

Iron complexes of tris(4-nitrophenyl)corrole, with emphasis on the (nitrosyl)iron complex

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Dedicated to Professor Emanuel Vogel in memoriam

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ABSTRACT: The iron complexes of 5,10,15-tris(4-nitrophenyl)corrole have been prepared and characterized by various spectroscopic techniques. The (nitrosyl)iron complex is diamagnetic and its X-ray structure reveals an almost perfectly linear Fe–N–O bond. EPR spectroscopy in conjunction with ¹⁵N labelling were used to deduce the redox centre of the one-electron reduction and oxidation products of the (nitrosyl)iron corrole.

KEYWORDS: corroles, synthesis, iron, ¹⁵N-, ⁵⁷Fe-labeled corroles, NMR, electrochemistry, EPR.

INTRODUCTION

Emanuel Vogel's tremendous achievements during his long and very fruitful carrier include also very critical contributions to the chemistry of corroles [1, 2]. Some of these were outlined in Jonathan Sessler's book "Expanded, Contracted & Isomeric Porphyrins," which includes a sub-chapter entitled "Recent work from Vogel: A New Interpretation" [3]. The discussion therein was mainly focused on Emanuel's proper assignment of nickel and copper corroles [4], although it also briefly mentioned phenyliron(IV) corrole and its one-electron oxidation product [5]. On top of these examples, Emanuel's research group also prepared and fully characterized the (pyridine)iron(III), (chloro)iron(IV) and (nitrosyl)iron complexes of octaalkylcorroles [6]. At the turn of the last century, the focus changed to the much more wide-ranging triarylcorroles that became accessible only as late as 1999 [7, 8]. Of the numerous metallocorroles that were introduced since [9], the iron complexes of triarylcorroles (ITC) stand out as the most extensively investigated [10]. It started with the demonstration that ITC are very useful catalyst for oxo-, carbene-, and nitrene-transfer reactions [11, 12]. The comparison with analogous iron porphyrins revealed that ITC are superior for the two latter purposes, but less so for oxygenation catalysis. The most unique group-transfer reaction catalyzed by ITC is the N-tosylation of olefins by Chloramine-T, a feature not shared by any other iron complex [13]. Only the (chloro)iron(IV) corrole, but not any iron(III) complex, was able to catalyze that reaction. This chemical reactivity novelty is related to another aspect- the proper assignment of oxidation states in ITC. Intensive debates regarding the (chloro)iron(IV) corrole vs. (chloro)iron(III) corrole radical formulation continued from Emanuel's time until most recently [14], but this issue has apparently been resolved by now [15]. The abovementioned low activity of metallocorroles as catalysts for oxygen atom transfer reactions relative to related porphyrin complexes was advantageously used for introducing corrole-based catalytic antioxidants [16–18]. Amphipolar and water soluble ITC have been shown to be excellent decomposition catalysts of reactive oxygen/nitrogen species and the medical relevance of

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these findings are under extensive investigation by using quite a large number of *in vitro* and *in vivo* models of various diseases [19]. Another unexpected reactivity of ITC, which is also shared with iron(III) porphyrins but no other metal complexes, is the ability to activate the NH and SH bonds of amines and thiols, respectively, with regard to their reactions with diazo compounds such as ethyldiazoacetate (EDA) [20, 21]. In sharp contrast with almost all other metal-catalyzed reactions of EDA, significant evidence points towards the non-involvement of metal-carbene intermediates in the ITC-catalyzed reactions [22].

The vast majority of the research activity on ITC was performed on the iron complexes of tris(pentafluorophenyl)corrole, **2-H**₃, and its β -pyrrolesubstituted derivatives. The underlying reasons for this choice are: (a) this corrole is particularly stable, since its electron withdrawing C_6F_5 substitutents remove electron-density from the very electron-rich macrocycle [23]; (b) its synthetic accessibility is very high [24]; and (c) its structural assignment is assisted by ¹⁹F NMR [25]. The first two of the above factors are also shared by tris(4-nitrophenyl)corrole, 1-H₃, which has been reported to be accessible in 21% chemical yield by the cyclocondensation between pyrrole and 4-nitrobenzaldehyde [26]. It is hence quite surprising that the coordination chemistry of 1-H₃ remains quite unexplored [27, 28], taking into account also the large difference in the price of the aldehydes required for the synthesis of 1-H₃ and 2-H₃, respectively. Based on the above, we have decided to explore the iron complexes of 1-H₃, with special emphasis on the properties of the nitrosyl complex regarding the NO stretching frequency and the redox processes, in comparison with (nitrosyl)iron complexes of other corroles and porphyrins.

EXPERIMENTAL

Materials

Ferrous chloride tetrahydrate (Fluka Chemika), pyridine (Merck), and deuterated solvents (Aldrich and Cambridge Isotopes products) were used as received. Solvents like dichloromethane and hexane were obtained from S. D. Fine Chemicals Ltd. Tetrabutyl ammonium perchlorate was obtained from Aldrich and was recrystallized twice from methanol. Sodium borohydride and tris-(4-bromophenyl)aminium hexachloroantimonate were obtained from Aldrich.

Physical measurements

The ¹H NMR spectra were recorded on a Bruker Avance 200 spectrometer operating at 200 MHz. Chemical shifts in the ¹H NMR spectra are reported in ppm relative to the residual hydrogens in the deuterated solvents. An HP 8452A diode array spectrophotometer was used to record the electronic spectra. Mass spectroscopy was performed on a Finnigan TSQ70 instrument with isobutane as carrier gas and IR spectra were recorded as thin films on KBr pellet on a FT-IR spectrometer Bruker Vector 22. Cyclic voltammetric measurements were recorded on a WaveNow USB potentiostat Galvanostat (Pine Research Instrumentation). using Pine AfterNath Data Organizer software. A three electrode system was used, consisting of a platinum wire working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. The CV measurements were performed in CH₂Cl₂ solutions, 0.1M in tetrabutylammonium perchlorate (TBAP, Fluka, recrystallized twice from methanol), and 1 mM substrate under N₂ atmosphere at ambient temperature. Scan rates of 10-1000 mV/s were applied. UV-visible spectroelectrochemical experiments were performed by using a commercial thin layer quartz glass spectroelectrochemical cell kit (Supplier: Bio-Logic SAS). The cell contains a thin layer quartz glass cell (light pass length: 0.5 mm), a platinum gauze working electrode (80 mesh), and a platinum wire counter electrode. An Ag/AgCl electrode was used as reference electrode. Potentials were applied with the WaveNow USB potentiostat/galvanostat. Time-resolved UV-visible spectra were recorded with a Hewlett-Packard Model 8453 diode array spectrophotometer. The EPR spectra were recorded on a Bruker EMX-10/12 X-band ($\nu = 9.3$ GHz) digital EPR spectrometer equipped with a Bruker N₂-temperature controller. EPR spectra processing and simulation were performed with the Bruker WIN-EPR and SimFonia software, respectively.

Synthesis

5,10,15-tris(4-nitrophenyl)corrole $1-H_3$ was prepared by the reaction between pyrrole and *p*-nitrobenzaldehyde in acetic acid as reported earlier [26]. $2-H_3$ and its complexes were synthesized as described in previous publications [24, 10a].

Synthesis of 1-Fe(py)₂. 1-H₃ (66 mg, 0.1 mmol) was dissolved in pyridine (40 mL) under N_2 and ferrous chloride tetrahydrate (0.25 g, 2 mmol) was added into it. The reaction mixture was refluxed for 20 minutes. After completing the iron insertion, the reaction mixture was cooled to 25 °C and the solvent was evaporated. The resulting solid material was dissolved in dichloromethane containing a few drops of pyridine and chromatographed over acidic alumina with CH₂Cl₂/hexane/pyridine (3:2:0.06) as an eluent. Compound **1-Fe(py)**₂ was obtained as a brown solid (yield 46 mg, 53%). UV-vis (benzene:pyridine 49:1): λ_{max} , nm (log ε) 428 (4.9), 583(2.2). ¹H NMR (200 MHz; pyridine- d_5): δ_H , ppm -1.7 (2H, s, pyrrole-*H*), -39.9 (2H, s, pyrrole-*H*), -54.2 (2H, s, pyrrole-*H*), -122.1 (2H, s, pyrrole-*H*), MS (ESI⁻, CH₃CN): m/z 750.9 (100%) $[M-2Py + 2H_2O]^-$, 792.8 (88%) $[M-2Py + 2H_2O]^-$ Py], 826.9 (28%) [M-2Py + 2CH₃CN].

Synthesis of 1-FeCl. 1-Fe(py)₂ (40 mg) was dissolved in CH₂Cl₂, the solution was washed twice with HCl (7%) and finally with water. During the acidic washing, the color of the mixture changed from red-brown to pale green. The solution was dried over Na₂SO₄ and the solvent was evaporated. Compound **1-FeCl** was obtained by recrystallization from CH₂Cl₂ and hexane as a green solid (yield 32 mg, 93%). UV-vis (CH₂Cl₂): λ_{max} , nm (log ε) 409 (6.3), 396 (4.6). ¹H NMR (200 MHz; CDCl₃): δ_{H} , ppm 5.1 (2H, s, pyrrole-*H*), -5.7 (2H, s, pyrrole-*H*), -7.3 (2H, s, pyrrole-*H*), 22.4 (2H, s, ortho-H of meso-Ph), 21.5 (2H, s, ortho-H of meso-Ph), -1.2 (2H, s, meta-H of meso-Ph), -1.3 (2H, s, meta-H of meso Ph), -2.1 (2H, s, meta-H of meso Ph). MS (ESI⁻, CH₂Cl₂): m/z 748.9 [M–H]⁻.

Synthesis of 1-Fe(NO) and 1-Fe(¹⁵NO). 1-FeCl (20 mg, 26.7 µmol) was dissolved in CH₂Cl₂ (20 mL) and a saturated solution of NaNO₂ (2 mL) was added into it. After 3 h of stirring at rt, the color of the solution became reddish orange. The organic solvent was washed with water, dried over Na₂SO₄ and evaporated. The compound was purified by column chromatography over silica gel using hexane/CH2Cl2 (2:3) as eluent. Compound 1-Fe(NO) was obtained as a red solid (yield 8.5 mg, 43%). UV-vis (CH₂Cl₂): λ_{max} , nm (log ε) 383 (11.22), 540 (1.81). ¹H NMR (300 MHz; CDCl₃): $\delta_{\rm H}$, ppm 7.37 (2H, d, ${}^{3}J(H,H) = 4.7$ Hz, pyrrole-*H*), 7.54 (2H, d, ${}^{3}J(H,H) = 4.7$ Hz, pyrrole-*H*), 7.76 (2H, d, ${}^{3}J(H,H) = 4.7$ Hz, pyrrole-*H*), 7.85 (1H, dd, ${}^{3}J(H,H) = 8.3$ Hz, phenyl-H), 7.98 (1H, dd, ${}^{3}J(H,H) = 8.3$ Hz, phenyl-*H*), 8.04 (4H, d, ${}^{3}J(H,H) = 8.8$ Hz, phenyl-*H*), 8.10 (2H, d, ${}^{3}J(H,H) = 4.7$ Hz, pyrrole-*H*), 8.46 (1H, dd, ${}^{3}J(H,H) = 8.3$ Hz, phenyl-H), 8.50 (1H, dd, ${}^{3}J(H,H) = 8.3$ Hz, phenyl-*H*), 8.51 (4H, d, ${}^{3}J(H,H) = 8.6$ Hz, phenyl-H). IR (KBr): λ , cm⁻¹ 1775 (NO stretching). MS (ESI⁻, CH₂Cl₂): *m*/*z* 743.9 [M–H]⁻.

The ¹⁵N substituted analog of compound **1-Fe(NO)**, **1-Fe(¹⁵NO)**] was synthesized as described above, by using ¹⁵N-labelled NaNO₂.

Crystal data: $2(C_{37}H_{20}FeN_8O_7) \cdot 5(CHCl_3)$, Mr = 2085.76, monoclinic, space group Cc, a = 25.643(2), b = 16.4041(10), c = 21.3666(17) Å, β = 111.874(3)°, V = 8340.8(11) Å³, Z = 4, T/K = 110(2), Dc/g.cm⁻³ = 1.661. Final R1 = 0.123 for 11666 reflections with F > 4σ (F), R1 = 0.142 and wR2 = 0.30 for all 13989 data.

Preparation of [1-Fe(NO)]: **1-Fe(NO)** (10 mg, 13.4 μ mol) and sodium borohydride (1 mg, 26.9 μ mol) were dissolved in CH₂Cl₂ (5 mL) and ethanol (5 mL), respectively. An equal volume was taken from each solution and mixed within the quartz ESR cuvette. The ESR tube was sealed and kept frozen with liquid nitrogen until the measurements. The sample preparation was done in a glove box.

Preparation of [1-Fe(NO)]⁺. 1-Fe(NO) (5.7 mg, 7.7 μ mol) and tris(4-bromophenyl)aminium hexachloroantimonate (1.5 mg, 1.9 μ mol) were dissolved in CH₂Cl₂ (5 mL) in separate vials. An equal volume was taken from each vial and mixed within the quartz ESR cuvette. The ESR tube was sealed and kept frozen with liquid nitrogen until the measurements. The sample preparation was done in a glove box.

RESULTS AND DISCUSSION

Synthesis and NMR characterization

Free base corrole $1-H_3$ was prepared *via* the condensation of *p*-nitrobenzaldehyde with excess pyrrole in acetic acid medium. Methods for inserting iron into core of corrole were already fully described in previous publications [10]. We adopted the same procedure to insert iron into corrole $1-H_3$, by refluxing the solution of $1-H_3$ in pyridine with excess ferrous chloride under an inert atmosphere. Column chromatography in the presence of pyridine in the eluting solvent mixture led to isolation of the red colored bis-pyridine iron(III) complex $1-Fe(py)_2$ [10c,d]. The treatment of $1-Fe(py)_2$ with 7% HCl at room temperature provided the pale green iron complex 1-FeCl, due to aerobic oxidation (Scheme 1).

The iron complexes $1-Fe(py)_2$ and 1-FeCl are paramagnetic, which is demonstrated by their ¹H NMR spectra (Figs 1a and 1b, respectively). Their oxidation and spin states were assigned based on the paramagnetic shifts of the β -pyrrole CH resonances of iron corroles, in relation to previous publications [10]. In **1-Fe(py)**₂, all the β -pyrrole CH resonances appear at high field region (-1.7, -39.9, -54.2 and -122.1 ppm), thus pointing towards low spin iron(III). On the other hand, the spectrum of 1-FeCl is similar to that of the analogous [(tpfc)FeCl, 2-FeCl], with less shifted high field resonances for the β -pyrrole CH's (5.1, -5.7, -7.3 and -38.5 ppm). In this case, additional resonances attributable to the *p*-nitrophenyl groups are also seen. All the low field chemical shifts (~20 ppm) are confidently assigned to ortho-H protons, because they are absent in chloroiron complexes of tris(ortho-substitutedphenyl)corroles [10d]. The most straightforward ¹H NMR assignment of the iron corroles may be obtained by converting the paramagnetic complexes to diamagnetic (nitrosyl)iron corrole [10b,c]. This was achieved by the treatment of 1-FeCl with a saturated solution of sodium nitrite at room temperature, leading to the orange-colored (nitrosyl)iron corrole **1-Fe(NO**), a {FeNO}⁶ complex by the Enemark and Feltham nomenclature [29]. Using Na¹⁵NO₂ instead of sodium nitrite led to the ¹⁵N-labeled complex 1-Fe(¹⁵NO). The nitrosyl(iron) complexes 2-Fe(NO) and 2-Fe(15NO) of the most extensively studied trispentafluorophenylcorrole were also prepared by the same methodology. In addition, the isotopically pure ⁵⁷Fe complexes 2-57Fe(NO) and 2-57Fe(15NO) were prepared from 2-57FeCl, which was obtained via metallation of 2-H₃ by ⁵⁷Fe in acetic acid.

The ¹H NMR spectrum of **1-Fe(NO)** (Fig. 1c) displays four doublets (7.37, 7.54, 7.76, 8.1 ppm) with characteristic coupling constants of J ~ 4.7 Hz [25], which correspond to the eight β -pyrrole hydrogen atoms. The



Scheme 1. Synthetic scheme for the iron complexes of corrole 1-H₃



Fig. 1. ¹H NMR spectra of different iron complexes of corrole $1-H_3$ at 25 °C: (a) $1-Fe(py)_2$ in pyridine-d₅; (b) 1-FeCl in CDCl₃; (c) 1-Fe(NO) in CDCl₃

penta-coordinated **1-Fe(NO)** is of C_s symmetry, leading to magnetically identical C_5 and C_{15} aryls and a unique C_{10} aryl. This is reflected in a 2:1 ratio of *ortho*-H protons at 8.04 ppm (4H of the C_5 and C_{15} aryls) and 8.50 ppm (2H of the C_{10} aryl) characterized by J ~ 8.8 Hz coupling constants. Surprisingly, the *meta*-H resonances are more separated, as seen by the three double doublets at 7.85, 7.98 and 8.46 ppm (the three other signals overlap with the *ortho*-H protons).

The spectroscopy-based assignment of **1-Fe(NO)** was confirmed by X-ray crystallography, based on single



Fig. 2. Structure (ORTEP view) of the two crystallographically independent molecule of **1-Fe(NO)**, showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity

 Table 1. Selected bond lengths (Å) of the two molecules of 1-Fe(NO) in the asymmetric unit

Bond length	Molecule 1	Molecule 2		
Fe-N ₂₁	1.914(10)	1.897(9)		
Fe-N ₂₂	1.906(9)	1.967(10)		
Fe-N ₂₃	1.888(10)	1.966(9)		
Fe-N ₂₄	1.886(10)	1.910(9)		
Fe-N _(NO)	1.675(14)	1.648(11)		
N-O	1.144(15)	1.155(13)		
Fe-plane	0.468(5)	0.464(5)		

crystals that were obtained by the slow evaporation of a saturated solution of 1-Fe(NO) in chloroform.

Crystallography

The diffraction measurements were carried out on a Nonius Kappa CCD diffractometer, using graphite monochromated Mo K α radiation ($\lambda = 0.7107$ Å). The structure was solved by direct method (SIR-97) and refined by full-matrix least squares on F² (SHELX-97). All non-hydrogen atoms were refined anisotropically. The compound **1-Fe(NO**) crystallized with high content of uncoordinated solvent molecules, which are partly disordered in the crystal lattice, thus affecting the crystal quality and lowering the precision of the otherwise unequivocal structure determination.

The asymmetric unit of the **1-Fe(NO)** crystals contains two crystallographically independent (nitrosyl)iron corrole molecules (Fig. 2), along with five molecules of the chloroform solvent. The most important structural parameters are tabulated in Table 1.

The iron ion in the square pyramidal coordination sphere is displaced out of the basal plane of the four pyrrole N-atoms by 0.468(5) and 0.464(5) Å towards the axial ligand. As discussed earlier [28], the neutral (nitrosyl)iron corroles are similar to the cationic (nitrosyl) iron porphyrins by means of a linear Fe–N–O moiety, consistent with {FeNO}⁶. The structure of **1-Fe(NO**) reveals Fe–N–O angles of 173(1)°, similar to previously reported iron corroles (Table 2). This feature is also consistent with the earlier mentioned diamagnetism.

A diagnostic tool of the coordination mode of nitrosyl ligands is IR, because of the large differences between the v(N–O) stretching frequencies of linear and bent Metal–N–O moieties. The FT-IR spectra of the (nitrosyl)iron corrole complexes were obtained as thin films on KBr (Fig. 3), revealing that the NO stretching frequency in both **1-Fe(NO)** and **2-Fe(NO)** are well within the range of linear nitrosyl(iron) complexes expected for {FeNO}⁶ [30]. This assignment was reinforced by the isotope sensitivity of v(¹⁴N–O)

Table 2. Structural parameters and the NO stretching frequency of **1-Fe(NO)**, in comparison with previously characterized (nitrosyl)iron corroles (oec = octaethylcorrole, tdcc = tris(*o*-dichlorophenyl)corrole, ttc = tris(*p*-methylphenyl)corrole, tmopc = tris(*p*-methylphenyl)corrole)

Complex	FeN(corrole)(Å)	Fe-NO ang (deg)	Fe out-of-plane(Å)	N–O(Å)	NO stret. cm-1	Ref.
Fe(NO)(oec)	1.909(3)	176.9(3)	0.470(1)	1.171(4)	1767	6
2-Fe(NO) ^a	1.910(4), 1.910(4)	177.3, 178.0(4)	0.465, 0.464(2)	1.164, 1.166(4)	1790	10a
Fe(NO)(tdcc)	1.910(4)	172.3(4)	0.452(2)	1.169(5)	1783	10a
Fe(NO)(ttc)	1.913(2)	177.1(2)	0.455(1)	1.162(2)	1761	28
Fe(NO)(tmopc)	1.898(4)	172.0(4)	0.449(2)	1.076(4)	1767	28
1-Fe(NO) ^a	1.888(10), 1.935(9)	172.8(10), 173.3(9)	0.468(5), 0.464(5)	1.144(15), 1.154(13)	1775	this work

^a There are two crystallographically independent corrole species in the asymmetric unit of these structures.



Fig. 3. FT-IR spectra (films on KBr pellets) of (nitrosyl)iron corroles: (a) **1-Fe(NO)** (gray) and **1-Fe(¹⁵NO)** (black); (b) **2-Fe(NO)** (gray), **2-**⁵⁷**Fe(NO)** (black), **2-**⁵⁷**Fe(¹⁵NO)** (dotted), and **2-Fe(¹⁵NO)** (long dashed line)

vs. $v(^{15}N-O)$, shifting from 1775 cm⁻¹ in **1-Fe(NO)** to 1733 cm⁻¹ in the ¹⁵N-labeled complex **1-Fe**(¹⁵NO) (Δ_{exp} = 42 cm⁻¹). A practically identical shift of 41 cm⁻¹ was identified for the tpfc-ligated complexes, from 1797 cm⁻¹ in 2-Fe(NO) to 1756 cm⁻¹ in 2-Fe(¹⁵NO). As may have been expected, the effect of ⁵⁷Fe substitution was marginal: 1797 in 2-Fe(NO) vs. 1799 in 2-57Fe(NO) and 1756 cm⁻¹ in 2-Fe(¹⁵NO) vs. 1759 cm⁻¹ in 2-⁵⁷Fe(¹⁵NO). The main motivation for the preparation of the ⁵⁷Fe-labeled complexes was not for that purpose, but rather for possible determination of the Fe-NO modes. The spectral area where such bands may be suspected (600-400 cm⁻¹), based on investigation of natural and synthetic (nitrosyl)iron complexes by Resonance Raman spectroscopy [31], was examined. Unfortunately, no isotope-sensitive bands could be identified with large enough confidence by IR spectroscopy.

Additional insight was obtained from the data in Table 3, which lists the NO stretching frequencies of the corroles under study together two other selected {FeNO}⁶ (nitrosyl)iron complexes [32]. One interesting aspect is the quite large effect of the chelating macrocycle in these isoelectronic complexes on the v(NO) frequency: 1859, 1797, 1775, and 1767 cm⁻¹ for [Fe(NO)(tpfpp)]⁺, 2-Fe(NO), 1-Fe(NO), and Fe(NO)-(oec), respectively (tpfpp = the dianionic form of 5,10,15,20-tetrakispentafluorophenylporphyrin; oec = the trianionic form of 2,3,6,7,11,12,16,17-octaethylcorrole). This pattern clearly reflects the electron-richness: much larger for the trianionic corrolates than for the dianionic porphyrinates; and within the former series, largest for the β -pyrrole-alkyl-subsituted Fe(NO)(oec), followed by meso-nitrophenyl-substituted 1-Fe(NO), and least so for the meso-pentafluorophenyl-substituted 2-Fe(NO). We also note that the experimental isotope shifts in the (nitrosyl)iron triarylcorrole complexes are 38-42 cm⁻¹, much larger than the expected 32 cm⁻¹ for a simple diatomic model, but perfectly in the range of linear nitrosyl-metal complexes [33].

Table 3. FT-IR band stretching frequencies of the investigated (nitrosyl)iron corroles and of some analogous complexes reported in the literature

Complex	Isotope		e	N–O stret. (cm ⁻¹)	$\Delta_{\rm exp.}{}^{\rm a}$	Ref.
	Fe	N	0	-		
1-Fe(NO)	56	14	16	1775		b
1-Fe(¹⁵ NO)	56	14	16	1733	+42	b
2-Fe(NO)	56	14	16	1797		b
2-Fe(¹⁵ NO)	56	15	16	1756	+41	b
2- ⁵⁷ Fe(NO)	57	14	16	1799	-2	b
2- ⁵⁷ Fe(¹⁵ NO)	57	15	16	1759	+38	b
Fe(NO)(oec)	56	14	16	1767		6
[Fe(NO)(tpfpp)] ⁺	56	14	16	1859		32
[Fe(¹⁵ NO)(tpfpp)] ⁺	56	15	16	1837	+22	32

^aRelative to the ⁵⁶Fe-¹⁴N-¹⁶O complex. ^bThis work.

Electrochemistry

Given the limited information about the oxidized and reduced states of (nitrosyl)iron corroles, emphasis was given to their characterization. The cyclic voltammogram of **1-Fe(NO)** reveals reversible oxidation and reduction waves with $E_{1/2}$ values of 1.03 V and -0.11 V, respectively (Fig. 4).

The spectroelectrochemical results for **1-Fe(NO)** are shown in Fig. 5. Holding the applied potential at -0.3 V reveals that the intensity of the Soret band at 382 nm decreased and shifted to 395 nm, and that the single band at 544 nm was replaced by two new bands at 524 nm and 662 nm (Fig. 5a). Identical characteristics were obtained by the chemical reduction of **1-Fe(NO)** with sodium borohydride, in a CH₂Cl₂:C₂H₅OH (1:1) solvent mixture (Fig. 5b). Formulation of this reduced species by virtue of the redox centre, *i.e.* the metal or the macrocycle, was achieved by EPR spectroscopy (*vide infra*).



Fig. 4. Cyclic voltammogram of 1-Fe(NO) in CH₂Cl₂ containing 0.1 M TBAP

Upon oxidation of **1-Fe(NO)** at an applied potential of 1.2 V, the Soret band intensity decreased and its λ_{max} shifted to the red by 13 nm. In addition, the 544 nm band disappeared and a new band appeared at 636 nm (Fig. 6a). Chemical oxidation of **1-Fe(NO)** by tris(4bromophenyl)aminium hexachloroantimonate induced identical changes (Fig. 6b). Comparison of the spectral changes occurring by either oxidation or reduction of **1-Fe(NO)** reveals a surprising similarity: an intensity reduction and red shift of the Soret band, as well as the growth of a new absorbance at about 650 nm. This phenomenon is different from what has been observed in nitrosyl(iron) tetraarylporphyrins, where the Soret band of the {FeNO}⁷ complexes are slightly blue shifted and more intense than those of the {FeNO}⁶ complexes [34].

EPR spectroscopy

The chemically reduced iron complexes **[1-Fe(NO)]**⁻ and **[1-Fe(¹⁵NO)]**⁻ with coordinated ¹⁴NO and ¹⁵NO, respectively, were examined by EPR. The spectrum of **[1-Fe(NO)]**⁻ (Fig. 7a) in CH₂Cl₂:C₂H₅OH (1:1) at 290 K displays an intense triplet due to the interaction of the unpaired electron with the ¹⁴N nuclei, with g = 2.032 and $a_N(^{14}N) = 16.0$ G. The ¹⁵N- labeled complex **[1-Fe(¹⁵NO)]**⁻ discloses an intense doublet (g=2.032) (Fig. 7b), with $a_N(^{15}N) = 22.3$ G. The ratio of the hyperfine coupling constants $a_N(^{15}N)/a_N(^{14}N)$ is 1.4, perfectly consistent with the ratio of the nuclear magnetic moments of ¹⁵N and ¹⁴N; $\mu(15)/\mu(14) = 1.4$ [35].

The EPR spectrum of $[1-Fe(NO)]^{-1}$ in the frozen CH₂Cl₂:C₂H₅OH solvent mixture (130 K) is rhombic (Fig. 8a), displaying diagonal components of the *g*-tensor (g₁ = 2.014, g₂ = 2.037, and g₃ = 2.046). The hyperfine coupling tensor A with ¹⁴N (A_1 = 16.1 G, A_2 = 17.2 G, and A_3 = 16.0 G) may be deduced from the spectrum as well, as illustrated by the spectral simulation that is based on these parameters (Fig. 8b). The spectrum of the ¹⁵N-labeled complex [1-Fe(¹⁵NO)]⁻ reveals identical g-factors, as well as the expected 40% increase in the hyperfine coupling tensors A of A_1 = 22.8 G, A_2 = 24.0 G, and



Fig. 5. UV-vis spectral changes of **1-Fe(NO)** upon (a) controlled reduction potential at -0.3 V in CH_2Cl_2 containing 0.1 M TBAP, and (b) chemical reduction by sodium borohydride in $CH_2Cl_2:C_2H_5OH$ solvent mixture. Black line for **1-Fe(NO)** and gray line for the reduced species



Fig. 6. UV-vis spectral changes of **1-Fe(NO)** via (a) controlled oxidation potential at 1.2 V in CH_2Cl_2 containing 0.1 M TBAP, and (b) chemical oxidation by tris(4-bromophenyl)aminium hexachloroantimonate, in CH_2Cl_2 . Black line for **1-Fe(NO)** and gray line for the oxidized species



Fig. 7. EPR spectra of (a) $[1-Fe(NO)]^{-}$ (b) $[1-Fe(^{15}NO)]^{-}$, in CH₂Cl₂:C₂H₃OH at 290 K

 $A_3 = 22.0$ G (Fig. 8d). Taken together, the EPR results of the reduced (nitrosyl)iron complex are fully consistent with an FeNO-centered redox process [36]. This conclusion is substantiated *via* comparison with literature data on porphyrin-chelated {FeNO}⁷ complexes (Table 4) by virtue of the similarity of both the *g*-tensor and the hyperfine coupling constants.

The EPR spectrum of the one-electron oxidized derivative of **1-Fe(NO)** ([**1-Fe(NO**)]⁺, Fig. 9a) in frozen CH_2Cl_2 solution is a superposition of signals from two



Fig. 8. EPR spectra in frozen $CH_2Cl_2:C_2H_5OH$ solution at 130 K of (a) **[1-Fe(NO)]**⁻ and (c) **[1-Fe(¹⁵NO)]**⁻, together with the simulated spectra (b) and (d), respectively)

paramagnetic particles: the intensive isotropic part, due to the organic radical (tris(4-bromophenyl)aminium hexachloroantimonate) that was applied as oxidant, and two features marked by (*), which are attributed to the

Compound	Solvent, T(K)	g factor	A (Gauss)	Ref.
Fe ^{II} (NO)(tpp)	Toluene, 120	2.10, 2.06, 2.01	12.6, 17.2, 17.3	36
Fe ^{II} (NO)(tpp)	Toluene, 253	2.054	17.4	36
[Fe ^{II} (NO)(oec)] ⁻	PhCN, 120	2.08, 2.04, 2.00		6
[Fe(NO)(oec)] ⁺	CH ₂ Cl ₂ , 77	2.02, 2.00, 1.98		6
[1-Fe(¹⁴ NO)] ⁻	CH ₂ Cl ₂ :C ₂ H ₅ OH, 290	2.032	16	this work
[1-Fe(¹⁴ NO)] ⁻	CH ₂ Cl ₂ :C ₂ H ₅ OH, 130	2.046, 2.037, 2.014	16.1, 17.2, 16.0	this work
[1-Fe(¹⁵ NO)] ⁻	CH ₂ Cl ₂ :C ₂ H ₅ OH, 290	2.032	22.3	this work
[1-Fe(¹⁵ NO)] ⁻	CH ₂ Cl ₂ :C ₂ H ₅ OH, 130	2.046, 2.037, 2.014	22.8, 24, 22	this work
[1-Fe(¹⁴ NO)] ⁺	CH ₂ Cl ₂ , 130	2.038, 2.004, 1.97		this work

Table 4. g factors and coupling constants of various (nitrosyl)iron complexes (tpp=tetraphenylporphyrin)



Fig. 9. EPR spectrum (frozen CH_2Cl_2 at 130 K) of [**1-Fe(NO**)]⁺, obtained *via* oxidation of **1-Fe(NO**) by using tris(4-bromophenyl)aminium hexachloroantimonate as oxidant: (a) experimental spectrum; (b) simulated spectrum of the oxidant, (c) spectrum obtained by subtraction (b) from (a)

components of the *g*-tensor of $[1-Fe(NO)]^+$. Apparently, only partial oxidation was obtained, which is consistent with the almost identical redox potentials of (tris(4-bromophenyl)aminium hexachloroantimonate) [9b] and $[1-Fe(NO)]^+$.

Subtraction of the contribution from tris(4bromophenyl)aminium hexachloroantimonate (Fig. 9b) from the experimental spectrum discloses all components of the *g*-tensor of **[1-Fe(NO)]**⁺: $g_1 = 2.038$, $g_2 = 2.004$, $g_3 = 1.970$ (Fig. 9c). The hyperfine coupling tensor *A* values could not be obtained with meaningful confidence because of the applied procedure.

SUMMARY AND CONCLUSIONS

We report an in depth investigation of the (nitrosyl)iron complex of 5,10,15-tris(4-nitrophenyl)corrole **1-Fe(NO)** and its ¹⁵N-labeled analog, by a combination of X-ray crystallography, IR, NMR, and electrochemistry, as well as of the one-electron oxidized and reduced complexes by EPR. The comparison with other (nitrosyl)iron corrole and porphyrins reveals that **1-Fe(NO)** is a genuine {FeNO}⁶ complex, with an almost perfectly linear Fe–N–O bond and large isotope shifts of the nitrosyl moiety. The reduced complex displays EPR parameters at both high and low temperatures that imply that it is an authentic {FeNO}⁷ complex.

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Supporting information

Crystallographic data for 1-Fe(NO) have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under number CCDC-867402. Copies can be obtained on request, free of charge, *via* www. ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

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