The X-ray structure, magnetic susceptibility, and high-field (high-frequency) EPR spectrum of manganese 5,10,15-tris(pentafluorophenyl) corrole unambiguously establish that the complex contains an isolated, slightly rhombic, manganese(II) center.

Manganese(II) porphyrins are very efficient catalysts for functionalization of hydrocarbons in processes that involve high valent intermediates. Spectroscopic identification of odd-spin manganese(III) and spin-coupled manganese(IV) porphyrins by magnetic resonance measurements is relatively straightforward, via utilization of EPR and NMR, respectively. However, even-spin manganese(III) porphyrins are EPR-silent (X-band) and their NMR spectra are not easily interpretable. For example, an early assignment of the origin of the paramagnetic shifts in manganese(III) porphyrin radical cations was recently revised, and there is some evidence indicating that the complexes might better be described as manganese(III) porphyrin radical cations. A recent development relevant to this question is the utilization of high-field (high-frequency) EPR (HF-EPR) spectroscopy for elucidation of the electronic structures of high-spin manganese(III) complexes.

The close relationship of porphyrins and corroles suggests that metallocorroles could also be very interesting catalysts. This proposal was only recently explored, taking advantage of the novel electron-poor 5,10,15-tris(pentafluorophenyl) corrole, H3tpfc, whose substitution pattern matches that of the most active porphyrin-based catalysts. First, it was demonstrated that the iron and rhodium complexes of H3tpfc are potent catalysts for oxygen and carbene transfer to olefins and alkanes, followed by full characterization of H3tpfc12 and its CrV O complexes. The manganese corrole [tpfc]Mn was also found to be an epoxidation catalyst, as well as an excellent precursor to a relatively stable oxomanganese(IV) corrole. The apparent importance of this result together with the rather limited information on the electronic structures of manganese corroles were the driving forces for the current investigations. A combination of HF-EPR spectroscopy, X-ray crystallography, and magnetic susceptibility measurements, led to the conclusion that [tpfc]MnOPPPh3 is an authentic manganese(III) complex that does not experience significant intermolecular interactions. The X-ray structure, magnetic susceptibility, and high-field (high-frequency) EPR spectrum of manganese 5,10,15-tris(pentafluorophenyl) corrole unambiguously establish that the complex contains an isolated, slightly rhombic, manganese(II) center. Since the consequences of lowered symmetry on the magnetic susceptibility measurements on manganese(II) porphyrin complexes have been the focus of much attention, the close relationship of porphyrins and corroles suggests that metallocorroles could also be very interesting catalysts. This proposal was only recently explored, taking advantage of the novel electron-poor 5,10,15-tris(pentafluorophenyl) corrole, H3tpfc, whose substitution pattern matches that of the most active porphyrin-based catalysts. First, it was demonstrated that the iron and rhodium complexes of H3tpfc are potent catalysts for oxygen and carbene transfer to olefins and alkanes, followed by full characterization of H3tpfc12 and its CrV O complexes. The manganese corrole [tpfc]Mn was also found to be an epoxidation catalyst, as well as an excellent precursor to a relatively stable oxomanganese(IV) corrole. The apparent importance of this result together with the rather limited information on the electronic structures of manganese corroles were the driving forces for the current investigations. A combination of HF-EPR spectroscopy, X-ray crystallography, and magnetic susceptibility measurements, led to the conclusion that [tpfc]MnOPPPh3 is an authentic manganese(III) complex that does not experience significant intermolecular interactions.

Obtaining X-ray quality crystals of [(tpfc)Mn] was a difficult task; NMR examination of material from different crystallization batches revealed significant variations in chemical shifts. Since we suspected that these differences were due to solvent coordination, we added external ligands to the recrystallization mixtures. These attempts finally met with success: with triphenylphosphine oxide as additive, X-ray quality crystals of [(tpfc)MnOPPPh3] were isolated. The structure of [(tpfc)MnOPPPh3] (Fig. 1) is quite different from that of the previously reported square planar manganese(III) corrole. In the latter complex the metal is located almost perfectly within the N4 plane and the macrocycle is planar, whereas in [(tpfc)Mn(OPPh3)] the manganese is 0.29 Å out of both the N4 and the corrole core planes. This causes some elongation of the average Mn–Npyrrole bonds [from 1.894 in [(e-7,13-mc)Mn] to 1.916 Å in [(tpfc)Mn(OPPPh3))] with slight deviations of the tpfc atoms from the mean plane. Another significant difference is the absence of interactions between the corroles in [(tpfc)Mn(OPPPh3)], which is a dominant factor in the structure of [(e-7,13-mc)Mn]. Rather, the potential empty space is occupied by the triphenylphosphine oxide ligand (Fig. 2). The absence of intermolecular interactions is also reflected in the magnetic susceptibility measurements on [(tpfc)Mn(OPPPh3)], performed in the temperature range 2–300 K. The magnetic moment of 4.88 μB confirms that the complex possesses a simple high-spin (S = 2) ground state; and the very flat plateau in the Meff vs. temperature plot down to 10 K (Fig. 3) is perfectly in line with the molecular packing deduced from the X-ray structure (Fig. 2).

Since the consequences of lowered symmetry on the electronic structures of corrole vs. porphyrin complexes have
Experimental and simulated HF-EPR spectra of \((\text{tpfc})\text{Mn(OPPh}_3\)) at two different frequencies (285 and 345 GHz) and at two different temperatures (5 and 30 K). One of the most sensitive lines to deviation from axiality is quite small. We thus conclude that the electronic deviation from axiality is quite small. We thus conclude that treating a corrolate as a trianionic porphyrinate is not unreasonable.

We have fully characterized a manganese complex of H_3tpfc. Employing three different methods, we have shown that \([(\text{tpfc})\text{Mn(OPPh}_3\))] contains an authentic, isolated S = 2 manganese(II) center.

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Notes and references

1. A major part of this work was first presented as Poster 23 in Contemp. Inorg. Chem.-II, March 12–15, 2000, College Station, Texas, and as Paper 293 in the 219th national ACS meeting in San Francisco, March 26–30, 2000. (b) abbreviations: tpcf and H_3tpfc; the trianions of 5,10,15-tris(pentafluorophenyl)corrole and 2,3,8,12,17,18-hexaethyl-7,13-dimethylcorrole, respectively.


10. Z. Gross, N. Galili and I. Saltsman, Angew. Chem., Int. Ed., 1999, 38, 1427; (b) H_3tpfc is commercially available (Strem Chemicals Inc.).


18. Crystal data: (tpfc)(Mn(OPPh_3)), C_{20}H_{24}F_{15}MnN_4O: M = 1126.68, monoclinic, space group P2_1/a, a = 13.883(2), b = 12.802(1), c = 25.952(3) Å, β = 100.31(1)°, V = 4537.9(9) Å^3, Z = 4, T = 98 K. D_{c} = 1.649 g cm^(-3), μ(Mo-Kα) = 0.44 mm^(-1), 10384 unique reflections, R_1 = 0.044 for 5262 observations with F > 2σ(F), R_1 = 0.117 (wR = 0.075) for all unique data, [Δ(Δ) ≤ 0.44 e Å^(-3)]. CCDC 182/1771. See http://www.rsc.org/suppdata/cc/b0/b006299p/ for crystallographic files in cif format.

19. The measurement was done on a pressed powder sample in a static field of 100 G on a Quantum Design MPMS SQUID magnetometer.
