Supplementary Information

For

Nucleophilic Reactivity of a Series of Peroxomanganese(III) Complexes Supported by Tetradentate Aminopyridyl Ligands

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Contents of Supplementary Information

Specific Details of XRD Data Collection and Analysis.

$[Mn(L^6py_2)(NCCH_3)_3][ClO_4]_2$. A colorless parallelepiped shaped crystal of $[Mn(N_4C_{16}H_{20})(NCCH_3)_3][ClO_4]_2 \cdot CH_3CN$ was cut from a larger single crystal. It was, at 173(2) K, triclinic, space group $P\bar{1} - C_i^1$ (No. 2)[1] with a = 11.618(2) Å, b = 11.666(2) Å, c = 13.214(3) Å, α = 88.508(2)°, β = 71.869(2)°, γ = 69.296(2)°, V = 1585.0(5) $Å^3$ and Z = 2 molecules {d_{calcd} = 1.438 g/cm^3; μ_a(MoKα) = 0.642 mm^{-1}}. A full hemisphere of diffracted intensities (1850 20-second frames with an ω scan width of 0.30°) was measured for a single-domain specimen using graphite-monochromated MoKα radiation (λ= 0.71073 Å) on a Bruker SMART APEX CCD Single Crystal Diffraction System[2]. X-rays were provided by a fine-focus sealed x-ray tube operated at 50kV and 30mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 3845 reflections. A total of 15336 integrated reflection intensities having 2θ((MoKα)< 55.68° were produced using the Bruker program SAINT[3]; 7423 of these were unique and gave R_{int} = 0.029 with a coverage which was 98.3% complete. The data were corrected empirically for variable absorption effects using equivalent reflections; the relative transmission factors ranged from 0.872 to 1.000. The Bruker software package SHELXTL was used to solve the structure using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL Version 6.10 software package[4].

The final structural model incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. All methyl groups were incorporated into the structural model as rigid groups (using idealized sp^3-hybridized geometry and a C-H bond length of 0.98 Å) that were allowed to rotate about their C-C bonds during least squares refinement cycles. The remaining hydrogen atoms were included in the structural model as idealized atoms (assuming sp^2- or sp^3-hybridization of the carbon atoms and C-H bond lengths of 0.95 or 0.99 Å). The isotropic thermal parameters of all hydrogen atoms were fixed at values 1.2 (nonmethyl) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded. A total of 392 parameters were refined using no restraints, 7423 data and weights of $w = 1/ [\sigma^2(F^2) + (0.0961\ P)^2 + 0.6059\ P]$ where $P = [F_O^2 + 2F_C^2] / 3$. Final agreement factors at convergence are: R_1(unweighted,

based on F) = 0.059 for 5916 independent absorption-corrected "observed" reflections having $2\theta(MoK\alpha) < 55.68°$ and $I > 2\sigma(I)$; R_1(unweighted, based on F) = 0.073 and wR_2(weighted, based on F^2) = 0.170 for all 7423 independent absorption-corrected reflections having $2\theta(MoK\alpha) < 55.68°$. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.84 and -0.71 $e^-/Å^3$, respectively.

$[Mn(L^7py_2^{4\text{-}Me})(ClO_4)_2]$. A colorless parallelepiped shaped crystal of $[Mn(C_{19}H_{26}N_4)(O_3SCF_3)_2]$ was cut from a larger single crystal. It was, at 100(2) K, monoclinic, space group $P2_1/c - C_{2h}^5$ (No. 14)[1] with **a** = 16.801(7) Å, **b** = 8.582(4) Å, **c** = 19.054(8) Å, **β** = 99.020(7)°, V = 2713(2) $Å^3$ and Z = 4 molecules {d_{calcd} = 1.624 g/cm^3; $\mu_a(MoK\alpha)$ = 0.726 mm^{-1}}. A full hemisphere of diffracted intensities (1850 10-second frames with an ω scan width of 0.30°) was measured for a single-domain specimen using graphite-monochromated MoKα radiation (λ= 0.71073 Å) on a Bruker SMART APEX CCD Single Crystal Diffraction System[2]. X-rays were provided by a fine-focus sealed x-ray tube operated at 50kV and 30mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 5226 reflections. A total of 24171 integrated reflection intensities having $2\theta((MoK\alpha) < 58.31°$ were produced using the Bruker program SAINT[3]; 6823 of these were unique and gave R_{int} = 0.041 with a coverage which was 93.3% complete. The data were corrected empirically for variable absorption effects using equivalent reflections; the relative transmission factors ranged from 0.810 to 1.000. The Bruker software package SHELXTL was used to solve the structure using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL Version 6.10 software package[4].

The final structural model incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. All methyl groups were incorporated into the structural model as rigid groups (using idealized sp^3-hybridized geometry and a C-H bond length of 0.98 Å) that were allowed to rotate about their C-C bonds during least squares refinement cycles. The remaining hydrogen atoms were included in the structural model as idealized atoms (assuming sp^2- or sp^3-hybridization of the carbon atoms and C-H bond lengths of 0.95 or 0.99 Å). The isotropic thermal parameters of all hydrogen atoms

were fixed at values 1.2 (nonmethyl) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded. A total of 363 parameters were refined using no restraints, 6823 data and weights of $w = 1/ [\sigma^2(F^2) + (0.0692\ P)^2 + 0.3317\ P]$ where $P = [F_o^2 + 2F_c^2] / 3$. Final agreement factors at convergence are: R_1(unweighted, based on F) = 0.043 for 5777 independent absorption-corrected "observed" reflections having $2\theta(MoK\alpha) < 58.31°$ and $I > 2\sigma(I)$; R_1(unweighted, based on F) = 0.050 and wR_2(weighted, based on F^2) = 0.118 for all 6823 independent absorption-corrected reflections having $2\theta(MoK\alpha) < 58.31°$. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 1.46 and -0.67 $e^-/Å^3$, respectively.

$[Mn(L^7q_2)(ClO_4)_2]$. A colorless near cube-shaped crystal of $[Mn(N_4C_{25}H_{26})][ClO_4]_2$ was cut from a larger single crystal. It was, at 100(2) K, monoclinic, space group $P2_1/c - C_{2h}^5$ (No. 14)[1] with **a** = 9.012(2) Å, **b** = 8.305(2) Å, **c** = 34.494(6) Å, **β** = 92.618(3)°, V = 2578.9(8) $Å^3$ and Z = 4 molecules {d_{calcd} = 1.639 g/cm^3; $\mu_a(MoK\alpha)$ = 0.778 mm^{-1}}. A full hemisphere of diffracted intensities (1850 10-second frames with a ω scan width of 0.30°) was measured for a single-domain specimen using graphite-monochromated MoKα radiation (λ= 0.71073 Å) on a Bruker SMART APEX CCD Single Crystal Diffraction System[2]. X-rays were provided by a fine-focus sealed x-ray tube operated at 50kV and 30mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 8878 reflections. A total of 23188 integrated reflection intensities having $2\theta((MoK\alpha) < 58.35°$ were produced using the Bruker program SAINT[3]; 6423 of these were unique and gave R_{int} = 0.048 with a coverage which was 92.0% complete. The data were corrected empirically for variable absorption effects using equivalent reflections; the relative transmission factors ranged from 0.900 to 1.000. The Bruker software package SHELXTL was used to solve the structure using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL Version 6.10 software package[4].

The final structural model incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The first perchlorate anion is disordered with two preferred orientations about the Cl(1)-O(11) bond.

Atomic positions for oxygen atoms O(12), O(13) and O(14) correspond to the major orientation and are occupied 53% of the time; atomic positions for oxygen atoms O(12'), O(13') and O(14') correspond to the minor orientation and are occupied 47% of the time. All hydrogen atoms were located in a difference Fourier and included in the structural model as independent isotropic atoms whose parameters were allowed to vary in least-squares refinement cycles. A total of 493 parameters were refined using no restraints, 6423 data and weights of $w = 1/ [\sigma^2(F^2) + (0.0652 P)^2 + 0.3766 P]$, where $P = [Fo^2 + 2Fc^2] / 3$. Final agreement factors at convergence are: R_1(unweighted, based on F) = 0.044 for 5411 independent absorption-corrected "observed" reflections having $2\theta(MoK\alpha) < 58.35°$ and $I > 2\sigma(I)$; R_1(unweighted, based on F) = 0.053 and wR_2(weighted, based on F^2) = 0.113 for all 6423 independent absorption-corrected reflections having $2\theta(MoK\alpha) < 58.35°$. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.56 and -0.47 $e^-/Å^3$, respectively.

$[Mn(L^8py_2^H)(ClO_4)_2]$. Colorless crystals of $[Mn(N_4C_{18}H_{24})][ClO_4]_2$ are, at 173(2) K, monoclinic, space group $P2_1/c - C_{2h}^5$ (No. 14)[1] with **a** = 14.731(2) Å, **b** = 17.692(2) Å, **c** = 8.752(1) Å, β = 95.547(1)°, V = 2270.1(5) $Å^3$ and Z = 4 molecules {d_{calcd} = 1.610 g/cm^3; $\mu_a(MoK\alpha)$ = 0.870 mm^{-1}}. A full hemisphere of diffracted intensities (1850 10-second frames with a ω scan width of 0.30°) was measured for a specimen using graphite-monochromated MoKα radiation (λ= 0.71073 Å) on a Bruker SMART APEX CCD Single Crystal Diffraction System[2]. X-rays were provided by a fine-focus sealed x-ray tube operated at 50kV and 30mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 6611 reflections. A total of 18486 integrated reflection intensities having $2\theta((MoK\alpha) < 59.14°$ were produced using the Bruker program SAINT[3]; 6352 of these were unique and gave R_{int} = 0.036 with a coverage which was 99.7% complete. The data were corrected empirically for variable absorption effects using equivalent reflections; the relative transmission factors ranged from 0.961 to 1.000. The Bruker software package SHELXTL was used to solve the structure using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL Version 6.10 software package[4].

The final structural model incorporated anisotropic thermal parameters for all

nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. All hydrogen atoms were included in the structural model as idealized atoms (assuming sp^2- or sp^3-hybridization of the carbon atoms and C-H bond lengths of 0.95 or 0.99 Å). The isotropic thermal parameters of all hydrogen atoms were fixed at values 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded. A total of 298 parameters were refined using no restraints, 6352 data and weights of $w = 1/ [\sigma^2(F^2) + (0.0498 P)^2 + 0.9315 P]$, where $P = [Fo^2 + 2Fc^2] / 3$. Final agreement factors at convergence are: R_1(unweighted, based on F) = 0.037 for 5524 independent absorption-corrected "observed" reflections having $2\theta(MoK\alpha) < 59.14°$ and $I > 2\sigma(I)$; R_1(unweighted, based on F) = 0.043 and wR_2(weighted, based on F^2) = 0.095 for all 6352 independent absorption-corrected reflections having $2\theta(MoK\alpha) < 59.14°$. The largest shift/s.u. was 0.001 in the final refinement cycle. The final difference map had maxima and minima of 0.45 and -0.36 $e^-/Å^3$, respectively.

[Mn($L^8py_2^{6\text{-}Me}$)(OTF)$_2$]. Colorless crystals of $Mn(C_{20}H_{28}N_4)(O_3SCF_3)_2$ are, at 100(2) K, monoclinic, space group C2/c - C_{2h}^6 (No. 15)[1] with **a** = 13.546(3) Å, **b** = 10.324(2) Å, **c** = 19.340(4) Å, **β** = 99.912(3)°, V = 2664.4(8) $Å^3$ and Z = 4 molecules {d_{calcd} = 1.689 g/cm^3; $\mu_a(MoK\alpha)$ = 0.741 mm^{-1}}. A full hemisphere of diffracted intensities (1850 10-second frames with an ω scan width of 0.30°) was measured for a single-domain specimen using graphite-monochromated MoKα radiation (λ= 0.71073 Å) on a Bruker SMART APEX CCD Single Crystal Diffraction System[2]. X-rays were provided by a fine-focus sealed x-ray tube operated at 50kV and 30mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 9403 reflections. A total of 11982 integrated reflection intensities having $2\theta((MoK\alpha) < 58.21°$ were produced using the Bruker program SAINT[3]; 3356 of these were unique and gave R_{int} = 0.052 with a coverage which was 93.7% complete. The data were corrected empirically for variable absorption effects using equivalent reflections; the relative transmission factors ranged from 0.815 to 1.000. The Bruker software package SHELXTL was used to solve the structure using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL Version 6.10 software package[4].

The final structural model incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. All hydrogen atoms were located from a difference Fourier and included in the structural model as independent isotropic atoms whose parameters were allowed to vary in least-squares refinement cycles. A total of 242 parameters were refined using no restraints, 3356 data and weights of $w = 1/ [\sigma^2(F^2) + (0.0504\ P)^2 + 2.1167\ P]$ where $P = [Fo^2 + 2Fc^2] / 3$. Final agreement factors at convergence are: R_1(unweighted, based on F) = 0.030 or 3223 independent absorption-corrected "observed" reflections having $2\theta(MoK\alpha) < 58.21°$ and $I > 2\sigma(I)$; R_1(unweighted, based on F) = 0.031 and wR_2(weighted, based on F^2) = 0.085 for all 3356 independent absorption-corrected reflections having $2\theta(MoK\alpha) < 58.21°$. The largest shift/s.u. was 0.001 in the final refinement cycle. The final difference map had maxima and minima of 0.50 and -0.33 $e^-/Å^3$, respectively.

References

1. International Tables for Crystallography, Vol A, 4th ed., Kluwer: Boston (1996).
2. Data Collection: SMART Software Reference Manual (1998). Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.
3. Data Reduction: SAINT Software Reference Manual (1998). Bruker-AXS, 6300 Enterprise Dr., Madison, WI 53719-1173, USA.
4. G. M. Sheldrick (2000). SHELXTL Version 6.10 Reference Manual. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.

Table S1. Crystal data and structure refinement for $[Mn(L^6py_2)(NCCH_3)_3][ClO_4]_2 \cdot CH_3CN$.

Empirical formula	$C_{24}H_{32}Cl_2MnN_8O_8$	
Formula weight	686.42	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1} - C_i^1$ (No. 2)	
Unit cell dimensions	**a** = 11.618(2) Å	**α** = 88.508(2)°
	b = 11.666(2) Å	**β** = 71.869(2)°
	c = 13.214(3) Å	**γ** = 69.296(2)°
Volume	1585.0(5) $Å^3$	
Z	2	
Density (calculated)	1.438 Mg/m^3	
Absorption coefficient	0.642 mm^{-1}	
F(000)	710	
Crystal size	0.18 x 0.14 x 0.09 mm^3	
Theta range for data collection	3.72° to 27.84°	
Index ranges	$-15 \le h \le 15$, $-15 \le k \le 15$, $-17 \le l \le 17$	
Reflections collected	15336	
Independent reflections	7423 [R_{int} = 0.029]	
Completeness to theta = 27.84°	98.3 %	
Absorption correction	Multi-scans	
Max. and min. transmission	1.000 and 0.872	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7423 / 0 / 392	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R_1 = 0.059, wR_2 = 0.161	
R indices (all data)	R_1 = 0.073, wR_2 = 0.170	
Largest diff. peak and hole	0.84 and -0.71 $e^-/Å^3$	

$R_1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$

$wR_2 = \{ \, \Sigma \, [w(F_o^2 - F_c^2)^2] \, / \, \Sigma \, [w(F_o^2)^2] \, \}^{1/2}$

Table S2. Crystal data and structure refinement for $[Mn(L^7py_2^{4\text{-}Me})(OTf)_2]$.

Empirical formula	$C_{21}H_{26}F_6MnN_4O_6S_2$	
Formula weight	663.52	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c - C_{2h}^5$ (No. 14)	
Unit cell dimensions	a = 16.801(7) Å	α = 90.000°
	b = 8.582(4) Å	β = 99.020(7)°
	c = 19.054(8) Å	γ = 90.000°
Volume	2713(2) $Å^3$	
Z	4	
Density (calculated)	1.624 Mg/m^3	
Absorption coefficient	0.726 mm^{-1}	
F(000)	1356	
Crystal size	0.50 x 0.34 x 0.18 mm^3	
Theta range for data collection	2.31° to 29.15°	
Index ranges	$-22 \le h \le 22$, $-11 \le k \le 11$, $-25 \le l \le 25$	
Reflections collected	24171	
Independent reflections	6823 [R_{int} = 0.041]	
Completeness to theta = 29.15°	93.3 %	
Absorption correction	Multi-scans	
Max. and min. transmission	1.000 and 0.810	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6823 / 0 / 363	
Goodness-of-fit on F^2	1.082	
Final R indices [I>2sigma(I)]	R_1 = 0.043, wR_2 = 0.115	
R indices (all data)	R_1 = 0.050, wR_2 = 0.118	
Largest diff. peak and hole	1.464 and -0.673 $e^-/Å^3$	

$R_1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$

$wR_2 = \{ \Sigma \, [w(F_o^2 - F_c^2)^2] \, / \, \Sigma \, [w(F_o^2)^2] \}^{1/2}$

Table S3. Crystal data and structure refinement for $[Mn(L^7q_2)][ClO_4]_2$.

Empirical formula	$C_{25}H_{26}Cl_2MnN_4O_8$	
Formula weight	636.34	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c - C_{2h}^5$ (No. 14)	
Unit cell dimensions	**a** = 9.0119(17) Å	**α** = 90.000°
	b = 8.3049(15) Å	**β** = 92.618(3)°
	c = 34.494(6) Å	**γ** = 90.000°
Volume	2578.9(8) $Å^3$	
Z	4	
Density (calculated)	1.639 Mg/m^3	
Absorption coefficient	0.778 mm^{-1}	
F(000)	1308	
Crystal size	0.28 x 0.26 x 0.24 mm^3	
Theta range for data collection	2.50° to 29.18°	
Index ranges	$-12 \le h \le 12$, $-10 \le k \le 10$, $-45 \le l \le 46$	
Reflections collected	23188	
Independent reflections	6423 [R_{int} = 0.048]	
Completeness to theta = 29.18°	92.0 %	
Absorption correction	Multi-scans	
Max. and min. transmission	1.000 and 0.900	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6423 / 0 / 493	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R_1 = 0.044, wR_2 = 0.109	
R indices (all data)	R_1 = 0.053, wR_2 = 0.113	
Largest diff. peak and hole	0.56 and -0.47 $e^-/Å^3$	

$R_1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$

$wR_2 = \{ \Sigma \, [w(F_o^2 - F_c^2)^2] \, / \, \Sigma \, [w(F_o^2)^2] \}^{1/2}$

Table S4. Crystal data and structure refinement for $[Mn(L^{8}py_2^{H})][ClO_4]_2$.

Empirical formula	$C_{18}H_{24}Cl_2MnN_4O_8$	
Formula weight	550.25	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c - C_{2h}^5$ (No. 14)	
Unit cell dimensions	**a** = 14.731(2) Å	α = 90.000°
	b = 17.692(2) Å	β = 95.547(1)°
	c = 8.752(1) Å	γ = 90.000°
Volume	2270.1(5) $Å^3$	
Z	4	
Density (calculated)	1.610 Mg/m^3	
Absorption coefficient	0.870 mm^{-1}	
F(000)	1132	
Crystal size	0.27 x 0.24 x 0.22 mm^3	
Theta range for data collection	3.97° to 29.57°	
Index ranges	$0 \le h \le 20$, $-24 \le k \le 0$, $-12 \le l \le 12$	
Reflections collected	18486	
Independent reflections	6352 [R_{int} = 0.036]	
Completeness to theta = 29.57°	99.7 %	
Absorption correction	Multi-scans	
Max. and min. transmission	0.8317 and 0.7991	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6352 / 0 / 298	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R_1 = 0.037, wR_2 = 0.092	
R indices (all data)	R_1 = 0.043, wR_2 = 0.095	
Largest diff. peak and hole	0.45 and -0.36 $e^-/Å^3$	

$R_1 = \Sigma \, ||F_O| - |F_C|| \, / \, \Sigma \, |F_O|$

$wR_2 = \{ \Sigma \, [w(F_O^2 - F_C^2)^2] \, / \, \Sigma \, [w(F_O^2)^2] \}^{1/2}$

Table S5. Crystal data and structure refinement for $Mn(L^8py_2^{6\text{-}Me})(OTF)_2$.

Empirical formula	$C_{22}H_{28}F_6MnN_4O_6S_2$	
Formula weight	677.54	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c - C_{2h}^6 (No. 15)	
Unit cell dimensions	**a** = 13.546(3) Å	**α** = 90.000°
	b = 10.324(2) Å	**β** = 99.912(3)°
	c = 19.340(4) Å	**γ** = 90.000°
Volume	2664.4(8) $Å^3$	
Z	4	
Density (calculated)	1.689 Mg/m^3	
Absorption coefficient	0.741 mm^{-1}	
F(000)	1388	
Crystal size	0.52 x 0.48 x 0.33 mm^3	
Theta range for data collection	2.49° to 29.10°	
Index ranges	$-18 \le h \le 18$, $-13 \le k \le 13$, $-25 \le l \le 25$	
Reflections collected	11982	
Independent reflections	3356 [R_{int} = 0.052]	
Completeness to theta = 29.10°	93.7 %	
Absorption correction	Multi-scans	
Max. and min. transmission	1.000 and 0.815	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3356 / 0 / 242	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R_1 = 0.030, wR_2 = 0.084	
R indices (all data)	R_1 = 0.031, wR_2 = 0.085	
Largest diff. peak and hole	0.50 and -0.33 $e^-/Å^3$	

$R_1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$

$wR_2 = \{ \, \Sigma \, [w(F_o^2 - F_c^2)^2] \, / \, \Sigma \, [w(F_o^2)^2] \, \}^{1/2}$

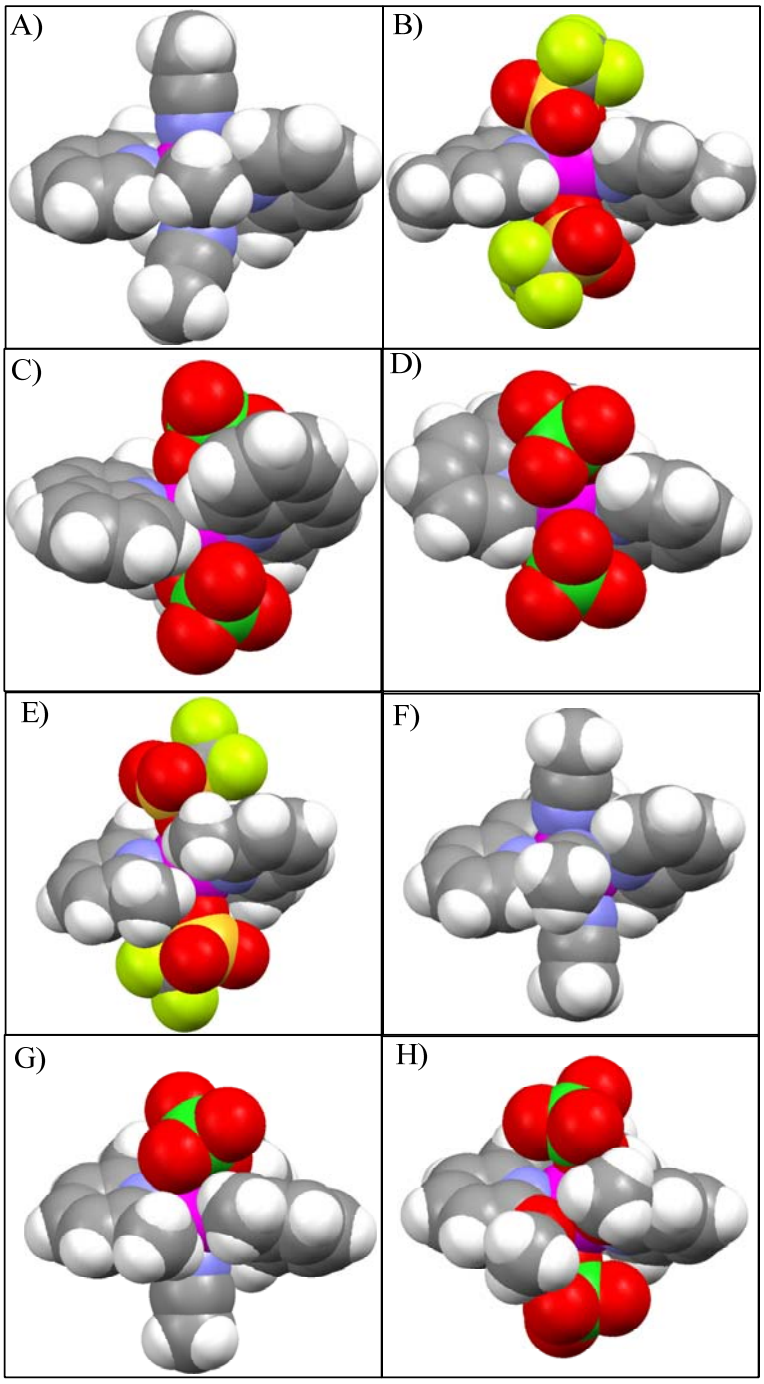

Figure S1. Space-filling diagrams of A) $[Mn^{II}(L^{6}py_2^{H})(NCMe)_3](ClO_4)_2$, B) $[Mn^{II}(L^{7}py_2^{4\text{-}Me})(OTf)_2]$ C) $[Mn^{II}(L^{7}q_2)(ClO_4)_2]$, D) $[Mn^{II}(L^{8}py_2^{H})(ClO_4)_2]$, and E) $[Mn^{II}(L^{8}py_2^{6\text{-}Me})(OTf)_2]$ F) $[Mn^{II}(L^{7}py_2^{6\text{-}Me})(ClO_4)_2]$ (reference 20) G) $[Mn^{II}(L^{7}py_2^{6\text{-}MeO})(ClO_4)_2]$ (reference 20) based on X-ray crystal structure data. Non-coordinating perchlorate counter anions or triflate counter anions have been removed for clarity.

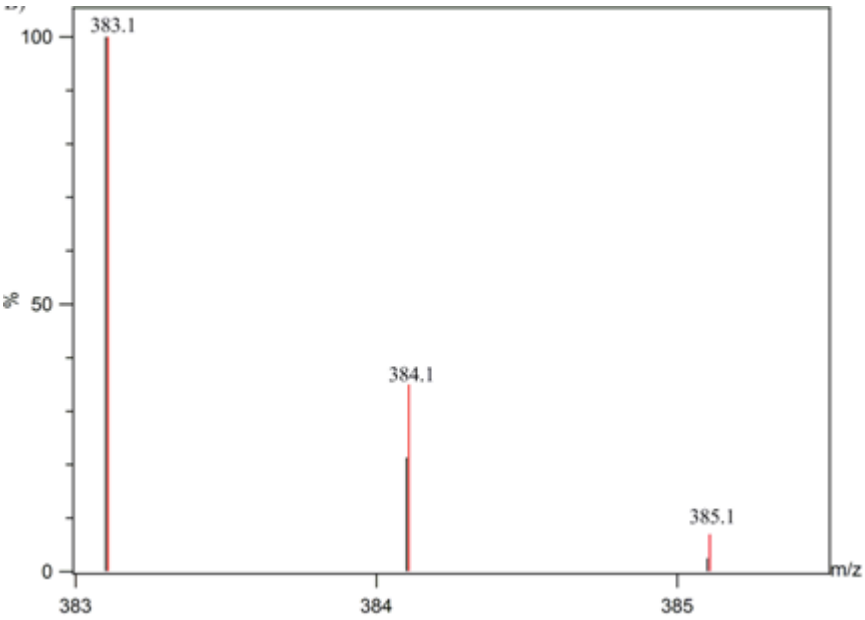

Figure S2. Experimental ESI-MS spectrum of $[Mn^{III}(O_2)(L^8py_2{}^H)]^+$ ({$[Mn^{III}(O_2)(L^8py_2{}^H)]^+$, M^+, 383.1)}). Red and black sticks correspond to the experimental simulated isotope patterns of $[Mn^{III}(O_2)(L^8py_2{}^H)]^+$.

Table S6. Cartesian coordinates for DFT optimized model of $[Mn^{III}(O_2)(L^7py_2^H)]^+$.

Atom	x	y	z
Mn	-0.278039	3.034828	1.014223
O	-0.530305	4.859658	0.740655
O	-0.465168	4.514143	2.141256
N	-2.317116	2.194425	0.577825
N	-0.078869	2.390066	-1.093472
N	1.927974	2.504719	0.632849
N	0.268396	1.650337	2.593571
C	-3.322184	2.010708	1.463726
C	-4.503722	1.331376	1.140523
C	-4.641411	0.811159	-0.157280
C	-3.613618	1.026398	-1.088321
C	-2.471888	1.743733	-0.691357
C	-1.425796	2.186651	-1.690302
C	0.648120	3.432208	-1.906270
C	2.155548	3.503896	-1.646692
C	2.577884	3.573907	-0.177665
C	1.900181	1.194508	-0.073690
C	0.675030	1.101141	-1.030678
C	-0.590734	0.961349	3.380083
C	-0.179480	0.238707	4.505421
C	1.186704	0.221011	4.828353
C	2.084240	0.915868	4.004365
C	1.595669	1.625589	2.896411
C	2.511141	2.411294	1.982433
H	-1.650313	0.987444	3.088341
H	-0.924374	-0.301387	5.108938
H	1.552324	-0.336729	5.705353
H	3.166225	0.909450	4.211218
H	2.616851	3.448600	2.374032
H	3.531738	1.960528	1.972863
H	-3.172322	2.441754	2.466748
H	-5.293985	1.210349	1.897455
H	-5.546270	0.252723	-0.446125
H	-3.696845	0.654605	-2.121462
H	-1.376148	1.493387	-2.560048
H	-1.759925	3.171551	-2.085078
H	0.490980	3.207261	-2.987450
H	0.157694	4.404307	-1.687563
H	2.536410	4.413640	-2.159475
H	2.663571	2.651322	-2.145422
H	2.295474	4.548807	0.276252
H	3.689178	3.474600	-0.115001
H	1.820144	0.397089	0.690882
H	2.857508	1.023183	-0.615632
H	0.983031	0.792755	-2.055881
H	-0.035488	0.334608	-0.657343

Table S7. Cartesian coordinates for DFT optimized model of $[Mn^{III}(O_2)(L^7py_2^{6\text{-}Me})]^+$.

Atoms	x	y	z
Mn	-0.010842	0.095253	0.495449
O	-0.688271	0.281369	2.268111
O	0.517331	-0.523306	2.175018
N	-1.973742	-0.890898	-0.172400
N	-0.823722	1.528735	-0.881397
N	1.440974	1.851885	0.478487
N	1.852991	-0.745970	-0.252437
C	-2.595424	-1.884041	0.526700
C	-3.987895	-2.067748	0.424103
C	-4.752404	-1.229497	-0.402558
C	-4.095348	-0.217583	-1.123466
C	-2.710950	-0.083283	-0.980245
C	-1.895894	0.937875	-1.747728
C	-1.423382	2.588126	0.028798
C	-0.400180	3.518720	0.692445
C	0.814257	2.870690	1.371788
C	-1.748460	-2.805510	1.372782
C	2.056048	-1.911850	-0.934629
C	3.342309	-2.473030	-1.024592
C	4.431553	-1.839473	-0.407691
C	4.215612	-0.627952	0.258826
C	2.914129	-0.104306	0.309603
C	2.655641	1.231888	0.998374
C	1.566742	2.350614	-0.910856
C	0.286457	2.066187	-1.737239
C	0.877047	-2.577344	-1.586203
H	-4.470292	-2.875712	0.995789
H	-5.842984	-1.367715	-0.477574
H	-4.640539	0.466492	-1.792721
H	-1.385005	0.453085	-2.605428
H	-2.546363	1.742461	-2.159594
H	-2.037461	2.048531	0.778364
H	-2.107293	3.215161	-0.587725
H	-0.055564	4.268386	-0.050870
H	-0.940540	4.108162	1.465520
H	0.544432	2.349278	2.311182
H	1.550080	3.675469	1.616764
H	-1.050952	-2.241883	2.027278
H	-1.130551	-3.460962	0.719501
H	-2.404493	-3.440418	2.003846
H	3.485822	-3.409171	-1.584697
H	5.432584	-2.295011	-0.472075
H	5.033808	-0.066525	0.736042
H	3.556036	1.874714	0.844743
H	2.530258	1.066665	2.087786
H	2.438841	1.865799	-1.392672
H	1.792432	3.440273	-0.915224
H	-0.054208	2.990317	-2.257335

H	0.482937	1.287316	-2.498476
H	0.134737	-2.917651	-0.831608
H	1.200277	-3.463907	-2.168069
H	0.340955	-1.889571	-2.275607

Table S8. Cartesian coordinates for DFT optimized model for $[Mn^{III}(O_2)(L^7py_2{}^{4\text{-}Me})]^+$

Atoms	x	y	z
Mn	-0.469549	2.634620	1.182838
O	-0.956405	4.398556	0.781838
O	-0.841302	4.156933	2.200683
N	-2.492751	1.846130	0.743326
N	-0.149251	1.726470	-0.810429
N	1.783775	2.613029	0.783718
N	0.317168	1.512035	2.769293
C	-3.591431	2.197368	1.446931
C	-4.875042	2.215736	0.889940
C	-5.050996	1.880034	-0.469302
C	-3.892410	1.523062	-1.195500
C	-2.642529	1.509732	-0.563662
C	-1.389496	1.022023	-1.261995
C	-6.404388	1.912006	-1.130775
H	-3.423776	2.482705	2.498462
H	-5.734074	2.502201	1.516954
H	-3.964287	1.249262	-2.260635
H	-1.274765	-0.054768	-1.012237
H	-1.502009	1.084712	-2.367630
H	-6.615525	0.951417	-1.651092
H	-6.441991	2.711638	-1.905824
H	-7.214089	2.103240	-0.396669
C	0.156418	2.897320	-1.714091
C	1.574764	3.471854	-1.547624
C	2.063717	3.761537	-0.118743
C	2.149525	1.314621	0.164349
C	1.006517	0.779608	-0.743802
H	0.050717	2.559023	-2.772356
H	-0.622487	3.666675	-1.531657
H	1.611762	4.422447	-2.122173
H	2.297525	2.796482	-2.054432
H	1.555014	4.650022	0.309111
H	3.161225	3.968781	-0.151680
H	2.326072	0.586930	0.980220
H	3.107650	1.409318	-0.394850
H	1.373798	0.553968	-1.770489
H	0.620294	-0.166867	-0.319831
C	-0.381628	0.676439	3.573144
C	0.167294	0.111074	4.725786
C	1.501567	0.407455	5.083860
C	2.219879	1.266758	4.224330
C	1.608836	1.808257	3.086836
C	2.326615	2.762686	2.146235
C	2.124667	-0.155513	6.333123
H	-1.416191	0.458284	3.265744
H	-0.448214	-0.303942	5.339493
H	3.232797	-0.180140	6.263054
H	3.274391	1.316933	4.498343
H	1.750060	-1.178744	6.546916
H	2.135084	3.809766	2.472848

H	1.856623	0.480314	7.208920