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Expected and Unexpected Transformations of Manganese(III) Tris(4-nitrophenyl)corrole

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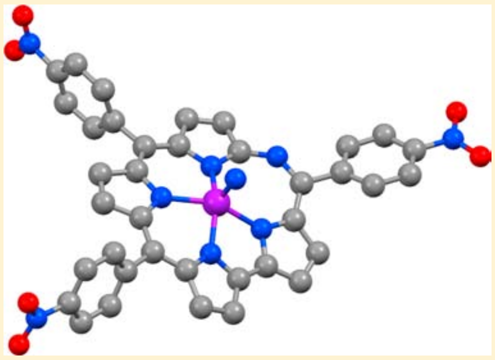
Supporting Information

ABSTRACT: The synthesis and characterization of manganese complexes of 5,10,15-tris(4-nitrophenyl) corrole in different oxidation states are described. Adoption of established protocols for the synthesis of (nitrido)manganese(V) complexes led to the expected corrole derivative as a minor product, accompanied by nitrogen atom insertion into the macrocycle. The major product was fully characterized via the combination of spectroscopy and X-ray crystallography as (nitrido)manganese(V) 6-azahemiporphycene.



INTRODUCTION

Metallocorroles are receiving increased interest in recent years because of the exceptional properties that the trianionic corrole macrocycle induces onto metal ions chelated by it.[1] This includes the strong reducing power of trivalent metals and the large stability of high (+4 to +6) oxidation states.[2] These non-independent features are responsible for the large utility of metallocorroles for prime importance aspects relevant to energy and medicine, such as the activation of small molecules: O_2,[3] CO_2,[4] H^+,[5] H_2O_2,[6] HOONO,[7] and more. This is particularly true for manganese and iron complexes of corroles, which have already been introduced as catalysts for quite different applications: oxidation of and group transfer to organic substrates,[8] reduction of oxygen,[9] carbon dioxide,[4] and protons,[5] and as antioxidants in biological media.[10] The majority of the above achievements were reported on corroles that contain C_6F_5 groups on their three *meso*-C atoms, particularly so for the metal complexes of 5,10,15-trispentafluorophenylcorrole (H_3tpfc)[11] and 2,17-bis-sulfonato-5,10,15-trispentafuorophenylcorrole (**1-Fe** and **1-Mn**, Chart 1).[12] While such corroles have the advantages of stability and the benefits associated with having ^{19}F NMR spectroscopy as an excellent characterization tool, it is very important to develop also corroles that do not contain the strong electron withdrawing and very expensive C_6F_5 groups. The 5,10,15-tris(4-nitrophenyl) corrole (**2-H$_3$**, Scheme 1) is one interesting candidate in terms of synthetic accessibility and stability.[13] What is more, reduction of its nitro groups may be expected to have a very strong effect on the corrole's electron-richness and the such formed 4-aminophenyl moieties may be used as synthetic handles for further modifications. There are indeed several reports on the manganese, iron, and cobalt complexes of corrole **2-H$_3$** (**2-Mn**,[14] **2-Fe**,[15] and **2-Co**,[13] respectively) that focused on both their physical and chemical properties. We have now decided to investigate the coordination chemistry of the complexes of corrole **2-H$_3$**, with particular emphasis on obtaining them in various oxidation states and with the hope of obtaining crystal structures of the yet elusive nitrido-manganese corrole. The results revealed that the manganese(III) and chloro-manganese(IV) complexes of corrole **2-H$_3$** are of similar stability compared to the analogous complexes of 5,10,15-trispentafluorophenylcorrole. However, methodologies that work so well for conversion of other manganese(III) corroles to the corresponding nitrido-manganese(V) derivatives[2b,16] led to nitrogen atom insertion into the macrocycle when applied on **2-Mn**. The expected [**2-Mn(N)**]$^-$ complex was obtained as the minor product, while neutral nitrido-manganese(V) complexes of two isomeric azahemiporphycene[17] were formed via ring expansion of the corrole macrocycle. Azahemiporphycenes were also obtained via oxidative expansion of free-base corroles by Paolesse and co-workers, albeit in those cases the reaction did not take place with electron-poor corroles such as **2-H$_3$**.[17a] All new compounds were characterized by a combination of spectroscopic methods, and the X-ray crystallography based molecular structure of the (nitrido)-manganese(V) azahemiporphycene is reported as well.

EXPERIMENTAL SECTION

Materials. Manganese acetate tetrahydrate, 99 + % (Aldrich Chemical Co., Inc.), pyridine (Merck), and deuterated solvents (Aldrich and Cambridge Isotopes products) were used as received.

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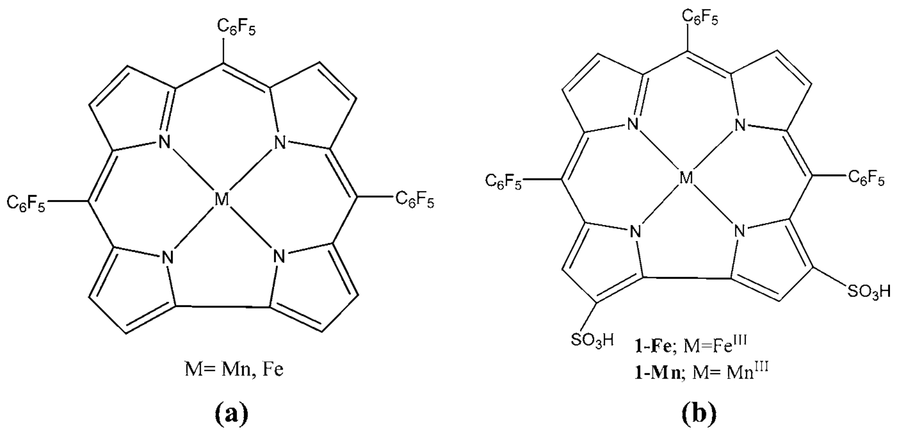
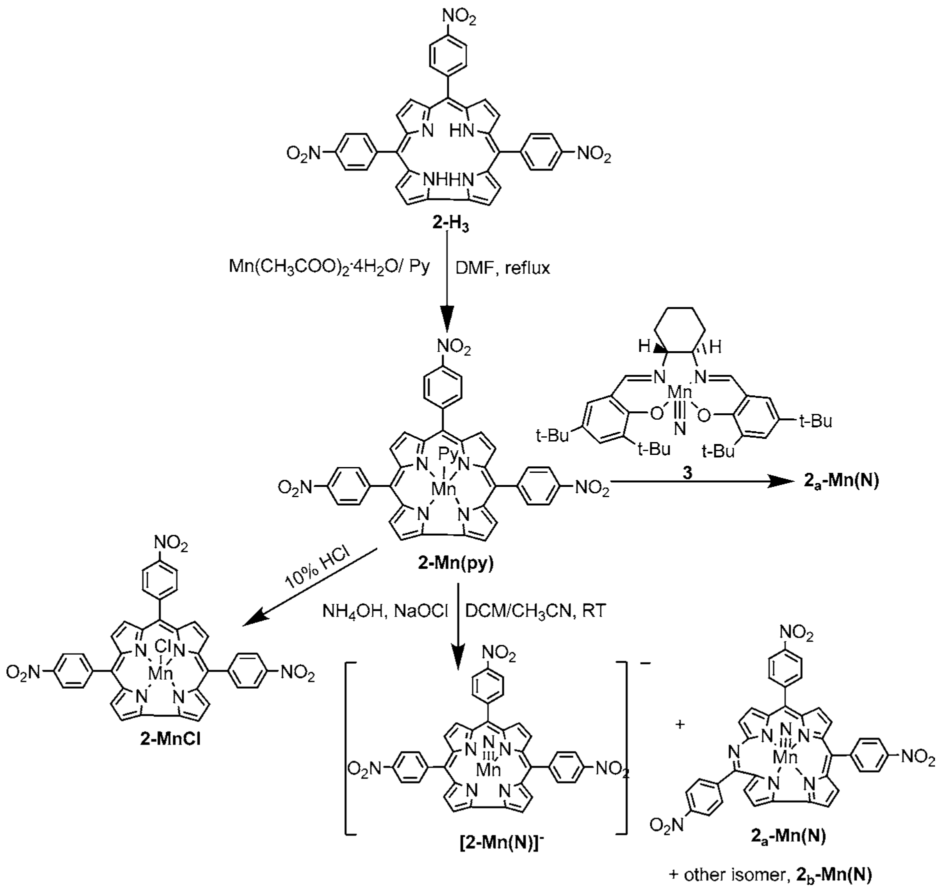
Chart 1. Structures of (a) tpfc Metal Complexes and (b) the Iron(III) and Manganese(III) Complexes of the 2,17-Bis-sulfonated Analogue



Scheme 1. Synthetic Approaches That Led to Manganese Corroles in Different Oxidation States and to the (Nitrodo)Manganese(V) Complexes of Azahemiporphycenes



Solvents like dichloromethane and hexane were obtained from S. D. Fine Chemicals Ltd.

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. The X-ray diffraction measurements (Nonius KappaCCD diffractometer, MoKα radiation) were carried out at about 293(2) K (for **2-Mn(py)** and **2-MnCl** compounds and 110(2) K (**2-Mn(N)**). The structures were solved by direct methods and refined (all non-hydrogen atoms anisotropically) by full-matrix least-squares, using standard software (SIR-97, SHELXL-97). All three compounds were found to contain crystallization solvent (pyridine, toluene, and dichloromethane), which could be precisely modeled only in **2-Mn(N)**. Despite the solvent disorder in **2-Mn(py)** and **2-MnCl**, and the rotational disorder of the aryl substituents in the latter, the crystallographic evaluations provided in all cases adequately precise models of the Mn-corrole structures. All electrochemical experiments were performed using a WaveNow USB potentiostat Galvanostat (Pine Research Instrumentation), using Pine AfterMath Data Organizer Software. A three-electrode system was used, consisting of a mini glassy carbon electrode (diameter of the active zone: 2.8 mm;

Metrohm) working electrode and a platinum wire counter electrode. Measurements were performed on dichloromethane solutions with 0.1 M tetrabutylammonium perchlorate (TBAP, Fluka, recrystallized twice from methanol) and 1 mM substrate, under N_2 atmosphere at ambient temperature.

Syntheses. The 5,10,15-tris(4-nitrophenyl)corrole (**2-H$_3$**) was prepared as reported earlier.[13]

Synthesis of 2-Mn(py). A dimethylformamide (DMF) solution (30 mL) of **2-H$_3$** (66 mg, 0.1 mmol) and manganese(II) acetate tetrahydrate (245 mg, 1.0 mmol) was heated to reflux for 30 min under nitrogen. The green colored solution was evaporated and redissolved in ethyl acetate with few drops of pyridine. The crude product was purified by column chromatography over acidic alumina using *n*-hexane/ethyl acetate/pyridine (75:49:1) as eluent, resulting in 86 mg (90% yield) of **2-Mn(py)**. Dark green colored X-ray quality crystals were obtained by slow evaporation of a solution of **2-Mn(py)** in toluene containing a few drops of pyridine. UV−vis (EtOAc): λ_{max} (relative ε): nm 359(75), 425(82), 477(100), 590(34), 657(32). Elemental analysis calculated for $C_{37}H_{20}MnN_7O_6{\cdot}2C_5H_5N{\cdot}0.5C_7H_8$: C, 66.09; H, 3.73; N, 13.73. Found: C, 66.32; H, 3.61; N, 13.55. HRMS (ESI$^+$, m/z) for $C_{37}H_{20}MnN_7O_6$: 713.0852 (cal. 713.0856)

Crystal data of **2-Mn(py)**: $C_{37}H_{20}MnN_7O_6{\cdot}2(C_5H_5N){\cdot}C_7H_8$, M = 963.87, triclinic, space group $P\bar{1}$, a = 9.045(2) Å, b = 11.071(2) Å, c = 23.842(5) Å, α = 101.135(2)°, β = 96.94(3)°, γ = 94.83(2)°, V = 2311.1(8) Å^3, Z =2, T = 293(2) K, D_c = 1.385 Mg/m^3, μ = 0.349 mm^{-1}. A total of 15836 reflections were measured, of which7454 were unique (R_{int} = 0.090) and 4066 with $I > 2\sigma(I)$ to $2\theta_{max}$ = 49.8°. Final R1 = 0.105 and wR2 = 0.263 for the 4066 data above the intensity threshold and R1 = 0.168 and wR2 = 0.280 for all data. The relatively high R-factors are due to the presence of a severely disordered toluene crystallization solvent in the crystal lattice, which could not be positioned reliably. The structural model of the **2-Mn(py)** compound is, however, well-defined. CCDC 940694. An ORTEP view of the molecular structure is shown in the Supporting Information.

Synthesis of 2-MnCl. **2-Mn(py)** (68 mg, 85.8 μmol) was dissolved in CH_2Cl_2 (50 mL) and stirred with a 10% HCl solution (50 mL) for 1 h at room temperature. The organic solution was washed with distilled water several times, dried over anhydrous sodium sulfate, and evaporated. The crude product was recrystallized from a CH_2Cl_2/*n*-hexane (1:2) solvent mixture as to afford 62 mg (95% yield) of pure purple colored crystals. UV−vis (CH_2Cl_2): λ_{max} (relative ε): nm 418 (100), 618(12). Elemental analysis calculated for $C_{37}H_{20}ClMnN_7O_6{\cdot}0.25C_6H_{14}{\cdot}0.25CH_2Cl_2$: C, 59.44; H, 3.41; N, 12.06. Found: C, 59.81; H, 3.06; N, 12.28. HRMS (ESI$^+$, m/z) for $C_{37}H_{20}ClMnN_7O_6$: 748.0503 (cal. 748.0544).

Crystal data for **2-MnCl**: $C_{37}H_{20}ClMnN_7O_6{\cdot}(CH_2Cl_2)_x$ ($x \cong 1/4$), M = 760.85, triclinic, space group $P\bar{1}$, a = 7.656(2) Å, b = 16.410(3) Å, c = 17.539(3) Å, α = 62.94(2)°, β = 80.64(2)°, γ = 77.22(2)°, V = 1908.8(7) Å^3, Z = 2, T = 293(2) K, D_c = 1.324 mg/m^3, μ = 0.486 mm^{-1}. A total of 17062 reflections were measured, of which 6523 were unique (R_{int} = 0.070) and 4752 with $I > 2\sigma(I)$ to $2\theta_{max}$ = 50.0°. Final R1 = 0.077 and wR2 = 0.238 for the 4752 data above the intensity threshold and R1 = 0.101 and wR2 = 0.260 for all data. The relatively high R-factors are due to the presence of a severely disordered CH_2Cl_2 crystallization solvent in the crystal lattice, which could not be modeled reliably, as well as rotational disordered of two of the aryl rings. CCDC 940696. An ORTEP view of the molecular structure is shown in the Supporting Information.

Synthesis of [2-Mn(N)]$^-$. *Method 1, Using Ammonium Hydroxide and Bleach.* **2-Mn(py)** (26.2 mg, 26.9 μmol) was dissolved in a mixture of dichloromethane (1 mL) and acetonitrile (14 mL). NH_4OH (15 μL, 383 μmol) and NaOCl (8 mL, 151 μmol) were added sequentially, the reaction mixture was stirred vigorously at room temperature for 1 min, after which sodium sulfate (200 mg) was added to quench the reaction. The solution was filtered and evaporated to dryness. The crude product was redissolved in dichloromethane and purified by separation on preparative thin-layer chromatography (alumina) using CH_2Cl_2/*n*-hexane (3:1) mixture as eluent. The light pink fraction was collected and recrystallized from CH_2Cl_2/*n*-pentane (1:2) to afford pure [**2-Mn(N)**]$^-$ (4 mg, 20.40%).

[2-Mn(N)]$^-$. UV−vis (CH_2Cl_2): λ_{max} (relative ε): 409(100), 529(7), 565(16) nm. MS (FAB: m/z 727 [M$^+$]. ^{1}H NMR (400 MHz; $CDCl_3$): δ_H, ppm 9.36 (2H, d, ^3J(H,H) = 5.2 Hz, pyrrole-*H*), 9.03 (2H, d, ^3J(H,H) = 4.7 Hz, pyrrole -*H*), 8.84 (2H, d, ^3J(H,H) = 4.6 Hz, pyrrole-*H*), 8.79 (2H, d, ^3J(H,H) = 4.6 Hz, pyrrole-*H*), 8.67 (6H, m, phenyl-*H*), 8.40 (3H, d, ^3J(H,H) = 8.4 Hz, phenyl-*H*), 8.31 (2H, d, ^3J(H,H) = 7.8 Hz, phenyl-*H*), 8.25 (1H, d, ^3J(H,H) = 8.0 Hz, phenyl-*H*)

Somewhat later eluting green fractions were also collected and further separated and purified by preparative alumina TLC using a CH_2Cl_2/*n*-hexane (1:1) mixture. The less and more polar bands provided [**2$_a$-Mn(N)**] (9 mg, 45%) and [**2$_b$-Mn(N)**] (3 mg, 13.4%), respectively.

2$_a$-Mn(N). UV−vis (CH_2Cl_2): λ_{max} (relative ε): 451(100), 618(15) nm. MS (FAB: m/z 741 [M$^+$]. ^{1}H NMR (400 MHz; $CDCl_3$): δH, ppm 9.28 (1H, d, ^3J(H,H) = 4.2 Hz, pyrrole -H), 9.14 (1H, d, ^3J(H,H) = 4.6 Hz, pyrrole -H), 8.99 (1H, d, ^3J(H,H) = 4.3 Hz, pyrrole -H), 8.88 (2H, m, pyrrole -H), 8.79 (1H, d, ^3J(H,H) = 4.9 Hz, pyrrole -H), 8.71 (3H, d ^3J(H,H) = 8.6 Hz, phenyl-H), 8.68 (2H, d, ^3J(H,H) = 8.6 Hz, phenyl-H), 8.62 (3H, d, ^3J(H,H) = 8.4 Hz, phenyl-H), 8.57 (1H, d, ^3J(H,H) = 4.8 Hz, pyrrole-H), 8.50 (1H, dd, ^3J(H,H) = 8.4 Hz, phenyl-H), 8.45 (1H, d, ^3J(H,H) = 4.7 Hz, pyrrole-H), 8.36 (2H, s, phenyl-H), 7.82 (1H, d, ^3J(H,H) = 8.1 Hz, phenyl-H)

Crystal Data for 2$_a$-Mn(N). $C_{37}H_{20}MnN_9O_6{\cdot}CH_2Cl_2$, M = 826.49, monoclinic, space group $C2/c$, a = 25.7597(5) Å, b = 17.3201(3) Å, c = 15.3600(4) Å, β = 93.3604(8)°, V = 6841.2(3)Å^3, Z = 8, T = 110(2) K, D_c = 1.605 mg/m^3, μ = 0.608 mm^{-1}. A total of 24262 reflections were measured, of which 6071 were unique (R_{int} = 0.102) and 3657 with $I > 2\sigma(I)$ to $2\theta_{max}$ = 50.1°. Final R1 = 0.049 and wR2 = 0.099 for the 3657 data above the intensity threshold and R1 = 0.104 and wR2 = 0.118 for all data. CCDC 940695.

2$_b$-Mn(N). UV−vis (CH_2Cl_2): λ_{max} (relative ε): 442 (100), 634 (14) nm. MS (FAB: m/z 741 [M$^+$]. ^{1}H NMR (400 MHz; $CDCl_3$): δ_H, ppm 9.49 (1H, d, ^3J(H,H) = 4.6 Hz, pyrrole -*H*), 9.39 (1H, d, ^3J(H,H) = 4.8 Hz, pyrrole -*H*), 9.24 (1H, d, ^3J(H,H) = 4.6 Hz, pyrrole -*H*), 9.06 (1H, d, ^3J(H,H) = 4.6 Hz, pyrrole -*H*), 8.93 (1H, d, ^3J(H,H) = 4.8 Hz, pyrrole -*H*), 8.88 (1H, d, ^3J(H,H) = 5.1 Hz, pyrrole -*H*), 8.77 (2H, m, phenyl-*H*), 8.68 (2H, d, ^3J(H,H) = 8 Hz, phenyl-*H*), 8.65 (1H, d, ^3J(H,H) = 4.8 Hz, pyrrole-*H*), 8.58 (2H, d, ^3J(H,H) = 8.4 Hz, phenyl-*H*), 8.51 (3H, d, ^3J(H,H) = 4.8 Hz, pyrrole-*H*, phenyl-*H*), 8.46 (1H, d, ^3J(H,H) = 9.6 Hz, phenyl-*H*), 8.39 (2H, d, ^3J(H,H) = 7.5 Hz, phenyl-*H*), 7.69 (1H, d, ^3J(H,H) = 7.7 Hz, phenyl-*H*).

Method 2: Via Nitrogen Atom Transfer. Solid (nitrido)manganese(V) salen-jc (**3**) (8.4 mg, 13.8 μmol) was added to a solution of **2-Mn(py)** (10 mg, 10.3 μmol) in acetonitrile (12 mL). The solvent was evaporated after 5 min to dryness, and the crude product was purified by preparative tlc over alumina using dichloromethane/*n*-hexane mixture(3:5) as eluent. The sole product was **2$_a$Mn(N)** (4 mg, 47%).

■ RESULT AND DISCUSSION

As part of our plan to explore the chemistry of corroles that do not contain the expensive and very electron-withdrawing C_6F_5 rings,[13] we now report on the manganese complexes of tris(4-nitrophenyl)corrole (**2-H$_3$**) in three oxidation states and the nitrogen atom insertion reactions that led to novel (nitrido)-manganese(V) complexes of azahemiporphycenes.

Insertion of manganese into **2-H$_3$** was achieved using DMF as solvent, in a manner similar to previously reported procedures.[2c] The crude product was purified over silica gel with ethyl acetate and dichloromethane mixtures as eluents, but the yield of pure Mn(III) corrole (**2-Mn**) was poor since two more bands were also obtained during chromatographic separation. We suspected that **2-Mn** might have been oxidized during the aerobic workup procedure, based on the precedents of intentional aerobic oxidation of manganese(III) corroles.[16] The addition of minute amounts of pyridine to the eluent mixture prevented this phenomenon, and **2-Mn(py)** was isolated in almost quantitative yields. The presence of

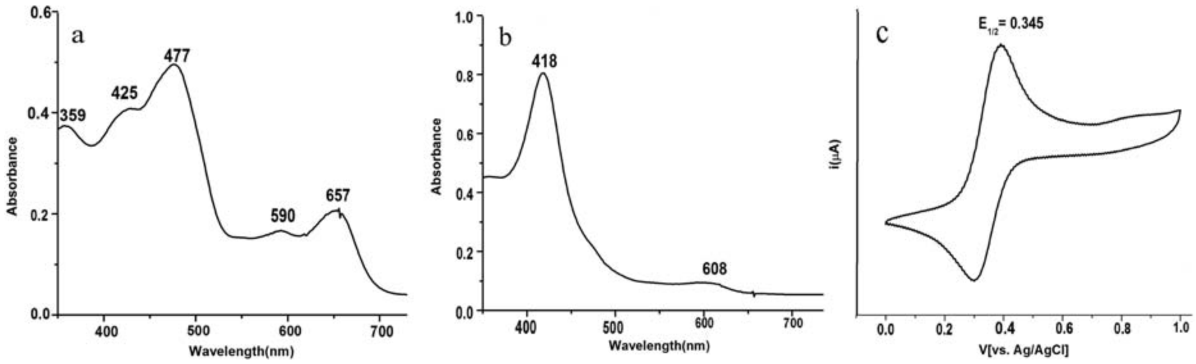


Figure 1. UV–vis spectra of (a) **2-Mn(py)** in ethyl acetate and (b) **2-MnCl** in CH_2Cl_2, and (c) the cyclic voltammogram of **2-MnCl** in CH_2Cl_2 (0.1 M TBAP electrolyte, 100 mV/s scan rate).

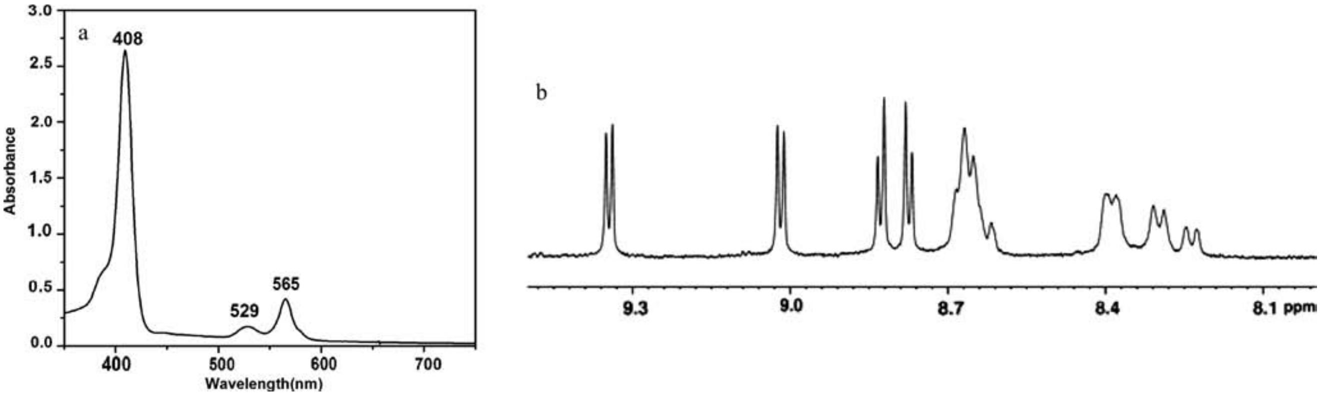


Figure 2. Spectroscopic features of $[\mathbf{2\text{-}Mn(N)}]^-$: (a) UV–vis spectrum in CH_2Cl_2; (b) ^1H NMR spectrum in $CDCl_3$.

manganese-coordinated pyridine was evident from the visible spectrum (Figure 1a), which disclosed a band at 477 nm that is characteristic of corrole- (and porphyrin-) chelated manganese(III) complexes with strongly bound axial ligands. This hypothesis was confirmed by X-ray crystallography (moderate quality crystals, Supporting Information, Figure S1), performed on green colored long blocks of **2-Mn(py)** obtained from a toluene solution that contained a few drops of pyridine. The coordinated pyridine group is characterized by a Mn–N bond length of 2.385(6) Å (the four Mn–$N_{pyrrole}$ bond distances being within 1.900–1.923(5) Å), with the Mn ion displaced 0.08 Å from the basal plane of the four pyrrole N-atoms toward it.[16] There is another pyridine molecule located on the concave side of the corrole ring, approaching the Mn-center at an Mn–N distance of 2.642(7) Å. The low tendency of hexacoordination is reminiscent of what has been observed for many other metallocorroles.[8h]

The earlier mentioned suspicion that this manganese(III) corrole is sensitive to aerobic oxidation was confirmed and taken advantage of for the synthesis of a manganese(IV) derivative. This was achieved by treating an organic solution of **2-Mn(py)** with aqueous HCl (10%), under aerobic conditions at room temperature. The Mn^{III} to Mn^{IV} conversion was facile, allowing for the isolation of the chloromanganese(IV) corrole **2-MnCl** in 95% yield. The UV–vis spectral changes are very indicative: in contrast with the rich spectrum of **2-Mn(py)** (Figure 1a), **2-MnCl** (Figure 1b) displays only a single Soret band of high intensity (λ_{max} = 418 nm) and a low-intensity Q-band (λ_{max} = 608 nm). These characteristics are identical to those of previously reported manganese(IV) corroles.[19,20] Moderate quality single crystals of **2-MnCl** were obtained by the slow diffusion of dichloromethane and *n*-hexane solvent mixture. The molecular structure (Supporting Information, Figure S2) revealed a 5-coordinate complex, wherein the central manganese(IV) ion is displaced by 0.429 Å from out of the basal plane of the corrole macrocycle. The Mn–Cl bond length of 2.284(2) Å (the Mn–$N_{pyrrole}$ bonds are within 1.913–1.941(3) Å) is comparable to the 2.310 Å and 2.312 Å Mn–Cl distances reported for the previously characterized **(OEC)-MnCl** and **(tpfc)MnCl** corroles.[16,18]

Cyclic voltammetry (CV) was used for estimating the electron-withdrawing power of the 4-nitrophenyl groups in **2-MnCl** relative to the pentafluorophenyl groups in **(tpfc)MnCl.** The CV of **2-MnCl** (Figure 1c) displays a reversible Mn^{IV}/Mn^{III} redox process with $E_{1/2}$ = 0.34 V, which is 70 mV less positive than that of **(tpfc)MnCl** ($E_{1/2}$ = 0.41 V). A similar comparison that has been reported for the (nitrosyl)iron complexes **2-Fe(NO)** and **(tpfc)Fe(NO)** revealed a 100 mV difference for the Fe^{II}/Fe^{III} redox couple.[15c] We may hence conclude that high-valent metal complexes of $\mathbf{2\text{-}H_3}$ are of larger thermodynamic stability.

The above data encouraged the preparation of (nitrido)-manganese(V) corroles, not at least because there is still no crystallographic information about such complexes.[19] The previously reported bleach oxidation of manganese(III) porphyrins and corroles to the corresponding (nitrido)-manganese(V) complexes was the obvious choice.[2b] Of the three suitable solvents for this reaction, CH_3CN, tetrahydrofuran (THF), and MeOH, the two latter were excluded because **2-Mn** is almost insoluble in MeOH and the results obtained in THF were discouraging in terms of the colors developed during reaction. Using a mixture of dichloromethane-acetonitrile

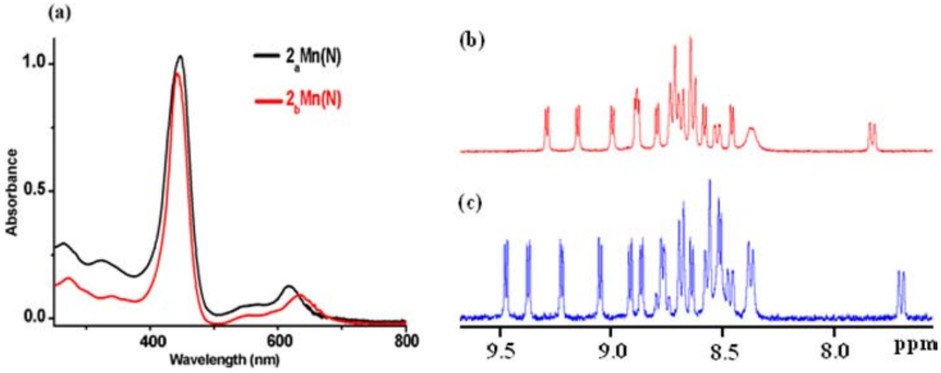


Figure 3. (a) UV−vis spectra of $\mathbf{2_aMn(N)}$(black line) and $\mathbf{2_bMn(N)}$ (red line) in CH_2Cl_2; (b) ^1H NMR spectra of $\mathbf{2_aMn(N)}$ (red); and (c) $\mathbf{2_bMn(N)}$ (blue) in $CDCl_3$.

(1:14) for dissolving **2-Mn**, the reaction with bleach was complete within 1−2 min at room temperature. Surprisingly, along with the expected $[\mathbf{2\text{-}Mn(N)}]^-$ (20.4%), 6-azahemiporphycene $\mathbf{2_aMn(N)}$ (45%) and $\mathbf{2_bMn(N)}$ (13.4%) formed as byproducts. The exact ratio of these three products varied as a function of the ammonia and sodium hypochlorite concentration that were applied.

The (nitrido)manganese(V) corrole $[\mathbf{2\text{-}Mn(N)}]^-$ was isolated as a pink complex by preparative thin-layer chromatography (alumina) using dichloromethane/*n*-hexane mixture as eluent. Following recrystallization from dichloromethane/*n*-pentane mixtures, it was characterized by ^1H NMR, UV−vis spectroscopy, and CV (Figure 2). The electronic spectrum of $[\mathbf{2\text{-}Mn(N)}]^-$ consists of an intense Soret band at 408 nm with a characteristic Q-band at 565 nm. The diamagnetism (low spin, d^2) of this complex is apparent from its ^1H NMR spectrum, with four well resolved doublets (8.77, 8.83, 9.02, 9.34 ppm, $J \sim 4.8$ Hz) that correspond to the eight β-pyrrole protons. The phenyl protons resonate at 8.24, 8.30, 8.39, and 8.66 ppm. CV of $[\mathbf{2\text{-}Mn(N)}]^-$ shows one oxidative response with $E_{1/2} = 0.56$ V, only slightly less positive than that of the previously reported $[\mathbf{(tpfc)}Mn^V(N)]^-$ ($E_{1/2} = 0.59$ V).[2b]

^1H NMR examinations of the green fraction revealed it to be a mixture of two products, which were separated by another preparative TLC over alumina using a mixture of dichloromethane and *n*-hexane (1:1). The yield of the less polar product, $\mathbf{2_aMn(N)}$, was much larger than that of the more polar green band $\mathbf{2_bMn(N)}$. The UV−vis spectra of the complexes were quite similar, with one Soret band and one dominant Q-band: 451 and 618 nm for $\mathbf{2_aMn(N)}$, and 442 and 634 nm for $\mathbf{2_bMn(N)}$ (Figure 3a). These spectral features are characteristic of (nitrido)manganese(V)porphyrins, and the same holds for the very positive and irreversible redox process (1.23 V) obtained in the CV of $\mathbf{2_aMn(N)}$. High resolution ^1H NMR spectra were obtained for both complexes (Figure 3b), which also strongly implied a manganese(V) oxidation state therein. Different from $[\mathbf{2\text{-}Mn(N)}]^-$, eight rather than four β-pyrrole doublets are clearly seen [at 9.28, 9.14, 8.99, 8.88, 8.79, 8.71, 8.56, and 8.45 ppm for $\mathbf{2_aMn(N)}$ and at 9.49, 9.39, 9.24, 9.06, 8.93, 8.88, 8.65, and 8.51 ppm for $\mathbf{2_bMn(N)}$]. This led to the conclusion that these new complexes are of lower symmetry, lacking any symmetry element that would induce magnetic equivalence of different protons.

These spectroscopy-based conclusions were confirmed by the determination of the molecular structure of the main product, on green X-ray quality crystal obtained via evaporation of $\mathbf{2_aMn(N)}$ solutions in dichloromethane/*n*-hexane. This revealed it to be a neutral (nitrido)manganese(V) complex of 6-azahemiporphycene,[17] obtained via N atom insertion and ring expansion of the corrole macrocycle. The metalated corrole core is characterized by a domed structure with the Mn-ion deviating upward by 0.460(2) Å from the mean plane of the four pyrrole N-atoms toward the nitride axial ligand, at $Mn\equiv N_{nitrido} = 1.521(3)$ Å (as compared to a single Mn—Npy bond distance of 2.385 Å in $\mathbf{2\text{-}Mn^{III}(py)}$). The pyrrole rings bent slightly downward from the N4-plane in opposite direction, the dihedral angles between the individual pyrrole fragments, and the N4-plane ranging from 9.5(2) to 15.7(2)°. The N-atom insertion into the triaryl corrole moiety modifies the shape and geometry of the latter. It caused some disparity of the observed Mn-Npyrrole bond lengths: 1.946(3), 1.995(3), 1.987(3), and 2.020(3) Å, and also affected the relative orientation of the aryl substituents with respect to the core ring. The aryl group at the *meso* position near the expanded site is considerably flattened in comparison with the two aryls at the other *meso* positions, as a result of smaller hindrance between the H-atoms at the β-pyrrole C-atoms of the corrole and at the *ortho* positions of the proximate phenyl rings, but an increased π-electron delocalization in the molecule. The corresponding dihedral angles between the aryl rings and the N4-plane are 65.0(1) and 76.3(1)° at the nonexpanded *meso* sites (as usually observed in triaryl corroles and tetra-aryl porphyrins) and 32.9(1)° at the expanded site. Moreover, in the former case the nitrophenyl rings point outward in equatorial directions, the "*meso*" C-atom and the aryl connected to it in the expanded section are folded by about 20° upward toward the axial nitrido ligand. In all three nitrophenyl residues the nitro groups are nearly coplanar with the phenyl rings.

The identical MS spectra of $\mathbf{2_aMn(N)}$ and $\mathbf{2_bMn(N)}$, as well as the similar NMR spectra, clearly suggested that these two complexes are isomers obtained via N atom insertion between different C atoms of the corrole skeleton (Figure 4). Insertion between the directly bound (not bridged) pyrrole rings, as reported for ammonia/bleach treatment of **(tpfc)Ir**,[20] could be ruled out because the NMR spectra of such complexes (azaporphyrins) are characterized by 4 rather than 8 β-prrole protons. Distinction between the remaining possibilities, 5-, 9-, or 10-azahemiporphycene, could not be currently achieved because all attempts of obtaining X-ray quality crystals of $\mathbf{2_bMn(N)}$ were unsuccessful.

Another interesting observation was obtained when a different approach to synthesize $[\mathbf{2\text{-}Mn(N)}]^-$ was applied. Nitrogen atom transfer from the (nitrido)manganese(V) salen **3** to **(tpfc)Mn** was reported as an excellent pathway for clean

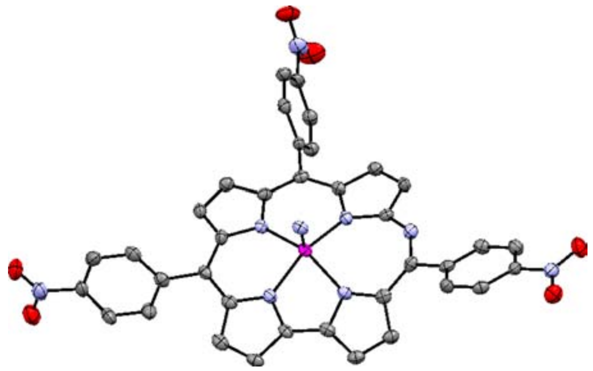


Figure 4. ORTEP diagram of **2$_a$Mn(N)** with ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

transformation into [**(tpfc)Mn(N)**]$^-$.[2b] But when **3** was reacted with **2-Mn** (Scheme 1), **2$_a$Mn(N)** was obtained as the only product. Its yield relative to **2-Mn** was 47%, which is quite high considering that two N atoms were supplied by complex **3**. An intriguing observation is that [**2-Mn(N)**]$^-$, once isolated from the earlier described bleach reaction, did not transform to **2$_a$Mn(N)**. This suggests that oxidative conditions are required for the nitrogen insertion reaction. Support for this hypothesis comes from the work of Paolesse and co-workers who have reported that nucleophilic attack of amines on oxidized free-base corroles lead to the formation of 6-azahemicorphycenes.[17]

■ CONCLUSION

We report the syntheses of 5,10,15-tris(4-nitrophenyl)corrole complexes with (pyridine)manganese(III), (chloro)manganese(IV), and (nitrido)manganese(V), and their characterization by UV−vis, ^{1}H NMR, X-ray crystallography, and CV. A comparison with the analogous 5,10,15-tris(pentafluorophenyl)corrole complexes reveals that the high-valent manganese oxidation states are more accessible when chelated by 5,10,15-tris(4-nitrophenyl)corrole, but also that they are more vulnerable to oxidative ring expansion. The exposure to ammonia/bleach leads to (nitrido)manganese(V) complexes of isomeric azahemiporphycene, of which the 6-aza isomer was fully characterized by X-ray crystallography.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures S1 and S2 with ORTEP diagrams of the complexes **2-Mn(Py)** and **2-MnCl**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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