl}$				-2.5, -3.1, -12.1, -33.6	9a
$\text{Fe}^{\text{IV}}(\text{tmp})(\text{OCH}_3)_2$		7.7		-37.5	23, 24
$\text{Fe}^{\text{IV}}(\text{tmp})(\text{O})$		6.2, 6.8		5.9	25

complex	$\text{CH}_2$	$\text{CH}_3$	<i>meso</i> -H	ref
$\text{Fe}(\text{oep}^{\bullet+})(\text{Cl})(\text{ClO}_4)_2$	30.5, 29.6	3.16	18	20
$\text{Fe}(\text{oec})\text{Cl}$	-5.7, -29.9	-0.3, -2.5	177, 189	4a

**Figure 3.** The EPR spectra of (a)  $\text{Fe}(\text{tpfc})(\text{OEt}_2)_2$  (powder, 130 K, insert, magnetic susceptibility measurements) and (b)  $\text{Fe}(\text{tpfc})(\text{py})_2$  (1:1:1  $\text{CH}_2\text{Cl}_2$ /toluene/pyridine; 20 K).

confirmed by the corresponding EPR spectra (Figure 3a,b), which also follow the well-known general pattern of iron porphyrins. The spectrum of the bis(ether) complex consists of a broad feature with  $g = 3.8$  expected for  $S = 3/2$ , while the bis(pyridine) complex displays the characteristic  $g_x, g_y, g_z$  pattern for low-spin iron(III) around  $g = 2$ . Finally, the  $S = 3/2$  spin state of  $\text{Fe}(\text{tpfc})(\text{OEt}_2)_2$  was validated via magnetic susceptibility measurements (Figure 3a, inset), obtained by SQUID on a powdered sample. We may thus safely conclude that both complexes are authentic iron(III)

corroles, without any indications for oxidation of the corrole macrocycle therein.

As mentioned in the Introduction, the only supporting evidence for iron(III) corrole radicals comes from the unusual  $^1\text{H}$  NMR chemical shifts of *meso*-CH in  $\text{Fe}(\text{omc})\text{Cl}$ . Accordingly, we have analyzed the spectrum of  $\text{Fe}(\text{tdcc})\text{Cl}$  (Figure 4) with particular emphasis on *para*-H and *meta*-H of its *meso*-aryl groups. This allows a comparison with high-valent iron porphyrins (Table 3), for which a consensus about the metal vs porphyrin oxidation exists.<sup>18</sup> The distinction between the aryl and  $\beta$ -pyrrole protons was easily achieved, due to the similarity of the chemical shifts of the latter in  $\text{Fe}(\text{tdcc})\text{Cl}$  and  $\text{Fe}(\text{tpfc})\text{Cl}$ . The assignment shown in the figure is based on the following considerations: The aryl on C10 is different from the magnetically identical groups on C5 and C15 due to the  $C_{2v}$  symmetry of the complex. Each aryl carries two nonequivalent *meta*-H protons, syn and anti to the Fe-Cl bond; the spectral width of *para*-H resonances is smaller than of *meta*-H due to the larger distance from the paramagnetic metal ion. In Table 3 we have summarized both the chemical shifts and the differences between the *para* and *meta* protons,  $\Delta(p-m)$ , of the *meso*-aryl groups of all relevant complexes. The difference between  $\text{Fe}(\text{tdcc})\text{Cl}$  and the well-established iron(III) porphyrin radical complexes is highly significant:  $\Delta(p-m)$  is much smaller in  $\text{Fe}(\text{tdcc})\text{Cl}$  (<15 ppm vs > 35 ppm), and while the pattern of low-field *para*-H and high-field *meta*-H is shared by  $\text{Fe}(\text{tdcc})\text{Cl}$  and the pentacoordinated iron(III) porphyrin radical complexes, this is not true for the  $\beta$ -pyrrole protons (6.6 to -37.5 vs 66 to 69 ppm). In fact, the trend of both *meta*-H and *pyrrole*-H being located at low field, found in  $\text{Fe}(\text{tdcc})\text{Cl}$ , is only shared by the iron(IV) porphyrins  $\text{Fe}(\text{tmp})(\text{O})$  and  $\text{Fe}(\text{tmp})(\text{OCH}_3)_2$ . Accordingly, this analysis adds confidence to the conclusion that  $\text{Fe}(\text{tpfc})\text{Cl}$  and  $\text{Fe}(\text{tdcc})\text{Cl}$  are not iron(III) corrole radical complexes but authentic iron(IV) corroles. Finally, we have also put

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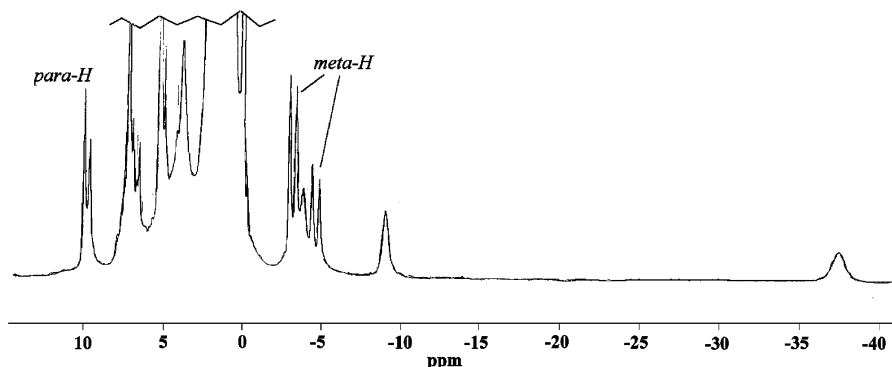


Figure 4.  $^1\text{H}$  NMR spectrum of  $\text{Fe}(\text{tdcc})\text{Cl}$  (25  $^\circ\text{C}$ ,  $\text{CDCl}_3$ ).

into Table 3 the information for the closely related corrole and porphyrin complexes  $\text{Fe}(\text{oec})\text{Cl}$  and  $[\text{Fe}(\text{oep}^+)\text{Cl}](\text{ClO}_4)$ , that demonstrates the large differences between the relevant protons therein. This suggests that  $\text{Fe}(\text{oec})\text{Cl}$  is also an iron(IV) corrole rather than an iron(III) corrole radical complex, as the data of Vogel et al indicate indeed.

### Conclusions

We have isolated several distinctively different iron complexes of tris(pentafluorophenyl)- and tris(2,6-dichlorophenyl)corrole. A combination of spectroscopic methods and X-ray crystallography allowed the conclusion that the bis(ether) and bis(pyridine) complexes are authentic intermediate-spin and low-spin iron(III) complexes, respectively. The diamagnetism and the linear  $\text{Fe}-\text{NO}$  bonds in the nitrosyl complexes were also perfectly consistent with a ferric ion supported by a closed-shell corrolato ligand. The spectral comparison of the iron(IV) corroles with high-valent iron porphyrins reveals highly significant differences relative to

iron(III) porphyrin cation radicals but some similarities to established iron(IV) porphyrins. Accordingly, we conclude that there is no indication for an open-shell corrole in any of the complexes; i.e., they are best formulated as authentic iron(III) and iron(IV) corroles.

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**Supporting Information Available:** Tables of crystal data, structure refinement details, atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles in CIF format for  $\text{Fe}(\text{tpfc})(\text{py})_2$ ,  $\text{Fe}(\text{tpfc})(\text{NO})$ , and  $\text{Fe}(\text{tdcc})(\text{NO})$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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