# Electrochemical formation of Mn<sup>III</sup>-peroxo complexes supported by pentadentate amino pyridine and imidazole ligands.

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# **Electronic Supplementary Information (ESI)**

Experimental	3
Scheme S1: setup for spectroelectrochemical experiments in a conventional cuvette	5
Data	
X-ray Diffraction	6
<b>Figure S1:</b> Crystal structure of $[Mn^{II}(imL_5^2)Cl]^+$	6
<b>Figure S2:</b> Crystal structure of $[Mn^{II}(imL_5^2)ClO_4]^+$	7
<b>Table S1:</b> Selected bond lengths [Å] and angles [°] for $[Mn^{II}(imL_5^2)Cl]PF_6$	
and [Mn <sup>II</sup> (imL <sub>5</sub> <sup>2</sup> )ClO <sub>4</sub> ]ClO <sub>4</sub>	8
<b>Table S2:</b> Crytallographic Data for $[Mn^{II}(imL_5^2)Cl]PF_6$ . 0.5(CH <sub>3</sub> OH) and	
$Mn^{II}(imL_5^2)ClO_4]ClO_4$	9
Electrochemical characterization	11
<b>Figure S3:</b> Cyclic votammetry in CH <sub>3</sub> CN of $[Mn^{II}(imL_5^2)Cl]PF_6$ , $[Mn^{II}(imL_5^2)ClO_4]ClO_4$	
and [Mn <sup>II</sup> (N4py)(OTf)]OTf	11
<b>Table S3:</b> $E^0$ or $E_p$ values for $[Mn^{II}(imL_5^2)Cl]^+$ , $[Mn^{II}(imL_5^2)(sol)]^{2+}$ in CH <sub>3</sub> CN,	
[Mn <sup>II</sup> (N4py)(sol)] <sup>2+</sup> in DMF and related complexes	12
Figure S4: Cyclic voltametry of O <sub>2</sub> in DMF	13
Spectroelectrochemistry	14
<b>Figure S5:</b> superposition of the UV-vis spectra of solutions of $[Mn^{II}(imL_5^2)]^{2+}$ , $[Mn^{II}(mL_5^2)]^{2+}$ and $[Mn^{II}(N4py)]^{2+}$ in DMF and TBAPF <sub>6</sub> 0.2M, O <sub>2</sub> 1mM upon reduction	
at $E = -1.2$ V vs SCE; $T = 243$ K.	14
<b>Table S4.</b> $\lambda$ (nm) and $\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> ) values of the various [Mn <sup>III</sup> (O <sub>2</sub> )(L)] species	15
Electron paramagnetic resonance	16
Figure S6: parallel mode EPR spectra for the peroxo complexes chemically generated	16
References	17

**Labels used in this work:**  $imL_5^2$ ,  $mL_5^2$  and N4Py labels has been used in our related previous work.<sup>1</sup>



## Experimental

*Caution:* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small quantities of these compounds should be prepared and they should be handled behind suitable protective shields.

## Synthesis of complexes:

[Mn<sup>II</sup>(imL<sub>5</sub><sup>2</sup>)Cl]PF<sub>6</sub>: Synthesis of the ligand imL<sub>5</sub><sup>2</sup> has been reported previously.<sup>1</sup> To a solution of ligand imL<sub>5</sub><sup>2</sup> (150 mg, 0.42 mmol) dissolved in methanol (7 mL) were added 83 mg of MnCl<sub>2</sub>•4(H<sub>2</sub>O) (0.42 mmol) in a minimum of methanol. The mixture was stirred, at air and room temperature for 15 minutes. One equivalent of NaPF<sub>6</sub> (70.54 mg, 0.42 mmol) were then added, yielding a white precipitate which was collected by filtration and washed with a minimum of ethanol and diethyl ether. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether to a methanolic solution of the complex, (overall yield 65 %). ESI-MS data are as follows: {Mn<sup>II</sup>(imL<sub>5</sub><sup>2</sup>)Cl}<sup>+</sup> m/z = 446.2 (calc.446.15)

 $[Mn^{II}(imL_5^2)ClO_4]ClO_4$ : Synthesis of  $[Mn^{II}(imL_5^2)ClO_4]ClO_4$  has been reported previously.<sup>1</sup> Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether to an ethanolic solution of the complex (overall yield 70 %).

 $[Mn^{II}(mL_5^2)(H_2O)](BPh_4)_2$ : Synthesis and X-ray analysis has been reported previously.<sup>2</sup> CCDC 792850 and 792851 contains the supplementary crystallographic data for  $[Mn^{II}(imL_5^2)Cl]PF_6$  and  $[Mn^{II}(imL_5^2)ClO_4]ClO_4$ . These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data\_request/cif</u>. [Mn<sup>II</sup>(N4py)(OTf)]OTf: Synthesis of [Mn<sup>II</sup>(N4py)(OTf)]OTf have been reported previously.<sup>1</sup> The X-ray crystal structure of this complex has been recently reported.<sup>3</sup>

**X-ray diffraction** data were collected on a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The temperature of the crystal

was maintained at the selected value (100 K) by means of a 700 series Cryostream cooling device within an accuracy of  $\pm 1$  K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97<sup>4</sup> and refined against  $F^2$  by full-matrix least-squares techniques using SHELXL-97 <sup>5</sup>with anisotropic displacement parameters for all non-hydrogen atoms. Treatment on H: H atoms of the ligand were added geometrically and refined by the riding model. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.<sup>6</sup>

Cyclic voltammetry. All electrochemical experiments were run under argon atmosphere. Cyclic voltammograms were recorded either on an EGG PAR potentiostat (M273 model) or a Metrohm potentiostat (AUTOLAB model). For cyclic voltammetry, the counter electrode used was a Pt wire and the working electrode a glassy carbon disk carefully polished before each voltammogram with a 1  $\mu$ m diamond paste, sonicated in ethanol bath and then washed with ethanol. The reference electrode used was an SCE (saturated calomel electrode), isolated from the rest of the solution by a fritted bridge.

Low Temperature UV/Visible Spectroelectrochemistry. Thin cell spectroelectrochemical data were obtained by a combination of a three electrode thin cell (optical length = 0.5 mm) mounted on a UV/Vis/NIR Varian Cary 5E Spectrophotometer. The apparatus for spectroelectrolysis experiments is described elsewhere.<sup>7</sup> It consists of a 0.5 mm quartz UV-Vis-NIR cell surmounted by a glass compartment. The working electrode was a 30 mm × 7 mm × 0.3 mm Pt grid with a wire covered with teflon to avoid electrolysis elsewhere than in the quartz window. The reference and the counter electrodes are located on the top of the cell. The entire solution was saturated with air (1 mM O<sub>2</sub>) and the cell was cooled to 243 K by a Julabo circulation cryostat.

Conventional cell spectroelectrochemical data were obtained by insertion of electrodes in a conventional spectroscopic curvette (optical length = 10 mm) mounted on a Specord S600 (Analytik Jena) spectrophotometer. 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. The working electrodes were two parallel vitreous carbon plates 50 mm × 10 mm × 0.18 mm (SIGRADUR<sup>©</sup>, HTW Hochtemperatur-Werkstoffe GmbH). The reference and the counter electrodes both separated by fritted glass bridge and are located near the top of the cell. The entire solution was saturated with air (1 mM  $O_2$ ), and the cell was cooled to 263 K by a Julabo circulation cryostat (Scheme. S1).



Scheme S1: setup for spectroelectrochemical experiments in a conventional cuvette

**EPR spectroscopy**: 9.4 GHz EPR (X-band) 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.

# Data

*X-ray Diffraction.* The crystal structures of  $[Mn^{II}(imL_5^2)C1]PF_6$  and  $[Mn^{II}(imL_5^2)(ClO_4)]ClO_4$  were determined by single-crystal X-ray diffraction. Views of the monocationic units are presented in Figure S1 and S2. Table S1 and S2 provides the principal crystallographic data with selected bond lengths and angles for  $[Mn^{II}(imL_5^2)C1]PF_6$  and  $[Mn^{II}(imL_5^2)(ClO_4)]ClO_4$ , respectively.



**Figure S1**. Crystal structure of  $[Mn^{II}(imL_5^2)CI]PF_6$  were. Hydrogen atoms, solvent molecules and counter anion (PF<sub>6</sub>) were omitted for clarity.

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**Figure S2**. Crystal structure of  $[Mn^{II}(imL_5^2)(ClO_4)]ClO_4$ . Hydrogen atoms, solvent molecules and counter anion (ClO<sub>4</sub>) were omitted for clarity.

$[Mn^{II}(imL_5^2)CI]PF_6$				
Mn - N(1)	2.3820(11)	Mn - N(4)	2.2194(11)	
Mn - N(2)	2.3550(11)	Mn - N(5)	2.2885(12)	
Mn - N(3)	2.2421(11)	Mn - Cl	2.3866(5)	
N(1) - Mn - N(2)	76.60(4)	N(3) - Mn - N(4)	101.17(4)	
N(1) - Mn - N(3)	72.36(4)	N(3) - Mn - N(5)	83.88(4)	
N(1) - Mn - N(4)	73.17(4)	N(1) - Mn - Cl	167.68(3)	
N(1) - Mn - N(5)	94.27(4)	N(2) - Mn - Cl	98.90(3)	
N(2) - Mn - N(3)	138.79(4)	N(3) - Mn - Cl	116.51(3)	
N(2) - Mn - N(4)	94.97(4)	N(4) - Mn - Cl	96.05(3)	
N(2) - Mn - N(5)	71.98(4)	N(5) - Mn - Cl	95.20(3)	
		[Mn <sup>II</sup> (imL <sub>5</sub> <sup>2</sup> )(ClO <sub>4</sub> )]ClO <sub>4</sub>		
Mn - N(1)	2.4094(7)	Mn - O(1)	2.4723(9)	
Mn - N(2)	2.4104(7)	Mn - O(2)	2.4604(8)	
Mn - N(3)	2.2198(7)	O(3) - Cl	1.4226(9)	
Mn - N(4)	2.1651(7)	O(4) - Cl	1.4264(8)	
Mn - N(5)	2.1621(7)			
N(1) - Mn - N(2)	74.68(2)	N(2) - Mn - N(4)	97.05(3)	
N(1) - Mn - N(3)	72.70(3)	N(2) - Mn - N(5)	73.30(3)	
N(1) - Mn - N(4)	75.15(3)	N(3) - Mn - N(4)	100.83(3)	
N(1) - Mn - N(5)	107.12(3)	N(3) - Mn - N(5)	90.38(3)	
N(2) - Mn - N(3)	136.99(3)	O(1) - Mn - O(2)	56.26(3)	

Table 1. Selected bond lengths [Å] and angles  $[\circ]$  for  $[Mn^{II}(imL_5^2)Cl]PF_6$  and  $[Mn^{II}(imL_5^2)(ClO_4)]ClO_4$ 

$[\operatorname{MII}(\operatorname{IIIIL}_5)(\operatorname{CIO}_4)] \subset \operatorname{IO}_4$		
Empirical formula	C <sub>18.5</sub> H <sub>30</sub> Cl F <sub>6</sub> Mn N <sub>8</sub> O <sub>0.5</sub> P	C <sub>18</sub> H <sub>28</sub> Cl <sub>2</sub> Mn N <sub>8</sub> O <sub>8</sub>
Formula weight (g mol <sup>-1</sup> )	607.86	610.32
Temperature (K)	100 (1)	100 (1)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	<i>P</i> -1	$P 2_1/n$
Unit cell dimensions		
a (Å)	9.5092(12)	8.5130(4)
b (Å)	10.8499(13)	21.2953(9)
c (Å)	14.270(3)	13.6687(6)
α (°)	97.998(3)	90
β(°)	98.664(3)	97.3070(10)
γ (°)	115.391(2)	90
$V(\mathring{A}^{3})$	1280.2(3)	2457.83(19)
Ζ	2	4
$D_{calc.}$ (Mg.m <sup>-3</sup> )	1.577	1.649
Absorption coefficient (mm <sup>-1</sup> )	0.753	0.817
F (0 0 0)	624	1260
Index ranges	-16 < h < 15 -16 < k < 18 -24 < 1 < 16	-14 < h < 12 -27 < k < 37 -21 < 1 < 24
Reflection collected	24 974	45 770
Independent reflections (Rint)	11793 (0.0215)	13247 (0.0274)
Observed reflections $[I > 2\sigma(I)]$	9 887	10 855
Refinement method	Full matrix least squares on F <sup>2</sup>	Full matrix least squares on F <sup>2</sup>
Final <i>R</i> indices $[I > 2\sigma I]$	R1 = 0.0486, wR2 = 0.1303	R1 = 0.0316, wR2 = 0.0826
R indices (all data)	R1 = 0.0602, wR2 = 0.1414	R1 = 0.0428, wR2 = 0.0868
S	1.025	1.022
$(\Delta/\sigma)_{\rm max}$	0.002	0.004
$(\Delta \rho)_{max, min} [e \text{ Å}^{-3}]$	1.369 ; -1.153	0.769 ; -0.751

Table	2.	Crytallographic	Data	for	[Mn <sup>II</sup> (imL <sub>5</sub> <sup>2</sup> )Cl]PF <sub>6</sub> .0.5(CH <sub>3</sub> OH)
[Mn <sup>II</sup> (im]	$L_5^2)(C$	lO <sub>4</sub> )]ClO <sub>4</sub>			

and

The mononuclear complex  $[Mn^{II}(imL_5^2)CI]PF_6$  (Figure S1) presents a distorted octahedral geometry. The  $Mn^{II}$  ion is wrapped by the pentadentate ligand and the coordination sphere is completed by a chloride ion. As reported in the case of the similar  $[Mn^{II}(mL_5^2)CI]^+$  cation,<sup>2</sup> the five-membered diamino bridge metallacycle imposes the shortening of the N(1)-Mn-N(2) angle compared to a regular octahedron. The Mn-N(imidazole) distances, (Mn-N(3), Mn-N(4) and Mn-N(5), respectively 2.2421(11), 2.2194(11) and 2.2885(12) Å) are slightly shortened compared to the corresponding Mn-N(pyridine) distances (2.274(3), 2.246(3) and 2.340(3), respectively in the  $[Mn^{II}(mL_5^2)CI]^+$  cation).<sup>2</sup> This observation is consistent with the electron-richer nature of imidazole compared to pyridine ligands. The Mn–Cl bond length (2.3866(5)) is consistent with those of related complexes with  $[N_5CI]$  donor set for which bond length values are reported between 2.35 and 2.53 Å.<sup>8-12</sup> The Mn–Cl bond is also slightly longer than the one in the  $[Mn^{II}(mL_5^2)CI]^+$  cation (2.3757(9) Å).<sup>2</sup>This variation is likely due to the shortening of the Mn-N (imidazole) distances compared to the Mn-N(pyridine) distances.

The X-ray crystallography of  $[Mn^{II}(imL_s^2)(CIO_4)]CIO_4$  (figure S2) reveals an heptacoordinated  $Mn^{II}$  ion adopting a distorted pentagonal geometry. The coordination sphere of manganese consists of the five nitrogen atoms from the ligand and two chelating oxygen atoms from the perchlorate ligand. The equatorial plane is occupied by one aromatic nitrogen atoms (Mn-N(3), 2.2198(7) Å), two nitrogen donor atoms from the amino bridge (Mn-N(1) and Mn-N(2) 2.4094(7) and 2.4104(7) Å, respectively) and two oxygen atoms from the chelating perchlorate ligand (Mn-O(1) and Mn-O(2), 2.4723(9) and 2.4604(8) Å, respectively). The axial positions are occupied by two nitrogen atoms from imidazoles (Mn-N(4) and Mn-N(5), 2.1651(7) and 2.1621(7) Å, respectively). The Mn-N(imidazole) bonds are slightly shorter than the one in cation  $[Mn^{II}(imL_s^2)CI]^+$ , whereas the two Mn-O bond distances from the perchlorate anions (2.4723(9) and 2.4603(8) Å) that complete the coordination sphere are longer than the Mn-Cl bond distance in  $1^+$  (2.3866(5) Å). In addition the O(1)-Mn-O(2) angle (56.26(3) °) is noticeably smaller than all of the N-Mn-N angles (ranging from 72.7 to more than 136.99 °). Electronic Supplementary Material (ESI) for Chemical Communications This journal is O The Royal Society of Chemistry 2013

## Electrochemical characterization:



**Figure S3.** Cyclic votammetry in acetonitrile (0.1 M TBAClO<sub>4</sub>) of a 1 mM solution of (a)  $[Mn^{II}(imL_5^2)Cl]PF_6$  (black line); (b)  $[Mn^{II}(imL_5^2)(ClO_4)]ClO_4$  (purple line), and  $[Mn^{II}(N4py)(OTf)]OTf$  (green line). Scan rate = 100 mV.s<sup>-1</sup>, T = 293 K. The cyclic voltammogram of  $[Mn^{II}(mL_5^2)(sol)]^{2+}$  in the same conditions (blue line).<sup>13</sup>

Complex  $[Mn^{II}(imL_5^2)Cl]^+$  exhibits two oxidation events. The first quasi-reversible anodic wave ( $E_p^a = 0.65 \text{ V} \text{ vs SCE}$ ) and the second irreversible anodic wave ( $E_p^a = 1.53 \text{ V} \text{ vs SCE}$ ) are attributed to the Mn<sup>II</sup> to Mn<sup>III</sup> and Mn<sup>III</sup> to Mn<sup>IV</sup> oxidation processes, respectively (figure S3). The reversibility of the second anodic wave increased at lower temperatures (not shown). These observations are similar to those reported for  $[Mn^{II}(mL_5^2)Cl]^+$ ,<sup>13</sup> but the  $E^0$  and  $E_p^a$  values are ca. 300 mV lower for  $[Mn^{II}(imL_5^2)Cl]^+$ .

**Table S3.**  $E^0$  or  $E_p$  values<sup>(a)</sup> (V vs SCE) for  $[Mn^{II}(imL_5^2)Cl]^+$ ,  $[Mn^{II}(imL_5^2)(sol)]^{2+}$  (solvated  $[Mn^{II}(imL_5^2)(ClO_4)]^+$ ) in acetonitrile (0.1 M Bu<sub>4</sub>NPF<sub>6</sub>),  $[Mn^{II}(N4py)(sol)]^{2+}$  (solvated  $[Mn^{II}(N4py)(OTf)]^+$ ) in DMF (0.1 M Bu<sub>4</sub>NPF<sub>6</sub>) and related complexes in acetonitrile.

	${E^0}\left( {\Delta E_p }  ight)$ or ${E_p}\left( V  ight)$ vs SCE ${Mn^{II}}/{Mn^{III}}$	$ \begin{array}{c} E^{0}\left(V\right)\left(\Delta E_{p}\right)\nu sSCE\\ Mn^{III}\!/Mn^{IV} \end{array} $	Ref
$[\mathrm{Mn}^{\mathrm{II}}(\mathrm{imL}_{5}^{2})\mathrm{Cl}]^{+}$	$E^0 = 0.65 \; (130 \; \mathrm{mV})$	1.53	this work
$[\mathrm{Mn}^{\mathrm{II}}(\mathrm{mL}_{5}^{2})\mathrm{Cl}]^{+}$	$E^0 = 0.95$	1.65	13
$[Mn^{II}(imL_5^2)(sol)]^{2+}$	$E_{p} = 1.16$	-	this work
$[Mn^{II}(mL_5^2)(sol)]^{2+}$	$E_{p} = 1.40$	-	13
$[Mn^{II}(N4py)(sol)]^{2+}$	$E_{p} = 1.55$	-	this work

(a)  $E^0$  is defined as  $(E_p^a + E_p^c)/2$ , where  $E_p^a$  is the potential value of the anodic peak and

 $E_p^c$  is the potential value of the cathodic peak.

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**Figure S4.** Cyclic voltametry of  $O_2^{14-15}$  (1mM in DMF and TBAPF<sub>6</sub> 0.1 M); T = 293 K. WE = glassy carbon, v = 0.2 V/s

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Spectroelectrochemistry:



**Figure S5**: superposition of the UV-vis spectra of solutions of  $[Mn^{III}(O_2)(imL_5^2)]^+$  (purple line),  $[Mn^{III}(O_2)(mL_5^2)]^+$  (blue line), and  $[Mn^{III}(O_2)(N4py)]^+$  (green line) (1 mM in DMF with TBAPF<sub>6</sub> 0.2M, O<sub>2</sub> 1mM) obtained from corresponding Mn(II) solution ( $[Mn^{II}(imL_5^2)]^{2+}$ ,  $[Mn^{II}(mL_5^2)]^{2+}$  and  $[Mn^{II}(N4py)]^{2+}$ ) upon reduction at E = -1.2 V vs SCE; T = 243 K. Path length l = 0.5 mm, working electrode: Pt grid

These are the same spectra presented in Figure 1 (left panels)

**Table S4.**  $\lambda$  (nm) and  $\varepsilon$  (M<sup>-1</sup>cm<sup>-1</sup>) values of the [Mn<sup>III</sup>(O<sub>2</sub>)(L)] peroxo species generated from cations [Mn<sup>II</sup>(imL<sub>5</sub><sup>2</sup>)(sol)]<sup>+</sup>, [Mn<sup>II</sup>(mL<sub>5</sub><sup>2</sup>)(sol)]<sup>2+</sup>, and [Mn<sup>II</sup>(N4py)(sol)]<sup>2+</sup> (1 mM in DMF and 0.2 M TBAPF<sub>6</sub>) upon reduction at E = -1.2 V vs SCE in presence of O<sub>2</sub> (1 mM) in a thin and 1cm spectroelectrochemical cells (T = 243 K, path length l = 0.5 mm, working electrode= Pt grid; T = 263 K, path length l = 1 cm, working electrode= vitreous carbon grid)

complex	$\lambda_1$ (nm); $\epsilon_1$ (M <sup>-1</sup> cm <sup>-1</sup> )	electrolysis time (s);	Ref
	$\lambda_2$ (nm); $\epsilon_2$ (M <sup>-1</sup> cm <sup>-1</sup> )	charge (C)	
$[Mn^{III}(O_2)(imL_5^2)]^+$	542; 484		this work thin cell
	430; 427		
	529; 159	200; 0.245	this work 1 cm cell (2.2 mL)
			()
	555; 180 <sup>(a)</sup>		1
	430; 170		
	370; 150		
$[Mn^{III}(O_2)(mL_5^2)]^+$	585; 335		this work thin cell
	430; 290		
	570; 139	150; 0.272	this work 1 cm cell (2.2 mL)
	581·80 <sup>(a)</sup>		1
	425: 90		
	120, 20		
	590; 165 <sup>(b)</sup>		16
	430; 100		
$[Mn^{III}(\Omega_2)(N4ny)]^+$	620: 278		this work thin cell
	432: 228		this work thin cen
	,		
	612; 67	150; 0.271	this work 1 cm cell
			(2.2 mL)
	$617.168^{(a)}$		1
	438.139		

(a): in butyronitrile/ethanol mixture

(b): in acetonitrile/dimethylsulfoxide mixture





**Figure S6**: parallel mode EPR spectra for the peroxo complexes generated chemically. Top spectrum: 10 equivalents of  $H_2O_2$  and 0.1 equivalent of NaOH were added to a 5 mM solution of  $[Mn^{II}(imL_5^{-2})(ClO_4)]$  in a 1:1 butyronitrile:ethanol mixture. The sample was immediately transferred to an EPR tube and frozen in liquid N<sub>2</sub>. Experimental conditions: microwave frequencies 9.35 GHz; microwave power 2 mW; field modulation amplitude 0.9 mT; T = 6 K

Bottom spectrum: 2 equivalents of KO<sub>2</sub> were added to a 5 mM solution  $[Mn^{II}(N4py)]^{2+}$  in butyronitrile at -40 °C. The sample was immediately transferred to an EPR tube and frozen in liquid N<sub>2</sub>. Experimental conditions: microwave frequencies 9.392 GHz; microwave power 2 mW; field modulation amplitude 0.4 mT; T = 5 K

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