

Inorganica Chimica Acta 339 (2002) 171-178



www.elsevier.com/locate/ica

Chloroiron *meso*-triphenylcorrolates: electronic ground state and spin delocalization

Sheng Cai^a, Silvia Licoccia^b, Cadia D'Ottavi^b, Roberto Paolesse^b, Sara Nardis^b, Véronique Bulach^c, Bertrand Zimmer^c, Tatjana Kh. Shokhireva^a, F. Ann Walker^{a,*}

^a Department of Chemistry, University of Arizona, Tucson, AZ 85721-0041, USA

^b Dipartimento di Scienze e Tecnologie Chimiche, Universitá di Roma Tor Vergata, Via della Ricerca Scientifica, 00133 Rome, Italy ^c Université Louis Pasteur, Laboratoire de Chimie de Coordination Organique, Institut Le Bel, 67000 Strasbourg, France

Received 6 November 2001; accepted 1 February 2002

Abstract

Four chloroiron meso-triphenyl-substituted corrolates have been synthesized and studied by ¹H NMR spectroscopy. As in the case of the β-pyrrole-octaalkylcorrolatoiron chloride complexes studied previously [Inorg. Chem. 39 (2000) 3466], these complexes were also found to be S = 3/2 Fe(III) corrolate(^{2-•}) π -cation radical species, where the macrocycle radical electron is antiferromagnetically coupled to the metal electrons to give an overall S = 1 complex. This conclusion is based upon the large alternating-sign contact shifts observed for the *meso*-phenyl protons. The ¹H isotropic shifts of the pyrrole-H of these chloroirontriphenylcorrolate complexes are similar to those of the chloroiron tri-(pentafluorophenyl)corrolate complex reported previously and said to be a S = 1 Fe(IV) complex bound to a simple corrolate(³⁻) ligand [Inorg. Chem. 39 (2000) 2704]. The ¹⁹F NMR spectrum of the latter complex shows that it has small (negative) phenyl-F isotropic shifts for all phenyl-F, which might suggest that this single compound has a different electronic structure than all other chloroiron corrolates investigated thus far. However, there have as yet been very few NMR investigations of paramagnetic metal macrocycles having fluorine substituents, and thus it is premature to conclude that the small phenyl-F isotropic shifts are definitive proof of small spin density at the meso positions of the corrolate ring. It is concluded that pyrrole-H chemical shifts alone cannot differentiate the two possible electron configurations, simple S = 1 Fe(IV) (Corr³⁻) and antiferromagnetically coupled S = 3/2 Fe(III) (Corr^{2-•}), and that based on the ¹H investigations reported in this and two previous papers, all chloroiron corrolates reported thus far, with the exception of one, have the electron configuration S = 3/2 Fe(III) (Corr^{2-•}), in which the corrolate unpaired electron is antiferromagnetically coupled to the three metal electrons, yielding an overall spin for the complex, S = 1. The electron configuration of the one exception, the strongly electronwithdrawing tri-(pentafluorophenyl)corrolate complex of iron chloride, cannot as yet be definitively assigned. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Iron complexes; Corrolate complexes

1. Introduction

Corroles are tetrapyrrole macrocycles that are related to porphyrins, except that they lack one *meso*-carbon, and, in order to retain the same number of π electrons, are thus, when fully deprotonated, trianionic ligands for transition metal ions. They have unique properties, including the capability of maintaining a planar conformation, the possibility of stabilizing high oxidation

* Corresponding author. Tel.: +1-520-621 8645; fax: +1-520-626 9300

states for coordinated metal ions [1], and/or the possibility of stabilizing a one-electron oxidized macrocycle [2]. We have reported NMR and EPR spectroscopic studies of two chloroiron octaalkylcorrolates ([(Me₈-Corr)FeCl] and [(7,13-Me₂Et₆Corr)FeCl]) and their bisimidazole complexes [2], as well as their complex formation with, and autoreduction by, cyanide ion [3]. The results of these studies have shown unambiguously that these five- and six-coordinate iron corrolates are actually iron(III) corrolate(^{2-•}) π -cation radicals [2,3], and that axial ligands such as cyanide can readily autoreduce the corrolate radical, leaving a low-spin Fe(III) cyanide complex [3]. The nature of the magnetic

E-mail address: awalker@u.arizona.edu (F. Ann Walker).

^{0020-1693/02/\$ -} see front matter 0 2002 Elsevier Science B.V. All rights reserved. PII: S 0 0 2 0 - 1 6 9 3 (0 2) 0 0 9 2 9 - 5

coupling between the unpaired electrons on the metal and the corrolate(^{2-•}) π -cation radical differs, depending on the axial ligand(s) present, with very strong antiferromagnetic coupling in the case of the chloride complexes [2], but weak ferromagnetic coupling in the case of the imidazole complexes [2], and much stronger ferromagnetic coupling in the case of the bis-cyanide complex, [(7,13-Me₂Et₆Corr)Fe(CN)₂]⁻ [3]. However, in all cases, the corrole π orbital used for the macrocycle unpaired electron is the 7b₁ orbital [4,5], which is analogous to the 3a_{2u} orbital of the porphyrin ring [5]. This orbital has large spin density at the *meso*-carbon positions and negligible spin density at the pyrrole β carbons [2,4,5].

In the present work we report a proton NMR spectroscopic study of several meso-phenyl-substituted iron corrolates—(5,10,15-triphenylcorrolato)iron perchlorate (TPCorr)FeClO₄ and (5,10,15-tri-(4-X-phenylcorrolato))iron chloride [T(4-X)PCorr]FeCl, where X =H, -NO₂ and -OCH₃. For comparison, the 5,10,15-tri-(pentafluorophenyl)corrolatoiron chloride [T(F₅P)Corr]FeCl, claimed to be an iron(IV) corrolate [6-8], was also investigated. As we will show, all of the chloroiron triphenylcorrolates, except for the tri-(pentafluorophenyl)corrolate complex, are unambiguously S = 3/2 Fe(III) corrolate(^{2-•}) π -cation radical complexes, as reported previously for the chloroiron octaalkylcorrolate analogs [2]. Additional investigations are necessary before the electron configuration of $[T(F_5P)Corr]FeCl can be defined.$

2. Experimental

5,10,15-Triphenylcorrole (TPCorrH₃), 5,10,15-Tri(4nitrophenyl)corrole [T(4-NO₂P)Corr]H₃, 5,10,15-Tri(4methoxyphenyl)corrole [T(4-MeOP)Corr]H₃ have been prepared as previously described [9]. 5,10,15-Tri(pentafluorophenyl)corrole, [T(F₅P)Corr]H₃, was purchased from Strem Chemicals (Illinois). The chloroiron derivatives of these meso-triarylcorroles were prepared by reaction of FeCl₂ in refluxing DMF [3,9], and the ⁵⁷Felabeled complex of TPCorrH₃ was prepared according to the procedure used for the corresponding 57 Fe porphyrinates [10]. The μ -oxo dimer is the first product of the reaction, and the corresponding chloroiron complex is obtained in quantitative yield after washing of a dichloromethane solution with diluted HCl [11]. The perchlorate complex was obtained after stirring (TPCorr)FeCl with 1.1 equiv. of AgClO₄ in dry toluene at room temperature (r.t.) under argon for 1 h, followed by filtration, evaporation and finally washing the residue three times with dry hexane. Caution! Perchlorate metal complexes are potentially explosive. Only small amounts of material should be prepared and it should be handled with caution. (TPCorr)FeCl: 82% yield. UV–Vis: λ_{max} 357 (ε 36000 M⁻¹ cm⁻¹), 409 (ε 45000), 504 (ε 11000) nm. LR MS (FAB): m/z 615 (M^+). (TPCorr)FeClO₄: 85% yield. UV–Vis: λ_{max} 357 (ε 37000), 420 (ε 45000), 518 (ε 12000) nm. LR MS (FAB): m/z 579 (M^+ –ClO₄). [T(4-NO₂P)Corr]FeCl: UV–Vis: λ_{max} 371 (ε 35000), 406 (ε 47000), 508 (ε 10000) nm. 63% yield. LR MS (FAB): m/z 750 (M^+). [T(4-MeOP)Corr]FeCl: UV–Vis: λ_{max} 361 (ε 32000), 410 (ε 44000), 511 (ε 11000) nm. 68% yield. LR MS (FAB): m/z 705 (M^+). NMR data are given in Table 1.

All samples for NMR spectroscopic experiments were prepared in 5 mm NMR tubes in CD₂Cl₂ (Cambridge) without degassing. ¹H NMR spectra were obtained over temperature ranges from -90 to +30 °C on a Unity 300 NMR spectrometer as described previously [2]. The temperature was calibrated using the Wilmad standard variable temperature sample. ¹⁹F NMR spectra were obtained at ambient temperature on the same instrument. ¹⁹F chemical shifts were referenced using an external sample of α, α, α -trifluorotoluene in benzine (-63.73 ppm relative to CFCl₃). The Mössbauer spectrum of (TPCorr)FeCl [11] was measured in zero applied field at 4.2 K in the Institut für Physik at the Universität zu Lübeck, Lübeck, Germany.

3. Results and discussion

Fig. 1 shows the 1D ¹H NMR spectrum of (TPCorr)FeCl at 25 °C. The [T(4-NO₂P)Corr]FeCl compound gives similar NMR spectra, except that the two peaks at 19.4 and 17.1 ppm in Fig. 1 are missing. Hence these two peaks must be from the para protons of the three phenyl groups (ratio = 2:1, total three protons). In the COSY spectrum (Fig. 2) of (TPCorr)FeCl, there are four pairs of cross peaks between these two resonances and the four resonances in the upfield region (from -1 to -7 ppm). These four peaks can be assigned to the *meta* protons of the three phenyl groups (ratio = 2:2:1:1, total six protons). Note that the two meta protons in each phenyl group are not equivalent, as expected for this five-coordinate complex. The last pair of cross peaks shown is between the 10-meta-H and a peak at 22.7 ppm, which can thus be assigned to the two ortho protons of the 10-phenyl group. Although they are not equivalent, the expected two resonances are not resolved at 300 MHz. It is reasonable to assign the other two downfield resonances to the four 5,15-ortho protons and the three upfield peaks to the pyrrole protons. The fourth pyrrole-H resonance is located at 7.8 ppm (Fig. 1). No cross peaks are observed among pyrrole-H resonances due to their short relaxation times. Only one pair of cross peaks, between the o-H and m-H of the 10-phenyl group, is shown in the COSY spectrum (supporting information Figure S1) of [T(4-NO₂P)Corr]FeCl, and again, no cross peaks are ob-

Table	1
1 4010	1

Isotropic shifts and assignments of (TPCorr)FeCl, [T(4-NO₂P)Corr]FeCl, [T(4-MeOP)Corr]FeCl, (TPCorr)FeCl₄ and [T(F₅P)CorrFeCl

Compound	(TPCorr)FeCl, CD ₂ Cl ₂ , 303 K	[T(4-NO ₂ P)Corr]FeCl, CD ₂ Cl ₂ , 303 K	Assignments
Isotropic shifts (ppm) a	16.36(2H), 15.27(2H)	14.6(2H), 13.6(2H)	5,15- <i>o</i> -H
	14.74(2H)	12.8(2H)	10- <i>o</i> -H
	-10.18(2H), -10.56(2H)	-9.5(2H), -9.8(2H)	5,15- <i>m</i> -H
	-11.22(1H), -11.47(1H)	-10.5(1H), -10.6(1H)	10- <i>m</i> -H
	11.71(2H)		5,15- <i>p</i> -H
	9.54(1H)		10- <i>p</i> -H
	-1.95(2H), -13.67(2H), -15.26(2H), -48.06(2H)	$-2.2(2H)^{b}$, $-14.2(2H)$, $-15.4(2H)$, $-46.1(2H)$	Pyrrole-H
Compound	[T(4-MeOP)Corr]FeCl, CD ₂ Cl ₂ , 293 K	(TPCorr)FeClO ₄ , CD ₂ Cl ₂ , 293 K	Assignments
Isotropic shifts (ppm) ^a	18.9(2H), 17.7(2H)	18.3(4H)	5,15- <i>o</i> -H
	17.0(1H), 16.8(1H)	17.8(2H)	10- <i>o</i> -H
	-11.3(2H), -11.5(2H)	-12.3(4H)	5,15- <i>m</i> -H
	-12.6(1H), -13.0(1H)	-13.6(2H)	10- <i>m</i> -H
		14.3(2H)	5,15- <i>p</i> -H
		11.7(1H)	10- <i>p</i> -H
	$-1.9(2H)^{b}$, $-12.6(2H)$, $-16.0(2H)$, $-50.0(2H)$	$-1.9(2H)^{b}$, $-19.6(2H)$, $-20.2(2H)$, $-61.9(2H)$	Pyrrole-H
Compound	[T(F ₅ P)Corr]FeCl, CD ₂ Cl ₂ , 294 K ^c	$[T(F_5P)Corr]FeCl, C_6D_6$, room temperature ^d	Assignments
Isotropic Shifts (ppm) a	-5.9(2H) -12.6(2H), -21.5(2H), -45.3(2H)	-11(2H), -12(2H), -21(2H), -42(2H) ^d	Pyrrole-H

^a The isotropic shifts were calculated by subtracting the corresponding diamagnetic shifts [9,27] from the chemical shifts. The average diamagnetic shift (8.7 ppm for triphenylcorrole free base [8], 8.9 ppm for [T(F_3P)Corr]Ga(Py) [27]) was used because the pyrrole peaks of neither the free base, the gallium complex, nor the iron complexes have been assigned.

^b Only three pyrrole proton resonances were positively detected in this case. The fourth one is located under the envelope of impurity peaks in the region of 1-9 ppm, and is tentatively assigned a chemical shift of 7.5-7.8 ppm.

^c This work. ^d Reference [6].



Fig. 1. ¹H NMR spectra of (TPCorr)FeCl at 298 K in CD₂Cl₂. The solvent resonance is marked with S, and those peaks marked with stars are due to impurities.

served among pyrrole-H resonances. Since this complex has a similar spectral pattern and chemical shifts to those of (TPCorr)FeCl, the assignments are likely the same.

[T(4-MeOP)Corr]FeCl and (TPCorr)FeClO₄ show similar NMR spectra (Fig. 3) at 20 °C to those of (TPCorr)FeCl and [T(4-NO₂P)Corr]FeCl, and thus they should have the same peak assignments. For [T(4-MeOP)Corr]FeCl, four *orth* o (2:2:1:1) and four *meta* (2:2:1:1) proton peaks were observed. One of the

pyrrole-H peaks happens to have same chemical shift (-4.1 ppm) as one of the *meta* proton peaks (they are resolved at lower temperature). In (TPCorr)FeClO₄, the perchlorate anion may exist as a dissociated counterion. In this case, the complex would have mirror symmetry (the corrolate plane) and the two meta protons within each phenyl group would now be equivalent, as would be the two ortho protons. We find that (TPCorr)FeClO₄ only shows two peaks each (2:1) for phenyl meta, para and ortho protons, respectively, hence supporting the assumption that the perchlorate anion is not bound to the metal, or that it exchanges rapidly between individual iron complexes. In the COSY spectra of [T(4-MeO)PCorr]FeCl and (TPCorr)FeClO₄ (supporting information Figure S2 and S3, respectively), all cross peaks are between para and meta protons of the phenyl groups. Not all protons expected to be J-coupled show cross peaks due to fast relaxation.

In Fig. 4 is shown the complete ¹H NMR spectrum of $[T(F_5P)Corr]FeCl$ at 21 °C. Although there is a prominent water peak at about 2 ppm, it is clear that the fourth pyrrole-H resonance is at 3.1 ppm, rather than at 7.8 ppm as observed for (TPCorr)FeCl (Fig. 1). For each of these five triphenylcorrolatoiron(III) chloride complexes the pyrrole-H resonances are slightly differently spaced (Table 1), yet all, including the perfluori-



Fig. 2. COSY spectrum of (TPCorr)FeCl at 303 K. Due to fast relaxation, not all coupled protons show cross peaks here. The cross peaks marked with 'M' are between *para* and *meta* protons of phenyl groups. The cross peaks marked with 'O' are between *ortho* and *meta* protons of the *meso*-10 phenyl groups. The cross peaks marked with 'I' are from an impurity in the sample used for the COSY experiment (not present in Fig. 1). T₁ noise stripes are observed from the solvent resonance and the impurity peak due to H₂O at ~1.5 ppm.

nated phenyl complex, have generally similar pyrrole-H shifts.

Table 1 lists the isotropic shifts of all peaks and their assignments for these four compounds according to the COSY results and relative peak areas. An important feature concerning the isotropic shifts (see Table 1) of the meso-phenyl protons of (TPCorr)FeCl and (TPCorr)FeClO₄ is that they alternate signs around the phenyl ring (e.g. p-H and o-H positive, m-H negative). This is solid evidence of large π spin density at the meso positions [4,5]. Furthermore, the signs of these shifts are opposite to those in [(TPP)Fe(t- $BuNC_{2}^{+}$, [12] which has been shown to have large positive π spin density on the *meso* carbons [5,12]. In this latter complex, the *p*-H and *o*-H shifts are negative, while the m-H shift is positive [12]. Hence, for the present complexes, there is large negative π spin density on the *meso* positions of (TPCorr)FeCl and (TPCorr)FeClO₄, indicating antiferromagnetic coupling of the corrolate unpaired electron to the three unpaired electrons of the metal. This is exactly the same electron configuration and coupling pattern as found previously for the octaalkyl-substituted corrolates (7,13-Me₂Et₆-Corr)FeCl and (Me₈Corr)FeCl [2]. Thus, we can conclude that these four tri-meso-phenyl-substituted corrolatoiron chloride complexes and the octaalkylcorrolatoiron chloride complexes studied previously [2] have the same electronic structure. They are all S = 3/2Fe(III) corrolate(^{2-•}) π -cation radical species, with the



Fig. 3. ¹H NMR spectra of (a) [T(4-MeOP)Corr]FeCl and (b) (TPCorr)FeClO₄] at 293 K in CD_2Cl_2 . The solvent peak is marked with S, and stars mark impurity peaks.

corrole unpaired electron antiferromagnetically coupled to the unpaired electrons on the metal center.

Based on their similar NMR spectra, (TPCorr)FeCl and (TPCorr)FeClO₄ are expected to have the same electronic structure, in both cases S = 3/2 intermediate spin Fe(III). This is quite different from the results for the corresponding porphyrins: TPPFeCl is a high-spin (S = 5/2) complex [5]. If the chloride is substituted by a perchlorate ion, the spin state of the porphyrin is lowered and changed to a spin admixed (S = 3/2, 5/2) complex [5,13,14]. The reason why the corrolates do not change electronic structure with change of anionic axial ligand from chloride to perchlorate is probably that in (TPCorr)FeCl the iron center is already intermediatespin (S = 3/2). Thus, substitution of perchlorate ion cannot lower the spin state any further.

Linear analysis of the temperature dependences of the proton resonances (supporting information Figures S4 and S5) shows non-Curie behavior (the intercepts of the isotropic shifts at 1/T = 0 are not zero) for all four complexes. This indicates that a thermally accessible excited state also contributes to the isotropic shifts. Using the two-level temperature-dependence fitting program [15], the spin distribution for both the ground state and excited state were calculated. The results, presented in Table 2, show that the ground state has



Fig. 4. ¹H NMR spectrum of $[T(F_5P)Corr]FeCl$ at 293 K in CD₂Cl₂. The solvent peak is marked with S, and impurities are marked with stars. The 'impurity' at 2 ppm is actually H₂O.

sizable spin densities on the pyrrole positions and phenyl rings, while the excited state has comparable spin densities on the pyrrole positions but much smaller spin densities on the phenyl rings (however, with some exceptions from [T(4-MeOP)Corr]FeCl, whose phenyl meta protons show larger spin densities for the excited state than for the ground state). The pattern of spin distribution for the ground state is consistent with that expected for an iron(III) center antiferromagnetically coupled to a π -cation radical. Based on the small spin density at the meso positions, the excited state probably has an Fe(IV)-TPCorr(³⁻) electron configuration. The excited state still has large spin density on the pyrrole positions. The energy separation, ΔE , between the ground and excited states, derived from the temperature-dependent fitting program [15], are all somewhat larger than kT at room temperature ($\sim 200 \text{ cm}^{-1}$), and, except for the pentafluorophenyl complex, is largest for the perchlorate complex, [(TPCorr)FeClO₄]. This seems reasonable based on the fact that perchlorate also stabilizes the S = 3/2 spin state of Fe(III) porphyrins [14]. The perfluorophenyl complex, [T(F₅P)Corr]FeCl, exhibits generally smaller spin densities for the excited state than for the ground state.

The Mössbauer isomer shift obtained for (TPCorr)FeCl is $\delta = +0.19$ mm s⁻¹ [11], and is indicative of a Fe(III) center [16]. The quadrupole splitting, $\Delta E_Q = +2.93$ mm s⁻¹ [11], is characteristic of either S = 3/2 Fe(III) or S = 1 Fe(IV), and hence this parameter is not useful for determining the oxidation state of the metal. More detailed magnetic Mössbauer

studies of a chloroiron and a phenyliron octaalkylcorrolate, presented elsewhere [16], also show that because the magnetic coupling between Fe(III) and the corrolate radical, where present, is very strong, the magnetic Mössbauer spectra of Fe(III)-Corr $(^{2-\bullet})$ π -cation radical and Fe(IV)-Corr $(^{3-\bullet})$ are almost identical, except for the isomer shift, and, therefore, only the latter is at all indicative of the oxidation state of the metal. Hence, the Mössbauer isomer shift of (TPCorr)FeCl is consistent with the conclusions reached from the ¹H NMR investigations discussed above, that this complex is a Fe(III)-Corr $(^{2-\bullet})$ π -cation radical.

In their recent papers, Gross et al. [6,7], have stated that $[T(F_5P)Corr]FeCl$ is an iron(IV) complex, but the only experimental evidence presented to support this statement were Fe-N(Corr) bond lengths [6] and the similarity in the one-electron oxidation potentials of the chlorotin(IV) and chloroiron complexes (1.20 and 1.24 V, respectively) [7], neither of which is definitive proof of the electron configuration of the complex. More recently, Gross has again stated that this, as well as the chloroiron, phenyliron and µ-oxo di-iron dimer complexes of all meso-triphenyl corrolates are iron(IV) complexes [7]. In contrast, Ghosh and coworkers have recently presented DFT calculations that favor the Fe(III)- $Corr^{2-}$ radical electron configuration for chloroiron corrolates [17], and our own DFT calculations are also consistent with this [16]. Since corrolate ligands in general are non-innocent [18], in the present work we address only the electronic structure of the chloroiron triphenylcorrolates. The ¹H NMR spectrum Table 2

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		Compound								
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		(TPCorr)FeCl	[T(4-NO ₂ P)-Corr]FeCl	[T(4-MeOP)-Corr]FeCl	[T(F5P)Corr]-FeCl	(TPCorr)-FeClO ₄				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Delta E \ (\mathrm{cm}^{-1})$	232	271	213	340	317				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C_I									
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<i>o</i> -H	-0.0140	-0.0120	-0.0150		-0.0130				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-0.0134	-0.0110	-0.0140		-0.0120				
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		-0.0124	-0.0100	-0.0140						
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				-0.0130						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	р-Н	-0.0110				-0.0110				
$ \begin{tabular}{ c c c c c c c } \hline m-H & 0.0067 & 0.0064 & 0.0058 & 0.0077 \\ 0.0071 & 0.0068 & 0.0066 & 0.0085 \\ 0.0077 & 0.0070 & 0.0075 & & & & & & & & & & & & & & & & & & &$		-0.0087				-0.0091				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<i>m</i> -H	0.0067	0.0064	0.0058		0.0077				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.0071	0.0068	0.0066		0.0085				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.0074	0.0068	0.0068						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.0077	0.0070	0.0075						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Pyrrole-H	0.0090	0.0083	0.0086	0.0050	0.0100				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.0090	0.0100	0.0094	0.0063	0.0110				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.0310	0.0300	0.0330	0.0125	0.0360				
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					0.0275					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C									
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0-H	-0.0006	0.0005	-0.0003		0.0021				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 11	0.0001	0.0010	-0.0001		0.0034				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-0.0001	0.0004	0.0021		0.0001				
p-H 0.0019 0.0038 0.0043 0.0043 0.0043 0.0043 0.0052 0.0036 0.0034 0.0075 a 0.0057 0.0051 0.0046 0.0089 a 0.0051 0.0046 0.0089 a 0.0043 0.0042 0.0080 a 0.0043 0.0042 0.0080 a 0.0057 0.0051 0.0046 0.0089 a 0.0043 0.0042 0.0080 a 0.0057 0.005		0.0001	0.0004	0.0012						
m-H 0.001/ 0.0022 0.0030/ 0.0043 0.0043 m-H 0.0048 0.0041 0.0093 a 0.0052 0.0051 0.0046 0.0089 a 0.0057 0.0043 0.0042 0.0080 a Pyrrole-H 0.0060 0.0099 0.0047 -0.0050 a 0.0170	<i>n</i> -H	0.0019		0.0012		0.0038				
m-H 0.0048 0.0041 0.0093 a 0.0052 0.0036 0.0034 0.0075 a 0.0057 0.0051 0.0046 0.0089 a 0.0043 0.0042 0.0080 a Pyrrole-H 0.0060 0.0099 0.0047 -0.0050 a 0.0170	<i>p</i> 11	0.0022				0.0043				
M M 0.0016 0.0011 0.0015 0.0012 0.0036 0.0034 0.0075 a 0.0057 0.0051 0.0046 0.0089 a 0.0057 0.0043 0.0042 0.0080 a 0.0075 a Pyrrole-H 0.0060 0.0099 0.0047 -0.0050 a 0.0170	m-H	0.0048	0.0041	0.0093 ^a		0.0052				
0.0051 0.0046 0.0089 a 0.0043 0.0042 0.0080 a Pyrrole-H 0.0060 0.0099 0.0047 -0.0050 a 0.0170		0.0036	0.0034	0.0075 ^a		0.0052				
0.0013 0.0042 0.0080 ^a Pyrrole-H 0.0060 0.0099 0.0047 -0.0050 ^a 0.0170 0.0100 0.0068 0.0097 0.0000 0.0170		0.0051	0.0046	0.0089 ^a		0.0007				
Pyrrole-H 0.0060 0.0099 0.0047 -0.0050 a 0.0170		0.0043	0.0042	0.0080^{a}						
	Pyrrole-H	0.0060	0.0099	0.0047	-0.0050^{a}	0.0170				
	1 ,11010 11	0.0100	0.0068	0.0097	0.0099	0.0170				
00230 00200 00210 00096 00410		0.0230	0.0200	0.0210	0.0096	0.0410				
0.0177		0.0200			0.0177	0.0.10				

Spin c	lensities	calculated	l from th	e two-level	data f	fitting	program	for th	e ground	state	(C ₁) ar	d the	excited	state	(C_2) of	of (Tl	PCorr)Fe	C1, ['	Γ(4-
NO ₂ P)Corr]Fe	Cl, [T(4-M	feOP)Co	rr]FeCl, [T(F ₅ P)Co	orr]Fe0	Cl and (T	PCorr)FeClO ₄										

 ΔE is the energy gap between these two states.

^a Exceptions which are inconsistent with the spin distribution patterns on other positions of [T(4-MeOP)Corr]FeCl or for other complexes.

of [T(F₅P)Corr]FeCl reported previously [6] shows four pyrrole proton peaks with negative chemical shifts (about -2.5, -3, -12 and -33.5 ppm in benzene-d₆ at room temperature). We obtain somewhat similar chemical shifts for three of the pyrrole protons for this complex in CD₂Cl₂, but the fourth (most downfield) pyrrole-H resonance is at +3.1 rather than -2.5 ppm, as shown in Fig. 4, suggesting that there are important solvent effects for this complex. Overall, the chemical shifts of the pyrrole protons of this complex in CD_2Cl_2 are not significantly different than those of the other triphenylcorrolatoiron chloride complexes of this study (Table 1). However, whether this is an Fe(IV) complex or an Fe(III) π -cation radical cannot be determined based on the ¹H NMR spectroscopic data, since both of these electron configurations are expected to give large negative pyrrole proton isotropic shifts due to one unpaired electron being present in each of the d_{π} orbitals, d_{xz} and d_{yz} in both cases, and the spin density expected at the β -pyrrole positions in an $a_{2u}(\pi)$ -type orbital is expected to be quite small [5]. Thus, to determine the electron configuration one must check the spin density at the *meso* positions and the isotropic shifts of the *meso* substituents.

To probe the spin density at the *meso* positions of $[T(F_5P)Corr]FeCl$, the ¹⁹F NMR spectrum was recorded in CD₂Cl₂ solution at 294 K (with α, α, α -trifluorotoluene (in C₆D₆) as external reference, -63.73 ppm vs. CFCl₃), as shown in Fig. 5. Since the *ortho*-phenyl fluorines are closest to the metal center, they are expected to give broad peaks due to rapid dipolar relaxation rates; [5] thus the four broad peaks (at -155, -160.7, -166 and -169 ppm) in Fig. 4 are from the *ortho*-fluorines. In the ¹⁹F COSY spectrum of this complex (not shown), two pairs of cross peaks were observed, one between *para*-5,15-F and *meta*-5,15-F, the other one between *para*-10-F and *meta*-10-F; these assignments are thus included in Fig. 5 and Table 3. The *ortho*-F resonances relax too



Fig. 5. ¹⁹F NMR spectrum of $[T(F_5P)Corr]$ FeCl at 293 K in CD_2Cl_2 , externally referenced against α, α, α -trifluorotoluene in C_6D_6 . Assignments are based on peak intensities and COSY crosspeaks.

rapidly to give any cross peaks. Based on the COSY results and relative peak areas, full assignments were made, and then the ¹⁹F isotropic shifts were calculated (Table 3).

Unlike the proton isotropic shifts of the four nonfluorine-substituted chloroiron corrolates summarized in Table 1, the ¹⁹F isotropic shifts of $[T(F_5P)Corr]FeCl$ (Table 3) are all negative and smaller in magnitude (decreasing in the order o > p > m, as expected for a very small contact contribution superimposed upon a small (negative) dipolar contribution) than might be expected possible for this nucleus. This might suggest that the ¹⁹F shifts of this complex may not have large contact shifts arising from large π spin delocalization to the phenyl substituents, and hence may not have an $a_{2\mu}(\pi)$ unpaired electron on the corrole macrocycle. However, there have been very few investigations of the ¹⁹F NMR spectra of fluorine-substituted paramagnetic metal macrocycles, and hence the definition of 'small' and 'large' has not yet been made for ¹⁹F. One

chloroiron porphyrin complex, the S = 5/2 octabromotetra-(pentafluorophenyl)porphyrinatoiron chloride, reported by Birnbaum, Grinstaff and coworkers [19], shows ¹⁹F isotropic shifts similar in magnitude, but opposite in sign to those of $[T(F_5P)Corr]FeCl$ (Table 3). The opposite sign could suggest that there is negative spin density at the meso positions of this corrolate complex, as is the case for the other chloroiron corrolates already discussed. However, we feel that it is not at present possible to evaluate these ¹⁹F shifts without additional investigations of complexes for which the electron configuration is known unambiguously. This is because of the unknown importance of the additional term, the ligand-centered dipolar shift [20,21], which is present for all atoms having more electron shells than hydrogen. For carbon atoms this term has been estimated to be quite large for atoms directly involved in a π system [20], but smaller for atoms adjacent to a π system [22–24], as in the case of the fluorine atoms of the complex of interest. Thus, addi-

Table 3

¹⁹F isotropic shifts and assignments of $[T(F_5P)Corr]FeCl$ at 293 K, and comparison to those of $[Br_8T(F_5P)P]FeCl$ [19]

Chemical shift ^a (ppm)	Diamagnetic shift ^b (ppm)	Isotropic shift ^c (ppm)	Assignment ^d		
-154.7, -166.0	-138.3	-16.4, -27.7	<i>o</i> -5,15-F		
-160.7, -170.0	-137.7	-23.0, -32.3	<i>o</i> -10-F		
-167.0	-161.9	-5.1	<i>m</i> -5,15-F		
-169.4, -169.6	-162.4	-7.0, -7.2	<i>m</i> -10-F		
-166.4	-152.8	-13.6	<i>p</i> -5,15-F		
-164.6	-153.4	-11.2	<i>p</i> -10-F		
$[Br_8T(F_5P)P]FeCl$					
-104.4, -108	-138.6 ^e	+33.9, +30.6	<i>o</i> -F		
-152.5, -153.3	-163.1 ^e	+10.6, +9.8	<i>m</i> -F		
-141.9	-152.0 °	+10.1	<i>p</i> -F		

^{a 19}F chemical shifts of [T(F₅P)Corr]FeCl in CD₂Cl₂ (vs. CFCl₃).

 $^{b\ 19}F$ chemical shifts of [T(F_5P)Corr]H_3 in CD_2Cl_2.

^c The ¹⁹F isotropic shifts were calculated by subtracting the corresponding chemical shifts (externally referenced to α, α, α -trifluorotoluene) of diamagnetic [T(F₅P)Corr]H₃ from the chemical shifts of [T(F₅P)Corr]FeCl.

^d Full peak assignments for [T(F₅P)Corr]H₃ were made based on the COSY spectrum (not shown) and relative peak areas.

^e Diamagnetic shifts taken from [Br₈T(F₅P)PFe(II)(Py)₂] [19].

tional investigations will be required in order to interpret quantitatively the observed ¹⁹F isotropic shifts of the chloroiron perfluorinated triphenyl corrolate, and on the basis of the data obtained thus far, it is not possible to reach a conclusion on the electron configuration of $[T(F_5P)Corr]FeCl$. Such investigations are currently underway in our laboratories.

Thus, we can conclude that, except in the presence of highly electronegative fluorine substituents, and possibly in that case as well, chloroiron corrolates have the ground state electron configuration S = 3/2 Fe(III) corrolate(^{2-•}) π -cation radical, with the macrocycle unpaired electron antiferromagnetically coupled to the metal electrons. In the case of the meso-triphenylcorrolates, the $Fe(IV)Corr(^{3-})$ excited state is at an energy of kT at room temperature or more higher than the ground state. It is therefore not at all clear, as has been frequently stated [1,6-8,18,25,26] that corrolate ligands have more tendency to stabilize high oxidation states of metal ions than do porphyrinate ligands. It is also not clear that the electron configuration of any other metal corrolate complexes can be stated without corroborating detailed magnetic resonance investigations of each individual complex. Rather, corrolates must be considered as non-innocent macrocyclic ligands in each of their metal complexes, and the electron configuration cannot be stated until each one is individually characterized by as many physical techniques as possible, most notably including a careful ¹H and other appropriate nucleus NMR spectroscopic investigation, where the isotropic shifts are analyzed in terms of their contact, dipolar, and, in the case of heavier nuclei, the ligand-centered dipolar contributions, as well as theoretical calculations.

The electron configurations of additional axial ligand complexes of iron corrolates will be addressed by this research team in future publications using a variety of physical and calculational techniques.

4. Supplementary material

Figures S1–S6: COSY spectra of [T(4-NO₂P)Corr]FeCl, [T(4-MeOP)Corr]FeCl, (TPCorr)Fe-ClO₄, Curie plots for the five complexes. This material is available upon request from the authors (awalker@-u.arizona.edu).

Acknowledgements

The support of the US National Institutes of Health, Grant DK 31038 (F. A.W.), NATO, Grant CRG971495 (S.L.) and MURST (S.L.) is gratefully acknowledged. The authors also wish to thank Professor Alfred X. Trautwein and Dr. Volker Schünemann, of the Institut für Physik, Medizinische Universität zu Lübeck, Lübeck, Germany, for measuring the isomer shifts and quadrupole splittings of chloroiron *meso*-triphenylcorrolate and chloroiron *meso*-tri-(pentafluorophenyl)corrolate.

References

- [1] S. Licoccia, R. Paolesse, Struct. Bonding 84 (1995) 71.
- [2] S. Cai, F.A. Walker, S. Licoccia, Inorg. Chem. 39 (2000) 3466.
- [3] S. Cai, S. Licoccia, F.A. Walker, Inorg. Chem. 40 (2001) 5795.
- [4] N.S. Hush, J.M. Dyke, M.L. Williams, I.S. Woolsey, J. Chem. Soc., Dalton Trans. (1974) 395.
- [5] F.A. Walker, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 5 (chapter 36), Academic Press, New York, 2000, pp. 81–183.
- [6] L. Simkhovich, N. Galili, I. Saltsman, I. Goldberg, Z. Gross, Inorg. Chem. 39 (2000) 2704.
- [7] L. Simkhovich, A. Mahammed, I. Goldberg, Z. Gross, Chem. Eur. J. 7 (2001) 1041.
- [8] Z. Gross, J. Biol. Inorg. Chem. 6 (2001) 733.
- [9] R. Paolesse, S. Nardis, F. Sagone, R.G. Khoury, J. Org. Chem. 66 (2001) 550.
- [10] F.A. Walker, B.H. Huynh, W.R. Scheidt, S.R. Osvath, J. Am. Chem. Soc. 108 (1986) 5288.
- [11] B. Zimmer, V. Bulach, M.W. Hosseini, S. Nardis, R. Paolesse, V. Schünemann, A.X. Trautwein, R. Weiss, ICPP-1 Proceedings, Dijon (2000), 628.
- [12] G. Simonneaux, F. Hindre, M. Le Plouzennec, Inorg. Chem. 28 (1989) 823.
- [13] H.M. Goff, in: A.B.P. Lever, H.B. Gray (Eds.), Iron Porphyrins Part 1, Addison-Wesley, Reading, MA, 1983, pp. 239–281.
- [14] M.J.M. Nesset, S. Cai, T.K. Shokhireva, N.V. Shokhirev, S.E. Jacobson, Kh. Jayaraj, A. Gold, F.A. Walker, Inorg. Chem. 39 (2000) 532.
- [15] N.V. Shokhirev, F.A. Walker, J. Phys. Chem. 99 (1995) 99 17795. Available at: http://www.chem.arizona.edu/faculty/walk/nikolai/ programs.html#tdfw.
- [16] O.Zakharieva, V.Schünemann, M. Gerdan, S. Licoccia, S. Cai, F.A. Walker, A.X. Trautwein, J. Am. Chem. Soc. 124 (2002), in press.
- [17] E. Steene, T. Wondimagegn, A. Ghosh, J. Phys. Chem. B 105 (2001) 11406.
- [18] A. Ghosh, E. Steene, J. Biol. Inorg. Chem. 6 (2001) 739.
- [19] (a) E.R. Birnbaum, J.A. Hodge, M.W. Grinstaff, W.P. Schaefer, L. Henling, J.A. Labinger, J.E. Bercaw, H.B. Gray, Inorg. Chem. 34 (1995) 3632;
 (b) M.W. Grinstaff, M.G. Hill, E.R. Birnbaum, W.P. Schaefer, J.A. Labinger, H.B. Gray, Inorg. Chem. 34 (1995) 4896.
- [20] H.M. Goff, J. Am. Chem. Soc. 103 (1981) 3714.
- [21] J. Mispelter, M. Momenteau, J.-M. Lhoste, in: L.J. Berliner, J. Reuben (Eds.), Biological Magnetic Resonance, vol. 12, Plenum, New York, 1993, pp. 299–355.
- [22] H. Santos, D.L. Turner, FEBS Lett. 194 (1986) 73.
- [23] L. Banci, I. Bertini, C. Luchinat, R. Pierattelli, N.V. Shokhirev, F.A. Walker, J. Am. Chem. Soc. 120 (1998) 8472.
- [24] D.L. Turner, Eur. J. Biochem. 227 (1995) 829.
- [25] R. Paolesse, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 2 (chapter 11), Academic Press, New York, 2000, p. 201.
- [26] C. Erben, S. Will, K.M. Kadish, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 2 (chapter 12), Academic Press, New York, 2000, p. 233.
- [27] J. Bendix, I.J. Dmochowski, H.B. Gray, A. Mahammed, L. Simkhovich, Z. Gross, Angew. Chem., Int. Ed. Engl. 39 (2000) 4048.