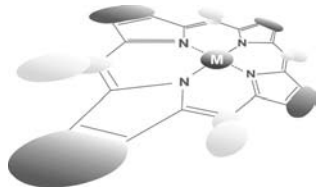
Journal of Porphyrins and Phthalocyanines
J. Porphyrins Phthalocyanines 2010; **14**: 615–620
DOI: 10.1142/S1088424610002434

Published at http://www.worldscinet.com/jpp/



Water-soluble manganese(III) corroles and corresponding (nitrido)manganese(V) complexes

Irena Saltsman[a◊], **Israel Goldberg***[b◊] **and Zeev Gross***[a◊]

[a] *Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel*
[b] *School of Chemistry, Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel*

Received 28 March 2010
Accepted 31 May 2010

ABSTRACT: Corroles that carry either two or three *ortho*-pyridyl groups at the *meso*-carbon atoms form stable manganese(III) complexes, from which corresponding water-soluble derivatives are obtained via *N*-alkylation. These syntheses and the spectroscopic features are disclosed, together with the molecular structure of the manganese(III) corrole that carries three *ortho*-pyridylium groups. All the manganese(III) corroles may be transformed to stable (nitrido)manganese(V) complexes, whose NMR spectra provide invaluable structural information regarding the identity and number of atropoisomers.

KEYWORDS: corroles, synthesis, manganese, NMR, X-ray crystallography.

INTRODUCTION

Manganese(III) corroles have lately been shown to display rich redox chemistry and to be effective oxidation catalysts [1, 2]. In addition, they serve as powerful catalytic antioxidants in models of various diseases [3]. Comparison with analogous porphyrins revealed that the chemistry of the corrole complexes is distinctively different and that they display unique chemistry in many cases [4]. One aspect where corroles outperform porphyrins is in the stabilization the [(nitrido)manganese(V)]$^{2+}$ moiety [2, 5], which is of importance regarding the development of catalytic systems for nitrogen atom transfer reactions and the fixation/activation of molecular nitrogen [6]. While the dianionic salen (sal) and porphyrin (por) ligands are long known to form quite stable [(por)Mn(N)] and [(sal)Mn(N)] complexes [7], their nitrogen atoms can still be transferred to manganese(III) complexes chelated by the trianionic corrolato ligands (cor) to form [(cor)Mn(N)]$^-$ complexes [2]. Electrochemical examinations further served to confirm the exceptional stability of the latter. The most recently introduced *para*-pyridylium-substituted corrole manganese(III) complexes were already used for two important medicine-oriented aspects: DNA intercalation, and the decomposition of reactive oxygen and nitrogen species in cellular models of various diseases [8]. We now present the synthesis and spectroscopic characterization of manganese(III) and (nitrido) manganese(V) corroles with *ortho*-pyridyl groups at the *meso*-carbon atoms, as well as the water-soluble *N*-alkylated analogs, including the molecular structure of the derivative with three *ortho*-pyridylium groups.

EXPERIMENTAL

General

NMR spectra were recorded at room temperature on a Bruker Avance 300 spectrometer (AV300) equipped with a QNP ^{1}H/^{19}F/^{13}C-2H 5 mm probe head (operating at 300 MHz for ^{1}H and 282 MHz for ^{19}F) or on a Bruker Avance 500 spectrometer (AV500) equipped with a bbo probe head (operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C). Chemical shifts are reported in ppm relative to solvent signals (δ_H = 1.94 for acetonitrile). Coupling constants (*J*) are reported in Hz. A HP 8452A diode array spectrophotometer was used to record the electronic spectra. Mass spectroscopy was performed by either ESI on a Waters Micromass LCT Premier instrument with nitrogen gas or by Waters MALDI-TOF instrument (direct

◊SPP full member in good standing

*Correspondence to: Zeev Gross, email: chr10zg@tx.technion.ac.il, fax: +972 4-8295703 and/or Israel Goldberg, email: goldberg@chemsg7.tau.ac.il, fax: +972 3-6409293

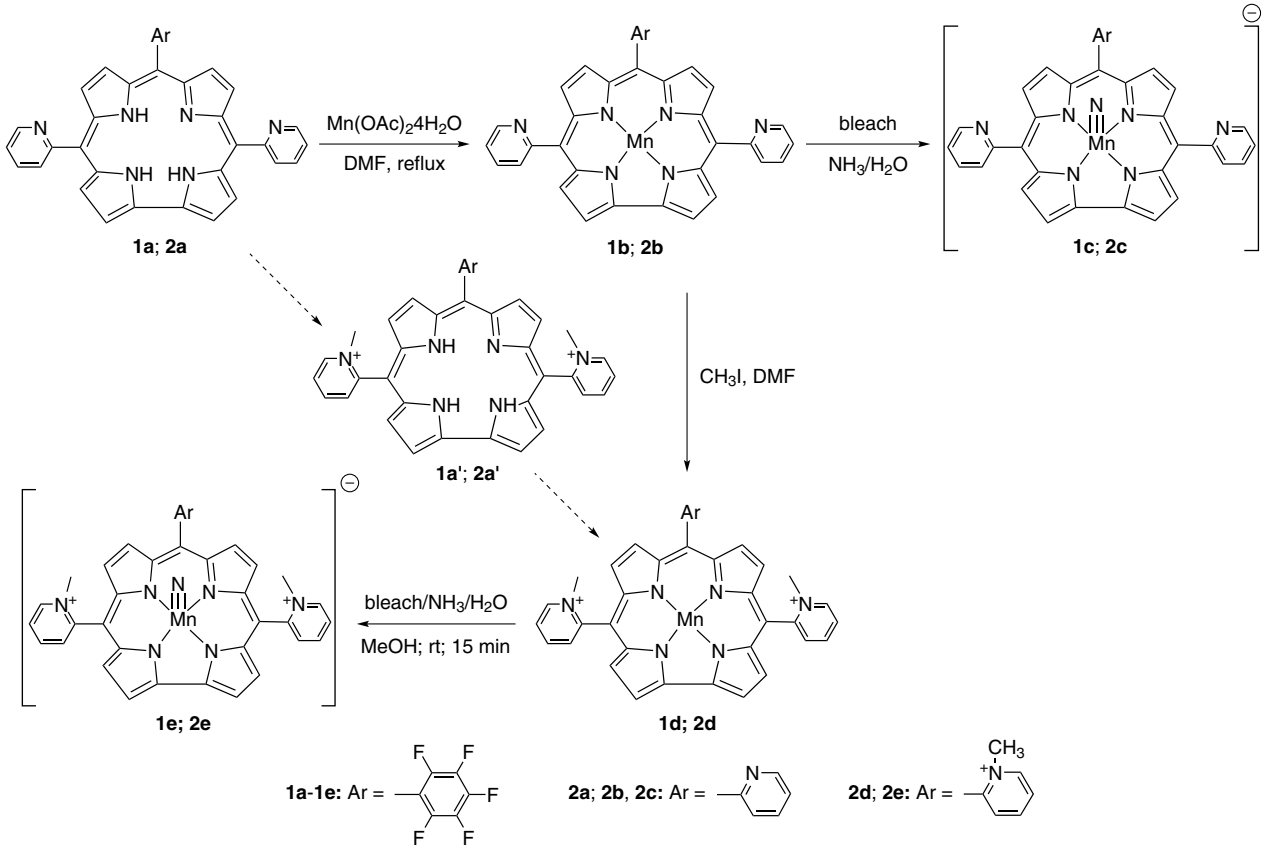
probe). All chemicals were used as received unless otherwise noted. Chromatography was performed on silica (Kieselgel 60, 230–400 mesh).

Synthetic methods

Compounds (**1a**) and (**2a**) were prepared according to the previously published procedure (Scheme 1) [9].

Preparation of the Mn(III) complex of 5,10,15-tris (*o*-pyridyl)corrole (2b), and the Mn(III) complex of 10-(pentafluorophenyl)-5, 15-bis(*o*-pyridyl)corrole (1b). Based on our previously published procedure [1b], samples of **2a** (50 mg, 86 μmol) or **1a** (50 mg, 75 μmol) and manganese(II) acetate tetrahydrate (221 mg, 900 μmol) were dissolved in DMF (10 mL) and heated to reflux for 20 min. Evaporation of the solvent, followed purification by column chromatography on silica gel (5% MeOH in ethyl acetate for **2b**; ethyl acetate/hexanes (9:1) for **1b**), resulted in the isolation of **2b** (49 mg, 89%) and of **1b** (37 mg, 69%). **2b.** R_f (silica, ethyl acetate) = 0.47. MS (MALDI-TOF) LD^+ (acetonitrile): *m/z* 583 $[M - H]^+$. UV-vis (acetonitrile): λ_{max}, nm (log ε) 408 (9.4), 476 (5.3), 592 (2.6), 642 (2.8). **1b.** R_f (silica, ethyl acetate) = 0.75. MS (MALDI-TOF) LD^+ (acetonitrile): *m/z* 670 $[M]^+$. UV-vis (methanol): λ_{max}, nm (log ε) 400 (9.1), 418 (10.3), 458 (6.6), 624 (2.8). ^{19}F NMR (282 MHz; CD_3CN): δ_F, ppm -140.82 (2F, br s, *ortho*-F), -156.18–156.48 (1F, m, *para*-F), -164.35–-164.93 (2F, m, *meta*-F).

Preparation of the Mn(III) complex of 5,10,15-tris (*N*-methyl-*o*-pyridylium)corrole (2d) and the Mn(III) complex of 10-(pentafluorophenyl)-5, 15-bis(*N*-methyl-*o*-pyridylium)corrole (1d). **1b** and **2b** were dissolved in the minimum volume of DMF and excess of methyl iodide (100 equiv.) was added to the solutions. Reaction mixtures were stirred at room temperature overnight. A small amount of methanol and threefold excess of diethyl ether were added to the reaction mixtures. Each precipitated product was collected and washed with additional portion of diethyl ether. The residues were dissolved in acetonitrile (grade HPLC) and carefully separated by chromatographic column (silica gel, $KCl(H_2O$, sat.$):H_2O$:acetonitrile, 1:1:8), resulted 75% of **2d** and 77% of **1d** yields, as dark-green solids. **2d.** R_f (silica, $KNO_3(H_2O$, sat.$):H_2O$:acetonitrile, 1:1:8) = 0.24. MS (MALDI-TOF) LD^+ (acetonitrile): *m/z* 596 $[M - (2 \times CH_3)]^+$. MS ESI^+ (acetonitrile:H_2O, 50:50): *m/z* 208 $[M]^{3+}/3$. UV-vis (methanol): λ_{max}, nm (log ε) 416 (9.2), 478 (20.1), 610 (4.2). **1d.** R_f (silica, $KNO_3(H_2O$, sat.$):H_2O$:acetonitrile, 1:1:8) = 0.78. UV-vis (acetonitrile): λ_{max}, nm (log ε) 402 (3.4), 476 (6.7), 630 (1.2). ^{19}F NMR (282 MHz; CD_3CN): δ_F, ppm -119.29 (2F, br s, *ortho*-F), -153.63–-154.31 (1F, m, *para*-F), -156.78–-157.91 (2F, m, *meta*-F). MS ESI^+



Scheme 1. Synthetic routes for the manganese(III) and (nitrido)manganese(V) corroles

(acetonitrile:H_2O, 50:50): *m/z* 350 $[M]^{2+}/2$, 370.5 [M + $CH_3CN]^{2+}/2$.

Preparation of the (nitrido)Mn(V) complexes of 5,10,15-tris(*o*-pyridyl)corrole (2c); of 10-(pentafluorophenyl)-5,15-bis(*N*-methyl-*o*-pyridylium)corrole (1e); of 10-(pentafluorophenyl)-5, 15-bis(*o*-pyridyl)corrole (1c); and of 5,10,15-tris(*N*-methyl-*o*-pyridylium)corrole (2e). Based on the previously published procedure [2b] samples 10 mg (17 μmol) of **1b**; **2b**; **1d** or **2d** (14 μmol) were added to a 25 mL flask and dissolved in 10 mL of methanol. 15 equiv. (7 μL, 17.6 μmol) of NH_4OH and 6 equiv. (3.7 mL, 70.7 μmol) of NaOCl were added to the solution. Immediately, the solution color changed from green to purple-green. The reaction was monitored by UV-vis. The solution was dried by sodium sulfate, filtered and evaporated to dryness, affording **2c** (9.5 mg, 93%), **1c** (9.3 mg, 91%), **1e** (9.2 mg, 90%) and **2e** (7.6 mg, 85%). **2c.** R_f (silica, ethyl acetate/methanol, 1:1) = 0.68. ^{1}H NMR (500 MHz, CD_3CN): δ_H, ppm 9.14 (2H, d, ^3J(H,H) = 4.03 Hz, pyrrole-*H*), 9.09 (2H, d, ^3J(H,H) = 5.50 Hz, pyrrole-*H*), 9.04 (1H, br s, pyridine-*H*), 8.96 (2H, d, ^3J(H,H) = 4.77 Hz, pyrrole-*H*), 8.79 (2H, d, ^3J(H,H) = 4.03 Hz, pyrrole-*H*), 8.61 (2H, d, ^3J(H,H) = 4.40 Hz, pyrrole-*H*), 8.44 (2H, d, ^3J(H,H) = 7.89 Hz, pyridine-*H*), 8.17 (2H, t, ^3J(H,H) = 7.52 Hz, pyridine-*H*), 8.13 (1H, t, ^3J(H,H) = 7.15 Hz, pyridine-*H*), 7.70-7.65 (4H, m, pyridine-*H*). MS (MALDI-TOF) LD$^-$ (acetonitrile): *m/z* 595 $[M]^-$. UV-vis (methanol): λ_{max}, nm (log ε) 434 (65.6), 546 (4.8), 588 (12.4). **1e.** R_f (silica, ethyl acetate:methanol, 1:1) = 0.80. ^{1}H NMR (500 MHz, CD_3CN): δ_H, ppm 9.37 (1H, d, ^3J(H,H) = 6.05 Hz, pyridine-*H*), 9.33 (1H, d, ^3J(H,H) = 4.77 Hz, pyrrole-*H*), 9.20 (1H, d, ^3J(H,H) = 6.24 Hz, pyridine-*H*), 9.10–9.07 (1H, m, pyridine-*H*), 9.03 (1H, d, ^3J(H,H) = 7.70 Hz, pyridine-*H*), 8.89 (1H, t, ^3J(H,H) = 7.70 Hz, pyridine-*H*), 8.82–8.78 (3H, m, pyrrole-*H*), 8.71 (1H, d, ^3J(H,H) = 4.58 Hz, pyrrole-*H*), 8.69 (2H, d, ^3J(H,H) = 4.03 Hz, pyrrole-*H*), 8.67 (1H, t, ^3J(H,H) = 4.95 Hz, pyrrole-*H*), 8.62 (1H, t, ^3J(H,H) = 7.70 Hz, pyridine-*H*), 8.46–8.40 (2H, m, pyridine-*H*), 4.38 (s) and 4.37 (3H, s, C*H*$_3$), 3.79 (s) and 3.77 (3H, s, C*H*$_3$). ^{19}F NMR (282 MHz, CD_3CN): δ_F, ppm -140.55–-141.37 (2F, m, *ortho*-F), -157.74 (1F, t, ^3J(F,F) = 20.9 Hz, *para*-F), -165.25–-165.32 (2F, m, *meta*-F). MS ESI$^+$ (acetonitrile:H_2O, 50:50): *m/z* 357 $[M]^+/2$. UV-vis (methanol): λ_{max}, nm (log ε) 430 (3.3), 582 (1.1). **1c.** R_f (silica, ethyl acetate) = 0.85. ^{1}H NMR (500 MHz, CD_3CN): δ_H, ppm 9.16 (2H, d, ^3J(H,H) = 3.67 Hz, pyrrole-*H*), 9.09 (2H, br s, pyridine-*H*), 8.99 (2H, d, ^3J(H,H) = 4.40 Hz, pyrrole-*H*), 8.82 (2H, d, ^3J(H,H) = 3.67 Hz, pyrrole-*H*), 8.59 (2H, d, ^3J(H,H) = 4.40 Hz, pyrrole-*H*), 8.44 (2H, d, ^3J(H,H) = 7.70 Hz, pyridine-*H*), 8.18 (2H, t, ^3J(H,H) = 7.34 Hz, pyridine-*H*), 7.74–7.68 (2H, m, pyridine-*H*). ^{19}F NMR (282 MHz, CD_3CN): δ_F, ppm -140.45 (1F, dd, ^3J(F,F) = 25.6 Hz, ^4J(F,F) = 7.9 Hz, *ortho*-F), -141.09 (1F, dd, ^3J(F,F) = 25.4 Hz, ^4J(F,F) = 7.9 Hz, *ortho*-F), -158.87 (1F, t, ^3J(F,F) = 19.7 Hz, *para*-F), -165.90–-166.45 (2F, m, *meta*-F). MS (MALDI-TOF) LD$^-$ (acetonitrile): *m/z* 684 $[M]^-$. UV-vis (acetonitrile): λ_{max}, nm (log ε) 432 (41.5), 548 (4.2), 584 (6.9). **2e.** R_f (silica, KCl(H_2O, sat.):H_2O: acetonitrile, 1:1:8) = 0.31. MS ESI$^+$ (acetonitrile:H_2O, 50:50): *m/z* 640 $[M]^{2+}$. UV-vis (methanol): λ_{max}, nm (log ε) 432 (78.6), 552 (17.8), 588 (23.7).

Crystallography

The diffraction measurements were carried out on a Nonius KappaCCD diffractometer, using graphite monochromated MoKα radiation (λ = 0.7107 Å). Crystal data: $(C_{37}H_{35}MnN_8O_2)^{3+}\cdot 3I^-$, orthorhombic, space group *Pbcn*, MW = 1059.37, *a* = 10.0388(2), *b* = 18.7942(5), *c* = 20.1470(7) Å, *V* = 3801.2(2) Å^3, T =110(2) K, *Z* = 4, D_{calc} = 1.851 g.cm^{-3}, μ(MoKα) = 2.83 mm^{-1}, 4531 unique reflections, R_1 = 0.068 for 3677 reflections with $I_o > 2\sigma(I_o)$, wR_2 = 0.221 for all unique data.

RESULTS AND DISCUSSION

The corrole ligands **1a** and **2a** were prepared via the condensation of 5-(2-pyridyl)dipyrromethane with either pentafluorophenylbenzaldehyde or 4-pyridinecarboxaldehyde, followed by subsequent oxidation by DDQ, as described by Saltsman and co-workers [9]. This was followed by insertion of manganese to afford complexes **1b** and **2b**, which were *N*-methylated by iodomethane, leading to the water-soluble complexes **1d** and **2d** (Scheme 1). This reaction scenario is preferable to the *N*-alkylation/metal insertion route (indicated by the broken arrows in Scheme 1), since we observed that the inner nitrogen atoms in the free-base corroles also react with iodomethane (easily observable by new ^{1}H NMR resonances at <0 ppm due to N-CH_3 moieties). Treatment of complexes **1d** and **2d** with bleach/ammonia led to the (nitrido)manganese(V) corroles **1e** and **2e**, respectively. The analogous complexes **1c** and **2c**, with non-alkylated pyridine substituents, were also prepared by the same procedure, from **1b** and **2b**, respectively.

The manganese(III) complexes are paramagnetic and the constitution of these compounds can hence not be confirmed by ^{1}H NMR spectroscopy. On the other hand, changes in the electronic spectra are very distinctive when it comes to the transformation of manganese(III) to (nitrido)manganese(V) corroles. This is shown in Fig. 1, for the transformation of **1b** to **1c**. While the electronic spectra of the manganese(III) corroles is characteristically rich throughout the visible range (bands I → VI in Boucher's nomenclature) [10], the products display a sharp Soret band and a prominent absorption centered about 580 nm that is distinctive of (nitrido)manganese(V) porphyrinoids.

The most valuable tool regarding unambiguous identification of a (nitrido)manganese(V) moiety in **1c** and **2c** is NMR spectroscopy, which is characterized by high-resolution resonances indicative of diamagnetic complexes. The diamagnetism by itself is fully (and only)

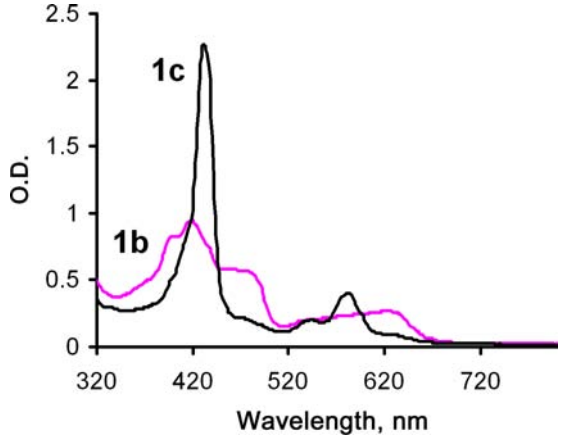


Fig. 1. Spectral changes upon treatment of manganese(III) corrole **1b** (λ_{max} = 418 nm; ~10^{-5} M) in MeOH with ammonia (3.6×10^{-4} M)/bleach (1.4×10^{-4} M) in H_2O at 25 °C, indicating its transformation to (nitrido)manganese(V) complex **1c** (λ_{max} = 432 nm)

consistent with a Mn^{5+} ion whose low-spin d^2 is enforced by a strong π-donating (and triply bound) N^{3-} ligand. The additional information that is obtainable from the ^{1}H NMR spectra is shown in Fig. 2(a), for complex **1c**. The four doublets (between 9.16 and 8.59 ppm) with small *J* coupling constants (3.67 and 4.40 Hz) are safely assigned to the four kinds of β-pyrrole protons [11], while the four other resonances are fully consistent with the hydrogen atoms on the *meso*-pyridine substituents. Complex **1c** should be a mixture of three different atropoisomers with respect to the relative orientations of the N-atoms of the pyridine rings (α or β) and the (nitrido)manganese(V) moiety (A or B): αAα, αBα and αAβ (≡ αBβ), where α *vs.* β and A *vs*. B are used as abbreviations for "above *vs.* below the corrole plane". This phenomenon is, however, not reflected in the ^{1}H spectrum, suggesting that rotation of the pyridine rings is fast on the ^{1}H NMR time scale at

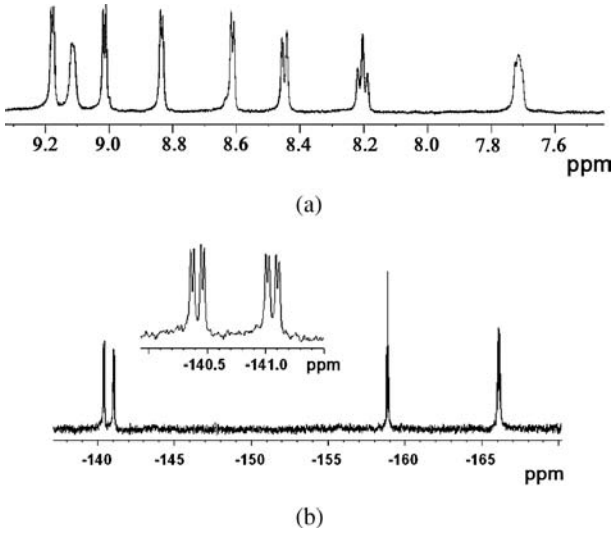


Fig. 2. ^{1}H (a) and ^{19}F (b) NMR spectra of (nitrido)manganese(V) complex **1c**

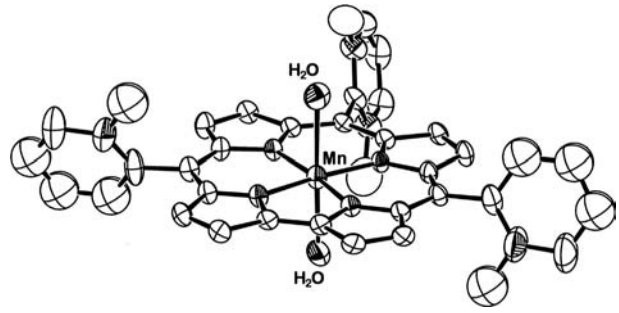


Fig. 3. ORTEP view of the molecular structure of complex **2d·(H$_2$O)$_2$**, characterized by a *C*2 symmetry. The empty ellipsoids indicate the two disordered orientations of the methylpyridinium group on *C*10 around the two-fold axis

room temperature. Nevertheless, the non-equivalency of the above and below corrole plane due to the presence of the (nitrido)manganese(V) moiety in complex **1c** is evident in its ^{19}F NMR spectrum (Fig. 2(b)), since the differences in chemical shifts (in Hz) are larger. Particularly indicative for that purpose are the two sets of double doublets (rather than one set) of *ortho*-F resonances at -140.4 and -141.1 ppm that are obtained for the *meso*-C_6F_5 ring.

N-alkylation of the pyridine groups may safely be predicted to stop the abovementioned dynamic atropoisomerization progress, which we have previously verified by HPLC separation of the free-base αα and αβ isomers of **1a′** and the ααα, ααβ, and αβα– isomers of **2a′**. This is further illustrated in Fig. 3, which displays the molecular structure of the manganese(III) corrole **2d·(H$_2$O)$_2$** (with two additional weakly coordinated axial water ligands). The corrole molecule is located in the crystal on a *C*2 axis, which passes through the C1-C19 bond, the metal ion and the center of the methylpyridylium group at C10. Correspondingly, the latter exhibits a two-fold orientational disorder, while the methyl groups of the aryls located on C5 and C15 (which also reveal partial disorder due to loose crystal packing) point in opposite directions. The corrole macrocycle is essentially planar. The manganese ion is six-coordinate with a distorted octahedral environment characterized by Mn-N(pyrrole) equatorial distances of 1.894(5) and 1.912(5) Å and Mn-O(water) axial coordination bonds of 2.328(6) Å. The iodide counter ions are located in intermolecular voids between the corrole units.

Similar to the earlier discussion, the (nitrido) manganese(V) complexes of the *N*-alkylated corroles could be fully analyzed by NMR spectroscopy. What is more, it also allows for the appreciation of the relative amounts of the different atropoisomers. This is shown in Fig. 4, which compares the ^{1}H NMR spectra of the resonances due to the methyl groups in the *ortho*-pyridylium-alkylated free-base corrole **1a′** and in its corresponding (nitrido)manganese(V) complex **1e**. The two singlets at about 4.15 ppm in Fig. 4(a) may be straightforwardly assigned as reflecting the one kind only of methylpyridylium groups in each of the atropoisomers of **1a′** (αα and

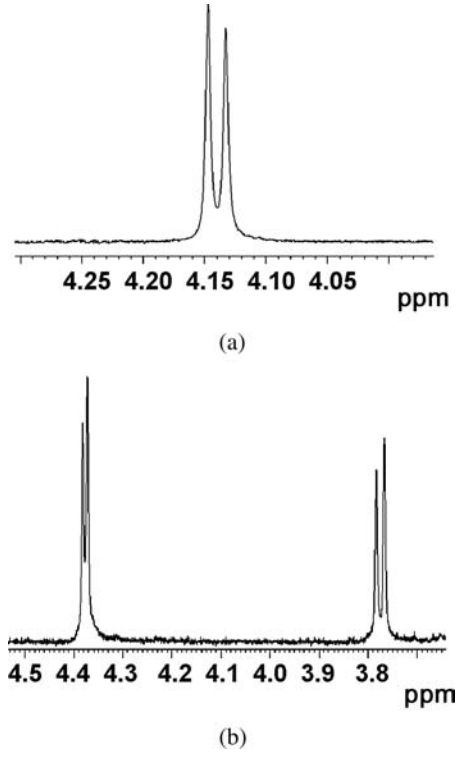


Fig. 4. Partial ^{1}H NMR spectra of a) **1a′** and b) **1e**, emphasizing the two and four different resonances assigned to methylpyridinium singlets, respectively

αβ). They are identical due to a σ_h symmetry operation in the former and due to a C_2 symmetry operation in the latter isomer, considering their effective C_s and C_2 point groups *(i.e.* taking into account that NH tautomerism is fast on the NMR scale), respectively. Due to the $[Mn{\equiv}N]^{2+}$ moiety in the corresponding (nitrido)manganese(V) corrole **1e**, its αα atropoisomer is actually a mixture of two different complexes with C_s symmetry: one wherein the two methyl groups and the nitrogen atom are syn to each other, and the other wherein they are anti (αAα and αBα, respectively). The αβ atropoisomer is a single complex (since αAβ ≡ αBβ), but its two methylpyridylium groups are now in a different magnetic environment because there is no symmetry operation that converts one into the other (*i.e.* it is of C_1 symmetry). Altogether, this readily explains the four singlets obtained between 3.77 and 4.38 ppm for **1e** (Fig. 4(b)) rather than only two singlets for **1a′** (Fig. 4(a))**.**

SUMMARY AND CONCLUSION

We have devised synthetic access to manganese(III) corroles with either two or three *ortho*-pyridyl *meso*-substituents, which upon *N*-alkylation are converted into water-soluble derivatives. These complexes have most recently disclosed as catalysts for decomposition of reactive oxygen and nitrogen species in both chemical and biochemical environments [3c, 12]. The X-ray crystal structure of 5,10,15-tris-(*ortho*-methylpyridylium)-corrolato manganese(III) revealed one particular atropoisomer, which displays a planar macrocycle due to the coordination of two axial water molecules to the metal. The corresponding (nitrido)manganese(V) derivatives are very stable low-spin d^2 complexes, whose diamagnetism allows for a detailed NMR-based structural analysis. The ^{19}F NMR spectra are particularly illuminating in terms of identifying that they are five-coordinated due to the strong *trans*-effect of the $[Mn{\equiv}N]^{2+}$ moiety.

Acknowledgements

This research was supported by the Israel Science Foundation, Grants 890015 (ZG) and 502/08 (IG). The funding of I.S. by the Center for Absorption in Science, Ministry of Immigration, is also acknowledged (KAMEA Foundation).

Supporting information

Crystallographic data for compound **2d·(H$_2$O)$_2$** have been deposited at the Cambridge Crystallographic Data Center (CCDC) under deposition number 780238. Copies can be obtained on request, free of charge, *via* www.ccdc.cam.ac.uk/conts/retrieving.html 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).

REFERENCES

1. a) Gross Z and Gray HB. *Adv. Synth. Catal.* 2004; **346**: 165–170. b) Gross Z, Golubkov G and Simkhovich L. *Angew. Chem. Int. Ed.* 2000; **39**: 4045–4048. c) de Visser SP, Ogliaro F, Gross Z and Shaik S. *Chem. Eur. J.* 2001; **7**: 4954–4960. d) Shen J, Ojaimi ME, Chkounda M, Gros CP, Barbe J-M, Shao J, Guilard R and Kadish KM. *Inorg. Chem.* 2008; **47**: 7717–7727. e) Broring M, Hell C and Brandt CD. *Chem. Commun.* 2007; 1861–1862. f) Bendix J, Golubkov G, Gray HB and Gross Z. *Chem. Commun.* 2000; 1957–1958.
2. a) Golubkov G, Bendix J, Gray HB, Mahammed A, Goldberg I, DiBilio AJ and Gross Z. *Angew. Chem., Int. Ed.* 2001; **40**: 2132–2134. b) Golubkov G and Gross Z. *J. Am. Chem. Soc.* 2005; **127**: 3258–3259. c) Lansky DE, Kosack JR, Narducci Sarjeant AA and Goldberg DP. *Inorg. Chem.* 2006; **45**: 8477–8479. d) Hai-Yang L, Tat-Shing L, Lam-Lung Y and Chang CK. *Org. Lett.* 2003; **5**: 617–620. e) Liu HY, Zhou H, Liu LY, Ying X, Jiang HF and Chang CK. *Chem. Lett.* 2007; **36**: 274–275. f) Aviv I and Gross Z. *Chem. Commun.* 2007; 1987–1999. g) Liu AU, Yam HY, Xie F, Li YT and Chang CK. *J. Am. Chem. Soc.* 2009; **131**: 12890–12891.
3. a) Mahammed A and Gross Z. *Angew. Chem., Int. Ed.* 2006; **45**: 6544–6547. b) Okun Z, Kupershmidt L, Amit T, Mandel S, Bar-Am O, Youdim MBH and

Gross Z. *ACS Chemical Biology* 2009; **4**: 910–914. c) Kanamori A, Catrinescu M-M, Mahammed A, Gross Z and Levin LA. *J. Neurochem.* 2010; **113**: 363–373.

4. a) Aviv-Harel I and Gross Z. *Chem. Eur. J.* 2009; **15**: 8382–8394. b) Goldberg DP. *Acc. Chem. Res.* 2007; **40**: 626–634. c) Gross Z and Gray HB. *Comments Inorg. Chem.* 2006; **27**: 61–72. d) Nardis S, Monti D and Paolesse R. *Mini-Rev. Org. Chem.* 2005; **2**: 355–374. e) Gryko DT. *Eur. J. Org. Chem.* 2002; 1735–1743.
5. a) Eikey RA, Khan SI and Abu-Omar MM. *Angew. Chem., Int. Ed.* 2002; **41**: 3591–3595. b) Zdilla MJ and Abu-Omar MM. *J. Am. Chem. Soc.* 2006; **128**: 16971–16979. c) Zdilla MJ, Dexheimer JL and Abu-Omar MM. *J. Am. Chem. Soc.* 2007; **129**: 11505–11511. d) Leeladee P and Goldberg DP. *Inorg. Chem.* 2010; **49**: 3083–3085.
6. a) Woo LK, Goll JG, Czapla DJ and Hays JA. *J. Am. Chem. Soc.* 1991; **113**: 8478–8484. b) Schrock RR. *Chem. Commun.* 2003; **19**: 2389–2391. c) Shaver MP and Fryzuk MD. *Adv. Synth. Catal.* 2003; **345**: 1061–1076.
7. a) Bottomley LA and Neely FL. *Inorg. Chem.* 1997; **36**: 5435–5439. b) Neely FL and Bottomley LA. *Inorg. Chim. Acta* 1992; **192**: 147–149. c) Groves JT and Takahashi T. *J. Am. Chem. Soc.* 1983; **105**: 2073–2074.
8. a) Gershman Z, Goldberg I and Gross Z. *Angew. Chem., Int. Ed.* 2007; **46**: 4320–4324. b) Fu BQ, Huang J, Ren L, Weng XC, Zhou YY, Du YH, Wu XJ, Zhou X and Yang GF. *Chem. Commun.* 2007; **31**: 3264–3266. c) Fu BQ, Zhang D, Weng XC, Zhang M, Ma H, Ma YZ and Zhou X. *Chem. Eur. J.* 2008; **14**: 9431–9441. d) Ma H, Zhang M, Zhang D, Huang R, Zhao Y, Yang H, Liu YJ, Weng XC, Zhou YY Deng MG, Xu L and Zhou X. *Chemistry–An Asian Journal* 2010; **5**: 114–122. e) Kupershmidt L, Okun Z, Amit T, Mandel S, Saltsman I, Mahammed A, Bar-Am O, Gross Z and Youdim MBH. *J. Neurochem.* 2010; **113**: 363–373.
9. Saltsman I, Botoshansky M and Gross Z. *Tetrahedron Lett*. 2008; **49**: 4163–4166.
10. Gouterman M. In *The Porphyrins*, Dolphin D. (Ed.) Academic Press: New York, 1978; pp 62–64.
11. Balazs YS, Saltsman I, Mahammed A, Tkachenko E, Golubkov G, Levine J and Gross Z. *Magn. Reson. Chem.* 2004; **42**: 624–635.
12. Eckshtain M, Zilbermann I, Mahammed A, Saltsman I, Okun Z, Maimon E, Cohen H, Meyerstein D and Gross Z. *Dalton Trans*. 2009; 7879–7882.