

Cyanide Complexes of Iron Corrolates: Spin Delocalization and Auto-reduction

Sheng Cai,[#] Silvia Licoccia,[‡] and F. Ann Walker^{*,#}

Department of Chemistry, University of Arizona, Tucson, Arizona 85721-0041, and Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00133 Rome, Italy

Received March 22, 2001

Complex formation of (7,13-dimethyl-2,3,8,12,17,18-hexaethylcorrolato)iron chloride, [(7,13-Me₂Et₆C)FeCl], with cyanide ion in dimethylformamide, DMF-*d*₇, was studied by ¹H NMR spectroscopy. It is found that a bis-cyanide complex is formed initially, in which the electron configuration is a low-spin Fe(III) corrolate(2-•). This complex is not stable, and it is readily reduced with an excess of cyanide in the solution. The reduction occurs at the corrole ring instead of on the iron center giving the monocyanide complex of the low-spin Fe(III) corrole, [(7,13-Me₂Et₆C)FeCN]⁻. Thus, this is a case where an axial ligand serves as a reducing agent of the macrocycle and not of the metal.

Introduction

Porphyrin-related tetrapyrrole macrocycles have recently become of interest to a number of researchers. Among these, the corroles are particularly interesting. Corroles are aromatic macrocycles with a direct link between two pyrrole rings (top, Figure 1) that, when fully deprotonated, are trianionic ligands. They have some unique properties such as the capability of maintaining a planar conformation, the possibility of stabilizing high oxidation states for coordinated metal ions,¹ and/or the possibility of stabilizing a one-electron oxidized macrocycle.²

Recently, we reported the NMR and EPR studies of two chloroiron corrolates, [(Me₈C)FeCl] and [(7,13-Me₂Et₆C)FeCl], and their bis-imidazole complexes.² The results showed clearly that these iron(IV) corrolates are actually iron(III) corrolate π cation radicals. In this article, we report an NMR study of the cyanide complexes of [(7,13-Me₂Et₆C)FeCl], including the one-electron reduction of the π cation radical by cyanide.

Experimental Section

Materials and Sample Preparation. (7,13-Dimethyl-2,3,8,12,17,18-hexaethylcorrolato)iron chloride was prepared as described previously.³ Meso-deuterated [(7,13-Me₂Et₆C)FeCl] was prepared by dissolving the complex in a 1:1 mixture of dichloromethane and trifluoroacetic acid-*d* (Aldrich) and by allowing the solution to stand at room temperature for 15 h. The solvent mixture was then evaporated under vacuum, and the residue was purified by column chromatography on neutral alumina with dichloromethane as the eluant. Cyanide ligand complexes were prepared in 5 mm NMR tubes immediately prior to the recording of the NMR spectra by direct addition of 3 equiv of NaCN in D₂O to saturated (~0.2 mM) DMF-*d*₇ solutions of [(7,13-Me₂Et₆C)FeCl]. All samples were prepared without degassing.

NMR Spectroscopy. ¹H NMR spectra were recorded on a Varian Unity-300 spectrometer operating at 299.955 MHz and equipped with a Varian variable temperature unit. The spectra were taken in DMF-*d*₇ (Cambridge Isotope Laboratories) over temperature ranges from -50

°C to +60 °C and were referenced to the resonance of the residual solvent formyl -CH. The temperature was calibrated using the Wilmad standard methanol sample. ²H spectra were recorded on a Bruker Avance 500 spectrometer operating at 76.755 MHz. The sample was dissolved in anhydrous DMF (Aldrich) with about 1% DMF-*d*₇ added as reference, and then sodium cyanide in H₂O was added.

EPR Experiments. EPR samples were directly taken from the NMR tubes after NMR measurements were completed. The samples were transferred to EPR tubes and were frozen in liquid nitrogen. The EPR spectra were obtained on a Bruker ESP-300E continuous wave spectrometer operating at X-band using 0.2 mW of microwave power and a 100 kHz modulation amplitude of 2 G. A Systron-Donner microwave counter was used for measuring the frequency. The EPR measurements were performed at 4.2 K using an Oxford continuous flow cryostat, ESR 900.

Magnetic Susceptibility Measurements. The magnetic susceptibility was measured by the modified Evans method^{4,5} as described previously.² Approximately 0.4 mL of a stock solution of [(7,13-Me₂Et₆C)FeCl] (1.00 × 10⁻⁴ mol/L, in CH₂Cl₂) was transferred to the Wilmad co-axial inner tube. The solvent was allowed to evaporate, and then 0.2 mL of DMF-*d*₇ stock solution (made by adding a molar excess (at least 3 equiv, based upon the amount of iron corrolate) of a D₂O solution of NaCN and 0.1% DMF-*h*₇ as the reference to pure DMF-*d*₇) was added to the inner co-axial tube giving a final concentration of 0.2 mM for the iron corrolate species. The Wilmad co-axial outer tube contained about 0.2 mL of the same DMF-*d*₇ stock solution. The difference in reference resonance between the inner and outer tubes was monitored on the Varian Unity-300 at room temperature, and it was used to calculate the molar magnetic susceptibility^{2,4,5} of complex **II** as a function of mole fraction.

Results and Discussion

Figure 1a is the ¹H spectrum acquired immediately after the addition of an excess of NaCN. The spectrum shows that the sample is an unstable mixture of two species, complexes **I** (reddish-orange) and **II** (yellow-orange, see spectra, Figure S1), whose ratio changes slowly with time (the concentration of complex **I** increases and that of complex **II** decreases). After several hours, complex **I** dominates the mixture, and its NMR spectrum can be obtained in the absence of complex **II** (Figure

[#] University of Arizona.[‡] Università di Roma Tor Vergata.(1) Licoccia, S.; Paolesse, R. *Struct. Bonding* **1995**, *84*, 71.(2) Cai, S.; Walker, F. A.; Licoccia, S. *Inorg. Chem.* **2000**, *39*, 3466.(3) Licoccia, S.; Paolesse, R.; Tassoni, E.; Boschi, T. *J. Chem. Soc., Dalton Trans.* **1995**, 3617.(4) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.(5) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169.

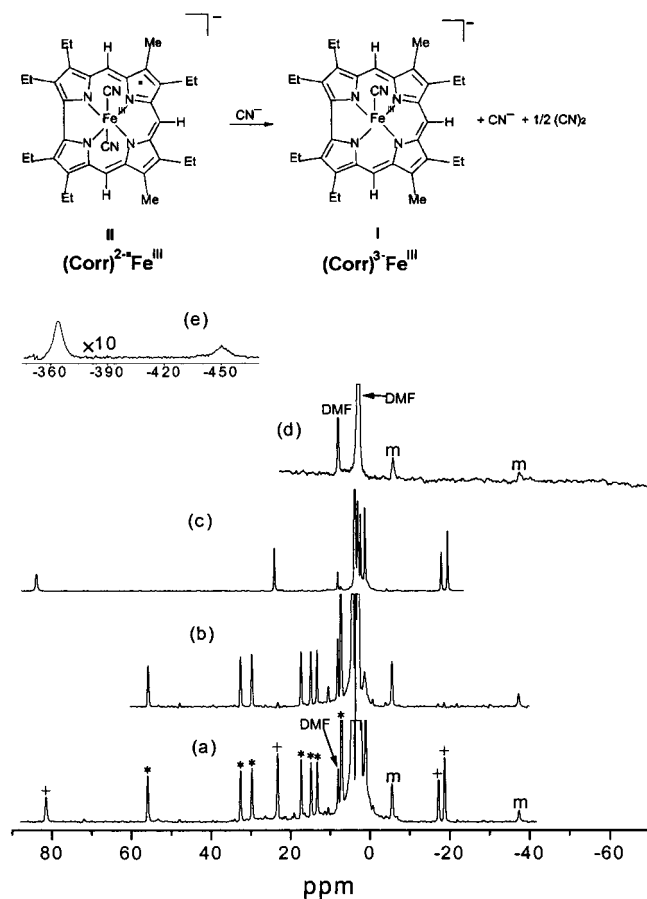


Figure 1. ¹H NMR spectra of cyanide complexes of [(7,13-Me₂Et₆C)-FeCl] (a) immediately after the addition of NaCN, (b) several hours later, and (c) after the addition of a small amount of ZnCl₂. The solvent is DMF-*d*₇. Mark "*" stands for pyrrole CH₂ (or CH₃) protons and "m" for meso protons, respectively, from complex I, while "+" stands for pyrrole CH₂ (or CH₃) protons from complex II. Please note that the meso-H resonances of [(7,13-Me₂Et₆C)Fe(CN)₂]⁻ are not included in (a) and (b). [(7,13-Me₂Et₆C-5,10,15-*d*₃)FeCl] with 3 equiv of cyanide added showed the same spectra with the same relative peak intensities, except that the two meso resonances observed in (a) and (b) were missing. (d) ²H spectrum of [(7,13-Me₂Et₆C-5,10,15-*d*₃)Fe(CN)₂]⁻. The solvent is DMF; 0.1 μL of DMF-*d*₇ was added as a reference. (e) Highly shielded ¹H spectrum of the meso-H resonances of [(7,13-Me₂Et₆C)-Fe(CN)₂]⁻, complex II. Spectra (a), (b), and (d) were collected at 30 °C, while spectra (c) and (e) were obtained at 21 °C.

1b). The rate of change from complex II to I depends on the concentration of NaCN in the solution, but the reaction rate has not been quantified beyond the general finding that more NaCN favors a faster change. If an oxidizing agent such as H₂O₂ or (NH₄)₂Ce(NO₃)₆ is added to the mixture, the NMR spectrum recorded immediately thereafter shows almost pure complex II present in the solution (see Figure 1c). Complex II changes back to complex I upon addition of the reducing agent hydrazine, but an aqueous solution of dithionite does not reduce complex II back to complex I. Taken together, these results suggest that both I and II are cyanide complexes of [(7,13-Me₂Et₆C)FeCl]. Complex I is more stable than II in the presence of excess cyanide. The conversion of complex II to I is a reduction reaction, and cyanide is the reducing agent. The proton NMR resonances of both complexes I and II show approximate Curie behavior (Figure 2).

The ¹H spectrum of complex II shows three pyrrole CH₂ and one pyrrole CH₃ groups. The fact that the methylene protons are not diastereotopic indicates that II is the bis-cyanide complex, [(7,13-Me₂Et₆C)Fe(CN)₂]⁻. The spectrum has a pattern

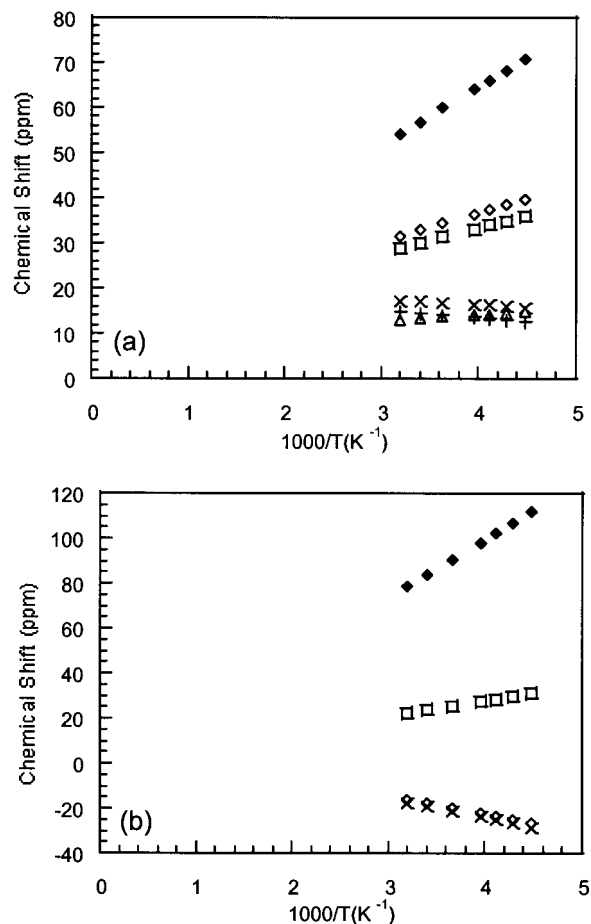


Figure 2. Curie plot of (a) the six CH₂ resonances of complex I and (b) the three CH₂ and one CH₃ (x) resonances of complex II.

of ¹H resonances similar to that of [(7,13-Me₂Et₆C)Fe(ImH)₂]⁺Cl⁻, which has been shown to be an iron(III) π cation radical.² The chemical shifts are summarized in Table 1, where they are compared to those of the bis-imidazole complex.² Thus, it is also reasonable to assign [(7,13-Me₂Et₆C)Fe(CN)₂]⁻ to an iron(III) π cation radical, for example, [(7,13-Me₂Et₆C^{2•-})Fe^{III}(CN)₂]⁻, where the charge and dot within the parentheses represent those of the corrolate anion, while the charge outside of the square brackets indicates the overall charge on the complex ion. The meso protons have very large isotropic shifts of -364 (2H) and -450 (1H) ppm at 303 K (Figure 1e). These meso-H chemical shifts are over a factor of 2 more negative at a comparable temperature than observed for the corresponding bis-imidazole complex (-161.3 (2H) and -188.5 (1H) ppm at 203 K).² The fact that the meso protons have very negative chemical shifts argues strongly against the formulation of this complex as containing S = 1 Fe(IV) bound to a corrolate trianion, since the two unpaired electrons would most likely be in the d_{xz} and d_{yz} orbitals of the iron, which would allow spin delocalization to the two π-symmetry orbitals of the corrole ring that are the analogues of the 3e(π) orbitals of the porphyrin.⁶⁻⁹ By analogy, meso-substituent resonances of Fe-

(6) Hush, N. S.; Dyke, J. M.; Williams, M. L.; Woolsey, I. S. *J. Chem. Soc., Dalton Trans.* **1974**, 395.

(7) Walker, F. A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, CA, 2000; Chapter 36, Vol. 5, pp 81-183.

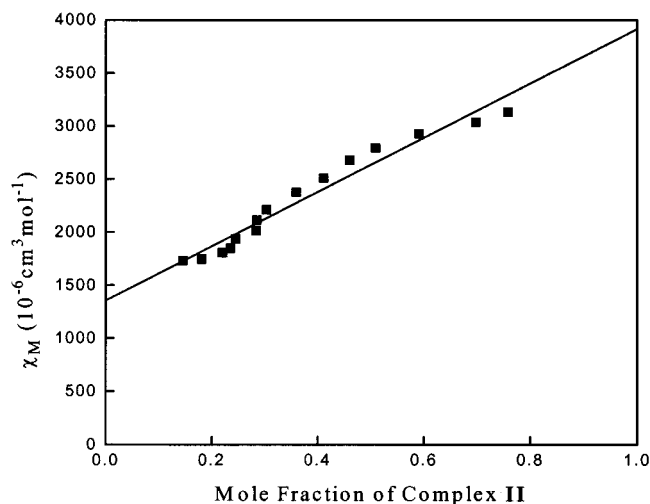
(8) Groves, J. T.; Quinn, R.; McMurry, T. J.; Nakamura, M.; Lang, G.; Boso, B. *J. Am. Chem. Soc.* **1985**, *107*, 354.

(9) Balch, A. L.; Renner, M. W. *J. Am. Chem. Soc.* **1986**, *108*, 2603.

Table 1. ^1H Chemical Shifts (ppm) and Assignments of the Protons of Complexes **I** and **II**, with Comparisons to the Simple Fe(III) Complexes of $[(\text{R}_8\text{C})\text{Fe}(\text{Py})]^{2,11}$ and the Low-Spin Fe(III) Cation Radical Complex $[(7,13\text{-Me}_2\text{Et}_6\text{C})\text{Fe}(\text{ImH})_2]^+\text{Cl}^-$

complex I ($T = 303\text{ K}$)	$[(\text{R}_8\text{C})\text{Fe}(\text{Py})]^{2,11}$ ($T = 298\text{ K}$)	assignment	complex II ($T = 303\text{ K}$)	$[(7,13\text{-Me}_2\text{Et}_6\text{C})\text{Fe}(\text{ImH})_2]^+\text{Cl}^-$ ($T = 203\text{ K}$)	assignment
-37.4	-62.2	meso-10	-450	-188.5	meso-10
-5.6	-16.0	meso-5,15	-364	-161.3	meso-5,15
7.2	14.1	pyrrole-7,13- CH_3	-18.7	-9.7	pyrrole-7,13- CH_3
55.9, 29.6 (42.8) ^a	66.5 ² or 67.7 ¹¹	pyrrole- CH_2	81.5, 23.3, -17.2	37.1, 11.9, -11.1	pyrrole- CH_2
32.6, 13.2 (22.9) ^a	38.2 ² or 37.9 ¹¹	pyrrole- CH_2			
17.2, 14.8 (16.0) ^a	27.2 ² or 28.5 ¹¹	pyrrole- CH_2			

^a In parentheses, the average chemical shift for the two inequivalent protons of each pyrrole- CH_2 group.

**Figure 3.** Plot of the magnetic susceptibility of the mixture of complexes **I** and **II** versus the mole fraction of **II**. The intercepts on the left and right edges are the magnetic susceptibilities of pure complexes **I** and **II**, respectively.

(IV) tetra-arylporphyrins show very small shifts^{8,10} which is indicative of spin delocalization to the $3e(\pi)$ orbitals of the porphyrin which has very small spin density at the meso positions.^{6,7}

It is clear from Figure 1b that complex **I** contains only one cyanide ligand, since the pyrrole CH_2 protons are diastereotopic (six resonances from the three CH_2 groups). The ^1H spectrum of **I** is similar to those of the one-electron reduced iron corrolate complexes bound to one pyridine ligand^{2,11} with large-to-medium positive shifts of the pyrrole substituents and negative shifts of the meso-H as summarized in Table 1. However, the average shifts of the methylene protons (in parentheses in Table 1) and the shifts of the methyl and meso protons of complex **I** are smaller in magnitude than those of the $[(\text{R}_8\text{C})\text{Fe}(\text{Py})]$ complexes,^{2,11} and the spin state is apparently different, since the mono-pyridine complexes were reported to have $S = 3/2$,¹¹ while, as discussed and shown in Figure 3 below, complex **I** has $S = 1/2$. It appears that the redox reaction (from complex **II** to **I** or vice versa) occurs on the corrole ring thus keeping the oxidation and spin state of the iron center unchanged. Redox reactions on the macrocycle instead of on the metal center have been observed for porphyrins as well.¹²⁻¹⁵

Full resonance assignments cannot be made for either complex **I** or **II** due to their poor stability and short relaxation times. However, partial assignments can be made for complex **I** based on its high quality COSY spectrum (supplementary Figure S2), for which the pairs of proton chemical shifts belonging to individual methylene groups are included in Table 1. The assignments of meso proton resonances of complex **I** are made from the ^2H spectrum (Figure 1d) of meso-deuterated $[(7,13\text{-Me}_2\text{Et}_6\text{C})\text{FeCl}]$ in the presence of 3 equiv of cyanide, while those of complex **II** were readily assigned by their large chemical shifts and intensities. The possible structures of complex **I** could be $[(7,13\text{-Me}_2\text{Et}_6\text{C}^{3-})\text{Fe}^{\text{III}}(\text{CN})]^-$ or $[(7,13\text{-Me}_2\text{Et}_6\text{C}^{3-})\text{Fe}^{\text{III}}(\text{CN})\text{Cl}]^{2-}$, where the charges in parentheses represent those on the corrolate anion, while the charges outside the square brackets represent the total charges on the complex ions. The former formulation seems to be more reasonable, since it has a lower negative charge. The stability of this monocyanide complex in $\text{DMF-}d_7$ is consistent with the loss of one axial anionic ligand upon the reduction of complex **II** to **I**, such that the overall negative charge on the complex does not exceed -1.

Magnetic susceptibilities have been measured for complexes **I** and **II**. Since it is difficult to obtain either of these in pure form, especially complex **II**, the measurement was made on the mixture. The magnetic susceptibility, which decreased slowly with time, was monitored by the NMR method.^{4,5} Immediately after the measurement, a normal 1-D NMR spectrum of the mixture was acquired, and the percentage of complexes **I** and **II** was calculated from the relative peak areas. Figure 3 shows the approximately linear fit of the experimental magnetic susceptibility of the mixture versus the mole fraction of complex **II**. The magnetic moments of pure complexes **II** and **I**, calculated from the intercepts, are $3.02 \mu_{\text{B}}$ ($S = 1$) and $1.79 \mu_{\text{B}}$ ($S = 1/2$), respectively. These results are consistent with the formulation of complex **I** as a normal low-spin Fe(III) complex and of complex **II** as a low-spin Fe(III) π cation radical with ferromagnetic coupling between the iron center and the corrole ring. The unpaired electron in the $7b_1$ orbital^{6,7} of the corrole ring is expected to lead to a very large positive π spin density at the meso positions. Hence, the meso proton resonances of complex **II** are shifted far upfield to -364 and -450 ppm at ambient temperature. In comparison, the meso-H resonances of the bis-imidazole complexes of $(\text{Me}_8\text{C})\text{Fe}^{\text{III}}$ were found at -95.1 (1H) and -82.8 (2H) ppm, while those of $(7,13\text{-Me}_2\text{-Et}_6\text{C})\text{Fe}^{\text{III}}$ were found at -188.5 (1H) and -161.3 (2H) ppm.² The difference in the meso-H shifts for these two complexes was ascribed to a difference in the strength of coupling between the $S = 1/2$ electrons on the metal and the macrocycle² which may indeed be the case. If so, then the bis-cyanide complex of $(7,13\text{-Me}_2\text{Et}_6\text{C})\text{Fe}^{\text{III}}$ has much stronger ferromagnetic coupling

(10) Wolowiec, S.; Latos-Grazynski, L. *Inorg. Chem.* **1998**, *37*, 2984.

(11) Vogel, E.; Will, S.; Tilling, A. S.; Neumann, L.; Lex, J.; Bill, E.; Trautwein, A. X.; Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 731.

(12) Buisson, G.; Deronizer, A.; Duee, E.; Gans, P.; Marchon, J.-C.; Regnard, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6793.

(13) Goff, H. M.; Phillippi, M. A. *J. Am. Chem. Soc.* **1983**, *105*, 7567.

(14) Balch, A. L.; Latos-Grazynski, L.; Noll, B. C.; Sztrenberg, L.; Zovinka, E. P. *J. Am. Chem. Soc.* **1993**, *115*, 11846.

(15) Scheidt, W. R.; Song, H.; Haller, K. J.; Safo, M. K.; Orosz, R. D.; Reed, C. A.; Debrunner, P. G.; Schulz, C. E. *Inorg. Chem.* **1992**, *31*, 941.

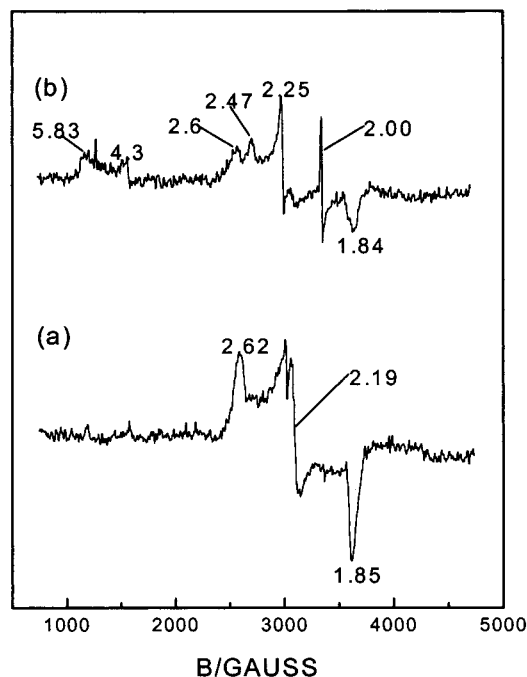


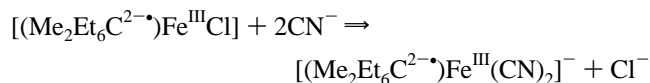
Figure 4. EPR spectra of (a) complex **I** and (b) complex **II**, each in CD_2Cl_2 at 4.2 K. The crystal field parameters⁷ for complex **I** (rhombic splitting, $V/\lambda = 3.23$, tetragonal splitting, $\Delta/\lambda = 6.47$) are similar to those for the bis-imidazole complex,² and while those of the second species in the spectrum of complex **II** (rhombic splitting, $V/\lambda = 3.96$, tetragonal splitting, $\Delta/\lambda = 4.43$) are somewhat different, both are within the range of the parameters observed for low-spin Fe(III) complexes with $(d_{xy})^2(d_{xz}, d_{yz})^3$ electron configurations.⁷

than the bis-imidazole complexes of either iron(III) corrolate. However, the difference in meso-H shifts could also be due to a difference in the amount of aggregation between the molecules, such that the spins on the macrocycles are able to pair, as was postulated to occur to explain the low-temperature EPR spectra of the bis-imidazole complexes, which were those of normal low-spin Fe(III) complexes with no sign of a radical signal.² If aggregation/dimerization does occur to some extent in solution, then it would have to be concluded that the bis-cyanide complex **II** is probably not as aggregated in solution as are either of the bis-imidazole complexes, and, therefore, exhibits even larger chemical shifts for the meso-H than those observed for either of the bis-imidazole complexes.² The EPR spectrum at 4.2 K (Figure 4) also shows that complex **I** is a low-spin Fe(III) species, while the EPR sample of complex **II** is not pure but contains two low-spin Fe(III) species (one the same as complex **I**), some free radical signal, and minor amounts of high- or intermediate-spin Fe(III) ($g = 5.83$). A small resonance from a non-heme iron impurity ($g = 4.2$) is also observed.

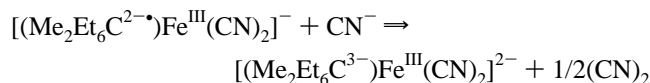
Complex **I** could also be converted to complex **II** when oxidizing agents such as H_2O_2 were added, or even when some salts containing di- or tripositive metal cations such as FeCl_2 , FeCl_3 , or ZnCl_2 were added in the absence of known oxidizing agents. In the latter case, the only possible oxidizing agent is dicyanogen, $(\text{CN})_2$, which is the product of the reduction of

complex **II** to complex **I**. With the presence of Fe^{2+} , Fe^{3+} , or Zn^{2+} , all of which have high affinity for CN^- , $(\text{CN})_2$ apparently becomes a strong enough oxidizing agent to be capable of oxidizing complex **I** back to **II**. The possible redox reactions (where the charge on the corrolate macrocycle is included within the parentheses, but the resulting overall charge on the complex ion is given outside of the brackets) are

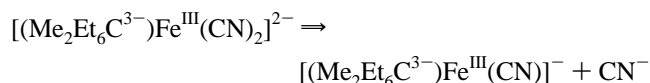
- (1) Two cyanides bind to the iron center upon the addition of cyanide:



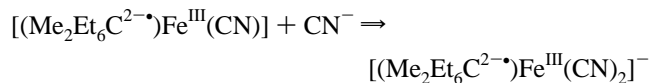
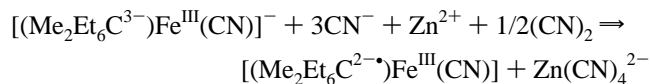
- (2) The Fe(III) π cation radical complex is reduced to a simple Fe(III) complex by cyanide:



- (3) The simple Fe(III) complex cannot support two negative charges and loses one cyanide:



- (4) The simple Fe(III) complex is oxidized back to the Fe(III) π cation radical in the presence of $(\text{CN})_2$ with Zn^{2+} or some other divalent or trivalent metal cation present:



While the finding that the cyanide ion can act as a one-electron reductant of iron tetrapyrroles is not new,^{16,17} this is the first case to our knowledge in which cyanide acts to reduce the tetrapyrrole macrocycle and not the metal. These findings stress the uniqueness of the corrole macrocycle in its ability to undergo facile redox reactions.

Acknowledgment. The support of the U.S. National Institutes of Health, Grant DK 31038 (F.A.W.), NATO, Grant CRG971495 (S.L.), and MURST (S.L.) is gratefully acknowledged. Thanks are due to Dr. Arnold M. Raitisimring for the EPR measurements.

Supporting Information Available: Figure S1, UV-visible spectra of $[(7,13\text{-Me}_2\text{Et}_6\text{C})\text{FeCl}]\text{Cl}$ and its two cyanide complexes; Figure S2, COSY spectrum of complex **I** at 303 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC010312I

(16) La Mar, G. N.; del Gaudio, J. *Adv. Chem. Ser.* **1977**, 162, 207.

(17) Dixon, D. W.; Barbush, M.; Shirazi, A. *Inorg. Chem.* **1985**, 24, 1081.