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NMR and Structural Investigations of A Nonplanar Iron Corrolate: Modified Patterns of Spin Delocalization and Coupling in A Slightly Saddled Chloroiron(III) Corrolate Radical

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An undecasubstituted chloroiron corrolate, octamethyltriphenylcorrolatoiron chloride, (OMTPCorr)FeCl, has been synthesized and studied by X-ray crystallography and ^{1}H and ^{13}C NMR spectroscopy. It is found that, although the structure is slightly saddled, the average methyl out-of-plane distance is only 0.63 Å, while it is much greater for the dodecasubstituted porphyrinate analogue (OMTPP)FeCl (1.19 Å) (Cheng, R.-J.; Chen, P.-Y.; Gau, P.-R.; Chen, C.-C.; Peng, S.-M. *J. Am. Chem. Soc.* **1997**, *119*, 2563–2569). In addition, the distance of iron from the mean plane of the four macrocycle nitrogens is also smaller for (OMTPCorr)FeCl (0.387 Å) than for (OMTPP)FeCl (0.46 Å). The ^{1}H and ^{13}C NMR spectra of (OMTPCorr)FeCl, as well as the chloroiron complexes of triphenylcorrolate, (TPCorr)FeCl; 7,13-dimethyl-2,3,8,12,17,18-hexaethylcorrolate, (DMHECorr)FeCl; 7,8,12,13-tetramethyl-2,3,17,18-tetraethylcorrolate, (TMTECorr)FeCl; and the phenyliron complex of 7,13-dimethyl-2,3,8,12,17,18-hexaethylcorrolate, (DMHECorr)FePh, have been assigned, and the spin densities at the carbons that are part of the aromatic ring of the corrole macrocycle have been divided into the part due to spin delocalization by corrole → Fe π donation and the part due to the unpaired electron present on the corrole ring. It is found that although the spin density at the β-pyrrole positions is fairly similar to that of (TPCorr)FeCl, the *meso*-phenyl-carbon shift differences $\delta_m - \delta_p$ are opposite in sign of those of (TPCorr)FeCl. This finding suggests that the radical electron is ferromagnetically coupled to the unpaired electrons on iron, rather than antiferromagnetically coupled, as in all of the other chloroiron corrolates. The solution magnetic moment was measured for (OMTPCorr)FeCl and found to be $\mu_{eff} = 4.7 \pm 0.5\ \mu_B$, consistent with $S = 2$ and ferromagnetic coupling. From this study, two conclusions may be reached about iron corrolates: (1) the spin states of chloroiron corrolates are extremely sensitive to the out-of-plane distance of iron, and (2) pyrrole-H or -C shifts are not useful in delineating the spin state and electron configuration of (anion)iron corrolates.

Introduction

The investigation of porphyrins and their metal complexes is an intriguing arena for researchers, because the richness of the properties of these compounds is of interest to scientific disciplines ranging from medicine to materials science.[1,2] Metalloporphyrins in living systems play many functions essential for life, and the elucidation of both the geometric and the electronic structures of these compounds is of paramount importance for the detailed understanding of the complex mechanisms of biological systems.[3] Furthermore, the possibility of mimicking the complex chemistry exhibited by metalloporphyrins in living organisms with

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synthetic models opens the possibility of exploiting them in a wide range of different applications, from medical fields[4] to catalysts and sensors.[5]

This appealing scenario is even more enriched by the preparation of porphyrin analogues, that is, macrocycles with modified molecular skeletons.[6] These porphyrin analogues are interesting from both theoretical and applicative points of view, because they allow investigation of the structure–property relationships and, consequently, the rational modification of a metal derivative for a specific application.

Among the plethora of porphyrin analogues reported in the literature, corroles have received increasing attention in the past few years.[7–9] The reason for the interest in these porphyrin-related macrocycles is mainly due to the coordination chemistry of corroles, which show unique and intriguing behaviors that are clearly distinguishable from those of porphyrins. The electron configuration of metallocorrolates has been the focus of particular attention because the formal oxidation state of the coordinated metal in corrole derivatives is sometimes higher than that of the corresponding metalloporphyrinates.[10,11] However, the noninnocent character of corrole ligands makes difficult and elusive the exact definition of the electronic configuration of some metal derivatives.[12] Recent careful analysis of ^{1}H NMR data has greatly helped this definition.[13]

The seminal work in the field of iron corrolates was the report of the Vogel group on iron derivatives of 2,3,7,8,12,13,17,18-octaethylcorrole (OECorr).[14] In these complexes, the formal oxidation state is Fe(IV), and this feature is particularly intriguing because Fe(IV) porphyrinates have been proposed as reactive intermediates in some enzymes.[15] It was thus interesting to determine if Fe(IV) could be stabilized when coordinated to corroles. However, the characterization of these iron corrolates did not completely elucidate their electronic configurations, because two different structures are compatible with some of the experimental data: Fe(IV)Corr(3−) or Fe(III)Corr(2−•), where the macrocycle is a one-electron oxidized radical. We contributed to this field by reporting and interpreting ^{1}H NMR and EPR spectroscopic data for chloroiron β-octaalkylcorrolates and their bis-imidazole complexes,[16] as well as their complex formation with and autoreduction by the cyanide ion,[17] and we unambiguously showed their characterization as Fe(III)-Corr(2−•) π-cation radicals. A more detailed study, corroborated by magnetic susceptibility, NMR, and Mössbauer spectroscopies, as well as DFT calculations, showed that the data were only consistent with the chloroiron β-octaalkylcorrolates having the electron configuration Fe(III) corrolate(2−•) π-cation radical, while for a phenyliron β-octaalkylcorrolate, the results indicated the Fe(IV) corrolate(3−) formulation, although in this case, the corrole also behaves as a noninnocent ligand,[18] with significant positive and negative spin densities at various sites on the macrocycle, where the sum equals zero.

Significant input into the characterization of metallocorrolate complexes has been the definition of synthetic routes for the preparation of 5,10,15-triarylcorroles.[19–31] In this case, in fact, corroles can be prepared in gram quantities by using facile synthetic procedures from commercially available starting materials; furthermore, different substituents can be introduced both at the β-pyrrole and at the *meso*-carbon positions, thus allowing a fine-tuning of the electronic characteristics of the corrole ligand.

We have reported studies of a series of chloroiron triphenylcorrolates by ^{1}H and ^{19}F NMR spectroscopy;[32,33] the results obtained showed that in all of these complexes, including the chloroiron tris(pentafluorophenyl)corrolate, the electronic structure is Fe(III)Corr(2−•). In contradiction to these results, Gross and co-workers claimed that there is "...no indication for corrole radicals" but rather simply stated that the chloroiron complexes have the Fe(IV) corrole(3−) electronic configuration.[34] More recently, this group has claimed that all halogen anion iron triphenylcorrolates contain

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Fe(IV), on the basis of the changes in pyrrole-H shifts as a function of the halide ion.[35] In particular, this group has assigned and compared the pyrrole-H shifts of the four halide complexes of haloiron triphenylcorrolates (F^-: +16, +3, −4, −3l ppm; Cl^-: +3, −8, −3, −34 ppm; Br^-: −4, −14, −2, −35 ppm; I^-: −24, −26, +1, −36 ppm, respectively, at 20 °C, listed in the order 2,18-, 8,12-, 7,13-, and 3,17-H) to those of the halomanganese(III) tetraphenylporphyrinates[36] and have noted that the pyrrole-H chemical shifts become larger in magnitude upon going through the series F, Cl, Br, I[36] and that the same thing happens for haloiron(III) porphyrinates, although the signs of the shifts are opposite.[37] On the basis of this similarity, which did not include the actual chemical shifts, or even their signs, they concluded that the electron configuration of the haloiron triphenylcorrolates is that of Fe(IV) Corr(3−).[35] However, the oxidation states and electron configurations of these systems differ, with halomanganese(III) porphyrinates being d^4, $S = 2$, with the electron configuration being $d_{xz}^1d_{yz}^1d_{xy}^1d_{z^2}^1$; haloiron(III) porphyrinates being d^5, $S = {}^5/_2$, with the electron configuration being $d_{xz}^1d_{yz}^1d_{xy}^1d_{z^2}^1d_{x^2-y^2}^1$; and the supposed haloiron(IV) corrolates being d^4, $S = 1$, with the electron configuration being either $d_{xy}^2d_{xz}^1d_{yz}^1$ or $d_{xz}^2d_{yz}^1d_{xy}^1$. The first two of these three systems have pyrrole-H chemical shifts that differ by ∼110 ppm (−30 and +78 ppm, respectively, at 35 °C) and different patterns of spin delocalization, with σ spin delocalization from the $d_{x^2-y^2}$ electron having a marked effect upon the chemical shifts of high-spin Fe(III) porphyrinates in comparison to those of Mn(III) porphyrinates, where that orbital is empty.[36]

The haloiron triphenylcorrolates, on the other hand, with the pyrrole-H chemical shifts given above, have average pyrrole-H chemical shifts that vary widely with the halide, with $\langle\delta_{\text{pyrr}-\text{H}}\rangle = -9, -21, -27.5$, and -42.5 ppm for the F^-, Cl^-, Br^-, and I^- complexes, respectively, while for the Mn(III) and Fe(III) tetraphenylporphyrinates, the chemical shifts vary by less than 2 ppm through the series, at a given temperature. Thus, it is difficult to ascertain how the authors could come to the conclusion that a simple comparison of chemical shift *trends* for three different metal complexes, having different electron configurations and using different orbitals for spin delocalization and having different chemical shifts (even different signs), nevertheless, have the "same" orbitals of the macrocycle being involved in spin delocalization in all three cases, and that this proves that the haloiron corrolates are Fe(IV) Corr(3−) rather than $S = {}^3/_2$ Fe(III) Corr(2−•), with antiferromagnetic coupling between iron and macrocycle electrons.

One system that would have been a better analogue for the comparison of ^{1}H NMR shifts to those of the supposed haloiron(IV) corrolates is the phenyliron(IV) porphyrinates, which have been shown to have $S = 1$ with $d_{xy}^2d_{xz}^1d_{yz}^1$ electron configurations.[38] These complexes, as the noncoordinating ClO_4^- salts, have extrapolated pyrrole-H chemical shifts of about −45 ppm at 25 °C.[38] Note that only the iodoiron triphenylcorrolate of the haloiron series[35] has an average pyrrole-H shift in this range at ambient temperatures.

As mentioned above, for $S = 1$ Fe(IV), the electron configuration is expected to be either $d_{xy}^2d_{xz}^1d_{yz}^1$ or $d_{xz}^2d_{yz}^1d_{xy}^1$, while for $S = {}^3/_2$ Fe(III), the electron configuration could be either $d_{xy}^2d_{xz}^1d_{yz}^1d_{z^2}^1$ or $d_{xz}^2d_{yz}^1d_{xy}^1d_{z^2}^1$. For the first configuration of each of these oxidation states listed, there is one unpaired electron in each of the π-symmetry orbitals, d_{xz} and d_{yz}, while in the second configuration of each, there is only one unpaired electron present, which is shared between the two d_π orbitals. Such d_π unpaired electrons can be readily delocalized to the π-symmetry orbitals of the corrolate macrocycle that have a nodal plane between two opposite nitrogens, that is, those that would be called the *3e(π)* or *4e(π)* orbitals of a porphyrin ring. In comparison, if the macrocycle is planar, or at least not ruffled, no delocalization to the corrolate is expected as a result of an unpaired electron in the d_{xy} orbital.[39] All chloro- and phenyliron corrolate structures reported previously exhibit no ruffling of the macrocycle.[14,40] Thus, for the three lowest-energy d orbitals of both $S = 1$ Fe(IV) and $S = {}^3/_2$ Fe(III), only the d_π unpaired electron(s) is (are) expected to be involved in spin delocalization to the corrolate ring, by Corr → Fe π donation to the half-filled d_π orbital(s). However, as we will show below, the $S = {}^3/_2$ Fe(III) state also has an unpaired electron in the d_{z^2} orbital, and this unpaired electron has important consequences for the pattern of spin delocalization observed for complexes of $S = {}^3/_2$ Fe(III) as compared to $S = 1$ Fe(IV).

Six of the frontier orbitals of the corrolate macrocycle, plus the two d_π orbitals of the metal, are shown in Figure 1A.[41] The four lowest-energy π orbitals are usually filled; the two d_π orbitals contain either two or three electrons, depending upon electron configuration, while the *4e(π*)*-like orbitals are empty. Spin delocalization can occur from the metal d_π orbitals to the corrolate ring by Corr → Fe π donation utilizing the *3e(π)*-like orbitals, the symmetry interaction for which is shown in Figure 1B, or by Fe → Corr π donation utilizing the *4e(π*)*-like orbitals, which also have proper symmetry to interact with the d_π orbitals. For low-spin Fe(III) porphyrinates, it has been shown conclusively over many years that the *3e(π)* orbitals are used exclusively,[42−45] and while it was thought for many years,

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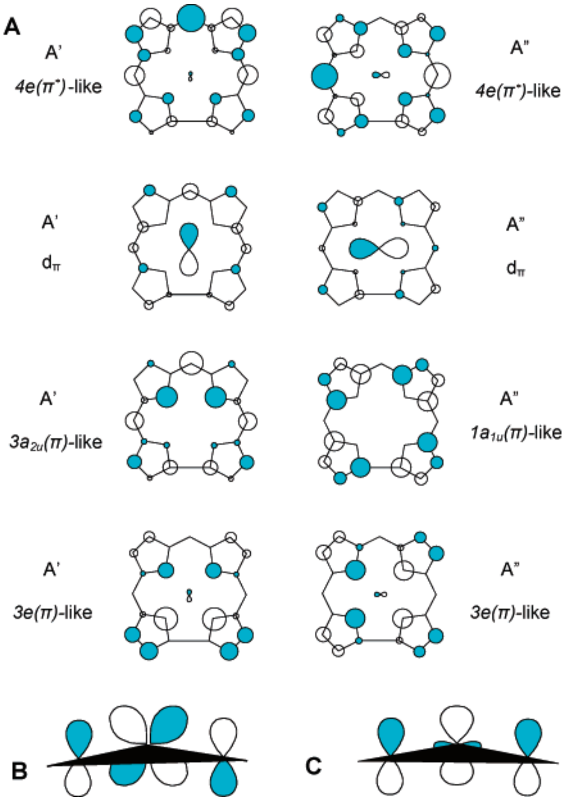

Figure 1. (A) The nodal properties and electron density distributions of the frontier π molecular orbitals of a metal corrolate such as chloroiron octamethyltriphenyl corrolate, of C_s symmetry, and the metal d orbitals of π symmetry with respect to the corrolate macrocycle. The names of the analogous frontier orbitals of a metalloporphyrin are also given [3e(π)-like, *1a$_{1u}$(π)*-like, *3a$_{2u}$(π)*-like, and *4e(π*)*-like]. Only the top pair of orbitals is empty; the relative energies of each member of the pairs of orbitals is not shown. The metal d_π orbitals are of proper symmetry to overlap with the *3e(π)*-like or the *4e(π)*-like orbitals of the corrolate, but in analogy to what is found for metalloporphyrinates,[13,45] the filled *3e(π)*-like orbitals are expected to interact much more strongly with the d_π orbitals than are the empty *4e(π)*-like orbitals. (B) Overlap of two opposite nitrogens of the corrolate ring for the *3e(π)*-like orbitals with one of the metal d_π orbitals, drawn to show this interaction when the metal is out of the plane of the four macrocycle nitrogens. (C) Overlap of two opposite nitrogens of the corrolate ring for the *3a$_{2u}$(π)*-like orbital with the metal d_{z^2} orbital, drawn to show the symmetry interaction of the corrolate ring with this metal orbital, which can only occur when the metal is out of the plane of the four macrocycle nitrogens.

based upon the experimental observation of significant spin density at the *meso*-carbons, that high-spin Fe(III) porphyrinates utilized mainly the *4e(π*)* orbitals,[42] it has recently been shown that the spin density observed at the *meso*-carbons of chloroiron(III) porphyrinates arises from a symmetry-allowed interaction between the unpaired electron in the d_{z^2} orbital of high-spin Fe(III) and the *3a$_{2u}$(π)* porphyrin orbital that arises because the metal is out of the plane of the macrocycle.[46] Thus, at the present time, there is no evidence that the *4e(π*)* orbitals are involved at all in the spin delocalization of high-spin Fe(III) porphyrinates, and thus, we would not expect them to be involved in either intermediate-spin Fe(III) porphyrinates or in Fe(IV) porphyrinates. Thus, for both $S = 1$ Fe(IV) and $S = {}^3/_2$ Fe(III) corrolates or porphyrinates, we expect to have at least the same amount of spin delocalization from the metal to the β-pyrrole carbons as is observed for $S = {}^1/_2$ Fe(III) corrolates or porphyrinates and approximately twice as much, if there are two d_π unpaired electrons on the metal, rather than one, as in the case of low-spin Fe(III), where each of the *3e(π)*-like orbitals of Figure 1A is involved in Corr → Fe π donation and their contributions are additive. That this is a reasonable assumption is clearly shown by the chemical shift of the pyrrole-H of the phenyliron(IV) tetraphenylporphyrinates quoted above: −45 ppm at 25 °C.[38] This corresponds to a paramagnetic shift of −54 ppm, or −27 ppm per d_π unpaired electron. In comparison, as shown previously,[42−44] $[(TPP)Fe(HIm)_2]^+$, which has one d_π unpaired electron, has a pyrrole-H paramagnetic shift of −26 ppm at 25 °C.

Thus, spin delocalization that takes place as a result of Corr → Fe π donation to the half-filled d_π orbital(s) of the metal should lead to positive spin density at the β-pyrrole carbons. As has been known for more than 30 years, positive spin density at carbons that are part of the π system yields negative chemical shifts for protons attached directly to those carbons (the McConnell equation),[42,47] and hence, negative spin density leads to positive chemical shifts of directly bound protons. In light of this known relationship,[42−45,47] it is interesting that the chemical shifts of the *meso*-H resonances of the chloroiron octaalkylcorrolates are +170 to +190 ppm at ambient temperatures.[14,16] These *meso*-H shifts are opposite in sign and much larger in magnitude than those observed for high-spin iron(III) porphyrinates such as (OEP)FeCl, where the *meso*-H chemical shift is −56 ppm at 21 °C,[45] and for the $(d_{xz},d_{yz})^4d_{xy}^1$ low-spin ruffled complex $[(OEP)Fe(t\text{-}BuNC)_2]^+$, where the *meso*-H chemical shift is about −53 ppm at 21 °C.[48] Such large positive chemical shifts for these chloroiron corrolate protons, directly bound to the *meso*-carbons, which represent *negative* spin densities at the *meso*-carbons of the corrolate, thus, *cannot* arise from delocalization of the d_π electron(s) to the macrocycle but, rather, indicate *antiferromagnetic coupling* between an unpaired electron on the macrocycle and the unpaired electrons on the metal.

As has been shown previously by both ^{1}H NMR spectroscopy[16,18,32,49] and DFT calculations,[18,50] the total spin density at the eight β-pyrrole carbons of chloroiron triphenyl- and octaalkylcorrolates is far smaller in magnitude than that present at the three *meso*-carbons of the chloroiron corrolates ($\sum|\rho_{\text{meso}}| \sim 0.75$, $\sum|\rho_{\text{pyrrole}}| \sim 0.25$), and the sign of the sum of the spin densities at the meso positions is negative, while

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the sum of the spin densities at the β-pyrrole positions is approximately zero.[18] This is because the *positive* spin at those β-pyrrole carbons that results from Corr → Fe π donation is approximately *canceled* by the *negative* spin at those β-pyrrole carbons that results from the corrolate radical electron in the $3a_{2u}(\pi)$-like orbital. As we have shown,[18] it is *antiferromagnetic coupling* between the unpaired electron in the metal d_{z^2} orbital of $S = {}^3/_2$ Fe(III) and that in the macrocycle $3a_{2u}(\pi)$-like orbital, an interaction that only becomes possible because the metal is out of the plane of the macrocycle,[18] that produces the very positive *meso*-H shifts observed for chloroiron octaalkylcorrolates.[14,16] This interaction is shown in Figure 1C. These large, positive *meso*-H chemical shifts translate into the *very negative spin densities* obtained either from NMR spectral shifts by using the McConnell equation[13,42−45,47] or from DFT calculations.[18,50] Thus, the observation of *very positive meso*-H chemical shifts for chloroiron corrolates, *of itself*, definitively shows that a corrolate radical, antiferromagnetically coupled to the metal electrons, is present. This was concluded and published in this journal by us over 5 years ago.[16] In that paper, we quoted the work of Balch and co-workers on the π-cation radical of the oxidation product of the *meso*-hydroxy OEPFe(III) complex, OEPO•FeBr,[51] an Fe(III) macrocycle radical with *meso*-H resonances at about 230(2) and 345(1) ppm at 24 °C. In this work, published in 1993, the complex was shown to be an overall $S = 2$ complex consisting of $S = {}^5/_2$ Fe(III) antiferromagnetically coupled to an oxophlorin radical, in which the radical electron is in the $3a_{2u}(\pi)$-like orbital of that macrocycle. Despite this, and our publications on the similar NMR spectra of the chloroiron octaalkylcorrolates[16] and the *meso*-phenyl shifts of the chloroiron triphenylcorrolate,[13,32] Gross and co-workers insist upon ignoring *meso*-substituent shifts.

An additional problem with the recent report of Simkhovich and Gross is that, although a major point is made by these authors concerning the difference in line widths of the four halide complexes and that this leads to the conclusion that they contain Fe(IV),[35] none of the literature cited in that paper with respect to these line widths mentions effects of the halide ligand on the line widths of the resonances. However, it has been known for more than 30 years that a large contribution to the ^{1}H line widths of haloiron(III) complexes, in particular, is due to changes in the electron spin relaxation rate, $R_{1e} = T_{1e}^{-1}$, which is proportional to the line width of the resonance, whose magnitude is inversely proportional to the square of the zero-field splitting constant, D, for the halide, which increases in the order F < Cl < Br < I[52] ($R_{1e} = T_{1e}^{-1} \propto \text{LW} \propto D^{-2}$).[53] This information has been included in comprehensive reviews on the NMR spectra of iron porphyrinates for the past 27 years.[42,45] Hence, it should have been no surprise that the iodoiron corrolate has much sharper signals than does the corresponding fluoroiron corrolate,[35] and this observation has nothing to do with the authors' statements that the electron configuration is $S = 1$ Fe(IV). The ^{1}H NMR spectroscopic behavior of the various spin and oxidation states of metal complexes of tetraphenylporphyrins has been known for many years, summarized in a number of comprehensive reviews,[13,42−45] and shown to obey very simple rules for the mechanisms of spin delocalization based upon the electron configuration of the metal; this body of knowledge should not be ignored by researchers who wish to interpret the chemical shifts obtained for new metal complexes.

The phenyl-H chemical shifts, previously shown to be very important in establishing the sign of the spin density at the *meso*-carbons of metallotetraphenylporphyrinates or -triphenylcorrolates,[13] were given in this work[35] only for the iodoiron 2,6-dichlorotriphenylcorrolate complex, and although only about half the chemical shift difference, $\delta_m - \delta_p$, is observed (−10.5 and −11.2 ppm for 5,15-Ph and −11.7 and −12.1 ppm for 10-Ph)[35] relative to those observed for the chloroiron triphenylcorrolate complex (−21.7 and −21.9 ppm for 5,15-Ph and −20.6 and −20.7 ppm for 10-Ph),[32] the pattern is exactly the same as that observed for the chloroiron complex,[32] with proton shift differences $\delta_m - \delta_p$ being negative, as outlined recently in detail.[13] Negative shift differences $\delta_m - \delta_p$, thus, indicated to us a negative spin density for the iodoiron triphenylcorrolate complex of that study.[35] That the iodoiron complex should show less negative spin density at the *meso*-carbons than does the chloroiron complex is consistent with the fact that it is usually found that iodide complexes of iron porphyrinates (and presumably corrolates as well) have the metal less shifted out of the mean plane of the four nitrogen atoms of the macrocycle than do the chloride complexes,[54] which would decrease the d_{z^2}−$3a_{2u}(\pi)$-type overlap[18] mentioned above and shown in Figure 1C. Thus, the recent paper of Simkhovich and Gross[35] that suggests that the haloiron triphenylcorrolates should be formulated as Fe(IV) Corr(3−), again, uses ^{1}H NMR shifts incorrectly. *Correct* interpretation of their results,[35] thus, indicates no need for any modification of the conclusion reached by us earlier[16,18,32,49] that the electronic ground state of the haloiron corrolates is mainly $S = {}^3/_2$ haloiron(III), $S = {}^1/_2$ corrolate(2−•) complexes, with antiferromagnetic coupling between metal and macrocycle unpaired electrons.

Although all of our previous experimental results are in agreement with the noninnocent character of corroles in their chloroiron complexes, a much more complete mapping of the spin density in iron corrolates may be obtained from ^{13}C NMR investigations, which can give additional insight into the electron configuration of these complexes. Therefore, in this paper, we report the ^{13}C NMR characterization of the chloroiron complexes of 7,13-dimethyl-2,3,8,12,17,18-hexaethylcorrole (H_3DMHECorr), 7,8,12,13-tetramethyl-2,3,17,-18-tetraethylcorrole (H_3TMTECorr), 5,10,15-triphenylcorrole (H_3TPCorr), and the phenyliron complex of H_3DMHECorr

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and the first characterization of the fully substituted chloroiron complex of 2,3,7,8,12,13,17,18-octamethyl-5,10,15-triphenylcorrole (H_3OMTPCorr). This latter complex is interesting because it contains both β-pyrrole and *meso*-substituents on the macrocycle frame; its molecular structure, determined by single-crystal X-ray diffraction, gives the necessary information on the deviations of the macrocycle from planarity, which allows us to interpret the influence of ring conformation on the electron distribution.

Experimental Section

Preparation of Complexes. DMHECorrFeCl,[16] DMHECorrFePh,[18] and TPCorrFeCl[32] from earlier work were used in these studies. H_3TMTECorr and its chloroiron complex were prepared as previously described.[32,55] The fully substituted H_3OMTPCorr was prepared as previously described.[26]

Chloroiron 2,3,7,8,12,13,17,18-Octamethyl-5,10,15-triphenylcorrolate. H_3OMTPCorr (0.142 g; 0.22 mmol) and diiron nonacarbonyl (0.142 g; 0.39 mmol) were dissolved in toluene, 50 mL, and the reaction mixture was refluxed under nitrogen. The progress of the reaction was monitored by UV−vis spectroscopy. After 2 h, the solution was cooled to room temperature and stirred under air for 10 min. The solvent was then removed under reduced pressure, and the crude product was purified by chromatography on silica gel. The red-brown fraction corresponding to the μ-oxo complex was eluted with a mixture of dichloromethane/methanol (98:2). The solvent was evaporated, and the solid residue, dissolved in dichloromethane, was stirred with hydrochloric acid (1 M; 30 mL) for 5 min. The organic phase was dried over anhydrous sodium sulfate, and the desired product was obtained after recrystallization from hexane/dichloromethane (2:1). Yield: 0.122 g, 76%. Thin-layer chromatography (TLC) studies after column chromatography, treatment with HCl, and recrystallization all continued to show the presence of a faster-moving brown spot attributable to the formation of the antiferromagnetically coupled μ-oxo dimer, [(OMTPCorr)Fe]$_2$O, presumably on the TLC plates. The possible presence of colorless impurities was not determined, although they are clearly present, as evidenced by the NMR spectra, discussed below. (OMTPCorr)FeCl has a much higher tendency than (TPCorr)FeCl to form the μ-oxo dimer and does so even upon standing in $CHCl_3$, presumably because of traces of water in the solvent. Repeated purification by column chromatography did not improve the purity of the sample.

Iron porphyrinates used for characterizing the ^{13}C chemical shifts of the carbons of $S = {}^5/_2$, $S = {}^3/_2$, and the two $S = {}^1/_2$ ground-state complexes were prepared as described elsewhere[56] or were obtained from Frontier Chemical or Mid-Century Chemical companies.

NMR Spectroscopy. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer operating at a ^{1}H Larmor frequency of 499.897 MHz and a ^{13}C frequency of 125.670 MHz. Chemical shifts were referenced to the residual solvent peak. The ^{1}H−^{13}C HMQC spectra were recorded using the 5 mm inverse-detection probe with decoupling during acquisition (HMQC = heteronuclear multiple-quantum coherence). A recycle time of 200 ms and a refocusing time of 2.5 ms were used. The water elimination by Fourier transform−nuclear Overhauser effect spectrometry (WEFT−NOESY) experiment utilized a relaxation delay of 100 ms and a recovery delay of 130 ms. The mixing time for the NOESY experiments was 20 ms. All 2D spectra were collected with 2048 data points in the t_2 dimension and 256−512 blocks in the t_1 dimension with 256−512 scans per block. 1D ^{13}C NMR spectra were acquired over 16 000 data points with a 50 ms acquisition time, a 50 ms relaxation delay, and 40−100 000 scans.

The magnetic susceptibility of (OMTPCorr)FeCl was measured by the NMR method of Evans[57] using the equation of Sur for the geometry of a superconducting magnet.[58] In a typical experiment, a 4.29 mg sample of solid (OMTPCorr)FeCl was dissolved in 0.5 mL of CD_2Cl_2 containing a small amount of tetramethylsilane (TMS) to yield a nominal concentration of 11.9 mM in the outer concentric NMR tube (Wilmad); CD_2Cl_2/TMS from the same stock solution was used in the inner tube. Because the NMR spectrum of (OMTPCorr)FeCl from the same sample showed the presence of large diamagnetic impurity resonances, as shown in the Results section, the intensities of the resonances of (OMTPCorr)FeCl as compared to those of the diamagnetic impurities at 1−2.5 ppm and 7−8 ppm were used to estimate that the complex contained impurities with approximately 14 C/H ∼ 1:1, 20 C/H ∼ 1:2, and about 10 C/H ∼ 1:3 per formula unit of (OMTPCorr)FeCl, or about 36−42% impurity; part of this impurity content may be due to the presence of some μ-oxo dimer, [(OMTPCorr)Fe]$_2$O, while the rest appears to be due to corrole decomposition products. Correction of the concentration of the paramagnetic complex for the approximate mass of the impurities yielded a concentration of 7.2 mM. From this concentration and the measured $\Delta\nu = 93.5$ Hz at 22 °C, using Pascal's constants[59] to estimate the diamagnetic susceptibility of the corrole ligand, a corrected $\chi_M' = 10.28 \times 10^{-3}$ K^{-1} was obtained, which yielded an approximate $\mu_{eff} = 4.92\ \mu_B$. If only the impurity peaks at 1−2.5 ppm were utilized for this correction, the approximate $\mu_{eff} = 4.50\ \mu_B$. Therefore, we take the approximate μ_{eff} to be the average of these estimates, 4.7 μ_B, with an estimated error of ±0.5 μ_B. The magnetic moment measurement was repeated twice.

X-ray Crystallography. Crystals suitable for X-ray characterization were obtained by crystallization from dichloromethane/*n*-hexane. Intensity data were collected at low temperatures, using graphite monochromated Mo Kα radiation on a Nonius KappaCCD diffractometer fitted with an Oxford Cryostream cooler. Data reduction included absorption corrections by the multiscan method, using HKL SCALEPACK.[60] Crystal data and experimental details are given in Table 1. The structure was solved by direct methods and refined by full-matrix least squares, using SHELXL97.[61] All H atoms were visible in difference maps but were placed in idealized positions. A torsional parameter was refined for each methyl group.

Results and Discussion

Synthesis and Optical Spectral Characterization. (TMTECorr)FeCl and (TPCorr)FeCl were prepared as previously reported[32] by reaction of the corrole free base and $FeCl_2$ in refluxing N,N-dimethylformamide. The intermediate μ-oxo dimer was then converted to the corresponding chloroiron derivative by treatment with dilute HCl. When the same method was used to prepare the (OMTPCorr)FeCl, very poor

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Table 1. Experimental Details and Crystal Data for [OMTPCorrFeCl]

compound	Fe corrole
CCDC deposit no.	253431
empirical formula	$FeN_4C_{45}H_{39}Cl$
color/shape	brown/fragment
fw	727.10
cryst syst	triclinic
space group	$P\bar{1}$
temp, K	100(2)
cell constants	
a, Å	10.833(3)
b, Å	13.153(3)
c, Å	14.140(6)
α, deg	64.200(12)
β, deg	87.175(13)
γ, deg	72.484(16)
cell volume, $Å^3$	1722.0(10)
Z	2
density (calc), g/cm^3	1.402
μ_{calc}, cm^{-1}	5.56
transm coeff	0.843−0.983
diffractometer/scan	Nonius KappaCCD/ω
radiation λ	Mo Kα (0.710 73 Å)
cryst dimension, mm^3	0.10 × 0.10 × 0.03
reflections measured	25 140
R_{int}	0.057
independent reflns	6082
2θ limits	$5.0 < 2\theta < 50.2°$
limiting indices	±12, ±14, ±16
reflns observed	4205
criterion for observed	$I > 2\sigma(I)$
data/params	6082/468
R(obs)	0.061
R(all data)	0.100
R_w, F^2(all data)	0.142
H-atom treatment	idealized
max. residual peaks ($eÅ^{-3}$)	1.20, −0.47

yields were obtained and significant decomposition of the starting macrocycle was observed during the reaction. We have, thus, used $Fe_2(CO)_9$ as a metal carrier in refluxing toluene to achieve the formation of the complex in good yield. A chromatographic workup on silica gel afforded the μ-oxo dimer, which was not isolated but, rather, quantitatively converted to the chloroiron derivative by treatment with dilute HCl.

The UV−visible spectrum of (OMTPCorr)FeCl is reported in Figure 2. The shape of the spectrum is intermediate among those of chloroiron complexes of β-octaalkyl- and of 5,10,-15-triarylcorrolates: it does not show, in fact, the split Soret band of 5,10,15-triarylcorrolatoiron chloride complexes,[62] but the main absorption band present at 379 nm is broader than that of the corresponding β-octaalkyl derivatives.[63] It is worth mentioning that the Soret band is not significantly red shifted, as observed in the case of dodecasubstituted porphyrin complexes.[64] This feature is similar to what was observed in the case of $(OMTPCorr)CoPPh_3$,[65] and it seems to further confirm the peculiar ability of the corrole ligand to accommodate the steric hindrance of peripheral substituents without undergoing the severe distortions from planarity observed for the fully substituted porphyrins (see also next section).

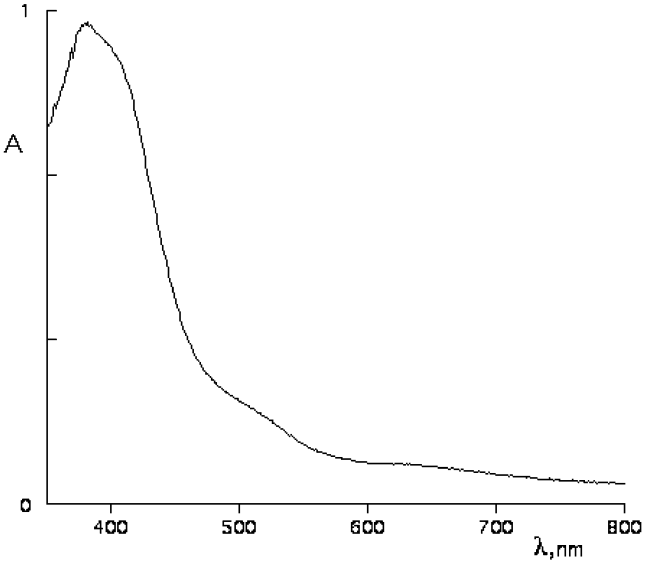

Figure 2. UV-visible spectrum of (OMTPCorr)FeCl in dichloromethane.

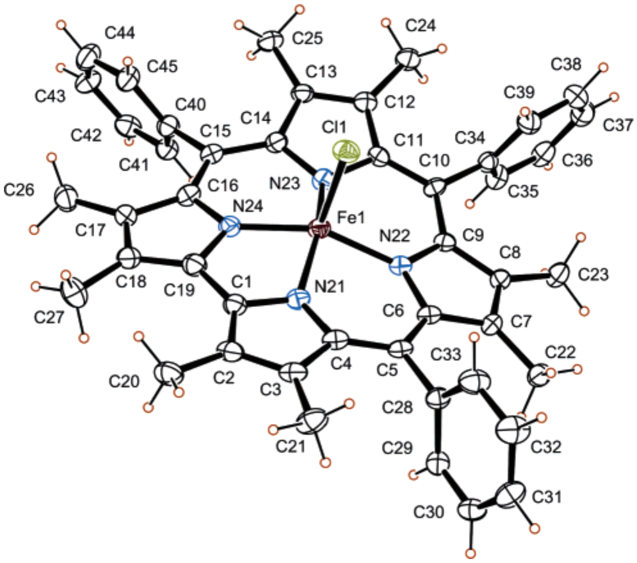

Figure 3. Molecular structure of (OMTPCorr)FeCl, showing the pentacoordination of the metal and the slight saddling of the macrocycle. The numbering of the methyl groups in the structure is not the same as the numbering used for assignment of the NMR spectra (Figure 4).

Structure. The molecular structure of (OMTPCorr)FeCl is shown in Figure 3. The iron atom is pentacoordinate, with a slightly distorted square pyramidal geometry. Fe−N distances are in the range 1.886(4)−1.927(4) Å, and those in the five-membered chelate ring are slightly shorter, by an average of 0.028 Å, than those involved in only six-membered chelate rings. The four N atoms are coplanar to within 0.035(5) Å, and the Fe atom lies 0.3865(8) Å out of this plane, less than in (OECorr)FeCl (0.42 Å)[14] or the dodecasubstituted porphyrinate complexes (OMTPP)FeCl (0.46 Å)[66] and $(TC_6TPP)FeCl$ (0.485 Å).[67] The Fe−Cl

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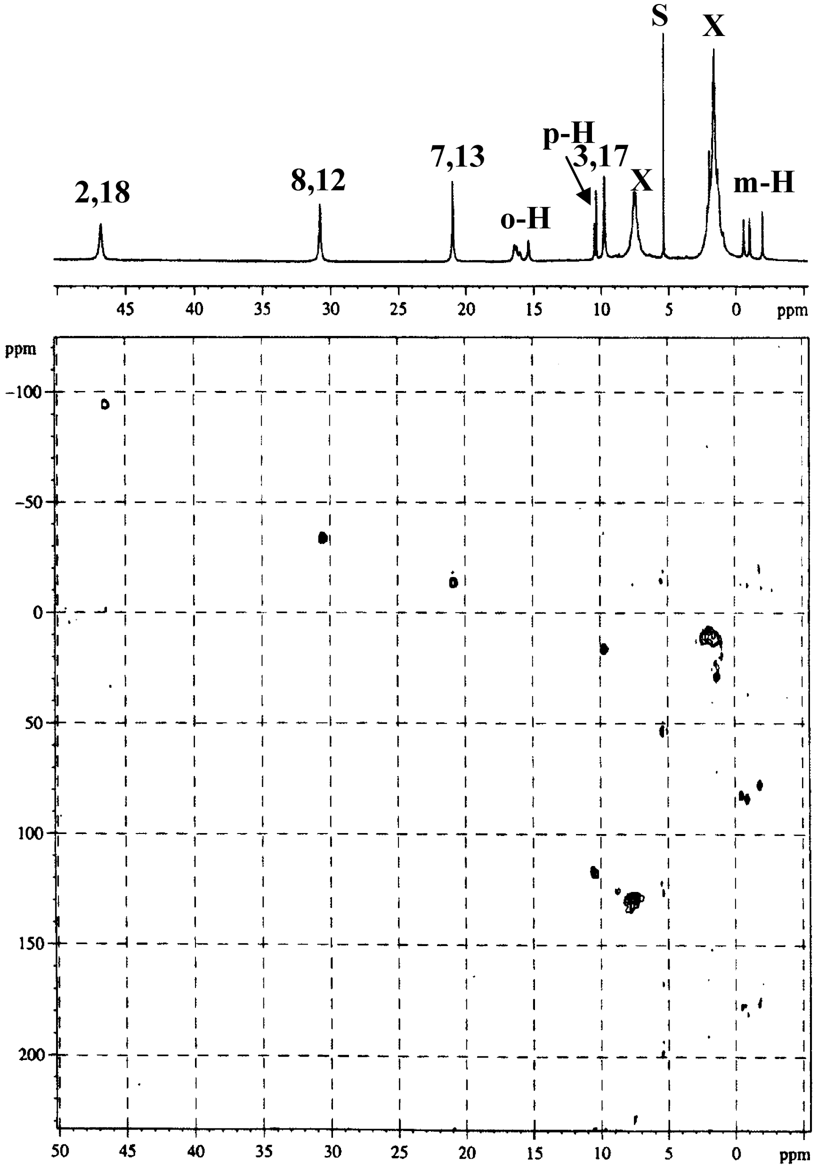

Figure 4. 1D ^{1}H and HMQC spectrum of (OMTPCorr)FeCl, using the numbering system appropriate for describing the pyrrole- and *meso*-carbons to which the substituents are attached, rather than the numbering system of those substituents used for the crystal structure shown in Figure 2. The ^{1}H$-$^{13}C correlations for the four methyl, two *para*-phenyl, and four *meta*-phenyl groups are shown; the relaxation times of the *ortho*-phenyl carbons are too short to allow the correlations to be detected. The ^{13}C chemical shifts of all detected HMQC crosspeaks are included in Table 2. Recorded in CD_2Cl_2 at 25 °C.

distance is 2.2420(14) Å, and the Fe$-$Cl bond tilts slightly away from the five-membered chelate ring, with N$-$Fe$-$Cl angles averaging 105.0° for the five-membered chelate ring and 98.7° for the six-membered chelate ring opposite it. As expected, the bite angle in the five-membered ring, 80.38(16)°, is smaller than those of the six-membered rings, 87.99(15)$-$93.84(15)°. The coordination of Fe imposes a flattened saddle shape on the octamethyltriphenylcorrolate ligand. Methyl groups C20, C21, C24, and C25 lie an average of 0.51 Å out of the N_4 plane on the same side as the Fe atom. Methyl groups C22, C23, C26, and C27 lie an average of 0.75 Å out of the plane on the opposite side. These deviations from the N_4 plane are much smaller than those observed for several dodecasubstituted porphyrin complexes, octamethyltetraphenylporphinatoiron(III) chloride—(OMTPP)FeCl (1.19Å)[66]—and two tetra-(β,β'-tetramethylene)tetraphenylporphyrinatoiron(III) anion complexes—(TC_6TPP)FeCl and (TC_6-TPP)$FeONO_2$ (0.86 and 1.19 Å, respectively).[67] The structure of (OMTPCorr)FeCl is very similar to that of (TPFPCorr)-FeCl, where TPFPCorr = 5,10,15-tris(pentafluorophenyl)-corrole.[68] That complex also has square pyramidal coordination geometry, with the Fe atom lying 0.3670(11) Å out of the N_4 plane, and all its Fe$-$L distances agree within experimental error with those of (OMTPCorr)FeCl.

NMR Spectroscopy. The 1D ^{1}H NMR spectrum and the corresponding HMQC spectrum of (OMTPCorr)FeCl are shown in Figure 4, where it can be seen that the crosspeaks for all four types of methyl groups, as well as the 5,15- and

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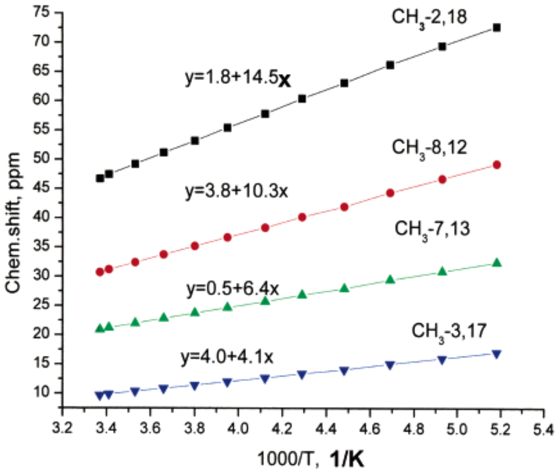

Figure 5. Curie plot for the four methyl resonances of (OMTPCorr)FeCl. The extrapolated diamagnetic shifts (assuming strict Curie behavior) are given as the constants in the linear regression of each line. As is clear from these values, the extrapolated diamagnetic shifts are within ±2 ppm of the expected diamagnetic shift of these methyl groups.

10-phenyl groups (except for the *ortho*-carbons), are clearly resolved. Assignments were made on the basis of the HMQC spectrum for the methyl groups and a comparison of the ^{1}H NMR shifts of this complex to those of (DMHECorr)FeCl, (TMTECorr)FeCl, and (TPCorr)FeCl. All assigned resonances are labeled. It should be noted that there are two large impurity peaks, labeled X, that extend from 1 to 2.5 ppm and from 7−8 ppm. Such impurity peaks are frequently observed for metallocorrolates, and even the ^{1}H NMR spectra of commercial samples of the free-base tris-(pentafluorophenyl)corrole, H$_3$TPFPCorr (Alfa), show large impurity peaks. As mentioned in the Experimental Section, these impurity peaks may arise, in part, from the formation of the μ-oxo dimer, [(OMTPCorr)Fe]$_2$O, but slow decomposition of the macrocycle during metal insertion and thereafter cannot be ruled out. These impurity peaks must be considered when the magnetic moment of the complex is calculated (see Experimental Section and below).

The temperature dependence of the proton resonances of (OMTPCorr)FeCl was investigated, and the Curie plot for the four types of methyl groups present in this complex is shown in Figure 5. As expected based upon previous work,[16,18,69] all resonances exhibit strict Curie behavior, with the methyl-H shifts extrapolating to within less than ±2 ppm of the diamagnetic shift expected for these protons. The complex is of fairly low solubility (∼13 mM), and 2- and 4-fold dilutions did not affect the chemical shifts of the resonances.

For comparison with the NMR spectra of the undecasubstituted (OMTPCorr)FeCl shown in Figure 4, the 1D ^{1}H and HMQC spectra of (TMTECorr)FeCl are shown in Figure 6, where all assigned resonances are labeled. The 1D ^{1}H and HMQC spectra of (DMHECorr)FeCl and (TPCorr)FeCl are shown in Supporting Information Figures S1−S2. All ^{1}H and ^{13}C chemical shift assignments for the chloroiron corrolates were made based upon NOESY and HMQC spectra for the ethyl groups and a comparison of the ^{1}H NMR shifts of the variably methyl/ethyl-substituted corrolates; these assignments are summarized in Table 2. The largest difference observed in these complexes is in the phenyl-carbon shifts of (OMTPCorr)FeCl and (TPCorr)FeCl. We will analyze these differences in more detail below.

Unfortunately, we have been unable to detect the HMQC or 1D ^{13}C signals for the *meso*-carbons of any of the iron corrolates; the proton signals [at +170 to +190 ppm at 25 °C for (DMHECorr)FeCl[16]] are very broad, and the ^{13}C signals are expected to be much broader as a result of very fast R_1 and R_2 relaxation rates (very short T_1 and T_2 relaxation times), which arise from both the metal and ligand dipolar relaxation mechanisms, both of which depend on the inverse distance between the unpaired electron and the carbon of interest to the sixth power.[45,70] In addition, the ligand-centered dipolar relaxation mechanism depends on the square of the amount of delocalized spin density present at the carbon of interest, ρ_C,[2,71] which is on the order of 5 times greater in magnitude for the *meso*-carbons of the chloroiron corrolates of this study than for the largest spin density of the β-pyrrole carbons. Thus, the *meso*-carbon resonances are expected to be at least 25 times broader than the broadest β-pyrrole carbon resonance of (TPCorr)FeCl, which we have only been able to detect in these natural-abundance ^{13}C samples by the 2D HMQC technique (Supporting Information, Figure S3), and we were unable to detect the HMQC crosspeak from the 3,17-carbon, whose ^{1}H resonance is at −40 ppm at 25 °C (1D ^{1}H spectrum shown in Figure S2 of the Supporting Information, although broad 1D ^{13}C resonances were detected for this and the α-carbons of this complex, Table 2). We have searched over the ^{13}C chemical shift region of ±2000 ppm but have found only one broad resonance at ∼ −1700 to −1800 ppm; however, this same broad resonance is also present when only CDCl$_3$ is present in the NMR tube, indicating that it is an artifact. It is unfortunate that the *meso*-C signals cannot be detected, because according to both the ^{1}H NMR spectra[14,16,32] and the DFT calculations,[18] most of the negative spin density of the chloroiron corrolates is present at the three *meso*-carbons.

For comparison to the chloroiron corrolates, the 1D ^{1}H and HMQC spectra of (7,13-DMHECorr)FePh are shown in Figure 7. The chemical shifts and assignments of these resonances are given in Table 3. The HMQC crosspeaks for the *meso*-H resonances observed at +49 and +53 ppm at ambient temperatures could not be found over the ^{13}C range of −150 to −650 ppm, although we estimate that they should occur at about −500 ppm.

Analysis of ^{13}C Paramagnetic Shifts of the Corrolate Complexes of This Study. The observed chemical shifts, δ_{obs}, of the complexes of this study, and all other paramagnetic complexes, are the sum of two contributions, the diamagnetic contribution, δ_{dia}, that is, the chemical shifts of the resonance(s) of interest of a diamagnetic complex of the

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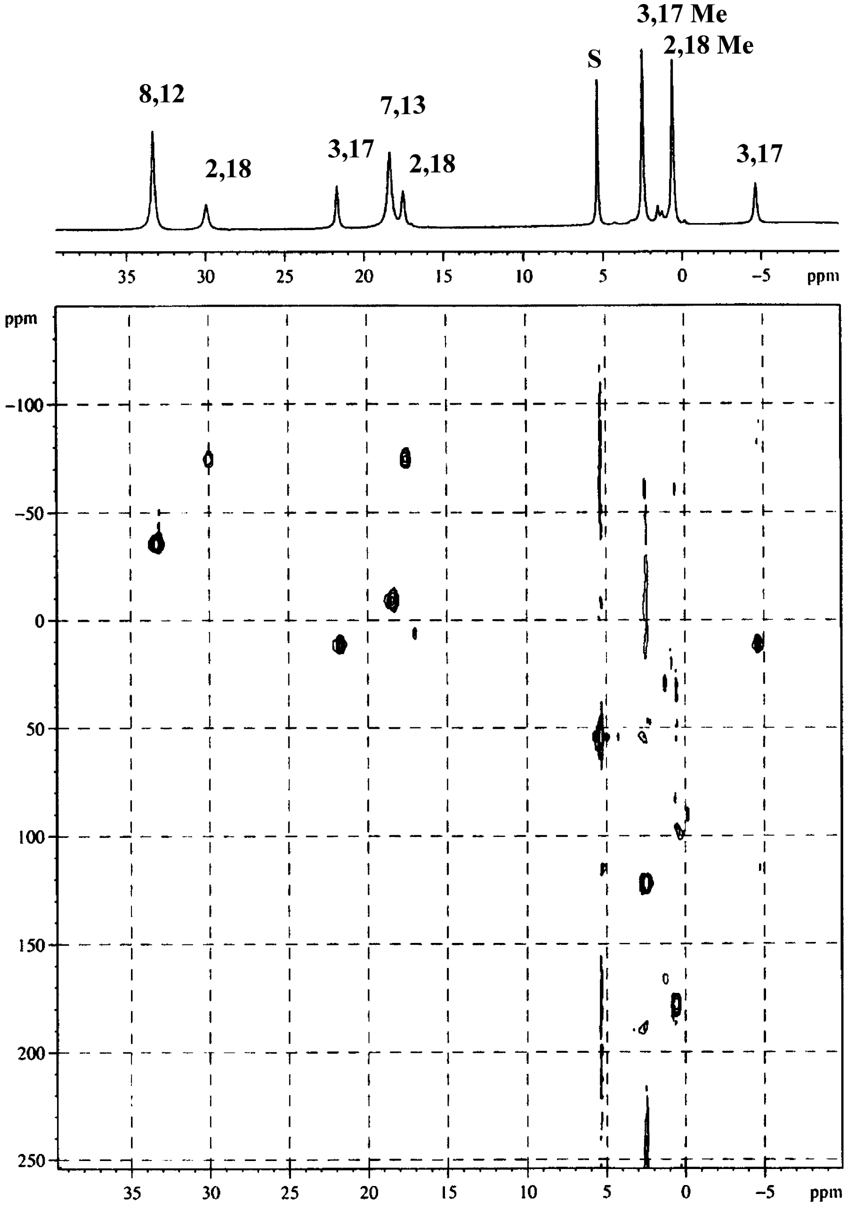

Figure 6. 1D ^1H and HMQC spectrum of (7,8,12,13-TMTECorr)FeCl, showing the $^1H-^{13}C$ correlations for the two methyl groups (8,12 and 7,18) and the two ethyl groups (2,18 and 3,17). The ^{13}C chemical shifts of all detected HMQC crosspeaks are included in Table 2. Recorded in CD_2Cl_2 at 25 °C.

same or similar structure to that of the paramagnetic complex of interest, and the paramagnetic contribution, δ_{para}:[13,42−45]

$$\delta_{obs} = \delta_{dia} + \delta_{para} \tag{1}$$

Thus, to determine the *paramagnetic* shifts of the protons and carbons of the complexes of this study, we must know the observed chemical shifts of diamagnetic complexes of the same or similar structure to those of the chloroiron and phenyliron corrolates. Although detailed ^{13}C chemical shifts are not available for many diamagnetic metal corrolates, they have been reported for (OECorr)SnCl and (OECorr)SnPh.[72] For the former, the $^{13}CH_2$ chemical shifts range from 20.89 (2,18) to 19.65 ppm (8,12), with an average chemical shift of 20.12 ppm, while for the latter, they range from 20.83 (2,18) to 19.65 ppm (8,12), with an average chemical shift of 20.09 ppm;[72] for both of these complexes, the average ^{13}C chemical shift is, thus, 20.1 ppm. The diamagnetic ^{13}C shift of the pyrrole-CH_2 group of [(ETIO)Co(1-MeIm)$_2$]Cl is 20.3 ppm;[75] the chemical shifts of diamagnetic complexes are not very sensitive to axial ligation, as shown by the fact that the ^{13}C chemical shift of the CH_2 carbon of (OEP)Zn is 20.2 ppm.[73] Thus, the diamagnetic shifts of porphyrin and corrole β-CH_2 groups are very similar. The chemical shift of the pyrrole β-CH_3 carbons of [(ETIO)Co(1-MeIm)$_2$]$^+$ is, however, somewhat different from the β-CH_2 shifts: 12.2 ppm. The (OECorr)SnCl and [(ETIO)Co(1-MeIm)$_2$]Cl chemical shifts just mentioned are summarized in Table 4.

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Table 2. Proton and Carbon Chemical Shifts of FeCl Corrolates at 25 °C (Solvent = CD_2Cl_2)

		7,8,12,13-(TMTECorr)FeCl		7,13-(DMHECorr)FeCl		(OMTPCorr)FeCl		(TPCorr)FeCl	
assignment[a]	spin density[b]	^1H (ppm)	^{13}C (ppm)	^1H (ppm)	^{13}C (ppm)	^1H (ppm)	^{13}C (ppm)	^1H (ppm)	^{13}C (ppm)
2,18	+0.05	30.0, 17.5 av: 23.8 (0.6)	−74.8 (178.5)	30, 17.5 av: 23.8 (0.6)	−73.7 (178.1)	46.4 (43.7)[c]	−93.3	+6.7	−18.8
3,17	−0.04	21.7, −4.6 av: 9.0 (2.5)	+11.7 (122.4)	21.2, −5.5 av: 7.9 (2.5)	+14.9 (118.4)	9.7 (18.0)[c]	+17.4	−40	428.9
7,13	+0.02	18.4	−8.8	18.3	−7.9	20.9 (18.2)[c]	−12.5	−5.0	172.8
8,12	−0.01	33.3	−35.3	27.6, 3.8 av: 15.7 (1.3)	−21.0 (158.6)	30.6 (33.8)[c]	−32.7	−6.5	210.0
other[d]								582.1, 605.2, 623.3, 631.0	
meso-5,15	−0.23			174	N. O.[e]				
meso-10	−0.26			187	N. O.[e]				
5,15-*o*-Ph						16.5 16.0	N. O.[e] N. O.[e]	25.0 23.8	−296.0 −279.5
10-*o*-Ph						15.3	N. O.[e]	23.0	−378.6
5,15-*m*-Ph						−0.5, −1.0	83.1, 84.7	−2.5 (av)	141.2
10-*m*-Ph						1.9	78.2	−3.5 (av)	115.5
5,15-*p*-Ph						10.5	117.8	19.5	68.4
10-*p*-Ph						10.6	118.2	17.3	80.5

[a] Based on methyl, ethyl substitution at 7,13-(DMHECorr)FeCl and 7,8,12,13-(TMTECorr)FeCl and calculated spin densities; ethyl CH_3 shifts given in parentheses. [b] Reference 18. [c] Methyl shifts of $Me_8CorrFeCl$[16] given in parentheses. [d] Quaternary carbons, probably the four α-carbons, although two *meso*-C's and two phenyl-C_1's are also quaternary carbons and should be observed; nevertheless, they are expected to have negative chemical shifts. [e] Not observed.

To determine the expected *paramagnetic* shift of the CH_2 or CH_3 carbons bound to the β-pyrrole positions of the iron corrolates because of a single d_π unpaired electron being delocalized from the metal to the *3e(π)* orbital(s) via macrocycle → Fe π donation, the best examples are the well-characterized low-spin Fe(III) porphyrinate complexes that are known to have a $d_{xy}{}^2(d_{xz},d_{yz})^3$ electron configuration, that is, those bound to imidazoles.[13,42−45] The chemical shift of the β-pyrrole-CH_2 carbon of [(OEP)Fe(1-MeIm)$_2$]Cl at 26 °C is −23.6 ppm, while that of [(ETIO)Fe(1-MeIm)$_2$]Cl is −23.2 ppm at the same temperature;[75] the chemical shift of the β-pyrrole-CH_3 carbons of [(ETIO)Fe(1-MeIm)$_2$]Cl is slightly different, −34.6 ppm, also at 26 °C. All of these values are included in Table 4. Thus, from eq 1, the ^{13}C paramagnetic shift of a CH_2 carbon attached to the β-pyrrole position of a low-spin Fe(III) porphyrin (having a single d_π unpaired electron) at ambient temperature is approximately −44 ppm, while that of a CH_3 carbon attached to the same position is approximately −47 ppm. As discussed in the Introduction, for two d_π unpaired electrons, which may be present for either $S = {}^3/_2$ Fe(III) or $S = 1$ Fe(IV) and which can be delocalized to the macrocycle by Corr → Fe π donation from the two *3e(π)*-like filled orbitals of the corrole, we would, thus, expect that the ^{13}C *paramagnetic* shift would be double this value, or about −88 and −94 ppm, respectively, for a β-CH_2 and β-CH_3 carbon. These values are presented in Table 5, where they are used to determine the amount of excess spin density due to the corrole π radical electron for each of the complexes having alkyl substituents on the β-pyrrole carbons.

For the pyrrole-β-carbon resonances themselves, the β-pyrrole carbon chemical shifts of (OECorr)SnCl range from 132.6 to 140.2 ppm[72] (Table 4), while the 3-nitro-substituted derivative of, presumably, (TF_5PCorr)GaPy (although the phenyl substituents are not defined in the table of ^{13}C shifts) has these resonances at ∼116.6 ppm (2,18), ∼124.3 ppm (17), ∼128.3 ppm (7,13), and ∼128.9 ppm (8,12).[74] These metallocorrolate ^{13}C chemical shifts may also be compared to those of appropriate diamagnetic Co(III) porphyrinates.[75] The ^{13}C shift of the β-pyrrole carbons of [(TPP)Co(1-MeIm)$_2$]Cl is 134.6 ppm,[75] and that of the β-pyrrole carbons of (TPP)Zn is 132.0 ppm,[76] both of which are more similar to the chemical shifts of (OECorr)SnCl[72] than to those of the 3-nitro-substituted derivative of the gallium(III) corrolate given above. The (OECorr)SnCl, (OECorr)SnPh, and [(TPP)Co(1-MeIm)$_2$]Cl data are included in Table 4. In comparison, the chemical shift of the β-pyrrole carbons of [(TPP)Fe(HIm)$_2$]Cl at 25 °C is 94.3 ppm (this work, Table 4), slightly different from that derived from Goff's data at 26 °C for the corresponding bis-1-MeIm complex (98.6 ppm).[75] Thus, using our data, the ^{13}C paramagnetic shift of a β-pyrrole carbon of a low-spin Fe(III) porphyrin having a single d_π unpaired electron is about −48 ppm, and the expected *paramagnetic* shift due to two d_π unpaired electrons, for either $S = {}^3/_2$ Fe(III) or $S = 1$ Fe(IV), would thus be double that amount, −96 ppm. These values are included in Table 5.

The *meso*-carbon chemical shifts of (OECorr)SnCl are +94.4 (5,15) and +89.0(10) ppm,[72] while the chemical shift of the *meso*-carbons of [(ETIO)Co(1-MeIm)$_2$]Cl is +96.7 ppm[75] (listed in Table 4) and that of (OEP)Zn is +96.5 ppm.[73] In comparison, the *meso*-carbon chemical shift of [(OEP)Fe(1-MeIm)$_2$]Cl is +23.6 ppm[75] (Table 4), that of [(OEP)Fe(5-MeImH)$_2$]Cl is +25.0 ppm,[75] and that of [(ETIO)Fe(1-MeIm)$_2$]Cl is +23.5 ppm, all at 26 °C.[75] Thus, the ^{13}C *paramagnetic* shift of a *meso*-carbon of a low-spin Fe(III) porphyrin (having a single d_π unpaired electron) is approximately −72 ppm. For two d_π unpaired electrons, which

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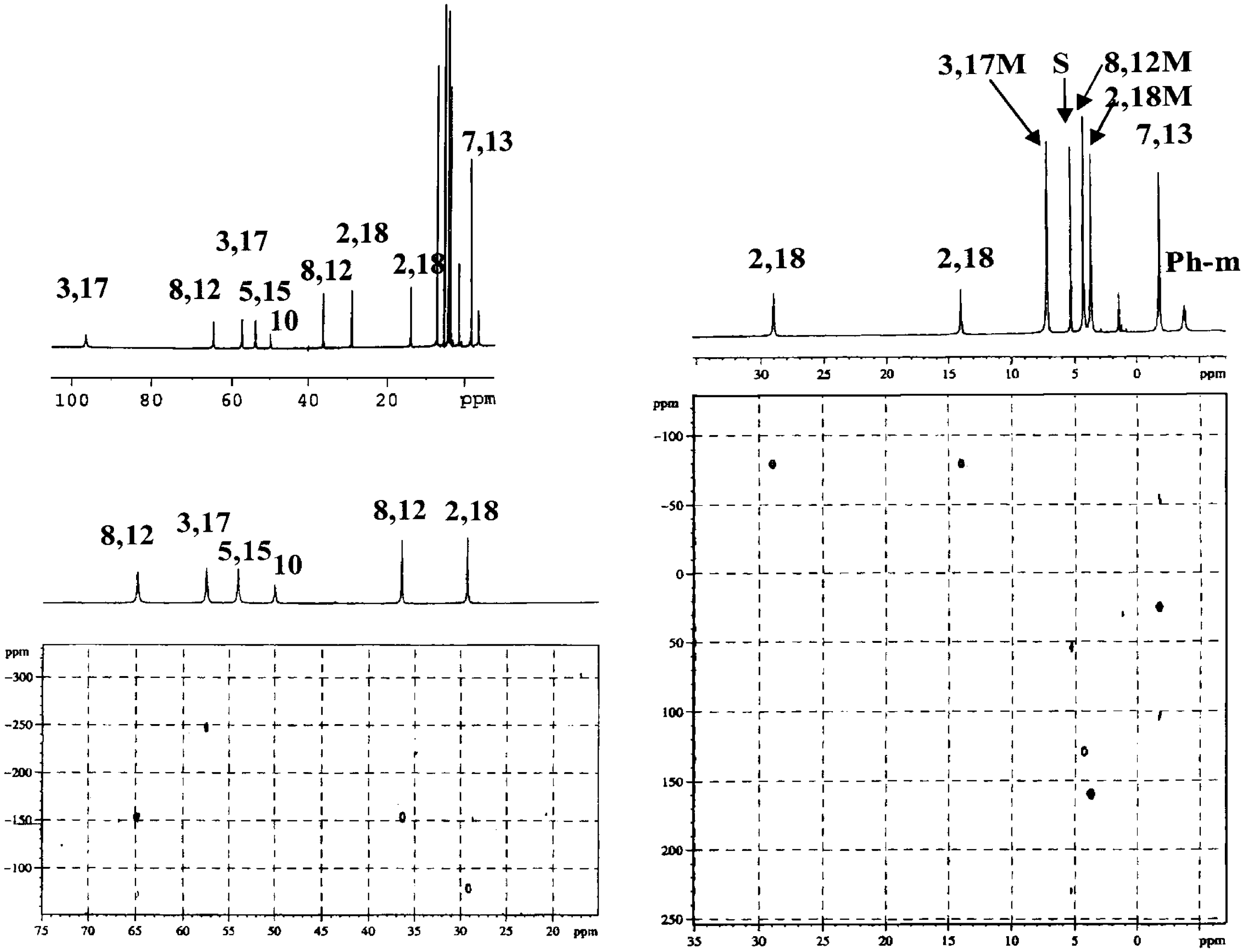

Figure 7. 1D ^{1}H (top left) and two expanded region HMQC spectra of (7,13-DMHECorr)FePh, showing the ^{1}H−^{13}C correlations for the 7,13 methyl group and the three ethyl groups (2,18; 3,17; and 8,12). One of the 3,17-CH$_2$ resonances is not included in the windows used for the HMQC spectra of this figure, but its ^{13}C shift is the same as that of the other 3,17-CH$_2$ carbon (−250 ppm). The window of the lower-left-hand HMQC spectrum is that of the expanded region of the ^{1}H spectrum between 75 and 20 ppm, and that of the right-hand HMQC spectrum is of the expanded region between 35 and −5 ppm. The phenyl resonances, including those of the *ortho*- (−149 ppm) and *para*-H (−74.9 ppm) are not shown in the 1D ^{1}H spectrum, and no HMQC crosspeaks were observed for any phenyl-carbon resonances because of their short relaxation times. The ^{13}C chemical shifts of all detected HMQC crosspeaks are included in Table 3. Recorded in CD$_2$Cl$_2$ at 25 °C.

Table 3. Proton and Carbon Chemical Shifts of the FePh Corrolate at 25 °C (Solvent = CD$_2$Cl$_2$)

		7,13-(DMHECorr)FePh	
assignment[a]	spin density[b]	^{1}H (ppm)	^{13}C (ppm)
2,18	−0.01	29.0, 14.0 av: 21.5 (3.7)	−78.9 (159.1)
3,17	+0.06	96.9, 57.5 av: 77.2 (7.2)	−250 (−)[c]
7,13	−0.002	−1.8	+24.7
8,12	+0.02	64.9, 36.3 av: 50.6 (4.3)	−154.3 (129.4)
meso-5,15	−0.04	54.0	
meso-10	−0.04	49.9	
Ph-*o*-H		−149	–[c]
Ph-*m*-H		−3.8	–[c]
Ph-*p*-H		−74.9	–[c]

[a] Based on calculated spin density and methyl substitution. Ethyl CH$_3$ shifts given in parentheses. [b] Taken from ref 18. [c] Not observed.

may be present for either $S = {}^3/_2$ Fe(III) or $S = 1$ Fe(IV), we would, thus, expect the ^{13}C *paramagnetic* shift to be about −144 ppm. Both of these values are presented in Table 5, where they are used to determine the amount of excess spin density present, beyond that expected for delocalization from the d$_\pi$ orbital(s) and, thus, due to the corrolate π radical. It should be noted that the *meso*-carbon paramagnetic shift of these low-spin Fe(III) porphyrinates is large, despite the fact that there are nodes at the *meso*-carbons of the *3e(π)* orbitals of the porphyrinate ring. This *paramagnetic* shift is due to spin polarization from the adjacent carbon atoms.[75]

The *ortho*-, *meta*-, and *para*-phenyl carbons of (TPP)Zn have ^{13}C chemical shifts of 134.4, 127.5, and 126.5 ppm, respectively,[76] while those of [TPPCo(1-MeIm)$_2$]Cl are 134.1, 127.1, and 128.2 ppm, respectively[75] (Table 4) and those of [TPPFe(ImH)$_2$]Cl are 130.8, 124.6, and 126.5 ppm, respectively[75] (Table 4). Thus, the *paramagnetic* shifts of *meso*-phenyl-carbons due to a single d$_\pi$ unpaired electron are −3.3, −2.5, and −1.7 ppm, respectively, values which are negligible to the accuracy of this desired separation of the chemical shifts observed for the chloroiron corrolates into the constituent contributions discussed in the sections on

Table 4. Proton and Carbon Chemical Shifts of Representative Cobalt(III) and Iron(III) Porphyrinates (Solvent = CD_2Cl_2 or as Marked)

porphyrin complex	spin state	T	meso		*meso*-phenyl		pyrrole		pyrrole CH_2		^{1}H	^{13}C	ref
			^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	$\delta_m - \delta_p$	$\delta_m - \delta_p$	
(OECorr)SnCl	$S = 0$	ambient	9.8	94.4 (5,15)				132.6 (2,18)	4.2	20.0			72
			9.7	89.0 (10)				140.1 (3,17)	4.0	19.9			
								140.2 (7,13)	4.1	20.0			
								136.6 (8,12)	4.1	19.7			
(OECorr)SnPh	$S = 0$	ambient						131.3 (2,18)	4.2−4.1	20.8			72
								139.0 (3,17)	4.2−4.1	20.0			
								139.3 (7,13)	4.2−4.1	19.9			
								135.7 (8,12)	4.2−4.1	19.7			
$[(ETIO)Co(1\text{-}MeIm)_2]^+$	$S = 0$	299	10.3	96.7				141.8	4.1	20.3 (CH_2)			75
									3.7	12.2(CH_3)			
$[(TPP)Co(1\text{-}MeIm)_2]^+$	$S = 0$	299		119.9	*o*	134.1		134.6					75
					m	127.1							
					p	128.2							
(OEP)FeCl	$S = {}^5/_2$	298	−55.9						43.7, 40.2	80.0			TW[a]
(OETPP)FeCl	$S \sim {}^5/_2$	298			o_1 10.7			− (1,4)	45.2,	53.9	5.9	0.3	TW[a]
					o_2 8.2				24.1		5.7	5.3	
					m_1 13.0	144.6		− (2,3)	38.5,	61.3			
					m_2 12.8	149.9			35.3				
					p 7.1	144.3							
		285			o_1 11.2	356.2							
					o_2 8.5	360.0							
$(TPP)FeClO_4$	$S = {}^3/_2$	298			*o* 10.0	269.8					3.4	2.5	TW[a]
					m 11.6	140.2							
					p 8.2	137.7							
$[(OEP)Fe(HIm)_2]^+$	$S = {}^1/_2$ d_π	298	3.0	23.6					6.6	−23.6			TW[a]
$[(OEP)Fe(1\text{-}MeIm)_2]^+$	$S = {}^1/_2$ d_π	299		23.6				146.7		−23.6			75
$[(ETIO)Fe(1\text{-}MeIm)_2]^+$	$S = {}^1/_2$ d_π	299	3.1	23.5				147.5	6.8	−23.2 (CH_2)			75
									16.0	−34.6 (CH_3)			
$[(TPP)Fe(HIm)_2]^+$	$S = {}^1/_2$ d_π	298			*o* 5.0	130.8	−16.9	94.3			−0.1	−1.9	TW[a]
					m 6.2	124.6							
					p 6.3	126.5							
$[(TPP)Fe(1\text{-}MeIm)_2]^+$	$S = {}^1/_2$ d_π	299		54.9				98.6					75
$[(TMP)Fe(2\text{-}MeHIm)_2]^+$	$S = {}^1/_2$ d_π	233			m_1 6.0	128	P_1[b] −12.0	77					TW[a]
					m_2 6.7	126	P_2[b] −15.5	89					
					m_3 6.9	122	P_3[b] −17.5	94					
					m_4 9.1	135	P_4[b] −19.2	98					
$[(OETPP)Fe(HIm)_2]^+$	$S = {}^1/_2$ d_π	298			*o* 5.5	104.1			12.4, 5.1		−1.0	−0.3	TW[a]
					m 5.9	125.0							
					p 6.9	125.3							
		285			*o* 4.6	106.6			10.8, 4.2	−25.5	1.0	4.6	
					m 6.6	125.1							
					p 5.6	124.5							
$[(OEP)Fe(t\text{-}BuNC)_2]^+$	$S = {}^1/_2$ d_{xy}	223	−58.2	491.1					7.4	1.7			80
$[(TPP)Fe(t\text{-}BuNC)_2]^+$	$S = {}^1/_2$ d_{xy}	223		997.3	*o* −2.4	579.6	11.2	60.0			15.6	−17.2	80
					m 16.5	149.3							
					p 0.9	166.5							
$[(OMTPP)Fe(t\text{-}BuNC)_2]^+$	$S = {}^1/_2$ d_{xy}	223		979.4	*o* 1.0	568.8			−2.1	18.9	10.8	23.6	80
					m 15.0	169.9							
					p 4.2	146.3							
$[(OETPP)Fe(t\text{-}BuNC)_2]^+$	$S = {}^1/_2$ d_{xy}	223		416.2	*o* 5.8	316.0			9.8	−11.0	5.1	7.0	80
					m 11.5	145.7							
					p 6.4	138.7							

[a] TW = this work. [b] P_1-P_4 = 4 β-pyrrole resonances observed as a result of the symmetry of the ruffled porphyrinate ring with this bulky ligand bound to Fe(III).

radical spin density at the *meso*-carbons of the chloro- and phenyliron corrolates.

Radical Spin Density at the β-Pyrrole Carbons of the Chloroiron Corrolates. Using the estimates of the contribution of spin delocalization from the metal d_π unpaired electron(s) to the spin density at the β-pyrrole and *meso*-phenyl carbons just discussed, we have constructed a table of estimated total *paramagnetic* shifts and the separation of these into the contributions expected from the delocalization of metal electrons to the macrocycle through Corr → Fe π donation, and the residual due to the corrole π radical electron, in order that we may see where this radical electron resides on the macrocycle. This is an approximate treatment, for we have not separately accounted for the metal- and ligand-centered pseudocontact contributions;[75] as justification for this neglect of the pseudocontact contributions, we cite the fact that metal-centered pseudocontact shifts are relatively small ($<$10 ppm),[45,75,77] and ligand-centered pseudocontact shifts parallel the contact shifts in magnitude and sign, but are much smaller than the contact shifts ($<$10%).[75,77] To

Table 5. ^{13}C Paramagnetic Shifts and Their Separation into Those Arising from the d_π and Corrole Radical Electrons

^{13}C Paramagnetic Shifts, ppm^a								
						or Ph		
complex/δ_{para}^a	2,18	3,17	7,13	8,12	*meso*-C	*o*	*m*	*p*
(TMTECorr)FeCl	−95	−8	−29	−55	N. O.^{b}			
$\delta_d\pi^c$	−44 (−88)	−44 (−88)	−47 (−94)	−47 (−94)	−73 (−146)			
$\delta_{\text{corr rad}}^c$	−51 (−7)	+36 (+80)	+18 (+65)	−8 (+47)				
radical spin density^{c,d}	+0.053 (+**0.007**)	−0.037 (−**0.083**)	−0.019 (−**0.068**)	+0.008 (−**0.049**)				
total β-pyrrole radical spin density^c		+0.01 (−**0.39**)						
total *meso* radical spin density^e		−0.72^e						
total β-pyrrole + *meso* radical spin density		−0.71 (−**1.11**)						
(DMHECorr)FeCl	−94	−5	−28	−41	N. O.^{b}			
$\delta_d\pi^c$	−44 (−88)	−44 (−88)	−47 (−94)	−44 (−88)	−73 (−146)			
$\delta_{\text{corr rad}}^c$	−20 (−6)	+39 (+83)	+19 (+66)	+3 (+47)				
radical spin density^{c,d}	+0.051 (+**0.006**)	−0.040 (−**0.084**)	−0.019 (−**0.067**)	−0.003 (−**0.048**)				
total β-pyrrole radical spin density^b		−0.02 (−**0.39**)						
total *meso* radical spin density^e		−0.72^e						
total β-pyrrole + *meso* radical spin density		−0.74 (−**1.11**)						
(TPCorr)FeCl	−151	+289	+33	+73	N. O.^{b}	−430, −414 −513	+14 −12	−58 −46
$\delta_d\pi^c$	−48 (−96)	−48 (−96)	−48 (−96)	−48 (−96)		−3 (−6)	−3 (−5)	−2 (−3)
$\delta_{\text{corr rad}}^c$	−103 (−55)	+337 (+385)	+81 (+129)	+121 (+169)		−423, −407 −506	+20 −6	−58 −46
radical spin density^{c,d}	+0.016 (+**0.009**)	−0.053 (−**0.060**)	−0.013 (−**0.020**)	−0.019 (−**0.026**)	N. O.^{b}			
total β-pyrrole radical spin density^c		−0.14 (−**0.19**)						
total *meso* radical spin density^e		−0.73^e						
total β-pyrrole + *meso* radical spin density		−0.87 (−**0.92**)						
(OMTPCorr)FeCl	−106	−5	−25	−45	N. O.^{b}	N. O.^{b}	−44,−42 −49	−10 −10
$\delta_d\pi^c$	−47 (−94)	−47 (−94)	−47 (−94)	−47 (−94)		−3 (−6)	−3 (−5)	−2 (−3)
$\delta_{\text{corr rad}}^c$	−59 (−12)	+42 (+86)	+22 (+69)	+2 (+49)		N. O.^{b}	−39, −37 −44	−8 (−7) −8 (−7)
radical spin density^{c,d}	+**0.048** (+0.010)	−**0.034** (−0.070)	−**0.018** (−0.056)	+**0.002** (−0.040)	(+)			
total β-pyrrole radical spin density^c		+**0.004** (−0.31)						
total *meso* radical spin density^e		+0.38						
total β-pyrrole + *meso* radical spin density		+**0.38** (+0.07)						
(DMHECorr)FePh	−99	−270	+5	−174	N. O.^{b}			
$\delta_d\pi^c$	−44 (−88)	−44 (−88)	−47 (−94)	−44 (−88)	−73 (−146)			
$\delta_{\text{corr rad}}^c$	−55 (−11)	−236 (−182)	+52 (+99)	−130 (−88)				
radical spin density^{c,d}	+**0.012** (+0.002)	+**0.048** (+0.037)	−**0.012** (−0.022)	+**0.026** (+0.018)	−0.061 (5,15)^f −0.058 (10)^f			
total β-pyrrole radical spin density^c		+**0.15** (+0.07)						
total meso radical spin density^e		−**0.12**^{e}; −0.18^f						
total β-pyrrole + meso radical spin density		+**0.03** (−0.05); −**0.03**^{f} (−0.23^f)						

[a] *Paramagnetic* shift $\delta_{para} = \delta_{obs} - \delta_{dia}$, where the diamagnetic shifts used are those of (OECorr)SnCl.[72] [b] N. O. = not observed. [c] Value for one d_π unpaired electron; values for two d_π unpaired electrons given in parentheses. For the chloroiron corrolates except for (OMTPCorr)FeCl, the spin densities are consistent with those of the $3a_{2u}(\pi)$-like corrolate orbital if there are two d_π unpaired electrons, while for the phenyliron corrolate, they are somewhat more consistent with that orbital if there is only one d_π unpaired electron; for (OMTPCorr)FeCl, the spin densities are marginally consistent with the presence of one d_π unpaired electron. [d] See text for the method of calculation of spin densities. [e] DFT-calculated value from ref 18. [f] Calculated from δ_{para}(*meso*-H) for (DMHECorr)FeCl (Table 2), the spin densities at the *meso*-carbons of the chloroiron corrolates,[18] and δ_{para}(*meso*-H) for (DMHECorr)FePh (Table 3).

convert *paramagnetic* shifts into spin densities, we have taken the difference in chemical shift between the 2,18- and 3,17-CH_2 carbons (Table 2) and divided that value by the difference in total β-pyrrole-carbon spin densities calculated by DFT methods for the 2,18- and 3,17-carbons ($+0.05 - (-0.04) = +0.09$)[18] to obtain the amount of spin density arising from all contributions that is represented by a 1 ppm shift. We have then multiplied this value by the *paramagnetic* shift due to the corrolate π radical electron derived in Table 5.

$$\{[\rho_C(2,18) - \rho_C(3,17)]/[\delta_{obs}(2,18) - \delta_{obs}(3,17)]\} \times \delta_{para}(7,13 \text{ or } 8,12) = \rho_C(7,13 \text{ or } 8,12) \quad (2)$$

Results obtained for the ^{13}C *paramagnetic* shifts of all complexes of this study are summarized in Table 5.

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As can be seen from the results presented in this table, for the two chloroiron octaalkylcorrolates, those of TMTECorr and DMHECorr, whether we consider one or two d_π unpaired electrons to be present, the spin density at each β-pyrrole carbon is quite similar for the two. Furthermore, the β-pyrrole spin densities for (OMTPCorr)FeCl at each position are very similar to those of the two octaalkylcorrolates. From the values given in Table 5, if it is assumed that there is only one d_π unpaired electron, then the largest corrole radical spin density is at the 2,18-carbons and is positive, about +0.05; for the 3,17-carbons, the spin density is about $^2/_3$ of this magnitude and is negative, about −0.04; at the 7,13-carbons, it is about $^1/_3$ of the 2,18-carbon spin density magnitude and also negative, about −0.01 to −0.02; at the 8,12-carbons, the spin density is very small and the sign varies. By having accounted for the contribution of the spin delocalization from the single metal d_π unpaired electron, we thus would conclude that the total β-pyrrole radical spin density at all eight carbons for the two chloroiron octaalkyl corrolates ranges from +0.02 to −0.02, very small values.

In the case of two d_π unpaired electrons, the ^{13}C chemical shifts of the 2,18 carbons of alkyl groups attached to the β-pyrrole carbons are largely accounted for by spin delocalization from the metal to the macrocycle, and thus, the radical electron contributes negligible spin density at the 2,18 carbons. In comparison, the ^{13}C shifts of the 3,17; 7,13; and 8,12 carbons are large and positive, indicating excess negative spin density at those β-pyrrole carbons due to the corrole radical electron, about −0.08, −0.06, and −0.03 to −0.05, respectively, a total of about −0.34 to −0.38 for the eight β-pyrrole carbons of the two octaalkylcorrolate complexes. Smaller values are found for low-spin Fe(III) porphyrinates, where only spin delocalization is possible, +0.10[78] and +0.06 to +0.07;[79] note that the sign of the spin density is the opposite of that observed for the chloroiron octaalkylcorrolates, again, indicating antiferromagnetic coupling of the radical electron.

Summarizing both possibilities, of one or two d_π unpaired electrons, either there is essentially zero radical spin density at the eight β-pyrrole carbons (one) or there is −0.34 to −0.38 radical spin density at the eight β-pyrrole carbons (two d_π unpaired electrons) of the chloroiron octaalkylcorrolates. The patterns of radical spin density obtained for these three complexes are more consistent for the case of two d_π electrons than for only one, when compared to the expected electron density distributions shown for the $3a_{2u}(\pi)$-like orbital of Figure 1A (small density at the 2,18-carbons, largest at the 3,17-carbons). Therefore, we will emphasize the case of two d_π electrons for the chloroiron octaalkyl- and triphenylcorrolates in the following discussion, and we have bolded those calculated spin densities in Table 5.

In comparison, for the triphenylcorrolate, (TPCorr)FeCl, the 2,18 β-carbons have the most negative ^{13}C shift (−18.8 ppm), while the 3,17 β-carbons have the most positive ^{13}C shift (+428.9 ppm). If the DFT-calculated total spin densities at the 2,18 and 3,17 positions, which included both metal and macrocycle contributions to the spin densities (+0.04, −0.03, respectively),[18] are used as were those of the β-pyrrole CH_2 or CH_3 groups in eq 2 to estimate the spin density at each β-pyrrole carbon that is due to the corrolate radical electron, one predicts that the spin density due to the corrolate unpaired electron at the 2,18 positions is about +0.009 for the presence of two d_π unpaired electrons, while that at the 3,17 carbons due to the radical electron is −0.060, that at the 7,13 carbons is −0.020, and that at the 8,12 positions is −0.026, a total of −0.19 for two d_π electrons that is due to the π radical electron. Thus, all four chloroiron corrolates of this study discussed thus far show similar patterns of positive and negative spin density at the β-pyrrole carbons of the macrocycle. Nevertheless, the sum of the spin densities at all eight β-pyrrole carbons for the triphenyl- or octaalkylcorrolates indicates that the eight β-pyrrole carbons carry only −0.2 to −0.4 of the corrole radical spin density and that *they are, thus, not the most definitive carbon positions to probe* in order to determine the existence and location of the spin of the corrolate π radical. Rather, we must investigate the *meso*-carbon *paramagnetic* shifts.

Radical Spin Density at the *meso*-Carbons of the Chloroiron Corrolates. One of the best systems for observing large spin delocalization from metal d orbitals to macrocycle π orbitals is the bis-*tert*-butylisocyanide complexes of iron porphyrinates.[13,45,48] These complexes have very large negative *meso*-H shifts or very large positive phenyl-H $\delta_m - \delta_o$ and $\delta_m - \delta_p$ shift differences for *meso*-phenyl-substituted porphyrins[13,45,48] and have very large positive *meso*-carbon shifts,[80,8180−81] as summarized in Table 4. These very large *positive* ^{13}C shifts represent large positive spin densities at the *meso*-carbons,[82] which suggest that, with negative spin density at the *meso*-carbons of the corrole ring, the chemical shifts should be very negative. [That *meso*-C resonances are shifted in an opposite direction to β-pyrrole-C resonances in paramagnetic iron porphyrinates (+ shifts → + spin density) was originally pointed out by Goff.[75]] We have looked as far as −2000 ppm (and as far positive as +2000 ppm) but have not found these resonances. Based on the spin density estimated for the *meso*-carbons of $[(TPP)Fe(PhNC)_2]^+$ ($\rho_C \sim +0.06$),[82] the chemical shift of the corresponding *t*-BuNC complex (+997 ppm) and that of the $[(OEP)Fe(t\text{-}BuNC)_2]^+$ complex (+491 ppm),[80] and the spin densities of the chloroiron corrolates calculated by DFT methods of about −0.25 each,[18] the *meso*-carbon resonances could be in the chemical shift range as negative as −1500 or even as negative as −3750 ppm. Thus, we cannot use ^{13}C NMR shifts to determine the spin density at the *meso*-carbons experimentally.

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We have shown previously that *meso*-phenyl-proton shifts can be useful for determining the *sign* of the spin density at the *meso*-carbons of iron tetraphenylporphyrinates.[13] To determine the *amount* of spin density at the *meso*-carbons of the phenyl-substituted chloroiron corrolates, (TPCorr)FeCl and (OMTPCorr)FeCl, we must have a means of converting *meso*-phenyl-H or -C shifts or shift differences (for example, $\delta_m - \delta_p$) into *meso*-carbon spin densities. While this cannot be done from first principles, we can estimate the meso ρ_C using the *meso*-H shift difference $\delta_m - \delta_p$ of [(TPP)Fe(*t*-BuNC)$_2$]$^+$, +15.6 ppm,[48] Table 4, and the estimated value of the meso ρ_C for this complex, +0.06,[82] along with the value of $\delta_m - \delta_p$ obtained for (TPCorr)FeCl, Table 1, −22 (5,15) and −20.8 (10) ppm, which yields values of meso $\rho_C = -0.087$ (5,15) and −0.080 (10). However, these values are much smaller than those obtained from the DFT calculations,[18] −0.225 (5,15) and −0.280 (10). Therefore, either the estimated spin density of the *meso*-carbons of [(TPPFe(*t*-BuNC)$_2$]$^+$ is too small by a factor of 3 (unlikely, based upon simulations of the pulsed electron-nuclear double resonance (ENDOR) spectra of [(OEP)Fe(PhNC)$_2$]$^{+}$ [82]) or the magnitude of the phenyl-H shift differences of the chloroiron corrolate radicals do not reflect the magnitude of the spin density at the *meso*-carbons. Thus, we have also investigated the behavior of the phenyl-^{13}C $\delta_m - \delta_p$ of (TPCorr)FeCl as compared to that of [(TPP)Fe(*t*-BuNC)$_2$]$^+$: the former has shift differences of +72.8 (5,15) and +35.0 (10) ppm (calculated from the phenyl-C shifts given in Table 2), while the latter has a $\delta_m - \delta_p = -17.2$ ppm. From these values and a meso $\rho_C = +0.06$ for the latter, the meso ρ_C values for (TPCorr)FeCl are −0.254 (5,15) and −0.122 (10). These spin densities for the 5,15-carbons are of similar magnitude to those obtained by DFT calculations,[18] and that for the 10-carbon is a factor of 2 smaller than calculated. Thus, it appears that, at least for the corrolate radical-containing complexes, and perhaps for other macrocycle complexes as well, phenyl-carbon $\delta_m - \delta_p$ values are much more reliable at predicting spin densities at the *meso*-carbons than are phenyl-proton shift differences. Detailed investigations of other systems will be required in order to determine the relative usefulness of ^{1}H and ^{13}C phenyl shift differences in cases where macrocycle radicals are not involved.

On the basis of the behavior of the phenyl-H and phenyl-C shift differences for (TPCorr)FeCl, we have used the shift differences $\delta_m - \delta_p$ for the phenyl carbons of (OMTPCorr)FeCl [−33.9 (5,15) and −40.0 (10) ppm] and the values of $\delta_m - \delta_p$ for the phenyl carbons of [(TPP)Fe(*t*-BuNC)$_2$]$^+$ (−17.2 ppm) to determine the spin densities, +0.118 (5,15) and +0.140 (10), respectively. From this estimate, it is clear that there is significant *positive* spin density at the *meso*-carbons of (OMTPCorr)FeCl. The total of the β-pyrrole spin densities found for (OMTPCorr)FeCl (Table 5) and the *meso*-carbon spin densities just calculated account for +0.40 (for one d_π unpaired electron; +0.09 for two) unpaired electron on the corrole ring that has positive spin, the same sign as that of the metal electrons.

Thus, depending upon whether (OMTPCorr)FeCl, with a somewhat saddled macrocycle, has one or two d_π unpaired electrons, it may have ferromagnetic coupling of metal and macrocycle electron spins. This could occur if the complex consists of intermediate-spin Fe(III) ferromagnetically coupled to a corrole radical to give an $S = 2$ system. To determine whether this is the case, we measured the value of μ_{eff} by NMR methods.[57,58] Based upon the mass of the sample used, an initial value of $\mu_{\text{eff}} = 3.8\ \mu_B$ was obtained. This value is larger than the 2.87 μ_B expected for an $S = 1$ system but considerably smaller than expected for an $S = 2$ system. However, because of the large impurity peaks in the ^{1}H NMR spectrum of (OMTPCorr)FeCl (Figure 3), which are probably due to a combination of the μ-oxo dimer [(OMTPCorr)Fe]$_2$O and polydimethylpyrrole/benzyl-unit-containing polymers or corrole ring decomposition products, we tried to account for this impurity based upon the intensity of the impurity resonances at 1−2.5 ppm and 7−8 ppm. On the basis of the intensity of those peaks, we estimate a purity of the paramagnetic (OMTPCorr)FeCl complex of about 61 ± 3%. Making this correction to the concentration of the complex shifts μ_{eff} to larger values, which indicates a value considerably larger than 3.8 μ_B and estimated to be within the range of 4.7 ± 0.5 μ_B; a value of $\mu_S = 4.90\ \mu_B$ is expected for four unpaired electrons. The solution magnetic moment supports the proposal of ferromagnetic coupling of the iron and corrole radical electrons to give $S = 2$ for (OMTPCorr)FeCl and the metal electron configuration $(d_{xz},d_{yz})^3 d_{xy}{}^1 d_{z^2}{}^1$, with only one d_π unpaired electron, although from the data at hand, we cannot determine the strength of the coupling.

That ferromagnetic coupling could be possible is supported by the smaller distance of the iron out of the mean plane of the four nitrogens (0.387 Å) as compared to that found for (OECorr)FeCl (0.42 Å),[14] which would decrease the $d_{z^2}-a_{2u}(\pi)$-type overlap (Figure 1C) shown previously by DFT calculations to be responsible for the antiferromagnetic coupling in the chloroiron octaalkyl- and triphenylcorrolates.[18] This out-of plane distance is larger than that found for the phenyliron complex (OECorr)FePh (0.27 Å)[14] discussed below, which was found to be best described as an $S = 1$ Fe(IV) center bound to a noninnocent corrolate(3−) anion.[18] Thus, the (OMTPCorr)FeCl complex gives us a view of how sensitive the electron configuration of the metallocorrolates is to not only the identity of the axial ligand but also the amount of out-of-plane displacement of the metal.

Radical Spin Density at the β-Pyrrole and *meso*-Carbons of the Phenyliron Corrolate. The phenyliron corrolate of this study, (7,13-DMHECorr)FePh, for which the *paramagnetic* shifts at the pyrrole-CH$_2$ and -CH$_3$ carbons and the residual *paramagnetic* shifts that are due to the corrolate π radical are also included in Table 5, shows a somewhat different pattern of residual spin densities. As summarized in Table 5, if we consider one d_π unpaired electron to be present, then there is small positive radical spin density at the 2,18-, 3,17-, and 8,12-carbons and small negative radical spin density at the 7,13-carbons (+0.011, +0.048, +0.026, and −0.011, respectively), for which the sum of the radical spin densities at the eight β-pyrrole carbons is +0.15. If, instead, we consider two d_π electrons to be present, then most of the observed negative ^{13}C *paramagnetic* shift of the 2,18-carbons is accounted for by delocalization of the metal d_π electrons to the corrole ring, yielding small positive spin density at these positions, with larger positive spin density at the 3,17 and 8,12 carbons, and negative spin density at the 7,13 carbons (+0.002, +0.037, +0.018, and −0.020, respectively) in this case, a total of +0.074 from the excess ^{13}C *paramagnetic* shifts at the β-pyrrole CH_2 and CH_3 positions of this study. Small spin density at the three *meso*-carbons, −0.04 each, was found from DFT calculations.[18] If we use the ^{1}H *paramagnetic* shifts of the *meso*-H of the chloroiron complex of this same corrolate [+164 (5,15) and +177 (10) ppm[16]], along with the calculated spin densities at these positions (−0.23 and −0.26, respectively[18]) and the *meso*-H *paramagnetic* shifts of the phenyliron corrolate [+43.6 (5,15) and +39.7 (10) ppm[18]] to calculate the spin densities, we find $\rho_C = -0.061$ (5,15) and −0.058 (10). These values are slightly larger in magnitude but of the same sign as the DFT-calculated spin densities.[18] These values lead to the total excess spin density being +0.03 (−0.05 for two d_π unpaired electrons) for the eight β-pyrrole and three *meso*-carbons due to the radical electron using the DFT-calculated spin densities or −0.03 (−0.23 for two d_π electrons) due to the radical electron using the *meso*-H shifts. Because the phenyl anion should be a much better π acceptor than the chloride ion, it should tend to lower the energies of the d_{xz} and d_{yz} orbitals; in addition, the metal is not shifted as far out-of-plane as it is for the chloroiron corrolates. Thus, we favor the $(d_{xz},d_{yz})^3(d_{xy})^1$ electron configuration and the presence of only one d_π unpaired electron for this complex. Therefore, as concluded previously,[18] the excess spin density on the corrolate ring at the β-pyrrole and *meso*-carbons of (7,13-DMHECorr)FePh due to a corrolate radical electron is very small. Thus, we conclude that, for the phenyliron corrolate, the metal is approximately Fe(IV) and the corrolate is approximately 3− in charge, but the macrocycle is non-innocent.

Conclusions. The undecasubstituted chloroiron corrolate, (OMTPCorr)FeCl, has a molecular structure that is much less distorted from planarity than its dodecasubstituted chloroiron porphyrinate counterpart, (OMTPP)FeCl.[66] Both have saddled macrocycles, but the average methyl out-of-plane distance is only 0.63 Å for the former, while it is 1.19 Å[66] for the latter. The Fe out-of-plane distance (from the mean plane of the macrocycle nitrogens) is also smaller for the undecasubstituted corrolate (0.387 Å) than for the octasubstituted corrolate (OECorr)FeCl (0.42 Å)[14] or the dodecasubstituted porphyrinates (OMTPP)FeCl (0.46 Å)[66] and (TC_6TPP)FeCl (0.485 Å).[67] This smaller out-of-plane distance is believed to be the reason for the ferromagnetic coupling between $S = {}^3/_2$ Fe(III) and the corrolate radical to yield an $S = 2$ (OMTPCorr)FeCl complex, as shown both by NMR shifts (^{13}C) of the phenyl carbons that are opposite in sign ($\delta_m - \delta_p$) from those of (TPCorr)FeCl (and the same sign as those of $[(TPP)Fe(t\text{-}BuNC)_2]^+$, Table 4), and by solution magnetic moment measurement. Interestingly, if we had only measured the ^{1}H chemical shifts of (OMTPCorr)-FeCl, we would not have discovered its different spin coupling pattern, for the ^{1}H shift differences ($\delta_m - \delta_p$) are of the same sign and approximately the same magnitude for (TPCorr)FeCl and (OMTPCorr)FeCl (Table 2). It is, thus, clear that ^{13}C chemical shifts are powerful tools for defining the sign and magnitude of the spin densities at various carbon positions of paramagnetic metallomacrocycles and appear to be more reliable than ^{1}H shifts and shift differences. The much smaller spin densities at the eight β-pyrrole carbons versus those at the three *meso*-carbons of all of the chloroiron corrolates, together with the fact that the *3e(π)*-like orbitals as well as the $3a_{2u}(\pi)$-like orbital of the corrolate macrocycle have similar patterns of electron density at the β-pyrrole carbons (Figure 1), which, with opposite spin contributions approximately canceling, makes it clear that the β-pyrrole carbon shifts (as well as β-substituent H or C shifts) are not useful for defining the electron configurations of metallocorrolates. Without analyzing the *meso*-H or *meso*-phenyl carbon shifts, the electron configurations of metallocorrolates cannot be reliably determined.

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Supporting Information Available: Figures S1−S3 [^{1}H and HMQC NMR spectra of (Me_2Et_6Corr)FeCl and (TPCorr)FeCl] are available free of charge via the Internet at http://pubs.acs.org.

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