# Electrochemical Formation and Reactivity of a Manganese Peroxo Complex: Acid Driven H<sub>2</sub>O<sub>2</sub> Generation vs. O-O Bond Cleavage

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# I. Formation of [Mn<sup>III</sup>L(O<sub>2</sub>)]

# I.1 CV analysis - Parameters for CV simulations

Simulations were obtained using Digielch program.[1] The electrochemical parameters of  $O_2$  and  $[Mn^{II}(L)]^+$  were first obtained separately before analysing the  $\{O_2 + [Mn^{II}(L)]^+\}$  system.

#### I.1.1. O<sub>2</sub> electrochemical characterization in DMF

O<sub>2</sub> in dry DMF leads to a one electron reversible wave. Simulation of this wave allows evaluating the following parameters taking into account that the electrode surface is 0.07 cm<sup>2</sup>:  $E_{O_2/O_2^{\bullet-}}^0 = -0.865$  V vs. SCE,

$$k_{O_2/O_2^{\bullet^-}}^S = 0.015$$
 cm/s (taking  $\alpha = 0.5$ ) and  $D_{O_2} = D_{O_2^{\bullet^-}} = 4.6 \times 10^{-5}$  cm<sup>2</sup>/s (figure S1a). Those parameters are

slightly different to those published in the literature.[2-3]

Upon scanning toward more negative potential, a second large one electron wave appears corresponding to the reduction of superoxide anion (through a CPET process)[4] thanks to the presence of residual water. No third wave is observed. A wave is observed on the reverse scan (figure S1b), tentatively attributed to OH<sup>-</sup> oxidation.



Figure S1. (black) CV of DMF with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> saturated with air (1.0 mM O<sub>2</sub>) at 0.2 V/s at a glassy carbon disk electrode at 293 K. (red) simulation with  $E_{O_2/O_2^{\bullet-}}^0 = -0.865$  V vs. SCE,  $k_{O_2/O_2^{\bullet-}}^S = 0.015$  cm/s and  $D_{O_2} = 4.6 \times 10^{-5}$  cm<sup>2</sup>/s.

#### I.1.2. [Mn<sup>II</sup>(L)]<sup>+</sup> electrochemical characterization in DMF

Cyclic voltammetry of  $[Mn^{II}(L)]^+$  complex leads to a quasi-reversible oxidation wave (figure S2). Simulation of this wave assuming a simple one electron Mn(III)/Mn(II) conversion leads to the following parameters  $E^0_{Mn^{III}/Mn^{II}} = 0.329$  V vs. SCE,  $k^S_{Mn^{III}/Mn^{II}} = 0.00095$  cm/s (taking  $\alpha = 0.5$ ) and  $D_{Mn} = 4 \times 10^{-6}$  cm<sup>2</sup>/s.



Figure S2. (black) CV of DMF with 0.1 M  $Bu_4NPF_6$  with [Mn<sup>II</sup>(L)]<sup>+</sup> (1.2 mM) at 0.2 V/s at a glassy carbon disk electrode at 293 K. (red) simulation.

X-ray structure has shown that  $[Mn^{II}(L)]^+$  is a bis-phenolato dinuclear species in the solid state.[5] However, there is no experimental indication that this dinuclear structure remains in solution at room temperature. Analysis of cyclic voltammetry experiments (absence of any additional wave that could be assigned to the oxidation of a putative Mn(II)Mn(III) species, no effect of concentration or scan rate variation) confirms the monoelectronic nature of the Mn(II)/Mn(III) oxidation wave. At more positive potential (1.54 V vs. SCE, see figure 2Sb), the complex leads to another oxidation wave attributed to ligand oxidation.[6]

Table S1. Parameters obtained from simulation of the CVs of the  $O_2$  to  $O_2$ <sup>-</sup> reduction and  $[Mn^{II}(L)]^+$  to  $[Mn^{II}(L)]^{2+}$  oxidation.

	O <sub>2</sub> /O <sub>2</sub> -	$[Mn^{II}(L)]^{+}/[Mn^{III}(L)]^{2+}$
E° (V vs. SCE)	-0.865	0.329
$k^{\mathrm{S}}$ (cm s <sup>-1</sup> )	$1.5 \times 10^{-2}$	$9.5  imes 10^{-4}$
$D (cm^2 s^{-1})$	$4.6 \times 10^{-5}$	4 0× 10 <sup>-6</sup>

### I.1.3. O<sub>2</sub> reduction in presence of Mn complex – wave 1 analysis

### I.1.3.1. Addition of increasing ammount of [MnIIL]+.

Upon addition of  $[Mn^{II}L]^+$  the  $O_2/O_2^-$  reduction wave reversibility decreases, in line with the formation of an  $[Mn^{III}L(O_2)]$  adduct. Simulations were performed using Digielch simulation program assuming a simple electrochemical reaction followed by a fast irreversible chemical reaction (EC mechanism). Due to the slow electron transfer kinetics of  $O_2$  reduction the following reaction is not rate-determining. Thus the pre-wave position is not determined by the coupling rate constant but by mixed control of electron transfer kinetics and  $[Mn^{II}L]^+$  diffusion.

EC mechanims:

$$O_2 + e^- \longrightarrow O_2^{--}$$
 (-0.865 V vs SCE) E

$$[Mn^{II}L]^+ + O_2 \stackrel{\leftarrow}{\longrightarrow} [Mn^{III}L(OO)]$$

Simulations reported in the manuscript have been performed using the parameters determined above and taking diffusion limited value ( $10^{10}$  M<sup>-1</sup>s<sup>-1</sup>) for *k* and a diffusion coefficient for [Mn<sup>III</sup>L(OO)] species equal to

$$D_{Mn} = 4 \times 10^{-6} \text{ cm}^2/\text{s}.$$

Experimental CV could not be modelled with a CE mechanism involving the formation of a Mn(II)-dioxygen adduct (C) followed by an electrochemical reaction (E). In that case the position of the pre-peak would vary with the quantity of  $[Mn^{II}L]^+$ .

### I.1.3.2. Oxidation of the [Mn<sup>III</sup>L(OO)] adduct.

The [Mn<sup>III</sup>L(O<sub>2</sub>)] species formed at the O<sub>2</sub> reduction wave can be re-oxidized at  $E^{\circ} \approx 0.2$  V vs. SCE in the reverse scan as shown on figure S3. The oxidation wave is much more intense than the wave expected from the simple oxidation of the Mn complex reaching the electrode by diffusion as seen from simulation without re-oxidation of the [Mn<sup>III</sup>L(O<sub>2</sub>)] product (red line on figure S3).



**Figure S3**. CV of DMF with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> saturated with air (1.0 mM  $O_2$ )with [Mn<sup>II</sup>(L)]<sup>+</sup> (1.2 mM) at 0.2 V/s at a glassy carbon disk electrode at 293 K (a); simulation based on mechanism omitting re-oxidation of the product (b).

The simulation shown on figure S4 was obtained using a simple mechanism (see below). The following hypothesis are made: the re-oxidation is irreversible and leads to  $Mn(II) + O_2$  with fast release of  $O_2$ .



Square reaction scheme used for simulation in figure S4

According to this mechanism, the re-oxidation current is due to the oxidation of the [Mn<sup>III</sup>L(O<sub>2</sub>)] product. To show that such a scenario is plausible, a simulation was performed using parameters for the [Mn<sup>III</sup>L(O<sub>2</sub>)] oxidation close to the Mn(II)/Mn(III) couple ( $k_s = 9.5 \times 10^{-4}$  cm s<sup>-1</sup>,  $E^\circ = 0.2$  V vs. SCE) (figure S4).



Figure S4. Simulation based on the above mentioned square reaction scheme.

# I.1.3.3.CV of the [Mn<sup>III</sup>L(OO)] adduct resulting from the addition of KO<sub>2</sub> to [Mn<sup>II</sup>L]<sup>+</sup>.

The [Mn<sup>III</sup>L(OO)] adduct was also chemically prepared according to the following procedure: [K(18-crown-6)]O<sub>2</sub> (1.2 mM)) was intoduced into the cell used cyclic volatmetry containing a 1.2 mM solution of [Mn<sup>II</sup>L]<sup>+</sup> under an argon atmosphere, thermostated at 263 K. Cyclic voltamograms immediately recorded after the addition are shown below:



Figure S5: CV of (a)  $[Mn^{II}(L)]^+$  (1.2 mM) +  $[K(18\text{-crown-6})]O_2$  (1.2 mM) under Ar, (blue curve) T= 263 K;  $[Mn^{II}(L)]^+$  (1.2 mM), solution saturated with air (1.0 mM  $O_2$ ), (black curve) T= 263 K; (b) same as (a), toward more negative potentials.

### I.2. EPR spectroscopic characterization

**Preparation of EPR samples**: Aliquots of the electrolyzed solution were collected directly from the UV-vis spectroelectrochemical cell with glassy carbon as working electrode, after two identical UV-Vis spectra were recorded, and immediately transferred into an EPR tube and frozen in liquid  $N_2$ . EPR spectra of samples containing the starting Mn(II) solution and of samples containing the electrolyzed solution were recorded in both parallel and perpendicular modes.



**Figure S6:** EPR signals of  $[Mn^{II}(L)]^+$  solution (1mM in DMF) saturated with air (1 mM O<sub>2</sub>) (black): starting  $[Mn^{II}(L)]^+$  solution; (blue) after electrolysis at -1.2 V vs. SCE. (a) parallel mode detection, microwave frequency 9.40 GHz; microwave power 1mW; field modulation amplitude 0.7 mT; T = 4 K (b) perpendicular mode detection, microwave frequency 9.63 GHz; microwave power 1 mW; field modulation amplitude 0.7 mT; T = 4 K

### **I.3. DFT Calculation**

*Computational Methods.* Initial models for  $[LMn^{III}(O_2)]$  were generated using the X-ray diffraction structure of  $[Mn^{IIL}_2], [5]$  removing one L ligand and placing a peroxo group within bonding distance of the Mn center  $(Mn-O \text{ distances of } \sim 1.88 \text{ Å})$ . The two specific initial models generated by this method are *cis*- $[LMn^{III}(O_2)]$  and *trans*- $[LMn^{III}(O_2)]$ , where the *cis* and *trans* terms mark the position of the peroxo unit relative to the phenolate ligand. Two additional models were generated by considering dissociation of methylimidazole arms. These are referred to as  $[LMn^{III}(O_2)-N(6)]$  and  $[LMn^{III}(O_2)-N(7)]$ , to indicate the specific methylimidazole arm that is dissociated (using the numbering scheme shown in figure S7, top). All models considered were energy minimized using unrestricted DFT methods that employed the BP functional[8-9] as well as TZVP (for Mn, N, and O) and SVP for C and H) basis sets.[10] The RI procedure with the SV/J and TZV/J auxiliary basis sets were used in these calculations. Solvation effects associated with DMF were incorporated using the COSMO model.[11] Each calculation was tightly converged to a quintet spin state. For all energy-minimized models, additional calculations were performed using the B3LYP functional[12-14] and the larger TZVPP basis set for all atoms. All calculations were performed using ORCA 2.9.1.[15]

*Optimized Structures*. Selected metric parameters for all DFT-optimized models are shown in table S2; corresponding molecular structures are shown in figure S7. The optimized structure of the *cis*-[LMn(O<sub>2</sub>)] model, where the phenolate ligand is oriented *cis* to the peroxo group, features a side-on peroxo ligand with Mn–O<sub>peroxo</sub> distances of 1.898 and 1.931 Å (table S2). The longer Mn–O<sub>peroxo</sub> distance is observed for the peroxo oxygen directly adjacent to the phenolate ligand. The Mn<sup>III</sup> center in *cis*-[LMn(O<sub>2</sub>)] is hexacoordinate, as the L ligand is bound in a tetradentate fashion with one amine nitrogen (N5) at a distance of 2.663 Å from the Mn<sup>III</sup> center. The geometry optimized structures of [LMn(O<sub>2</sub>)-N(6)] and [LMn(O<sub>2</sub>)-N(7)] likewise show hexacordinate Mn<sup>III</sup> centers with side-on peroxo ligands and a tetradentate L ligand. However, for these models, the tetradentate binding mode of the L ligand is achieved through dissociation of a methylimidazolyl arm. For [LMn(O<sub>2</sub>)-N(6)] and [LMn(O<sub>2</sub>)-N(7)], the phenolate ligand is also *cis* with respect to the peroxo ligand. In both componds, Mn–O<sub>peroxo</sub> distances are ~1.89 Å.



Figure S7. Hypothetical structures of geometry optimized models of [LMn<sup>III</sup>(O<sub>2</sub>)].

1.887

 $LMn(O_2)-N(7)$ ]

1.882

<b>Table S2.</b> Metal-Ligand Bond Lengths (Å) for Optimized Models of $[LMn(O_2)]$ Complexes								
	Mn-O(1)	Mn-O(2)	O(1)-O(2)	Mn-O(3)	Mn-N(4)	Mn-N(5)	Mn-N(6)	Mn-N(7)
cis-[LMn(O <sub>2</sub> )]	1.898	1.931	1.443	1.970	2.454	2.663	2.275	2.270
trans-[LMn(O <sub>2</sub> )]	1.858	2.836	1.417	2.008	2.339	2.327	2.162	2.180
$[LMn(O_2)-N(6)]$	1.886	1.892	1.459	1.941	2.408	2.230	5.240	2.276

1.460

The *trans*-[LMn( $O_2$ )] models is distinct from the others in that the peroxo ligand is bound in an end on fashion, with Mn– $O_{peroxo}$  distances of 1.858 and 2.836 Å (table S2). Presumably this is a consequence of having a strong donor ligand (in this case a phenolate) *trans* to the peroxo unit. The O–O distance in *trans*-[LMn( $O_2$ )] is 1.417 Å, which falls within the expected range for a peroxo ligand and is significantly longer than the O–O distance of a superoxo ligand (1.35 Å). Thus, a peroxomanganese(III) description for *trans*-[LMn( $O_2$ )] appears quite reasonable.[16]

1.928

2.211

2.382

2.313

5.534

A variety of density functionals[17-18]were employed to compare the energies of these models (table S3). The most notable result of these calculations is that the *trans*-[LMn(O<sub>2</sub>)] model with an end-on peroxo ligand is predicted at highest energy for all functionals employed. For the B3LYP functional, this result is true regardless of whether the energy calculations are performed in the gas phase or incorporating solvation effects from DMF using the COSMO method. The relatively high energy of *trans*-[LMn(O<sub>2</sub>)] suggests it is not the best model. The energies of the remaining three models, *cis*-[LMn(O<sub>2</sub>)], [LMn(O<sub>2</sub>)-N(6)], and [LMn(O<sub>2</sub>)-N(7)] are within ~2 kcal/mol of each other, with the lowest-energy structure depending on the functional. Given the very similar energies of these three models, none of these can be discounted on the basis of their computed energies.

(E/D) Ground state Zero neld Splitting I dianeters						
	B3LYP	B3LYP	PBE0	TPSSh	D	E/D
	gas phase	COSMO	COSMO	COSMO		
					(B3LYP g	as phase)
cis-[LMn(O <sub>2</sub> )]	0.00	0.00	0.00	0.00	-1.81	0.16
$trans-[LMn(O_2)]$	12.90	14.58	14.31	13.99	+1.12	0.09
$[LMn(O_2)-N(6)]$	-2.24	-1.00	0.52	-0.99	-1.89	0.16
$[LMn(O_2)-N(7)]$	-1.68	-2.14	-0.55	-2.01	-2.14	0.12

**Table S3.** Relative Energies (kcal/mol) of  $[LMn^{III}-O_2]$  Models and Calculated Axial (*D*, cm<sup>-1</sup>) and Rhombic (*E/D*) Ground-state Zero-field Splitting Parameters

*Calculated Spectroscopic Properties.* In an attempt to further discriminate between the computationally-derived models, ground-state zero-field splitting (ZFS) parameters (*D* and *E/D*) and electronic transition energies were calculated using the CP-DFT[19] and TD-DFT[10, 20-23] methods, respectively. The calculated *D* and *E/D* values for the models with side-on peroxo ligands, *cis*-[LMn(O<sub>2</sub>)], [LMn(O<sub>2</sub>)-N(6)], and [LMn(O<sub>2</sub>)-N(7)] are quite similar, spanning the narrow ranges of D = -1.81 to -2.14 cm<sup>-1</sup> and E/D = 0.12 to 0.16 (table S3). These calculated values are in good agreement with *D* and *E/D* values determined experimentally for side-on peroxomanganese(III) adducts. In contrast, *trans*-[LMn(O<sub>2</sub>)], which features an end-on peroxo ligand, displays a positive D (+1.12 cm<sup>-1</sup>). While these calculations predict large differences in ground-state properties when comparing side-on and end-on Mn<sup>III</sup>-O<sub>2</sub> adducts, they are unable to provide a means for distinguishing between *cis*-[LMn(O<sub>2</sub>)], [LMn(O<sub>2</sub>)-N(6)], and [LMn(O<sub>2</sub>)-N(7)], as the predicted ZFS parameters are so similar to one another. Even if experimental *D* and *E/D* values were to be determined with high precision for [LMn(O<sub>2</sub>)], the uncertainty in the corresponding calculated ZFS parameters is sufficient to make the three computationally-derived complexes appear equivalent.

We next turned to a comparison of the excited-state properties by performing TD-DFT computations. The TD-DFT-computed electronic absorption spectra for all models are shown in figure S8. The computed absorption spectrum for *cis*-[LMn(O<sub>2</sub>)] consists of a weak feature centred at 580 nm ( $\varepsilon = 230 \text{ M}^{-1}\text{cm}^{-1}$ ), a more intense band at 450 nm ( $\varepsilon = 850 \text{ M}^{-1}\text{cm}^{-1}$ ), and a shoulder at 380 nm that appears before the on-set of intense transitions in the UV (figure S14). The lower-energy band at 580 nm arises from a Mn<sup>III</sup>  $d_z^2 \rightarrow d_x^2 \cdot y^2$  transition, whereas the dominant feature at 450 nm is a mixed Mn<sup>III</sup> *d-d* and peroxo-to-Mn<sup>III</sup> charge-transfer (CT) transition. Notably, [LMn(O<sub>2</sub>)-N(6)] displays a TD-DFT-computed absorption spectrum nearly identical to that of *cis*-[LMn(O<sub>2</sub>)], with the major difference being a modest blue-shift of the absorption maxima to 560 and 420 nm (figure S13). This blue shift is likely due to the shorter Mn-O<sub>peroxo</sub> distances in [LMn(O<sub>2</sub>)-N(6)]. Because the Mn<sup>III</sup>  $d_x^2 \cdot y^2$  acceptor orbital for these transitions is a Mn<sup>III</sup>-O<sub>2</sub>  $\sigma$ -antibonding orbital, the shorter Mn-O<sub>peroxo</sub> bonds destabilize this orbital. Importantly, the TD-DFT-computed spectra for both *cis*-[LMn(O<sub>2</sub>)] and [LMn(O<sub>2</sub>)-N(6)] are in good agreement with the experimental spectrum of [LMn(O<sub>2</sub>)], which shows a prominent feature at 440 nm ( $\varepsilon = 600 \text{ M}^{-1}\text{cm}^{-1}$ ) and a shoulder at 540 nm ( $\varepsilon = 220 \text{ M}^{-1}\text{cm}^{-1}$ ).



**Figure S8.** TD-DFT-computed electronic absorption spectra for  $LMn^{III}-O_2$  Models. Sticks mark individual electronic transitions. The simulated spectra were achieved through by modelling the electronic transitions with Gaussian functions with widths (full-width at half maximum) of 2 500 cm<sup>-1</sup>. TD-DFT calculations for *cis*-[LMn(O<sub>2</sub>)] were performed with TZVP basis set on all atoms (basis set 1) and a combination of TZVP (Mn, O, and N) and SVP (C and H) basis sets (basis set 2). Given that the more economical basis set 2 performed equivalently as basis set 1, the former was used for TD-DFT computations on the remaining models.

For *trans*-[LMn(O<sub>2</sub>)], the agreement between TD-DFT-computed and experimental absorption spectra is not as favorable. In particular, the computed spectrum of *trans*-[LMn(O<sub>2</sub>)] displays an intense peroxo-to-manganese(III) CT transition at 550 nm ( $\varepsilon = 6~000 \text{ M}^{-1}\text{cm}^{-1}$ ), in clear contrast with the experimental spectrum of [LMn(O<sub>2</sub>)]. Thus, all available computational data (*i.e.*, the computed total energy, ZFS parameters, and electronic transition energies) strongly indicate that *trans*-[LMn(O<sub>2</sub>)] is a poor model for [LMn(O<sub>2</sub>)].

The computed absorption spectrum of  $[LMn(O_2)-N(7)]$  appears quite distinct from those of all other computational models (figure S8). This is somewhat surprising, given that the structures of *cis*-[LMn(O<sub>2</sub>)],  $[LMn(O_2)-N(6)]$ , and  $[LMn(O_2)-N(7)]$  initially appear quite similar (table S2). However, upon closer examination, the major difference between the TD-DFT-computed absorption spectrum of  $[LMn(O_2)-N(7)]$  and those of *cis*-[LMn(O<sub>2</sub>)] and  $[LMn(O_2)-N(6)]$  arises solely because of the appearance of a moderately intense phenolate-to-manganese(III) CT transition for  $[LMn(O_2)-N(7)]$  ( $\lambda_{max} = 460$  nm;  $\varepsilon = 1$  800 M<sup>-1</sup>cm<sup>-1</sup>; see figure S8). The spectrum for  $[LMn(O_2)-N(7)]$  still displays a lower-energy *d*-*d* transition (550 nm;  $\varepsilon = 150$  M<sup>-1</sup>cm<sup>-1</sup>) and a higher-energy mixed *d*-*d* peroxo-to-manganese(III) CT transition (404 nm;  $\varepsilon = 300$  M<sup>-1</sup>cm<sup>-1</sup>), similar to those observed for *cis*-[LMn(O<sub>2</sub>)] and  $[LMn(O_2)-N(6)]$ . The origin of this low-energy phenolate-tomanganese(III) CT transition for  $[LMn(O_2)-N(7)]$  is tentatively attributed to the unique orientation of the phenolate ligand in this complex (figure S7). Despite the distinctiveness of the TD-DFT-computed absorption spectrum of  $[LMn(O_2)-N(7)]$ , the computed spectrum remains within reasonable agreement with the experimental data, showing an absorption band at ~460 nm). The difference between the computed spectra of  $[LMn(O_2)-N(7)]$ , on the one hand, and *cis*- $[LMn(O_2)]$  and  $[LMn(O_2)-N(6)]$ , on the other, is the intensity of the absorption band at ~450 nm. The band for  $[LMn(O_2)-N(7)]$  is roughly twice as intense. Given that the most intense visible absorption feature in the experimental spectrum of  $[LMn(O_2)]$  is ~600 M<sup>-1</sup>cm<sup>-1</sup>, model  $[LMn(O_2)-N(7)]$  can probably be excluded from consideration.

### II. Reduction of [Mn<sup>III</sup>L(O<sub>2</sub>)] in presence of HClO<sub>4</sub>

II.1.Cyclic voltammetry analysis.

As detailed in the manuscript, the following mechanism is considered for simulation of CV in presence of strong acid:

# ECE/DISP

$$O_2 + e^- \longrightarrow O_2^-$$
 (1)

$$LH + O_2 - k_H \rightarrow HOO' + L^-$$
 (2)

$$HOO' + e^- \longrightarrow HOO^-$$
 (3)

$$HOO' + O_2' - \underbrace{k_{disp}}_{HOO'} + O_2$$
(4)

$$HOO^- + LH \qquad \xrightarrow{k_H} \qquad H_2O_2 + L^- \tag{5}$$

# ECE'/DISP'

$$O_2 + e^- \longrightarrow O_2^{--}$$
 (1)

$$[\mathrm{Mn}^{\mathrm{II}}\mathrm{L}]^{+} + \mathrm{O}_{2}^{-} \xrightarrow{k_{df}} [\mathrm{Mn}^{\mathrm{III}}\mathrm{L}(\mathrm{OO})]$$
(2')

$$[Mn^{III}L(OO)] + LH \xrightarrow{k_p} [Mn^{III}L]^{2+} + HOO^{-} + L^{-}$$
(3')

$$[\mathrm{Mn}^{\mathrm{III}}\mathrm{L}]^{2+} + \mathrm{O}_{2}^{--} \qquad \xrightarrow{\kappa \ disp} \qquad [\mathrm{Mn}^{\mathrm{II}}\mathrm{L}]^{+} + \mathrm{O}_{2} \qquad (5')$$

$$HOO^- + LH \qquad \xrightarrow{k_H} \qquad H_2O_2 + L^- \tag{5}$$

Diffusion coefficients $(cm^2/s)$						
O <sub>2</sub> , O <sub>2</sub> •-, HO <sub>2</sub>	$_{2}^{\bullet}, \mathrm{HO}_{2}^{\bullet}, \mathrm{H}_{2}\mathrm{O}_{2}$	4.6 x 10 <sup>-5</sup>				
All Mn	species	4 x	x 10 <sup>-6</sup>			
LH	I, L	4 x	x 10 <sup>-6</sup>			
	Electrochemical reactions					
couple	$E^{\circ}$ (V vs. SCE)	$k^{\rm S} ({\rm cm} {\rm s}^{-1})$	α			
O <sub>2</sub> /O <sub>2</sub> •-	-0.865	0.015	0.5			
$HO_2^{\bullet}/HO_2^{-}$	0	104	0.5			
$[Mn^{III}L]^{2+}/[Mn^{II}L]^{+}$	0.329	9.5x10 <sup>-4</sup>	0.5			
Homogeneous rate constants						
$k_H = k_{disp} = k'_{disp} = k_{dif} = 10^{10} \text{ M}^{-1} \text{ s}^{-1}$						
	$k_p = 10^{4}$	<sup>5</sup> M <sup>-1</sup> s <sup>-1</sup>				

Simulations (figure 3 in the manuscript) have been performed with the following parameters:



**Figure S9**. CV of DMF with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> saturated with air (1.0 mM  $O_2$ ) with [Mn<sup>II</sup>(L)]<sup>+</sup> (10 mM) and increasing concentration of HClO<sub>4</sub>: 0 (orange), 1 (yellow), 2 (green), 3 (cyan), 4 (blue), 5 (magenta), 6 (purple), 7 (pink) mM at 0.2 V/s at a glassy carbon disk electrode at 293 K.



**Figure S10**. Selected UV-vis spectrum of MeCN with  $[Mn^{II}L]^+$  (0.5 mM) and increasing concentration of HClO<sub>4</sub>: 0 (orange), 0.1 (yellow), 0.2 (green), 0.3 (cyan), 0.4 (blue), 0.5 (magenta), and 0.6 (purple) mM (experiment is not possible in DMF because it has an absorbance band in 200 -300 nm.

Upon addition of increasing amounts of  $HClO_4$ , the band at  $\lambda$ =289 nm assigned to  $[Mn^{II}(L)]^+$  decreases and a new band associated with the protonated form of the ligand LH appears at  $\lambda$ =275 nm.

II.2. UV-vis experiments.

[Mn<sup>III</sup>L(O<sub>2</sub>)] was prepared in bulk by electrolysis in a UV-vis cuvette (see figure 2, right panel ). Subsequent addition of equivalents of H<sup>+</sup> results in the growth of peaks at 400 nm ( $\varepsilon = 1580 \text{ M}^{-1}\text{cm}^{-1}$ ) and 650 nm ( $\varepsilon = 280 \text{ M}^{-1}\text{cm}^{-1}$ ) (figure S7, left panel), which are comparable to the [Mn<sup>III</sup>L]<sup>2+</sup> species prepared by bulk electrolysis at +0.7 V in DMF (growth of peaks at 400 nm ( $\varepsilon = 1750 \text{ M}^{-1}\text{cm}^{-1}$ ) and 650 nm ( $\varepsilon = 300 \text{ M}^{-1}\text{cm}^{-1}$ ) (figure S7, right panel). However, these bands are less intense that those observed in MeCN ( $\lambda = 403 \text{ nm}$ ,  $\varepsilon = 2181 \text{ M}^{-1}\text{cm}^{-1}$  and  $\lambda = 672 \text{ nm}$ ,  $\varepsilon = 432 \text{ M}^{-1}\text{cm}^{-1}$ ).[5] This is consistent with the release of H<sub>2</sub>O<sub>2</sub> upon protonation of [Mn<sup>III</sup>L(O<sub>2</sub>)] proposed in eq. 3'. The band at 400 nm has been attributed to phenolato to Mn(III) LMCT absorption.



**Figure S11**. *left panel*: Evolution of the UV-vis spectrum of DMF with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> with [Mn<sup>III</sup>(L)O<sub>2</sub>] (~1.0 mM, prepared by bulk electrolysis performed at -1.2 V vs. SCE for 200 s at 263 K, black trace) and HClO<sub>4</sub>: (1.1 mM, red trace). *right panel*: Evolution of the UV-vis spectrum of DMF with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> with [Mn<sup>II</sup>(L)]<sup>+</sup> (1.0 mM) during bulk electrolysis performed at +0.7 V vs. SCE at 263 K. Black trace: t=0, red trace: 500, 1000, 1500, 2000s

# III. Reduction of [Mn<sup>III</sup>L(O<sub>2</sub>)] in presence of a weak acid. O-O bond cleavage

III.1. CV analysis. Estimation of  $\Delta G_{peak}^{\neq}$  and of the reorganization energy  $\lambda$ .

The free enthalpy barrier  $\Delta G_{peak}^{\star}$  for electron transfer at the voltammetric peak could be calculated at every scan rate from the following equation:[7]

$$\Delta G_{peak}^{\neq} = \frac{RT}{F} \ln \left\{ Z \left( \frac{RT}{\alpha F v D} \right)^{1/2} - 0.78 \right\}$$

where *D* is the diffusion coefficient for the substrate ( $D = 4 \ 10^{-6} \ \text{cm}^2 \ \text{s}^{-1}$ ),  $Z = \sqrt{RT/2\pi M}$  the collision frequency, *M* the molar mass (440 g mol<sup>-1</sup>),  $\alpha$  the transfer coefficient, *T* the temperature (298 K), *F* the Faraday constant and *v* the experimental scan rate. Thus for v = 0.1 V/s:  $\Delta G_{peak}^{*} = 0.36 \text{ eV}$ .

From this value and the value for the transfer coefficient  $\alpha$ , one may calculate the reorganization energy :

$$\alpha = \frac{\partial \Delta G^*}{\partial \Delta G^0} = \frac{\partial}{\partial \Delta G^0} \left\{ \frac{\lambda}{4} \left( 1 + \frac{\Delta G^0}{\lambda} \right)^2 \right\} = \sqrt{\frac{\Delta G^*}{\lambda}} \text{ , thus } \lambda = 2.25 \text{ eV}.$$



**Figure S12**. CV of DMF with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> saturated with air (1.0 mM O<sub>2</sub>)with  $[Mn^{II}(L)]^+$  (1.2 mM) at 0.2 V/s at a glassy carbon disk electrode at 293 K, (black); in the presence of H<sub>2</sub>O (500 mM) (red).



**Figure S13**. CV of DMF with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> saturated with air (1.0 mM O<sub>2</sub>)with  $[Mn^{II}(L)]^+$  (1.2 mM) at 0.2 V/s at a glassy carbon disk electrode at 293 K, (black); in the presence of H<sub>2</sub>O (500 mM) (red). *The slight variation of the second reduction wave (at*  $\approx$  -1.8 V) *is an artifact of the large movement of the third reduction wave (at*  $\approx$  -2.5 V), which is currently under *further investigations*.



Figure S14. CV of DMF with 0.1 M  $Bu_4NPF_6$  saturated with air (1.0 mM  $O_2$ ) (black) and with  $[Mn^{II}(L)]^+$  (1.2 mM) at 0.2 V/s at a glassy carbon disk electrode at 293 K, (blue).

III.2. UV-vis spectroscopic characterization



**Figure S15**.  $[Mn^{II}L]^+$  (1.2 mM) and O<sub>2</sub> (1.0 mM, air saturated) in DMF + 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> (*T* = 263 K). *left panel* : evolution of UV-vis spectrum upon electrolysis performed at -1.2 V vs. SCE; *right panel* : evolution of UV-vis spectrum upon electrolysis performed at -1.2 V ), (200 s, 1 spectra per 50 s).

Of note, spectra recorded upon electrolysis performed at -1.9 V vs. SCE (*right panel*) do not show the intense band at 400 nm characteristic of phenolato to Mn(III) LMCT absorption (see Figure S11), thus supporting the decoordination of the phenolato moiety, shown in Scheme 3.

EPR spectra (in parallel mode) recorded on the same sample show disappearance of the Mn(III)-peroxo six-line signal and no appearance of Mn(II) species (in perpendicular mode).

### **III.3 DFT calculation**

One-electron Reduction of  $[LMn(O_2)]$  Models. The one-electron-reduced form of  $[Mn^{III}(O_2)(L)]$  was evaluated using the optimized structures of the previously developed peroxomanganese(III) complexes as a starting point for subsequent energy minimization of the corresponding  $[Mn^{III}(O_2)(L)]^-$  species. In this analysis, we did not include the *trans*- $[LMn(O_2)]^-$  species, as it was unambiguously discounted as a plausible model for the peroxomanganese(III) adduct. In addition, we were unable to locate a stable minima for cis-[LMn(O<sub>2</sub>)]; *i.e.*, all optimized geometries showed at least one imaginary frequency. In contrast, minimum energy structures with no imaginary frequencies were identified for [LMn(O<sub>2</sub>)-N(6)]<sup>-</sup> and LMn(O<sub>2</sub>)-N(7)]<sup>-</sup> (figure S16). In the optimized structures of both [LMn(O<sub>2</sub>)-N(6)]<sup>-</sup> and LMn(O<sub>2</sub>)-N(7)]<sup>-</sup>, the O–O and Mn–O bonds remain intact (table S4), although both are elongated relative to the peroxomanganese(III) analogues (cf. tables S4 and S2). The spin densities for the Mn centers in these models are increased relative to the corresponding peroxomanganese(III) complexes (Mulliken spin densities of 4.8 and 4.1, respectively), suggesting that both  $[LMn(O_2)-N(6)]^-$  and LMn(O<sub>2</sub>)-N(7)]<sup>-</sup> contain manganese(II) centers. By using the SCF energies of the [LMn<sup>II</sup>(O<sub>2</sub>)-N(6)]<sup>-</sup>/[LMn<sup>III</sup> (O<sub>2</sub>)-N(6)] and [LMn<sup>II</sup>(O<sub>2</sub>)-N(7)]<sup>-</sup>/[LMn<sup>III</sup>(O<sub>2</sub>)-N(7)] pairs of complexes at the B3LYP/TZVPP/COSMO level of theory, as well as the zero-point energies from the BP/TZVP/SVP/COSMO frequency calculations, we calculate reduction potentials of -1.96 and -2.11 V (versus SCE). We note that a test calculation, using the same level of theory (with the exception that water was used as the solvent), was performed for the related  $[LMn^{II}(OH_2)]^+/[LMn^{II}(OH_2)]$  pair of complexes. In that case, the calculated reduction potential of 0.14 V (versus SCE) was in reasonable agreement with the experimental data (0.199 V and 0.184 V versus SCE in PIPES and phosphate buffer, respectively).[5]

Table S4. Metal-Ligand Bond Lengths (Å) for Optimized Models of [LMn<sup>II</sup>(O<sub>2</sub>)]<sup>-</sup> Complexes

	Mn-O(1)	Mn-O(2)	O(1)-O(2)	Mn-O(3)	Mn-N(4)	Mn-N(5)	Mn-N(6)	Mn-N(7)
$[LMn(O_2)-N(6)]^{-1}$	2.062	2.078	1.541	2.126	2.327	2.634	5.025	2.238
$[LMn(O_2)-N(7)]^{-1}$	2.004	2.128	1.542	2.099	2.404	2.424	2.315	5.554



Figure S16. Hypothetical structures of geometry optimized models of [LMn<sup>II</sup>(O<sub>2</sub>)]<sup>-</sup> species.

Because the CV experiments provide strong evidence that the one-electron reduction of  $[LMn^{III}(O_2)]$  is coupled with O–O bond cleavage, we also developed models of dioxomanganese(IV) complexes,  $[LMn^{IV}(O)_2]^-$ , which would be formed under such a scenario. Stable structures with no imaginary frequencies were found for *cis*- $[LMn^{IV}(O)_2]^-$ ,  $[LMn^{IV}(O)_2-N(6)]^-$ , and  $[LMn^{IV}(O)_2-N(7)]^-$  (figure S17). Selected metric parameters for these models are shown in table S5. In all cases, the  $[LMn^{IV}(O)_2]^-$  complexes are approximately 25 kcal/mol lower in energy than the corresponding  $[LMn^{II}(O_2)]^-$  compounds, showing that O–O bond cleavage in the reduced species is thermodynamically favourable. Consequently, the calculated standard reduction potentials for the  $[LMn^{IV}(O)_2]^-/[LMn^{III}(O_2)]$  couples are significantly lower than those of the  $[LMn^{II}(O_2)]^-/[LMn^{III}(O_2)]$  couples (specifically, for *cis*- $[LMn^{IV}(O)_2]^-/$ *cis* $-<math>[LMn^{III}(O_2)]$ ,  $[LMn^{IV}(O)_2-N(6)]^-/[LMn^{III}(O_2)-N(6)]$ , and  $[LMn^{IV}(O)_2]^-/(LMn^{III}(O_2)-N(7)]^-/[LMn^{III}(O_2)]^-/(is)$ .

Table S5. Metal-Ligand Bond Lengths (Å) for Optimized Models of [LMn(O)<sub>2</sub>]<sup>-</sup> Complexes

Table 55. Metal L	Tuble 55. Metal Elgand Bond Eenguis (A) for optimized Models of [EMI(0)2] complexes							
	Mn-O(1)	Mn-O(2)	O(1)-O(2)	Mn-O(3)	Mn-N(4)	Mn-N(5)	Mn-N(6)	Mn-N(7)
cis-[LMn <sup>IV</sup> (O) <sub>2</sub> ] <sup>-</sup>	1.695	1.709	2.824	2.181	3.512	2.995	2.135	2.060
$[LMn^{IV}(O)_2 - N(6)]^{-1}$	1.712	1.712	2.809	2.000	2.175	2.432	5.628	2.271
$[LMn^{IV}(O)_2-N(7)]^{-1}$	1.681	1.699	2.900	1.987	2.168	2.392	4.591	5.554



Figure S17. Hypothetical structures of geometry optimized models of [LMn<sup>IV</sup>(O)<sub>2</sub>]<sup>-</sup> species.

# Cartesian Coordinates for Geometry-Optimized Models.

Mn	-0.408305	4.779661	-1.393895
0	1.291867	4.695621	-0.482269
0	1.216739	3.828499	-1.633570
Ν	-1.091811	3.215470	-3.156326
Ν	-1.519990	3.023424	-0.468141
Ν	0.281807	6.347435	-2.882736
Ν	-2.435068	5.811951	-2.779713
0	-1.248014	6.002724	-0.098045
С	-1.490789	1.896328	-1.183740
С	-0.962538	1.860796	-2.589277
Ν	-1.972285	0.844485	-0.454216
С	-2.056927	-0.553456	-0.880008
С	-0.506336	9.258598	-4.920693
С	-2.313826	1.337426	0.799947
С	-2.030195	2.690398	0.771475
С	-2.591423	4.980827	-3.988673
С	-0.576357	7.219852	-3.416899
С	-4.693190	7.335052	-0.276432
С	-2.381641	6.631997	0.177454
С	-2.433118	3.492007	-3.701950
Ν	0.082771	8.127523	-4.202491
С	1.435547	7.811435	-4.149774
С	1.538753	6.702302	-3.331355
С	-3.597522	8.132627	1.727249
С	-2.446307	7.420770	1.369287
С	-3.624479	5.738440	-1.901741
С	-4.739572	8.098135	0.902703
С	-2.049605	7.187081	-3.132262
C	-3.553467	6.594731	-0.656308
Н	-0.387718	3.336802	-3.895258
H	-1.486243	1.086567	-3.196271
H	0.114182	1.592843	-2.577943
H	-2.736342	-1.092621	-0.197100
H	-2.462902	-0.613085	-1.90/083
H	-1.058/92	-1.033295	-0.853231
H	0.229350	9.636493	-5.651913
H	-1.413836	8.934058	-5.4635/1
H	-0.//2010	10.074193	-4.21981/
п	-2./2/394	0.0838/2	1.5/41/0
п	-2.103824	5.441555	1.550/95
п	-3.3/8339	5.1040/1	-4.460423
п u	-1.606052	3.203/90	-4./1551/
н ц	-3.377343	2.014161	-0.930119
н	-3 178835	3 156311	-2 953139
н	2 177464	8 307120	-4 701249
н	2.177404	6 131951	-3.040211
н	-3 602432	8 725351	2 657044
Н	-1 547909	7 448665	2.037044
н	-4 550806	6 005838	-2 469450
н	-3 730420	4 671398	-1 609911
H	-5 647962	8 659832	1 169396
Н	-2.635867	7 593402	-3 992142
Н	-2.275541	7.842301	-2.264034

Table S6. Cartesian Coordinates for cis-[LMn<sup>III</sup>(O<sub>2</sub>)]Atomxyz

Alu		<b>y</b>	L 0.000007
Mn	0.906127	-0.085601	0.083927
Ν	-0.982871	1.240852	-0.291955
Ν	-0.867679	-1.577351	-0.128726
Ν	1.622211	1.954055	0.102718
Ν	1.901977	-2.016376	0.259402
0	-0.026382	0.715841	2.639234
0	0.820751	-0.178173	1.937712
0	1.169401	-0.207897	-1.902645
С	-2.247402	0.515507	-0.019907
Č	-1.974015	-0.878104	0.574865
Č	0.668971	2 872633	0 306304
č	2 831469	2 623165	0.113658
Ň	1 224044	4 114507	0.439205
Ċ	2 601474	3 968747	0.326013
c	0.513330	5 362623	0.719755
č	-0 783678	2 516277	0./15/35
c	1 085580	1 3/6310	2 502357
c	1.032760	3 023803	0.388778
C	2 156216	-3.023803	0.300770
N	3.130310	-2.380324	0.146066
IN C	1.080382	-4.225072	0.380438
C	3.040999	-3.955290	0.229934
C	-0.439578	-2.801/42	0.586/39
C	1.078594	-5.549/41	0.493029
C	-0.01/660	-2.252958	-2.429/61
C	2.095904	-1.6911/2	-3.5356/1
C	-0.055526	-3.445747	-3.178306
C	0.954846	-3.773394	-4.100/41
С	2.028377	-2.878909	-4.278181
С	-1.187464	-1.852746	-1.560882
Н	-0.878061	1.394420	-1.302811
Н	-2.841522	0.448872	-0.953674
Н	-2.870090	1.078647	0.704115
Н	-1.641953	-0.743127	1.624418
Н	-2.914585	-1.478354	0.560541
Н	3.782854	2.103151	-0.040052
Н	3.273123	4.829752	0.394215
Η	1.176877	6.211473	0.479273
Η	0.224494	5.417889	1.787935
Н	-0.394616	5.429957	0.092061
Н	-1.003057	2.316148	1.488114
Н	-1.437341	3.337509	0.044208
Н	4.056739	-1.971842	0.014816
Н	3.779761	-4.761319	0.191468
Н	-0.633118	-2.642925	1.667702
Н	-1.029385	-3.693454	0.274791
Н	1.873279	-6.310074	0.402597
Н	0.342401	-5.704419	-0.319297
Н	0.577188	-5.668269	1.472617
Н	2.938222	-0.992530	-3.663892
Н	-0.914234	-4.126155	-3.044294
Н	0.901478	-4.710348	-4.676481
Н	2.827935	-3.113635	-5.000509
Н	-1.617838	-0.916320	-1.969674
Н	-1.986179	-2.629166	-1.620415

Table S7. Cartesian Coordinates for trans-[LMn<sup>III</sup>(O2)]Atomxyz

Mn	1.764411	-0.671317	-0.187826
Ν	0.607411	1.395666	-0.622996
Ν	-0.355217	-1.329931	-0.405551
Ν	0.334352	4.252639	-1.267002
Ν	1.845646	-2.869712	0.395443
0	2,133407	-0.073118	1.562174
Ō	3.271217	0.092336	0.663741
Ô	2,183591	-1.008908	-2.052320
Č	-0.848776	1.118449	-0.706503
Č	-1.212702	-0.179990	0.020526
Č	0 499923	3 814335	-0.016072
Č	-0.047301	5.578132	-1.151707
Ň	0.238977	4.808778	0.899477
C	-0.107317	5.943813	0.181697
Č	0.336817	4.710365	2.356281
Č	0.973899	2.432685	0.360940
Ċ	1.764051	-2.142115	-2.642239
Č	0.618248	-3.378531	0.513225
Ċ	2,724505	-3.922054	0.553651
Ň	0.666559	-4.722585	0.752992
C	2.007828	-5.082247	0.783639
Č	-0.607121	-2.517060	0.460791
Č	-0.473376	-5.618676	0.955336
Ċ	0.403540	-2.573758	-2.520157
Ċ	2.658580	-2.927105	-3.415287
Ċ	-0.002214	-3.770068	-3.142247
С	0.896241	-4.546266	-3.896528
С	2.227389	-4.109953	-4.035553
С	-0.600641	-1.662771	-1.855965
Н	0.926930	1.723245	-1.544307
Н	-1.140302	1.066826	-1.772584
Н	-1.451264	1.943840	-0.269275
Η	-1.060976	-0.057417	1.111858
Η	-2.290006	-0.410352	-0.143762
Η	-0.261060	6.195173	-2.033414
Н	-0.364263	6.880822	0.685818
Н	-0.031116	5.651325	2.800820
Н	1.386884	4.551482	2.670607
Н	-0.285772	3.874934	2.730823
Н	2.080621	2.414954	0.459761
Н	0.585591	2.134917	1.354217
Н	3.809221	-3.785343	0.488390
Н	2.314145	-6.117887	0.959376
Н	-0.841702	-2.147268	1.481467
Н	-1.498458	-3.084752	0.113348
Н	-0.100030	-6.654983	1.021454
Н	-1.174139	-5.546375	0.101669
Н	-1.007174	-5.367053	1.892038
Н	3.701068	-2.585205	-3.513743
H	-1.054358	-4.087867	-3.047564
H	0.558020	-5.477343	-4.376598
H	2.9424/6	-4./01901	-4.629922
н	-0.391403	-0.090/40	-2.390814
11	-1.023024	-2.000004	-1.701300

Table S8. Cartesian Coordinates for  $[LMn^{III}(O_2)-N(6)]$ Atomxyz

Mn	1.321652	0.484571	-0.530342
Ν	-0.840057	0.948286	-0.536955
Ν	0.332851	-1.675349	-0.707842
Ν	1.123758	2.770170	-0.234648
Ν	0.466110	-4.981351	-0.670793
0	1.789296	0.180665	1.272600
Ō	2.923873	0.061641	0.361681
Ō	1.652443	0.462219	-2.429265
Ċ	-1.718680	-0.255612	-0.477092
Č	-0.948465	-1.485448	0.012561
Ċ	-0.043488	3.027414	0.364899
Č	1.881559	3.920199	-0.119150
N	-0.074148	4.302774	0.853446
C	1.152849	4.882247	0.555855
Č	-1.164699	4.927350	1.604140
Č	-1.125449	1.993777	0.475212
Ċ	2.091562	-0.634611	-3.075448
Č	0.610515	-4.017691	0.249513
Č	-0.138246	-6.039211	-0.021768
Ň	0.123355	-4.436685	1.476083
C	-0.357376	-5.723403	1.308346
Č	1.212843	-2.664536	-0.011441
č	0.074305	-3.698908	2.739290
Č	1 417380	-1 894188	-2.963978
č	3.230009	-0.545271	-3.921168
Č	1 912872	-3 004495	-3 676352
č	3.043584	-2.905532	-4.506938
Č	3 696429	-1 664031	-4 628035
č	0.145666	-2.000835	-2.153052
Ĥ	-0.951760	1.384497	-1.462883
Н	-2.134566	-0.426029	-1.488045
Н	-2.584540	-0.079301	0.192698
Н	-0.693719	-1.352917	1.083703
Н	-1.612911	-2.377879	-0.068743
Н	2,894263	3.988811	-0.531361
Н	1.378761	5.913618	0.843337
Н	-1.025570	6.022273	1.589586
Н	-1.169091	4.574678	2.654242
Н	-2.134834	4.684336	1.132124
Н	-1.115724	1.519968	1.480294
Н	-2.133542	2.442862	0.333962
Н	-0.373940	-6.976539	-0.541603
Н	-0.790105	-6.283748	2.143208
Н	2.109950	-2.791153	-0.646262
Н	1.540406	-2.183224	0.930424
Н	0.284125	-4.392730	3.573928
Н	-0.924408	-3.243736	2.893027
Н	0.839482	-2.903521	2.743179
Н	3.736838	0.428977	-4.008281
Н	1.388751	-3.968821	-3.571981
Н	3.410165	-3.787668	-5.054100
Н	4.582561	-1.565939	-5.276191
Н	-0.590016	-1.272715	-2.551012
Н	-0.293039	-3.016880	-2.268345

Table S9. Cartesian Coordinates for  $[LMn^{III}(O_2)-N(7)]$ Atomxyzxyz

Table S	10.	Cartesian	Coordinate	es for [LMn <sup>II</sup> (O <sub>2</sub> )-N(6)] <sup>-</sup>
Atom	х	v	Z	

Ato	m x	у	Z
Mn	0.232291	0.334129	-0.592416
Ν	-1.177606	2.184132	-0.642775
N	-2.257882	-0 520319	-0.685031
N	-1 330124	5 110343	-0 594479
N	0.076346	1 523375	0.645783
0	1.00000	1 222225	0.043783
0	1.009002	1.323335	0.608626
0	1./56/09	1.692863	-0.880004
0	0.387188	-0.736307	-2.423229
С	-2.565853	1.929118	-1.075543
С	-3.112832	0.653516	-0.421178
С	-1.328683	4.387954	0.529569
С	-1.585049	6.414772	-0.201859
Ν	-1.570351	5.180698	1.629624
C	-1.733783	6.481127	1.171638
Č	-1 626756	4 741325	3 023015
č	-1 025494	2 915136	0.627699
c	0.137277	1 020324	2 637470
c	1 069520	-1.929324	-2.037470
C	-1.008520	-2.210349	1.025792
U N	1.063248	-2.415455	1.025/82
N	-0.855635	-3.5189/0	0.983610
C	0.501339	-3.658885	1.243565
С	-2.400729	-1.584926	0.325944
С	-1.856536	-4.583964	1.043148
С	-1.547325	-2.180966	-2.456933
С	0.668249	-3.029313	-3.075534
С	-2.072649	-3.462319	-2.716608
С	-1.260205	-4.527977	-3.147669
С	0.119508	-4.294275	-3.324643
Ċ	-2.453840	-1.038697	-2.068072
Ĥ	-0 677073	2 723939	-1 361413
н	-2 558523	1 825345	-2 178536
ц	3 248001	2 777407	0.840722
п п	2 140066	2.777407	-0.840722
11	-3.149900	0.799370	0.077087
п	-4.100935	0.490775	-0./58005
H	-1.648486	7.232985	-0.930272
Н	-1.939304	7.306920	1.860209
Н	-1.851468	5.612315	3.662959
Н	-0.657001	4.307656	3.336364
Н	-2.423314	3.983825	3.161460
Н	0.033187	2.728987	0.951796
Η	-1.669866	2.439547	1.396995
Н	2.109728	-2.104049	1.117730
Н	0.924953	-4.620460	1.549633
Н	-2.783166	-1.122171	1.260760
Н	-3 148778	-2.357590	0.031358
н	-1 360079	-5 518360	1 357709
н	-2 308734	-4 736984	0.043471
н	2.500754	1 227/05	1 77/679
п	-2.030009	-4.33/493	1.//40/8
п	1./40040	-2.048040	-3.218291
H	-3.158018	-3.622645	-2.589119
H	-1.6956/2	-5.519545	-3.34/026
H	0.776322	-5.113292	-3.664572
Н	-2.269935	-0.183749	-2.751650
Н	-3.521290	-1.349241	-2.198456

Atom x		у	Z
Mn	0.053276	-0.004081	-0.093537
Ν	-2.292591	0.499218	-0.240554
Ν	-1.013206	-2.146869	-0.478220
N	-0.270173	2.245667	0.344355
N	-1 173690	-5 416802	0 124829
0	0.095508	-0 569482	1 957304
0	1 464618	0.451526	1 257217
0	0.524622	-0.451520	2 124116
Č	0.334033	-0.100284	-2.134110
C	-3.09/423	-0./3/393	-0.318089
C	-2.319384	-1.959832	0.189/00
C	-1.43/568	2.385/14	0.983657
C	0.489597	3.350157	0.684629
Ν	-1.461826	3.544320	1.713519
С	-0.232367	4.167067	1.534953
С	-2.545717	4.009721	2.578548
С	-2.533506	1.358600	0.927002
С	0.925830	-1.206106	-2.749150
С	-0.802960	-4.330304	0.818896
С	-1.768935	-6.264790	1.040011
Ν	-1.144228	-4.461969	2.153208
С	-1.757212	-5.694052	2.301833
С	-0.133345	-3.107903	0.261228
С	-0.885210	-3.521338	3.248273
С	0.170902	-2.437267	-2.675304
Č	2 122253	-1.222813	-3.536837
Ċ	0.632634	-3 581054	-3 355531
Č	1.812052	-3.572764	-4.125186
Č	2 552555	-2.375483	-4 208897
Č	-1.141243	-2.472995	-1.923648
H	-2.432431	1.056381	-1.091670
Н	-3.396908	-0.878735	-1.374952
Н	-4 043908	-0.655352	0 262576
Н	-2.100385	-1 819181	1 266746
Н	-2.974275	-2.860394	0.086477
н	1 504634	3 491701	0 296207
н	-0.003178	5 121893	2 018267
н	-2 378769	5 074327	2 818645
н	-2 576081	3 426519	3 520383
н	-3 516699	3 909503	2 057848
н	-2 486731	0 723089	1 838213
н	-3 537963	1 845862	0.915371
н	-2 169720	-7 243250	0.744504
ц	2.107720	6.040860	3 276880
н	0.657179	-3 /20239	-0 447049
ц	0.336301	2 515037	1 073836
н ц	0.330301	-2.313037	3 044535
и П	1 924484	2 228550	2 805701
н ц	-1.024404	-5.556559	2 8/1527
п U	-0.303988	-2.33028/	2.041337
н ц	2.701294	1 500/00	2 270555
н Ц	0.038273	-4.500400	-3.219333
н п	2.140204	-4.402420	-4.04609/
н Ц	3.4/9/00	-2.34110/	-4.000100
11	-1.010201	-1./06200	-2.330313
11	-1.0303/4	-2.400823	-2.004360

# Table S11. Cartesian Coordinates for $[LMn^{II}(O_2)-N(7)]^-$

Atom x		y z	
Mn	-0.126780	4.590807	-1.588106
0	1.138244	4.697236	-0.464507
Ô	0 400261	3 972213	-3 091843
Ň	-1 725089	2 354045	-3 77/392
N	0.831345	2.554045	0.864848
IN NI	-0.631343	2.709402	-0.004040
IN	0.006241	0.55/080	-2.188350
N	-2.501975	5.400/48	-3.222649
0	-1.671923	5.286429	-0.215282
С	-1.313020	1.577727	-1.405553
С	-1.441595	1.238333	-2.878934
Ν	-1.623074	0.685492	-0.406527
С	-2.144536	-0.670704	-0.578114
С	-1.207971	9.548009	-3.851340
Ċ	-1.315321	1.280257	0.809995
Č	-0.832568	2 535686	0 508329
č	-3.060672	4 391643	-4 147942
č	0.812758	7 181501	3 044806
c	2 764610	9 142550	1 107256
C	-3.704019	6.142330	-1.19/230
C	-2.225/88	0.4/551/	-0.213576
C	-3.041839	2.9/3660	-3.566960
Ν	-0.516839	8.519157	-3.075583
С	0.523953	8.742190	-2.185094
С	0.831993	7.513682	-1.636437
С	-2.581999	8.688222	0.846413
С	-1.960588	7.432043	0.821333
С	-3.560358	5.865285	-2.293454
С	-3.491072	9.061443	-0.165340
С	-1.826404	6.499452	-3.918680
Ċ	-3.157415	6.872475	-1.244160
Ĥ	-0.966025	3.068001	-3 593770
н	-2 218571	0.451248	-2 992463
ц	0.486041	0.768272	3 205010
п п	2 272840	1.0870272	-3.203910
11	-2.372640	-1.08/03/	1 1774401
п	-3.0/5215	-0.05/08/	-1.1//449
H	-1.399464	-1.321419	-1.0/6384
H	-0./25//9	10.520/15	-3.651122
Н	-1.144786	9.335182	-4.935548
Н	-2.271544	9.606440	-3.546707
Н	-1.475310	0.757452	1.757818
Η	-0.485085	3.343552	1.157264
Η	-4.103603	4.667718	-4.446241
Н	-2.457301	4.390486	-5.079394
Н	-4.488133	8.411112	-1.988091
Н	-3.824520	2.357898	-4.067970
Н	-3 328670	3 024200	-2,486569
Н	0.932484	9 744642	-2 027021
н	1 575553	7 231243	-0.885/113
и П	2 254127	0.201720	1 666052
11 11	-2.33413/	7.371/30 7.127177	1.000055
11	-1.24023/	( )020(2	2 005504
н	-4.41/088	0.283803	-2.883394
H	-3.931290	4.949849	-1./83/20
H	-3.981707	10.047478	-0.148811
Н	-1.286545	6.058259	-4.783476
Η	-2.536145	7.256900	-4.337411

Table S12. Cartesian Coordinates for cis-[LMn<sup>IV</sup>(O)<sub>2</sub>]<sup>-</sup>

Table S1	13. (	Cartesian	Coordir	nates for	$[LMn^{IV}(O)_2-N(6)]^-$
Atom	х	У	Z		

Atom x		у	Z
Mn	0.268471	0.079298	-1.436665
N	-0 663308	1 912596	-0 729579
N	-2 017562	-0.670439	-1.083209
N	0.295559	4 002154	0.174220
IN NI	-0.283338	4.003134	0.174320
IN O	0.062209	-0.782448	0.054/88
0	1.8/2494	0.530219	-1.043172
0	-0.136102	0.637397	-3.004050
0	0.492325	-1.826467	-2.002081
С	-2.108288	1.835444	-1.060370
С	-2.719431	0.525447	-0.559745
С	-0 727402	3 834962	0 878983
Č	-0 906420	5 991536	0 716729
Ň	-1 614837	4 236232	1 856193
Ċ	-1 729797	5 613745	1 764271
c	2 201229	2 202270	2 8 4 2 8 0 2
c	0.220825	2.393279	2.645802
c	-0.320823	2.406723	0.023323
C	-0.298542	-2.490229	-2.834950
C	-1.000561	-1.543069	0.916410
С	0.864410	-0.821665	1.773864
Ν	-0.922362	-2.070964	2.178952
С	0.271386	-1.621913	2.734628
С	-2.063658	-1.781722	-0.113708
С	-1.864557	-2.997396	2.806202
С	-1.708326	-2.233601	-3.040317
С	0.268984	-3.598655	-3.545711
С	-2.438266	-3.086476	-3.896972
Ċ	-1 856290	-4 165174	-4 585051
Č	-0.482182	-4 414614	-4 398988
c	-2 455090	-1.054719	-2 440037
н	-0.210946	2 524721	-1 422237
п	2 174400	1 880880	2 162707
11	-2.174400	2 604909	-2.102/9/
11 11	-2.070812	2.094696	-0.037839
п	-2.051988	0.489586	0.546829
Н	-3.806435	0.499546	-0.812315
Н	-0.726768	7.002078	0.328674
Н	-2.375988	6.178874	2.443303
Н	-2.979546	4.023448	3.433181
Н	-1.559457	2.926410	3.531335
Н	-2.883678	2.602867	2.344365
Η	0.779577	2.299530	0.708011
Н	-0.764329	1.731423	1.378086
Н	1.811562	-0.272036	1.804636
Н	0.567802	-1.907891	3.748661
Н	-3.072460	-1.905447	0.348287
н	-1 848723	-2 723764	-0.660995
н	-1 766859	-2 921506	3 903815
н	-1.659861	-4 041214	2 494760
ц	2 800309	731214	2.777700
н ц	-2.077300	2 700089	2.32102/
11 11	2 51(042	-3.130300	-3.370/41
н	-3.516042	-2.88528/	-4.028/88
H	-2.465198	-4.801042	-5.246228
H	0.00/336	-5.253898	-4.921006
Н	-2.256543	-0.159336	-3.068726
Н	-3.552510	-1.269576	-2.457080

Atom x		y z	
Mn	-0.085693	0.276062	-0.807584
Ν	-2 151316	0 741460	-0 341040
N	-1.019217	_1 010005	-0.648688
IN NI	-1.019217	-1.919995	-0.048088
IN N	-2.840039	5.055189	0.00/1/0
N	-1.143/94	-5.09/9/1	0.113/03
0	0.498911	0.117807	0.779761
0	0.031061	1.778249	-1.551891
0	1.242958	-0.544945	-2.035899
С	-2.990571	-0.399413	-0.772609
Ċ	-2.420855	-1 698559	-0 212138
č	2.126033	2 657810	1 23/050
c	2.120734	4 915664	1.234039
U N	-2.200373	4.813004	1.070182
N	-1.103113	3.1/1496	1.995682
C	-1.182955	4.549192	1.906682
С	-0.119559	2.418589	2.779119
С	-2.418851	1.198783	1.058696
С	1.448211	-1.778244	-2.483070
С	-0.962955	-3.982889	0.834454
С	-1.843516	-5.967162	0.926987
N	-1 523600	-4 119859	2 093897
C	-2.086652	-5 382813	2 158144
c	0.265072	2 744794	0.245242
C	-0.203972	-2.744704	2 1 90 4 6 4
C	-1.501143	-3.150583	3.189404
C	0.42/012	-2./88115	-2.51/425
C	2.738533	-2.123354	-2.992230
С	0.727275	-4.061778	-3.041027
С	1.999017	-4.379919	-3.549685
С	3.005555	-3.393942	-3.518488
С	-0.969846	-2.483908	-2.031814
Н	-2.309362	1.545004	-0.965971
Η	-2.996942	-0.411250	-1.880557
Н	-4.045430	-0.280397	-0.436488
Н	-2.424506	-1.636401	0.893329
Н	-3.075494	-2.555687	-0.491294
Н	-2.644405	5.792975	0.757374
Н	-0 475828	5 195615	2.436041
н	0 738062	3 081216	2 994227
н	0.217473	1 5/1859	2.77117
и Ц	0.561800	2 094424	2 720614
и П	1 802720	0.502055	1 748205
11	-1.602729	1.029194	1.746203
П	-3.493829	1.028184	1.290421
H	-2.128002	-6.9/1602	0.58/952
H	-2.588496	-5.738215	3.063752
Н	0.684218	-3.038645	-0.138701
Н	-0.004101	-2.051444	1.169813
Н	-1.242727	-3.639073	4.129742
Η	-2.586236	-2.750945	3.321863
Н	-0.871334	-2.316622	2.975678
Н	3.522430	-1.349084	-2.965529
Н	-0.069094	-4.824566	-3.042829
Н	2.203391	-5.382291	-3.956532
Н	4.013317	-3.619794	-3.905334
Н	-1 444322	-1 725810	-2.693906
н	-1 588712	-3 407950	-2 091020
11	1.500/12	J.TU/950	2.071020

Table S14. Cartesian Coordinates for [LMn<sup>IV</sup>(O)<sub>2</sub>-N(7)]<sup>-</sup>

### **IV. Experimental Details**

*Chemicals*. Anhydrous *N*,*N'*-dimethylformamide (DMF, Sigma Aldrich > 99.8%, stored on molecular sieves), the supporting electrolyte Bu<sub>4</sub>NPF<sub>6</sub> (Fluka, puriss.  $\geq$  99%), and HClO<sub>4</sub> (RP prolabo Nanopur 70%), CaCl<sub>2</sub> (Prolabo), KO<sub>2</sub> (Sigma Aldrich) were used as received. 18-crown-6 (Sigma Aldrich 99%) was recrystallized from acetonitrile and vacuum dried before use. Aqueous solutions were prepared from MilliQ water (TKA micropure). The metal complex [Mn<sup>II</sup>L]<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> was prepared according to our previously described method.[5] In *N*,*N'*-dimethylformamide (DMF) the complex is present as the solvated monomer [Mn<sup>II</sup>L]<sup>+</sup>.

### Methods and Instrumentation

**Cyclic voltammetry.** Electrochemical experiments were run under an argon atmosphere, or in air dehumidified *via* a CaCl<sub>2</sub> drying-tube. Cyclic voltammograms were recorded on a Metrohm potentiostat (AUTOLAB model). For cyclic voltammetry, the counter electrode used was an Au wire and the working electrode a glassy carbon disk carefully polished before each voltammogram with a 1 µm diamond paste, sonicated in ethanol bath, washed with ethanol and finally air dried. The reference electrode used was an SCE (saturated calomel electrode), isolated from the rest of the solution by a fritted bridge. The ohmic drop was systematically compensated using the adequate option within the commercial potentiostat. For scan rate higher than 0.2 V/s, cyclic voltammetry experiments were run using a potentiostat developed in the laboratory, equipped with positive feedback compensation and current measurer.[24] In these experiments Ohmic drop was also carefully compensated.

**Uv-Vis Spectroelectrochemistry.** Uv-Vis Spectroelectrochemical experiments were performed following our previously described method.[25] The apparatus for spectroelectrolysis experiments consists of a 40 mm x 10 mm x 10 mm quartz UV-Vis-NIR cell mounted in a thermostatic cell holder on a Specord S600 (Analytik Jena) spectrophotometer. The working electrodes were two parallel vitreous carbon plates 50 mm x 10 mm x 0.18 mm (SIGRADUR©, HTW Hochtemperatur-Werkstoffe GmbH). The reference and the counter electrodes are both separated by fritted glass bridge and are located near the top of the cell. The entire solution was saturated with dried air (1 mM  $O_2$ ), and the cell was cooled to 263 K by a Julabo circulation cryostat.

**EPR spectroscopy**. X-band EPR spectra were recorded on a Bruker ELEXSYS 500 spectrometer equipped with an Oxford Instrument continuous flow liquid helium cryostat and a temperature control system. A dual mode cavity (Bruker ER 4116DM) was used for perpendicular and parallel mode detection, respectively.

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