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COMMUNICATION

Dipyrrinphenol–Mn(III) complex: synthesis, electrochemistry, spectroscopic characterisation and reactivity†

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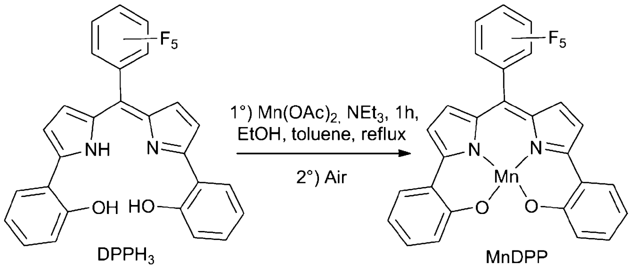
Herein, we report the manganese complex with a novel trianionic ligand, the pentafluorophenyldipyrrinphenol ligand $DPPH_3$. The X-ray crystal structure reveals that the Mn^{III} complex exists in a dimeric form in the solid state. Electrochemical studies indicate two quasi-reversible one electron oxidation processes. EPR data on the one electron oxidised species in solution support the formation of a monuclear Mn complex with an $S = 3/2$ spin system. Preliminary studies towards epoxidation reactions were tested in the presence of iodosylbenzene (PhIO) and are in favour of an oxygen-atom-transfer (OAT) reaction catalyzed by the Mn^{III} complex.

The development of robust molecular catalysts to drive oxidation reactions in environmentally benign conditions is an ongoing challenge and a priority for chemists. Prototypal metal complexes in this field are based on well-established porphyrin,[1] phtalocyanine,[2] corrole[3] and salen[4] derivatives. These molecular systems act as monooxygenase catalysts upon activation with oxygen containing oxidants to produce high valent metal–oxo species. TetraAmidoMacrocyclic Ligands (TAML) developed by Collins and collaborators are also known to give access to reactive high-valent metal–oxo derivatives that lead to degradation of persistent organic pollutants.[5] The difference in reactivity between these families of complexes bearing the same metal ion evidences the primary importance of the ligand set surrounding the metal ion that shapes the electronic structure of the active species. In this communication, we describe the synthesis, spectroscopic and structural characterisation of a manganese(III) derivative of a new ligand: pentafluorophenyldipyrrinphenol ($DPPH_3$). Preliminary results concerning the epoxidation of cyclooctene using iodosylbenzene (PhIO) as terminal oxidant are also presented.[6]

The dipyrrinphenol ligand can be seen as a combination of structural features from a porphyrin and a salen core. The synthesis of the ligand $DPPH_3$ was realised following the condensation of 2-*ortho*anisylpyrrole with pentaflurobenzaldehyde in acidic conditions followed by classical deprotection of the methoxy groups with BBr_3 according to Nabeshima's strategy.[7] Insertion of manganese in the free base $DPPH_3$ was realised by refluxing with an excess of $Mn(OAc)_2$ in a toluene–EtOH mixture in the presence of NEt_3 as base under aerobic conditions (Scheme 1). Color changes from blue to green and usual analytical techniques probe the insertion of the metal ion in the N_2O_2 coordination environment.



Scheme 1

Single crystals of MnDPP of suitable quality for X-ray analysis, were produced by slow evaporation of acetonitrile in air.

The crystal structure shows that the complex exists as a dimer of [MnDPP] in the solid state (see Fig. 1). The lack of counter anions attests the presence of a manganese(III) ion in the trianionic N_2O_2 coordinating site. Each manganese ion adopts a square pyramidal geometry, with the DPP ligand as the basal plane and the oxygen atom of a phenolato group bridging two monomeric units.[8] We note also a particularly short intradimer Mn–Mn distance at 3.146 Å.[9] The oxygen atom of the bridging phenol is tilted towards the opposite manganese ion and departs from the N_2O_2 mean plane by 0.773 Å, while the Mn ion is found at 0.337 Å outside the basal plane.

Mass spectrometry of the isolated compound using ESI technique shows a major peak at 569 corresponding to [MnDPP + $Na^+]^+$. A peak at 610 attributable to a monomeric manganese

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complex with an axial acetonitrile molecule to $[MnDPP(CH_3CN) + Na^+]^+$ was also detected under our experimental conditions.

Typically, Mn^{III} (d^4, $S = 2$) is spectroscopically silent in the conventional EPR experiment (X-Band, 9 GHz) but transitions can be observed using parallel polarisation EPR. The parallel mode EPR spectrum of $[MnDPP(CH_3CN)]$ in acetonitrile exhibits six well-resolved hyperfine lines centred at $g \approx 8.05$ that are split by 39.2 G. The morphology and field position of these signals are consistent with previously reported mononuclear Mn^{III} complexes in similar geometries.[10] Although MnDPP was evidenced in the monomeric form in solution by mass spectrometry and EPR spectroscopy, attempts to crystallise the manganese monomer were unfruitful to date.

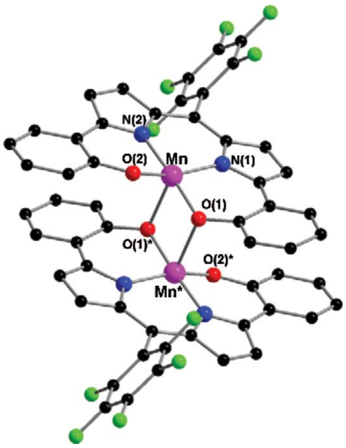


Fig. 1 Crystal structure of $[MnDPP]_2$. Hydrogen atoms are omitted for clarity. Selected metric distances (Å): Mn–N(1) 1.954(3), Mn–N(2) 1.942(3), Mn–O(1) 1.909(3), Mn–O(2) 1.854(3), Mn–O(1)* 2.206(3), Mn–Mn* 3.146(13). The asterisk indicates the symmetry operation ($1 - x$, $-y$, $-z$).

Running the cyclic voltammogram of the manganese complex in acetonitrile, (Fig. 2) we observed two quasi-reversible anodic processes of equal intensity at 0.67 V and 1.23 V *vs.* SCE, that were attributed to the Mn^{IV}/Mn^{III} couple and to a putative Mn^{V}/Mn^{IV} couple, respectively. Upon addition of water, we noticed a shift of the redox potential of the $Mn^{IV/III}$ couple by 60 mV to less positive values while the second oxidation process becomes irreversible. These effects on the electrochemical response in the presence of water imply the participation of water molecules in the coordination sphere of the manganese centre.[11]

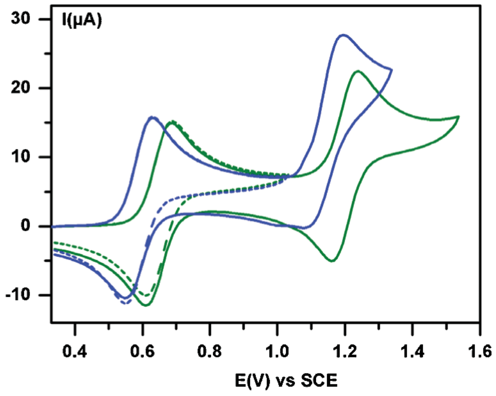


Fig. 2 Cyclic voltammetry of MnDPP (2 mM) at 0.1 V s^{-1}, $T = 253$ K, on a glassy carbon electrode in acetronitrile (0.2 M NBu_4PF_6), (green line) and in acetonitrile containing 6% water (blue line). The corresponding dotted lines indicate the reversible nature of the first oxidation wave.

Exhaustive bulk electrolysis was performed both in pure and wet acetonitrile at 253 K, at + 0.8 V/SCE and coulometry confirmed a one-electron oxidation process. Furthermore, the chemical reversibility of the oxidation process was supported by the identical electrochemical response on the electrolysed solution in comparison with the initial one. This process is associated with a colour change from green to intense dark green. Monitoring this oxidation process by UV-Visible spectroscopy shows among other changes the appearance of two absorption bands at 870 and 970 nm (Fig. 3). These electronic features are reminiscent to the formation of a metalloradical type species. The electrochemical re-reduction of the oxidised species generated gave a spectrum corresponding to that initially observed for MnDPP, demonstrating the chemical reversibility of the one-electron electrochemical process.

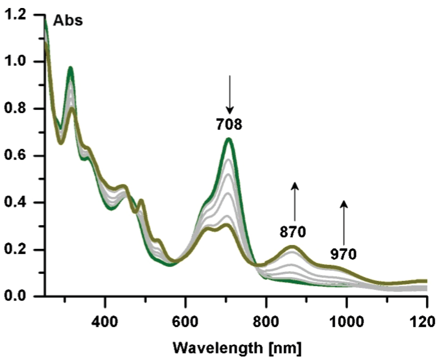


Fig. 3 UV-vis absorption spectra recorded in the course of the electrochemical oxidation of MnDPP at 0.8 V *vs.* SCE, Conditions: 0.2 M NBu_4PF_6, 1 mM solution in acetonitrile, $T = 253$ K, optical path: 0.5 mm.

Perpendicular mode X-band EPR data obtained at 5 K on the electrolysed solution in acetonitrile in the presence of water, indicate well-resolved (Fig. 4) signals with g_{eff} at 4.9, 3.0 and 1.8 compatible with the one electron oxidation of the Mn^{III} complex

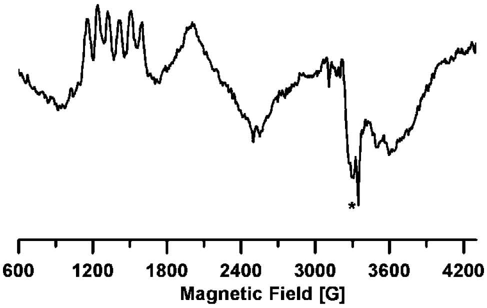


Fig. 4 Perpendicular mode EPR spectrum of a 2 mM solution of MnDPP in acetonitrile containing 6% water (0.2 M NBu_4PF_6) recorded after exhaustive reduction at 0.8 V *vs.* SCE; $T = 253$ K; working electrode: glassy carbon crucible; auxiliary electrode: Pt grid separated from the rest of the solution with a fritted glass. EPR recording conditions: microwave frequency 9.38 GHz; modulation frequency 100 kHz; microwave power 2 mW; modulation amplitude 1 mT; $T = 5$ K; time constant 160 ms. * trace of free Mn(II).

to a $S = 3/2$ spin system.[10,12] Only Mn^{55} hyperfine coupling was resolved for the $g = 4.9$ signal with an A value of 91 G.

Density functional theory (DFT) calculations were used to support this finding. The geometry optimisation of the pentacoordinated $[Mn(DPP)(OH_2)]$ monomer with a water molecule in apical position places the water molecule at 2.27 Å from the manganese centre, while the Mulliken atomic spin on manganese and the map of the spin density distribution are characteristic of a high-spin Mn^{III} centre (see SI†). Theoretical data on the oxidised complex $[Mn(DPP)(OH_2)]^+$ with a total spin state $S = 3/2$ lead to an optimised geometry with a $Mn–O_W$ distance of 2.24 Å. Interestingly, we found that the Mulliken atomic spin on manganese is 3.87 (a value close to four unpaired electrons) and the map of the spin density distribution (Fig. 5) reveals a spin density of essentially negative sign developed on the whole DPP ligand. In such a configuration, the quartet state of the oxidised complex results from an antiferromagnetic coupling between an $S_{Mn} = 2$ Mn^{III} ion and an $S_L = 1/2$ ligand radical. Thus the electronic structure is best described as $[Mn^{III}(DPP^{\bullet+})(OH_2)]^+$.

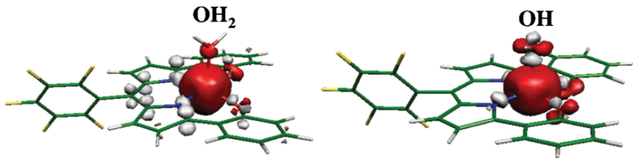
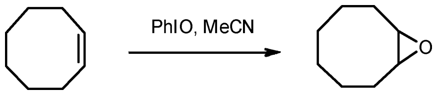


Fig. 5 Map of the spin density distribution for the quartet states of $[Mn(DPP)(OH_2)]^+$ (left) evidencing the antiferromagnetic coupling between a high spin Mn^{III} ion and a ligand $DPP^{\bullet+}$ radical and of $[Mn(DPP)(OH)]$ (right) showing a high spin Mn^{IV} ion.

As deprotonation of the water ligand may occur in the oxidised aqua complex under certain experimental conditions, a DFT study was also performed on the oxidised hydroxo monomer in the quartet state. A noticeable shrinking of the optimised $Mn–O_W$ distance was found at 1.79 Å and the Mulliken atomic spin on manganese ρ_{Mn} falls to 2.99 corresponding to three unpaired spins. As shown in Fig. 5, the spin density map now reflects a metal centred oxidation. Kurahashi *et al.* have recently proposed such an electronic reshuffling in the case of a SalenMn complex.[12]

The preliminary catalytic performances of DPPMn were evaluated towards the epoxidation of cyclooctene in the presence of iodosylbenzene, a nucleophilic mono oxidizing species (Table 1).

Table 1 Catalytic activity



Entry	DPPMn (μmol)	PhIO (μmol)	Temp.	Epoxide (GC-yield) (%)
1[a]	1	100	rt	38
2[a]	1	10	rt	97
3[a]	1	10	60 °C	78
4	0	100	rt	0

[a] Reaction conditions: 1 μmol of MnDPP, ξ μmol PhIO, 1000 μmol alkene, 2 mL solvent.

In acetonitrile, at room temperature, MnDPP catalyzed efficiently the oxidation of the alkene to the corresponding epoxide. Indeed, in the presence of 10 equiv., the GC yield of the epoxide was 97%. This observation pertains to the formation of a high valent Mn(V)–oxo species. A recent report has indeed shown the formation of a genuine manganese(V)–oxo species within the same family of ligands upon treatment of the corresponding Mn(III) complex with peroxynitrite ions ($ONOO^-$).[13] However no reactivity towards organic substrates was reported.

These preliminary catalytic results clearly indicate that MnDPP constitutes an efficient catalyst for the epoxidation of alkene. Further work on the catalytic activities of this novel manganese complex using other oxidising agents are currently ongoing in our labs.

Conclusion

We described here the manganese complex of the pentafluorophenyldipyrrinphenol ligand, DPPH$_3$. We have shown the ability to transfer an oxygen atom to organic substrates. Collected spectroscopic and theoretical data converge towards a structure–reactivity relationship similar to those of Salen and Corrole. We believe that the synthetic versatility of the DDPH$_3$ core will allow us to efficiently tune the reactivity of the corresponding metal complexes. Furthermore, the participation of the ligand in the redox properties of the metal complex holds the promise of an intriguing non-innocent ligand.[14] Work is underway in our labs to develop the coordination chemistry of the dipyrrinphenol ligand.

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