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Electrochemical formation of Mn^{III}-peroxo complexes supported by pentadentate amino pyridine and imidazole ligands[†]

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A novel and efficient method for preparing $[Mn^{III}(O_2)(L)]^+$ complexes using electrochemically generated superoxide is reported, with the reaction probed by low temperature electronic absorption and electron paramagnetic resonance spectroscopic techniques.

Manganese ions are found at the active sites of numerous enzymes involved in important reactions such as the activation of molecular oxygen,¹ the detoxification of superoxide anion $(O_2^{\bullet-})$ and hydrogen peroxide (H_2O_2) ,² or oxygen evolution from water-splitting.³ Although the reaction mechanisms involved are far from being understood, Mn^{III} -(hydro)peroxo species have been suggested to be key intermediates in many enzymatic cycles of Mn-containing enzymes such as MnSOD,² homoprotocatechuate 2,3-dioxygenase,⁴ catalase,⁵ and the oxygen evolving complex of photosystem II.⁶ Such intermediates have also been involved in catalytic oxidative reactions such as alkene epoxidation.⁷ In this

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 \dagger Electronic supplementary information (ESI) available: Synthesis and X-ray diffraction structures of $[Mn^{II}(imL_5^{-2})ClO_4)](ClO_4)$ (Fig. S1) and $[Mn^{II}(imL_5^{-2})Cl](PF_6)$ (Fig. S2). Experimental details of the electrochemical and spectroelectrochemical set-up; E^0 (V), λ (nm) and ϵ (M⁻¹ cm⁻¹) values tables; cyclic voltammograms of $[Mn^{II}(imL_5^{-2})ClO_4)](ClO_4)$, $[Mn^{II}(imL_5^{-2})Cl](PF_6)$, $[Mn^{II}(N4py)(OTf)](OTf)$ and $[Mn^{II}(mL_5^{-2})(OI_2)](BPh_4)_2\cdot 2H_2O$. Parallel mode EPR spectra of chemically prepared $[Mn^{III}(O_2)(imL_5^{-2})]^+$ and $[Mn^{III}(O_2)(N4py)]^+$. CCDC 792850 and 792851. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc41300d \ddagger Present address: Synchrotron Soleil, L'Orme des Merisiers, Saint-Aubin – BP 48, 91192 Gif-sur-Yvette, France.

context it is of great interest to prepare and characterise new Mn^{III} -(hydro)peroxo complexes. However owing to their inherent reactivity, only a handful of $[Mn^{III}(O_2)(L)]$ complexes have been isolated and structurally characterised.^{8–11} Other metastable $[Mn^{III}(O_2)(L)]$ species have also been generated *in situ* and characterised using various spectroscopic techniques.^{12–16} In all reported cases, $[Mn^{III}(O_2)(L)]$ species were prepared by chemical means using O_2 , H_2O_2 or KO_2 (often in large excess), which frequently results in poor yields and various undesired side-reactions. Herein, we report the first examples of $[Mn^{III}(O_2)(L)]$ complexes prepared by using electrochemically generated $O_2^{\bullet-}$. The formation of peroxo-species was monitored using low temperature electronic absorption spectroscopy, and electron paramagnetic resonance spectroscopy, which revealed a highly efficient and selective process that minimised the formation of side-products.

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The synthesis and selected characterisation of $[Mn^{II}(imL_5^2)-(ClO_4)]ClO_4$,¹⁷ $[Mn^{II}(mL_5^2)(OH_2)](BPh_4)_2 \cdot 2H_2O^{18}$ and $[Mn^{II}(N4py)-(OTf)]OTf^{17}$ $(imL_5^2 = N-methyl-N,N',N'-tris((1-methyl-4-imidazolyl)-methyl)ethane-1,2-diamine, mL_5^2 = N-methyl-N,N',N'-tris(2-pyridyl-methyl)ethane-1,2-diamine, and N4py = <math>N,N$ -bis(2-pyridyl-methyl)-N-bis(2-pyridyl)methylamine, Scheme 1) have been described previously. An X-ray diffraction structure was obtained for $[Mn^{II}(imL_5^{-2})(ClO_4)]^{\dagger}$, which has not been reported previously, and it reveals a hepta-coordinated Mn^{II} centre adopting a distorted pentagonal geometry (Fig. S1, ESI[†]).§ The equatorial plane is occupied by three N-donors from the pentadentate imL_5^{-2} (two at the diamino bridge, and one imidazolyl), and two O-donors from the chelating ClO_4^- , while the axial positions are occupied by the remaining two N-donors from imL_5^{-2} (two imidazolyl).





Cyclic voltammetry of [Mn^{II}(imL₅²)(ClO₄)]ClO₄ and [Mn^{II}(N4py)-(OTf)]OTf complexes were recorded in acetonitrile solution on a glassy carbon electrode. In solution, complex [Mn^{II}(imL₅²)(ClO₄)]⁺ shows one irreversible anodic wave at $E_p = 1.16$ V vs. SCE (Fig. S3, ESI[†]) attributed to the Mn^{II}/Mn^{III} oxidation process. This value is *ca.* 600 mV higher than the Mn^{II}/Mn^{III} oxidation potential of the chlorido-analogue (see ESI⁺). This variation is consistent with the labile ClO_4^{-} ligand dissociating or being displaced by a neutral MeCN solvent molecule. This $E_{\rm p}$ = 1.16 V vs. SCE value for $[Mn^{II}(imL_5^2)(sol)]^+$ is also *ca.* 300 mV lower than the value reported for its solvated pyridyl analogue [Mn^{II}(mL₅²)(sol)]²⁺ (sol = MeCN, E_p^a = 1.40 V vs. SCE).¹⁹ This difference is attributed to the replacement of the pyridyl groups by the more electron donating imidazolyl groups, thus stabilising the higher oxidation state of the Mn centre. In the case of [Mn^{II}(N4py)(OTf)]⁺, an anodic irreversible wave is observed at $E_p = 1.55$ V vs. SCE (Fig. S3, ESI[†]), which is also consistent with the dissociation or displacement of the anionic OTf⁻ ligand. These experimental results support the formation of solvated $[Mn^{II}(imL_5^2)(sol)]^{2+}$, $[Mn^{II}(N4py)(sol)]^{2+}$ and $[Mn^{II}(mL_5^2)(sol)]^{2+}$ species in solution.

Bulk electrolysis $(-1.2 \text{ V } \nu \text{s. SCE})$ of air saturated DMF solutions (by bubbling dried air for 10 min just before electrolysis giving 1 mM O_2)^{20–22} containing the above-mentioned complexes (1 mM) results in the reduction of dissolved O_2 to $O_2^{\bullet^-}$, (Fig. S4, ESI[†]) which readily reacts with the solvated $[\text{Mn}^{II}(\text{L})(\text{sol})]^{2+}$ complexes to generate the corresponding $[\text{Mn}^{III}(O_2)(\text{L})]^+$ species *in situ*.

This is confirmed by UV-vis spectroelectrochemical experiments using a Pt grid working electrode in a thin layer spectroelectrochemical cell thermally equilibrated at 233 K in a previously described experimental set up.²³ Upon application of the reductive potential, a major band develops in the UV-vis absorption spectra at $\lambda = 542$ nm (normalised absorbance $(A_{\text{norm}}) = 484 \text{ M}^{-1} \text{ cm}^{-1}$,¶ 585 nm $(A_{\text{norm}} = 335 \text{ M}^{-1} \text{ cm}^{-1})$ and 617 nm (A_{norm} = 280 M⁻¹ cm⁻¹), corresponding to the formation of $[Mn^{III}(O_2)(imL_5^2)]^+$, $[Mn^{III}(O_2)(mL_5^2)]^+$, and $[Mn^{III}(O_2)(N4py)]^+$, respectively (Fig. 1, left panels), which are comparable to literature values.^{14,15,17} For each sample, bulk electrolysis was terminated when absorbance at λ_{max} no longer increased. Accordingly, the λ_{max} values across the series $([\text{Mn}^{\text{III}}(\text{O}_2)(\text{imL}_5^2)]^+$ < $[Mn^{III}(O_2)(mL_5^2)]^+ < [Mn^{III}(O_2)(N4py)]^+)$ follow the same trend as the Mn^{II}/Mn^{III} oxidation potentials of the solvated parent compounds, highlighting the influence of the electron-donating properties of the supporting ligands on these two observables (Fig. S5, ESI⁺). However, the calculated A_{norm} values are significantly higher than the extinction coefficients reported for the same $[Mn^{III}(O_2)(L)]^+$ species prepared chemically by H_2O_2 or KO_2 , where complete transformation of the initial Mn^{II} complexes was assumed (Table S4, ESI[†]). This suggests a higher yield when the [Mn^{III}(O₂)(L)]⁺ species are generated electrochemically, particularly in the case of $[Mn^{III}(O_2)(imL_5^2)]^+$ and $[Mn^{III}(O_2)(mL_5^2)]^+$ where at least a two-fold increase in A_{norm} is observed. This difference is consistent with the view that the extinction coefficients derived from chemical generation of [Mn^{III}(O₂)(L)]⁺ species are at the lower limit, owing to incomplete conversion or side reactions (e.g. dinuclear [LMnO₂MnL] formation⁵). In the present electrochemical preparation, we propose that the in situ formed



Fig. 1 (left panels) Evolution of the UV-vis spectrum of air saturated (1 mM O₂) DMF solution containing 0.2 M TBAPF₆, and 1 mM [Mn^{II}(N4py)(OTf)](OTf) (top), [Mn^{II}(mL₅²)(OH₂)](BPh₄)2·2H₂O (middle), or [Mn^{II}(imL₅²)(CIO₄)](CIO₄) (bottom) before and at the completion of bulk electrolysis (300 s) performed at -1.2 V vs. SCE on a Pt grid in a thin layer spectroelectrochemical cell (0.5 mm optical pathlength) at 243 K. (right panels) Analogous experiments (0.1 M TBAPF₆, 150–200 s at -1.2 V vs. SCE) on parallel glassy carbon films in a conventional cuvette (10 mm optical pathlength) at 263 K.

 $O_2^{\bullet-}$ anion at the electrode can react instantly with the excess of Mn^{II} complexes and diffusion of the product away from the electrode renders side reactions less favourable, allowing for higher yields of $[Mn^{III}(O_2)(L)]^+$ species.

Similar UV-vis spectroelectrochemical experiments were also conducted using glassy carbon film working electrodes in a conventional cuvette thermostated at 263 K (Fig. 1, right panels), which allows for the collection of reaction mixture aliquots during electrolysis for perpendicular- and parallelmode EPR spectroscopic analysis. Briefly, two vitreous carbon plate working electrodes were inserted along the two sides parallel to the light path, with the reference and the counter electrodes, both separated by a fritted glass bridge, located near the top of the cell (Scheme S1, ESI⁺). Bulk electrolysis was performed with stirring and, in all cases, the total charge consumed at completion corresponded to one electron per $[Mn^{II}(L)(sol)]^{2+}$. However, lower A_{norm} values were observed which is consistent with the inherent instability of [Mn^{III}(O₂)(L)]⁺ species at higher temperatures. In the case of $[Mn^{III}(O_2)(N4py)]^+$ the major band is also ill-defined, suggesting that it is the most unstable of the series, in line with limited thermal stability of



Fig. 2 EPR spectra for the solutions of complexes before and after the *in situ* electrochemical generation of superoxide, recorded with perpendicular-mode (left panels) and parallel-mode (right panels) detection. Experimental conditions: microwave frequencies 9.63 GHz (\perp) and 9.41 GHz (II); microwave power 1 mW; field modulation amplitude 0.7 mT; T = 4 K.

samples prepared by chemical methods.¹⁷ For all starting solutions, the perpendicular-mode EPR spectra display characteristic mononuclear Mn^{II} complexes (Fig. 2). The resonances for $[Mn^{II}(imL_5^2)(sol)]^+$ are centred at *ca.* g = 4.6 (150 mT), while $[Mn^{II}(mL_5^2)(sol)]^+$ and $[Mn^{II}(N4py)(sol)]^+$ displayed features at ca. g = 2 (340 mT) indicating smaller zero-field splitting values for the latter complexes. This echoes the similarity of the X-band parallel-mode EPR spectra where for $[Mn^{II}(imL_5^2)(sol)]^+$ the spectrum is essentially silent, but for the other two complexes resonances are detected at ca. 130 mT with 6-line hyperfine patterns resolved. For the solutions collected after bulk electrolysis, the sample initially containing [Mn^{II}(N4py)(sol)]⁺ is the only one to still display some $Mn^{\rm II}$ species in the EPRspectrum although the signal intensity is significantly decreased. In all three cases, the X-band parallel-mode spectra display new resonances with well-resolved 6-line hyperfine coupling, clearly detected below 100 mT, which are characteristic of Mn^{III} complexes and attributed to the corresponding $[Mn^{III}(O_2)(L)]^+$ species. The spectrum for $[Mn^{III}(O_2)(N4py)]^+$ displays the lowest yield, which is consistent with the UV-vis absorption results (vide supra). The spectra are similar to those obtained chemically by addition of H₂O₂ or KO₂ (Fig. S6, ESI[†]).^{14,15,17} However, the amounts of dimeric Mn^{III}Mn^{IV} by-products are significantly diminished when [Mn^{III}(O₂)(L)]⁺ species are generated electrochemically. This observation further supports the fact that side-reactions are limited when electrochemical methodology is used.

In summary we have reported here the first examples of $[Mn^{III}(O_2)(L)]^+$ complexes prepared from a reaction between $[Mn^{II}(L)]^{2+}$ (L = amino-pyridine or imidazol pentadentate ligands) and electrochemically generated $O_2^{\bullet-}$. The formation of peroxo-species was monitored using low temperature electronic absorption and electron paramagnetic resonance spectroscopies, which revealed a highly efficient and selective process that minimised the formation of side-products. We anticipate that this method could easily be transposed to the preparation of other metal-peroxo species of interest.

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§ Selected X-ray crystallographic data for $[Mn^{II}(imL_5^{-2})(ClO_4)](ClO_4)$: chemical formula: $C_{18}H_{28}Cl_2MnN_8O_8$; $M_r = 610.32$; unit cell dimensions/Å: a = 8.5130(4), b = 21.2953(9), c = 13.6687(6); cell volume/Å³ = 2457.83(19); T/K = 100(1); space group = $P2_1/n$; Z = 4; no. of collected, independent and observed $[I > 2\sigma(I)]$ reflections = 45 770, 13 247, 10 855, respectively; $R_{int} = 0.0274$; $R[F^2 > 2\sigma(F^2)]R_1 = 0.0428$; $wR_2 = 0.0868$; CCDC no. 792851. X-ray diffraction structures were also obtained for the novel comparative complex $[Mn^{II}(imL_5^{-2})Cl](PF_6)$: chemical formula: $C_{18.5}H_{30}ClF_6MnN_8O_{0.5}P$; Mr = 607.86; unit cell dimensions/Å: a = 9.5092(12), b = 10.8499(13), c = 14.270(3); cell volume/Å³ = 1280.2(3); T/K = 100(1); space group = P-1; Z = 2; no. of collected, independent and observed $[I > 2\sigma(I)]$ reflections = 24 974, 11 793, 9887, respectively; $R_{int} = 0.0215$; $R[F^2 > 2\sigma(F^2)]R_1 = 0.0602$; $wR_2 = 0.1414$; CCDC no. 792850.

 $\P A_{norm}$ = absorbance normalised vs. $[Mn^{II}(L)(sol)]^{2+}$ concentration and optical pathlength.

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