Supporting Information for

Geometric and Electronic Structure of a Peroxomanganese(III) Complex Supported by a Scorpionate Ligand

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Table S1. Crystal data and structure refinement for $[Mn(Tp^{Ph2})(DMF)_3](OTf)$.

Empirical formula	$C_{59}H_{63}BF_3MnN_9O_7S$	
Formula weight	1164.99	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 17.6441(10) Å	α= 90°.
	b = 14.8052(8) Å	β= 93.243(4)°.
	c = 21.9441(11) Å	γ = 90°.
Volume	5723.2(5) $Å^3$	
Z	4	
Density (calculated)	1.352 Mg/m^3	
Absorption coefficient	2.805 mm^{-1}	
F(000)	2436	
Crystal size	0.22 x 0.01 x 0.01 mm^3	
Theta range for data collection	10.74 to 66.71°.	
Index ranges	-20<=h<=20, -17<=k<=16, -24<=l<=25	
Reflections collected	19229	
Independent reflections	9144 [R(int) = 0.1286]	
Completeness to theta = 66.71°	90.2 %	
Absorption correction	Multi-scan	
Max. and min. transmission	1.000 and 0.793	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9144 / 0 / 709	
Goodness-of-fit on F^2	0.928	
Final R indices [I>2sigma(I)]	R1 = 0.0638, wR2 = 0.1504	
R indices (all data)	R1 = 0.0984, wR2 = 0.1649	
Largest diff. peak and hole	1.402 and -0.894 $e.Å^{-3}$	

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

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

Table S2. Crystal data and structure refinement for [Mn(O_2)(Tp^{Ph2})(THF)].

Empirical formula	$C_{58}H_{62}BMnN_6O_5$	
Formula weight	988.89	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.928(2) Å	α= 90°.
	b = 21.642(4) Å	β= 103.572(4)°.
	c = 18.633(3) Å	γ = 90°.
Volume	5067.5(15) $Å^3$	
Z	4	
Density (calculated)	1.296 Mg/m^3	
Absorption coefficient	2.562 mm^{-1}	
F(000)	2088	
Crystal size	0.23 x 0.20 x 0.06 mm^3	
Theta range for data collection	3.18 to 66.52°.	
Index ranges	-15<=h<=15, -25<=k<=19, -21<=l<=21	
Reflections collected	45183	
Independent reflections	8594 [R(int) = 0.0482]	
Completeness to theta = 66.52°	96.2 %	
Absorption correction	Multi-scan	
Max. and min. transmission	1.000 and 0.810	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8594 / 30 / 693	
Goodness-of-fit on F^2	1.077	
Final R indices [I>2sigma(I)]	R1 = 0.0514, wR2 = 0.1460	
R indices (all data)	R1 = 0.0528, wR2 = 0.1474	
Largest diff. peak and hole	0.944 and -0.535 $e.Å^{-3}$	

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

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

Table S3. Cartesian coordinates (Å) for DFT energy minimized [$Mn^{III}(O_2)(Tp^{Ph2})$(THF)] model.

Atom	x	y	z
Mn	2.311278	5.168113	8.572887
O	3.759224	4.994203	7.408479
O	3.702012	3.944327	8.39639
O	3.642094	6.494182	10.025693
N	0.531187	4.095032	7.443028
N	1.29661	6.924038	8.086569
N	1.148728	4.746492	10.261434
N	-0.182102	5.072468	10.203946
N	-0.675955	4.675571	7.737045
N	0.002915	7.007179	8.533482
B	-0.777242	5.703335	8.899954
C	-1.695933	4.029288	7.074486
C	-1.115549	2.982868	6.349993
C	0.278409	3.060868	6.59728
C	-0.446171	8.298971	8.418836
C	0.597253	9.057491	7.86571
C	1.672346	8.164192	7.669132
C	-0.75983	4.883731	11.434879
C	0.246276	4.439276	12.307237
C	1.423074	4.346505	11.533707
C	-3.122816	4.41319	7.087925
C	-3.54652	5.755614	6.936598
C	-4.913374	6.0725	6.883498
C	-5.883315	5.057732	6.973848
C	-5.475734	3.718441	7.116625
C	-4.108853	3.39927	7.172456
C	1.30298	2.165797	6.016736
C	2.617277	2.598687	5.724944
C	3.542085	1.72037	5.134432
C	3.177311	0.397649	4.823422
C	1.871992	-0.04476	5.110218
C	0.945819	0.829963	5.700579
C	-1.782401	8.793367	8.814209
C	-2.36368	8.482828	10.065985
C	-3.606851	9.02433	10.429283
C	-4.289297	9.888691	9.554043
C	-3.71636	10.213329	8.310792
C	-2.473499	9.67219	7.944217
C	2.987638	8.483451	7.077143
C	3.620911	9.706662	7.406037
C	4.844505	10.061323	6.815830

C	5.45373	9.201693	5.882800
C	4.827141	7.989516	5.541610
C	3.603509	7.632058	6.130691
C	-2.188855	5.066142	11.768434
C	-2.529037	5.709462	12.984204
C	-3.871567	5.841674	13.374697
C	-4.898018	5.33189	12.558414
C	-4.571156	4.683966	11.353178
C	-3.22971	4.547236	10.961781
C	2.73614	3.843311	11.987691
C	3.221705	4.221099	13.263644
C	4.440482	3.716821	13.745588
C	5.192825	2.821935	12.961949
C	4.712988	2.431209	11.698561
C	3.493368	2.933361	11.214475
C	3.214411	7.534751	10.950286
C	4.458382	7.897943	11.769279
C	5.597298	7.621325	10.769254
C	5.096992	6.365083	10.052628
H	-1.633772	2.301757	5.664913
H	0.573997	10.127612	7.630868
H	0.117627	4.134897	13.352104
H	-2.798897	6.558025	6.835146
H	-5.222622	7.123673	6.760456
H	-6.956171	5.310218	6.927996
H	-6.227323	2.914172	7.187294
H	-3.795155	2.348989	7.294857
H	2.918763	3.630836	5.962713
H	4.561822	2.077277	4.912743
H	3.907777	-0.287954	4.361568
H	1.573301	-1.080472	4.877377
H	-0.067449	0.466800	5.937741
H	-1.830297	7.827967	10.772099
H	-4.042706	8.770735	11.409456
H	-5.266041	10.310907	9.842117
H	-4.242647	10.890437	7.617011
H	-2.034985	9.920592	6.963872
H	3.152575	10.380976	8.142642
H	5.326333	11.015049	7.088299
H	6.414766	9.479021	5.419004
H	5.291717	7.314972	4.803005
H	3.108311	6.694600	5.835317
H	-1.728767	6.118134	13.622552

H	-4.117554	6.347139	14.323221
H	-5.952724	5.435496	12.864199
H	-5.367271	4.272972	10.711187
H	-2.989236	4.012554	10.029806
H	2.638872	4.927288	13.878533
H	4.804938	4.026285	14.738921
H	6.149941	2.424872	13.338375
H	5.289454	1.720031	11.083498
H	3.111419	2.594062	10.240319
H	2.377791	7.134522	11.563455
H	2.839901	8.401869	10.357583
H	4.548801	7.229166	12.652852
H	4.433434	8.948472	12.128501
H	6.581008	7.462723	11.259597
H	5.697716	8.464468	10.05032
H	5.441171	6.266887	9.00275
H	5.355249	5.434518	10.608295
H	-1.937045	5.988601	9.095838

Table S4. Cartesian coordinates (Å) for DFT energy minimized [$Mn^{III}(O_2)(Tp^{Ph,Me})(THF)$] model.

Atom	x	y	z
Mn	0.000000	0.000000	0.000000
O	-1.854526	-0.208260	0.000000
O	-1.146840	-1.465504	0.000000
O	-0.005152	0.023431	-2.374784
N	0.554751	0.222984	2.288960
N	0.422438	2.040054	-0.095163
N	1.996603	-0.607940	-0.156403
N	2.941567	0.180790	0.448265
N	1.645044	1.035517	2.467048
N	1.679688	2.407126	0.310880
B	2.503175	1.458400	1.240795
H	1.965103	0.401315	-2.965131
H	0.811331	1.778758	-3.177974
H	1.094151	-0.767126	-4.910694
H	0.826253	0.924577	-5.468045
H	-1.346370	-0.758565	-5.322228
H	-1.507980	0.897011	-4.630129
H	-2.023934	-0.417048	-2.630224
H	-0.879026	-1.733182	-3.114965
C	1.952702	1.143215	3.805244
C	1.035736	0.348942	4.501687
C	0.171948	-0.203017	3.522113
C	1.934412	3.698883	-0.076457
C	0.790612	4.170579	-0.739223
C	-0.136448	3.106179	-0.731116
C	4.197678	-0.263296	0.117264
C	4.041581	-1.362002	-0.742549
C	2.650747	-1.560981	-0.875946
C	-0.976385	-1.094036	3.796608
C	-2.144382	-1.100905	2.999333
C	-3.225688	-1.936912	3.326875
C	-3.165543	-2.779826	4.451711
C	-2.007546	-2.782201	5.252257
C	-0.925333	-1.948628	4.927554
C	-1.507375	3.126127	-1.281144
C	-1.753936	3.779178	-2.513289
C	-3.055885	3.861944	-3.032318
C	-4.134627	3.297766	-2.326143
C	-3.901288	2.656452	-1.096238
C	-2.600070	2.571823	-0.574954

C	1.985969	-2.652351	-1.617856
C	2.486468	-3.035666	-2.886368
C	1.910216	-4.104372	-3.591907
C	0.826309	-4.811774	-3.039042
C	0.330039	-4.446494	-1.774390
C	0.904071	-3.377344	-1.066210
C	3.214759	4.419824	0.225905
C	3.086361	1.970499	4.335954
C	5.460792	0.367289	0.624043
C	0.933721	0.674864	-3.277404
C	0.565863	0.184153	-4.682396
C	-0.949525	-0.062209	-4.553541
C	-1.062399	-0.634444	-3.138688
H	3.492381	2.046726	1.615276
H	0.957352	0.250788	5.590734
H	0.649626	5.168311	-1.169924
H	4.840432	-1.993399	-1.147665
H	-2.207079	-0.447402	2.115160
H	-4.128744	-1.926589	2.693807
H	-4.016544	-3.435210	4.703125
H	-1.943596	-3.441719	6.133777
H	-0.016637	-1.972864	5.550875
H	-0.911633	4.216276	-3.075513
H	-3.228510	4.369022	-3.996197
H	-5.157363	3.361839	-2.732977
H	-4.742160	2.221369	-0.530538
H	-2.432990	2.092598	0.401633
H	3.331422	-2.480029	-3.326602
H	2.309877	-4.384938	-4.580270
H	0.372393	-5.651080	-3.591267
H	-0.510326	-5.003867	-1.327723
H	0.531657	-3.124044	-0.063106
H	3.369838	4.549662	1.319588
H	3.194452	5.427419	-0.239545
H	4.101007	3.875328	-0.167488
H	3.068625	1.962994	5.445390
H	3.021343	3.029507	4.001104
H	4.079329	1.584314	4.012533
H	5.570631	1.418656	0.277484
H	6.337323	-0.204244	0.255003
H	5.502460	0.379169	1.734679

Table S5. Cartesian coordinates (Å) for DFT energy minimized (for hydrogen atoms only) brown isomer of [$Mn^{III}(O_2)(Tp^{iPr2})(pz^{iPr2}H)$] (253 K structure).

Atom	x	y	z
Mn	2.01447016	1.349043599	0.00327932
O	1.712240055	-0.326615503	0.730450237
O	2.367811342	0.559555395	1.639152294
N	2.569381402	3.340234155	0.001640721
N	2.792937349	3.972397518	-1.216212397
N	3.947886629	1.192752816	-1.177116358
N	4.117912651	2.102260045	-2.181296997
N	1.233897449	1.353811255	-1.909490532
N	1.672062199	2.330093985	-2.778835509
N	-0.159210252	2.109086546	0.699998912
N	-0.859296861	1.210045325	1.455327724
B	2.996300519	3.110552737	-2.462206373
C	3.787454413	3.454165474	2.993131239
C	1.86674869	4.974279105	3.237830859
C	2.455886111	3.869399126	2.418020921
C	2.616025286	4.266356113	0.959478637
C	2.860665187	5.504302762	0.396868278
C	2.970945886	5.293455297	-0.961904885
C	3.206054857	6.279747046	-2.063200645
C	1.874698219	6.828050971	-2.581475962
C	4.100847387	7.409017388	-1.59887337
C	6.003852607	-1.709410189	-0.494142106
C	6.088006664	0.098564147	1.193591245
C	5.315811129	-0.479740088	0.039542604
C	5.115977525	0.542211131	-1.042664969
C	6.040407695	1.030692222	-1.984553008
C	5.395657495	2.031762905	-2.688598938
C	5.925747057	2.985736292	-3.698944342
C	7.013596091	2.3730936	-4.546516414
C	6.423755122	4.212885809	-2.993617443
C	0.005324619	-1.705801692	-2.234321956
C	-2.048508986	-0.272497035	-1.992474278
C	-0.54458949	-0.370445183	-1.790810439
C	0.173855566	0.757666042	-2.468428894
C	-0.096685621	1.329517019	-3.714056819
C	0.862719409	2.324906221	-3.883583598
C	1.012792478	3.292288786	-5.011830047
C	2.034732059	2.779515382	-6.042506001
C	-0.333044931	3.544417767	-5.687733624

C	-1.450967226	4.155911148	-1.772148596
C	-1.002356082	5.525750777	0.237017502
C	-0.697443735	4.238458396	-0.443479224
C	-1.045907053	3.063013439	0.401085442
C	-2.295185976	2.757532126	0.959845089
C	-2.14972163	1.565167769	1.645280252
C	-3.097687502	0.748491441	2.40258236
C	-4.227705953	0.248965874	1.454545173
C	-3.723190819	1.539803196	3.527792252
H	-0.354361262	0.371998824	1.763691879
H	3.676292935	3.113065177	4.043772568
H	4.243273132	2.620107226	2.422992438
H	4.508410111	4.299281277	2.989795352
H	2.531783118	5.864013248	3.268240347
H	0.88062472	5.311221898	2.857078781
H	1.720589634	4.650506619	4.289054889
H	1.77573158	2.990844382	2.432308421
H	2.956159891	6.462479438	0.916085913
H	3.70437125	5.747437944	-2.898844762
H	1.334904717	7.375482022	-1.781174982
H	2.036146543	7.53277926	-3.42385506
H	1.208160533	6.017947568	-2.940294259
H	5.071812333	7.03982647	-1.21063067
H	4.314761818	8.111391529	-2.430743835
H	3.623063284	8.002044043	-0.79118299
H	6.109518663	-2.48261377	0.295768753
H	5.448301939	-2.168280216	-1.33787537
H	7.028599246	-1.480176919	-0.858130307
H	6.200823511	-0.644397389	2.011363574
H	7.109121353	0.411150477	0.885499576
H	5.582222854	0.986677743	1.62294455
H	4.303149229	-0.759236209	0.400778435
H	7.073389873	0.69534377	-2.126099346
H	5.086809832	3.278952675	-4.367033247
H	6.669122714	1.459838887	-5.073103477
H	7.368016027	3.092569673	-5.313302373
H	7.897092322	2.092119443	-3.935361836
H	7.278520559	3.965969435	-2.329104861
H	6.773051745	4.985932299	-3.711523812
H	5.645817098	4.677143115	-2.356449856
H	-0.488178326	-2.54014218	-1.692472192
H	-0.156837615	-1.872620312	-3.321042215
H	1.094385583	-1.780985407	-2.042690721

H	-2.449275581	0.696846903	-1.633958514
H	-2.327325608	-0.381171999	-3.062390422
H	-2.570412836	-1.082998676	-1.44260082
H	-0.33240542	-0.270904875	-0.705551579
H	-0.90404568	1.069261098	-4.403775521
H	1.389323155	4.251561273	-4.598116876
H	1.697531782	1.81699924	-6.479548044
H	2.161315683	3.506220351	-6.871859825
H	3.029009769	2.609204208	-5.583512946
H	-1.099558997	3.896796293	-4.969133068
H	-0.231788679	4.311622029	-6.482552527
H	-0.71988083	2.62432959	-6.172441027
H	-2.548237534	4.223727741	-1.611952554
H	-1.165037441	4.995726251	-2.440088451
H	-1.243499503	3.209296562	-2.305970988
H	-0.46299008	5.633502072	1.200144409
H	-0.719281511	6.392854455	-0.395755955
H	-2.087080987	5.630162473	0.456229108
H	0.386468577	4.181984348	-0.656693698
H	-3.210985307	3.354892561	0.887826743
H	-2.564875133	-0.134493521	2.817567651
H	-4.785319756	1.110287002	1.034505112
H	-3.821289915	-0.339514775	0.608619437
H	-4.948305457	-0.389209748	2.006268787
H	-2.96474	1.922830972	4.241348211
H	-4.281409147	2.415384522	3.136725249
H	-4.441569443	0.919544754	4.102939776
H	3.265055747	3.809138399	-3.404168309

Table S6. Cartesian coordinates (Å) for DFT energy minimized (for hydrogen atoms only) blue isomer of [$Mn^{III}(O_2)(Tp^{iPr2})(pz^{iPr2}H)$] (193 K structure).

Atom	x	y	z
Mn	0.003281554	0.003672271	0.002376072
O	1.846980039	0.00327784	0.003695983
O	1.326432464	1.339191421	0.001040796
N	-1.861465091	0.941560535	0.033207174
N	-2.941409734	0.252532817	-0.421690018
N	-0.516025497	-0.335937192	-2.15315674
N	-1.777189772	-0.836061885	-2.392659211
N	-0.764292583	-1.873011845	0.216061439
N	-2.026184365	-2.141236763	-0.222154884
N	0.031948506	0.142757329	2.407450238
N	1.129695761	0.86378811	2.775800075
B	-2.72792984	-1.075433928	-1.185044751
C	-1.552656131	3.364767215	2.516288994
C	-1.450831401	4.475637592	0.344920437
C	-1.340691782	3.148854546	1.053758624
C	-2.291002951	2.106809597	0.52709932
C	-3.657793996	2.15685687	0.367572915
C	-4.071108359	0.99984759	-0.241485724
C	-5.424988969	0.558578284	-0.653382682
C	-6.493564245	1.038168042	0.303182221
C	-5.765639362	1.107149374	-2.015629346
C	1.601316085	1.603421689	-3.942945422
C	2.354509855	-0.687017262	-4.181994343
C	1.515911379	0.23224641	-3.421663028
C	0.0967369	-0.238429858	-3.337643447
C	-0.78205607	-0.661760185	-4.327230716
C	-1.963325382	-1.023426823	-3.72472465
C	-3.204788904	-1.602707879	-4.251644467
C	-3.616371695	-0.894257191	-5.529591549
C	-3.141252816	-3.013750163	-4.601566573
C	1.187479521	-4.007810111	2.562823058
C	2.038231612	-3.473436935	0.369414843
C	1.064095451	-3.067134033	1.396923213
C	-0.346459717	-2.998149685	0.842789784
C	-1.348205897	-3.929988991	0.80687533
C	-2.415360957	-3.383398917	0.15199075
C	-3.783207604	-3.918578148	-0.116767411
C	-4.781452644	-3.349648104	0.890060228
C	-3.75193933	-5.46478775	-0.036680421

C	-3.016885958	-0.200868297	3.377613894
C	-1.973161701	-1.816397704	4.749495316
C	-1.812414665	-0.97283549	3.550789108
C	-0.559279259	-0.187283303	3.58012752
C	0.226239409	0.346670885	4.624334921
C	1.293169021	1.006278189	4.083621882
C	2.411386533	1.777825793	4.615596095
C	2.227133901	3.233354269	4.529163254
C	2.711057955	1.440490994	6.025066535
H	1.673851264	1.247732559	1.986035665
H	-1.422664591	2.436769085	3.108142906
H	-0.839816475	4.115305949	2.918534564
H	-2.574568728	3.749432264	2.725248028
H	-2.449454039	4.93830458	0.497852058
H	-0.696544089	5.188388614	0.737547984
H	-1.289898216	4.38793117	-0.749557463
H	-0.318260302	2.745804484	0.893718635
H	-4.308688078	2.987149494	0.666224577
H	-5.437877128	-0.550011213	-0.691498007
H	-6.319924141	0.695909834	1.344496928
H	-6.549819979	2.146327104	0.323423302
H	-7.491617302	0.668870142	-0.009506611
H	-5.772956872	2.216911285	-2.002395674
H	-5.037481727	0.796916048	-2.793659769
H	-6.769924858	0.769169811	-2.347040904
H	1.001840883	2.321060138	-3.346074027
H	2.648946033	1.974990731	-3.939451473
H	1.241521298	1.673163594	-4.994171953
H	2.053702572	-0.74846944	-5.252213966
H	3.418197371	-0.365088135	-4.176512937
H	2.329030555	-1.723177557	-3.783666189
H	1.875011818	0.242501922	-2.368407865
H	-0.574736784	-0.69986727	-5.403757705
H	-4.000378795	-1.444860263	-3.494913941
H	-3.724282223	0.20321527	-5.400594096
H	-2.866475452	-1.05687865	-6.331780198
H	-4.584493419	-1.283877792	-5.906286201
H	-4.118528496	-3.384396478	-4.975683545
H	-2.393987637	-3.205812759	-5.401419694
H	-2.856090667	-3.669132207	-3.748948302
H	0.98665721	-5.058545975	2.26112186
H	2.216164606	-3.984621546	2.977133244
H	0.49014086	-3.76326832	3.391200995

H	2.026996345	-2.808661048	-0.519159864
H	3.074385906	-3.458038488	0.768991091
H	1.843898077	-4.506441423	0.006725637
H	1.307527909	-2.036927449	1.736890957
H	-1.302625373	-4.933553813	1.242809673
H	-4.091444475	-3.620051834	-1.140289929
H	-4.505598271	-3.644360744	1.923765902
H	-4.811850089	-2.242198892	0.856815963
H	-5.807433115	-3.724389031	0.692170337
H	-4.747587347	-5.887210003	-0.28174348
H	-3.012925408	-5.895984735	-0.740986501
H	-3.491524614	-5.804102017	0.986615673
H	-3.208039926	0.472545826	4.243518317
H	-3.006096449	0.443469685	2.476471192
H	-3.908209794	-0.857629089	3.28868026
H	-2.865564413	-2.470864608	4.666718453
H	-1.100576848	-2.476179265	4.942931423
H	-2.119033891	-1.202597694	5.665890234
H	-1.703851173	-1.646324323	2.670676072
H	0.021308796	0.237102947	5.696266931
H	3.30222586	1.506408385	3.99940545
H	1.374851379	3.571670446	5.157096959
H	3.129361386	3.774101411	4.883218184
H	2.02416239	3.590298321	3.497085984
H	2.897264726	0.357405455	6.182871877
H	3.607025414	1.984857007	6.386395748
H	1.872087028	1.725964463	6.695859394
H	-3.785877568	-1.512572101	-1.545398481

Table S7. Cartesian coordinates (Å) for DFT energy minimized (for hydrogen atoms only) brown isomer of $[Mn^{III}(O_2)(Tp^{iPr2})(pz^{iPr2}H)]$ (253 K structure).

Atom	x	y	z
Mn	1.841544249	1.622823228	-0.163209007
O	1.517299205	-0.05181286	0.695567336
O	2.220261861	0.917842393	1.513477577
N	2.418803064	3.607006142	-0.118279615
N	2.811588365	4.18741708	-1.300545407
N	3.845589071	1.285997299	-1.201209733
N	4.17127718	2.221227547	-2.151898905
N	1.146328873	1.707438728	-2.118406164
N	1.801346956	2.54417315	-2.992099894
N	-0.453133688	2.164718202	0.677798985
N	-0.821189834	1.132050295	1.477747968
B	3.103529459	3.280843024	-2.54072868
C	3.40730173	3.755162678	3.001226182
C	1.489391276	5.425727922	3.027383269
C	2.125018164	4.237980993	2.285818889
C	2.417904631	4.56425297	0.839602399
C	2.801885344	5.790230733	0.25465205
C	3.045185606	5.520809507	-1.101420163
C	3.422953886	6.47900693	-2.209209276
C	2.174672833	6.9231845	-3.004578282
C	4.197482457	7.693624194	-1.669424009
C	5.2529137	-2.006658557	-0.755697626
C	5.829116843	-0.395264984	1.130908309
C	4.897081997	-0.674039148	-0.066685186
C	4.912006212	0.475488819	-1.048242817
C	5.949273227	0.896831935	-1.917629027
C	5.450810011	2.011505687	-2.604152955
C	6.147074623	2.906828238	-3.604796088
C	7.117351434	2.114505079	-4.499440288
C	6.873547897	4.070978506	-2.893526591
C	-0.029703628	-1.34856496	-2.251028377
C	-2.128542846	-0.006084182	-2.772296103
C	-0.717426201	0.032815644	-2.161752568
C	0.146535079	1.097238555	-2.798186726
C	0.14783607	1.565218552	-4.129450392
C	1.209077466	2.477953171	-4.223902597
C	1.697109002	3.239758844	-5.4357979
C	2.765383441	2.430255837	-6.204779815
C	0.532483124	3.640266651	-6.359328901

C	-2.067632358	4.142699333	-1.452023849
C	-2.118968984	5.498501736	0.694740788
C	-1.439723801	4.338443037	-0.054643761
C	-1.469311495	3.0541103	0.746210682
C	-2.4877414	2.560341003	1.606424749
C	-2.035194489	1.31222328	2.061095643
C	-2.634583112	0.297879368	3.006861628
C	-4.025550662	-0.16680256	2.530407974
C	-2.683910916	0.83944621	4.45160654
H	-0.145080995	0.342961297	1.502401652
H	3.179890099	3.461682198	4.046884905
H	3.844646869	2.876232126	2.488054458
H	4.17354281	4.558271447	3.028131159
H	2.190092902	6.284728028	3.094173124
H	0.567107429	5.778362204	2.523523922
H	1.224055344	5.136225116	4.064386704
H	1.403647798	3.392984893	2.28299604
H	2.895998469	6.75825167	0.755535294
H	4.087635324	5.932497767	-2.911444787
H	1.470376335	7.479637512	-2.352021747
H	2.462641365	7.587144435	-3.845800867
H	1.630510456	6.05322151	-3.423308931
H	5.096916069	7.386092119	-1.099067204
H	4.525855477	8.343356722	-2.505799502
H	3.564611285	8.3124303	-0.999658523
H	5.185681675	-2.848177902	-0.035151365
H	4.566060522	-2.223473722	-1.598883922
H	6.288528481	-1.993455077	-1.157446231
H	5.776453521	-1.22308175	1.868615551
H	6.88683564	-0.298087166	0.805317467
H	5.542487755	0.541127881	1.649584537
H	3.858456191	-0.745684959	0.317114468
H	6.939779438	0.444952146	-2.035769167
H	5.365275535	3.350220291	-4.257135693
H	6.604477211	1.282170029	-5.022106136
H	7.568179649	2.778053211	-5.26557106
H	7.949619625	1.680986263	-3.906775694
H	7.677037153	3.686168205	-2.23167278
H	7.3360413	4.757787597	-3.632798728
H	6.176484243	4.66041411	-2.264554801
H	-0.638417145	-2.120197666	-1.735468351
H	0.095201413	-1.660954555	-3.309096771
H	0.971475397	-1.330201864	-1.776625518

H	-2.632308509	0.978894076	-2.70413991
H	-2.099101593	-0.3024415	-3.842070419
H	-2.757731427	-0.750134028	-2.242906323
H	-0.809399143	0.297336554	-1.087506668
H	-0.539652098	1.277002783	-4.930258736
H	2.180030375	4.17035071	-5.070436129
H	2.335297094	1.48674167	-6.60019657
H	3.158336571	3.015278331	-7.061947939
H	3.618530666	2.162342631	-5.55011695
H	-0.236140127	4.227494265	-5.817830636
H	0.905033536	4.25527499	-7.203713069
H	0.03538302	2.748686509	-6.795054888
H	-3.138249394	3.859440479	-1.368552359
H	-2.009524558	5.080373638	-2.043618644
H	-1.544854134	3.347748633	-2.019883294
H	-1.678764446	5.652267177	1.700851772
H	-2.015552409	6.445240748	0.12595938
H	-3.205481084	5.31152974	0.828120866
H	-0.367572729	4.593682903	-0.199587579
H	-3.431670866	3.049164319	1.870353366
H	-1.958368508	-0.585584031	2.999713874
H	-4.745546853	0.677966896	2.519487144
H	-3.983331757	-0.588764764	1.506267855
H	-4.431175059	-0.945974299	3.208266591
H	-1.676959845	1.137778315	4.806061054
H	-3.344881396	1.728587327	4.519558035
H	-3.079048152	0.068447875	5.145142235
H	3.505247264	3.965043589	-3.443683831

Table S8. Cartesian coordinates (Å) for DFT energy minimized (for hydrogen atoms only) blue isomer of [$Mn^{III}(O_2)(Tp^{iPr2})(pz^{iPr2}H)$] (193 K structure).

Atom	x	y	z
Mn	-0.143372466	0.009476672	0.09138829
O	1.706896913	-0.144021844	0.019318459
O	1.308922384	1.249699234	0.073251099
N	-2.007420749	0.919261156	0.150692529
N	-3.066550209	0.247068582	-0.414283184
N	-0.644228416	-0.205138617	-2.125270207
N	-1.861327267	-0.780887533	-2.393729509
N	-0.90512222	-1.904881998	0.249909592
N	-2.152205259	-2.146080069	-0.27455667
N	0.071423721	0.251332125	2.576980067
N	1.187791979	0.991341553	2.79418746
B	-2.815458843	-1.077874653	-1.203849824
C	-2.234183199	3.950310133	2.332716817
C	-0.975629283	4.054246186	0.120825321
C	-1.545870888	3.134686476	1.224844449
C	-2.469881989	2.100121146	0.62541067
C	-3.856638813	2.180212658	0.376872469
C	-4.206231117	0.993863378	-0.285223256
C	-5.555850774	0.572582729	-0.82225487
C	-6.699403168	1.026069567	0.103704497
C	-5.764803916	1.091301606	-2.262593478
C	1.438787853	1.723622858	-4.391274078
C	2.436011719	-0.508732232	-3.677426094
C	1.375595084	0.569742544	-3.371217116
C	-0.008860766	-0.033524927	-3.301988384
C	-0.83309734	-0.507868816	-4.352888696
C	-2.003519799	-0.980214923	-3.744956257
C	-3.199925109	-1.656032307	-4.377347755
C	-3.532789644	-1.051657707	-5.753676619
C	-2.981349648	-3.182688953	-4.479576319
C	0.951502741	-4.124308839	2.636529614
C	1.937902843	-3.525637186	0.36871249
C	0.906235871	-3.142073229	1.454153984
C	-0.477225237	-3.038465804	0.85476914
C	-1.479880875	-4.024192941	0.729843954
C	-2.528299182	-3.430663068	0.009368346
C	-3.876263284	-4.008619788	-0.360549115
C	-4.960654998	-3.571421527	0.649851318
C	-3.821409896	-5.540821754	-0.487208961

C	-2.899932317	0.00483887	3.982160126
C	-1.599705832	-1.777946001	5.239648955
C	-1.647673218	-0.89925148	3.977280204
C	-0.381877585	-0.086464447	3.805816604
C	0.473748946	0.455826717	4.803033797
C	1.479590737	1.148716462	4.111948863
C	2.671416328	1.948325936	4.584388108
C	2.232287184	3.259018422	5.271962664
C	3.585657491	1.110191665	5.500279008
H	1.642297895	1.350763682	1.931412503
H	-2.634722043	3.296277974	3.133003578
H	-1.515756354	4.656932597	2.795697512
H	-3.075229071	4.553225411	1.930073276
H	-1.785969077	4.627950357	-0.375891207
H	-0.256627198	4.781116931	0.55267445
H	-0.443623962	3.467233881	-0.653771718
H	-0.696682853	2.579980708	1.67521757
H	-4.528748247	3.000246669	0.647262771
H	-5.565921908	-0.536660571	-0.859579729
H	-6.563213601	0.647912476	1.136790204
H	-6.767659544	2.13271873	0.152758274
H	-7.672530247	0.652218633	-0.274921897
H	-5.769144986	2.200800164	-2.285035942
H	-4.957178045	0.74538577	-2.938120406
H	-6.733047626	0.735042294	-2.671126294
H	0.69493431	2.512562775	-4.158803521
H	2.445304829	2.19103994	-4.388494136
H	1.24109614	1.365823849	-5.424176116
H	2.265556474	-0.971398676	-4.672918417
H	3.454473221	-0.06724732	-3.677681986
H	2.415029547	-1.313714893	-2.916296078
H	1.589124841	0.981534947	-2.363099017
H	-0.608067946	-0.50553306	-5.424571869
H	-4.071481059	-1.487029809	-3.710301795
H	-3.699013953	0.042543413	-5.689571611
H	-2.713186176	-1.227520054	-6.481146386
H	-4.449777948	-1.516494573	-6.170324485
H	-3.881203069	-3.683391745	-4.893891127
H	-2.122930054	-3.412437323	-5.144344338
H	-2.764620463	-3.62864589	-3.4880798
H	0.7363651	-5.163579847	2.309632518
H	1.960025357	-4.12652275	3.097460542
H	0.216913837	-3.85666273	3.422441432

H	1.929410727	-2.795962	-0.464632738
H	2.961523647	-3.543346885	0.796531975
H	1.721210704	-4.531914929	-0.047573786
H	1.170355908	-2.127817054	1.82310785
H	-1.44819936	-5.048506397	1.112671182
H	-4.156468191	-3.592511168	-1.351499587
H	-4.731930461	-3.959484316	1.664036056
H	-5.028043313	-2.467375544	0.718832698
H	-5.95565304	-3.959644463	0.348934758
H	-4.801070695	-5.93387129	-0.826585447
H	-3.050170179	-5.864500343	-1.214694864
H	-3.59319603	-6.020198348	0.487507954
H	-2.875649786	0.710221637	4.839585283
H	-2.970027167	0.598243982	3.049223954
H	-3.823404531	-0.604932993	4.070024165
H	-2.497353059	-2.426853918	5.298091824
H	-0.702779028	-2.42984462	5.253961722
H	-1.580896907	-1.159301256	6.161701865
H	-1.718044546	-1.564759008	3.089647958
H	0.378550771	0.353144636	5.889178733
H	3.253681842	2.221233327	3.676522427
H	1.638067565	3.049162139	6.185593365
H	3.116488202	3.858907736	5.571652833
H	1.608543577	3.879858774	4.59804484
H	3.929861321	0.186437158	4.993602279
H	4.480142711	1.694276112	5.799784133
H	3.053114595	0.811555136	6.427278862
H	-3.86385969	-1.505101017	-1.607867231

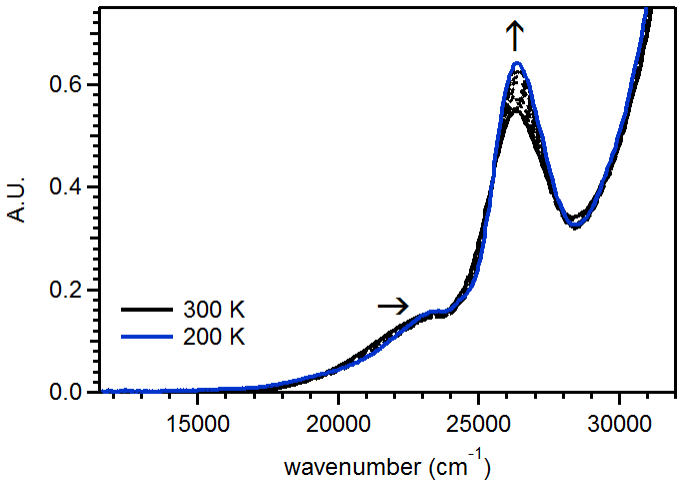


Figure S1. Variable-temperature absorption data collected for [$Mn^{III}(O_2)(Tp^{Ph2})(THF)$] in THF Data were collected from 300 – 200 K in 10 K increments.

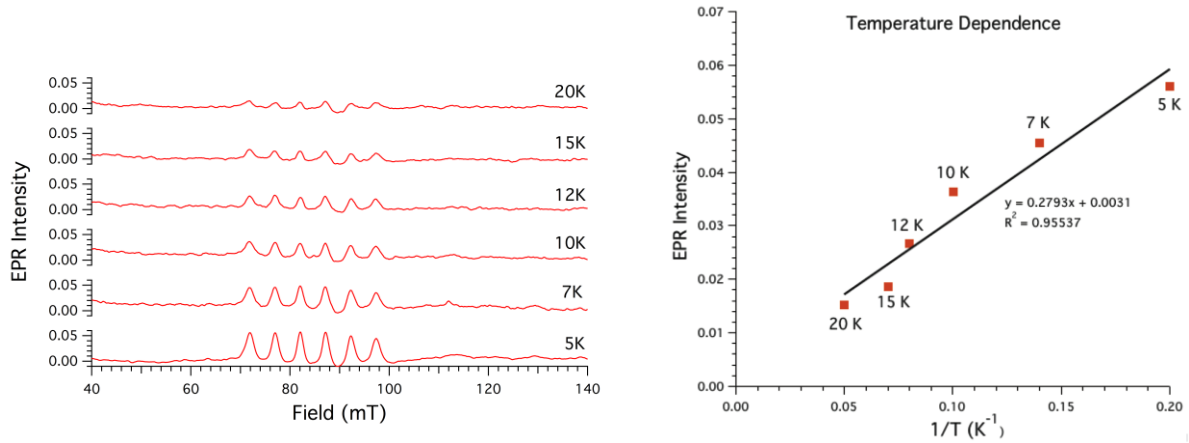


Figure S2. Variable-temperature parallel-mode EPR spectra collected for [$Mn^{III}(O_2)(Tp^{Ph2})$].

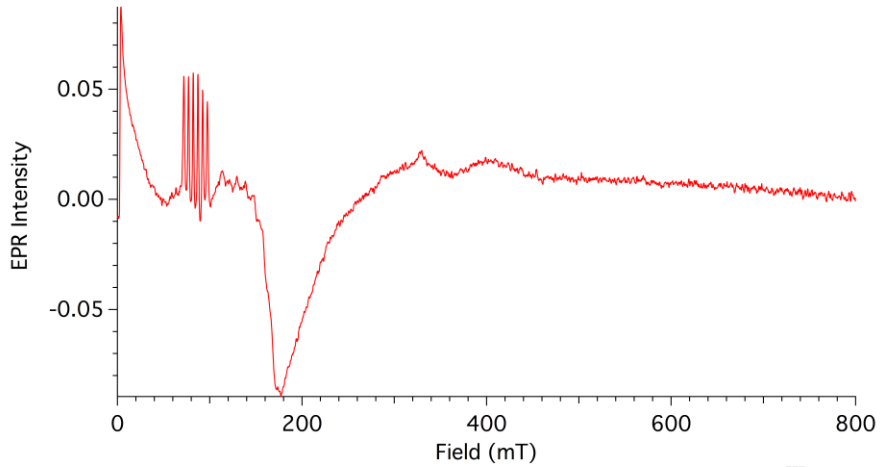


Figure S3. Full spectrum, parallel-mode X-band EPR of [$Mn^{III}(O_2)(Tp^{Ph2})$]. The large negative feature from 100 to 250 mT is due to O_2 dissolved in THF solution.

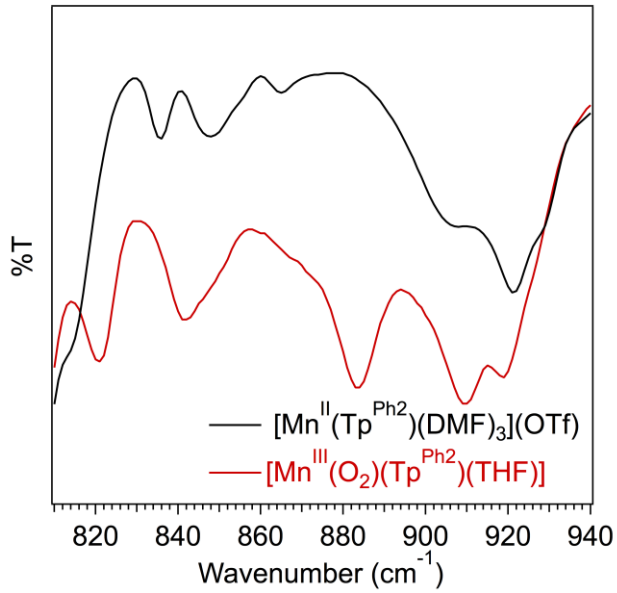


Figure S4. IR spectrum of $[Mn^{II}(Tp^{Ph2})(DMF)_3](OTf)$ (black) and $[Mn^{III}(O_2)(Tp^{Ph2})]$ (red) with a weak feature at 882 cm^{-1}.

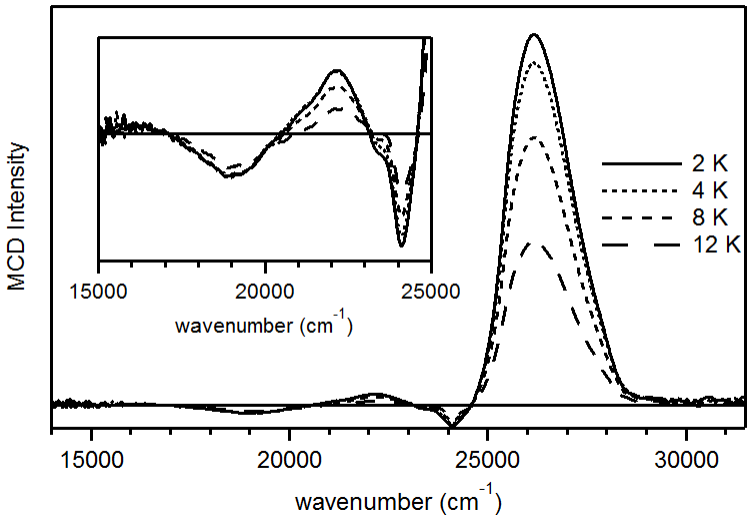


Figure S5. Variable-temperature 7 T MCD data collected for $[Mn^{III}(O_2)(Tp^{Ph2})(THF)]$ in THF. Inset: expanded view of low-intensity MCD features from 15 000 – 25 000 cm^{-1}. Data were collected at the temperatures indicated in the figure.

Table S9. Electronic transition energies (cm^{-1}), oscillator strengths (f_{exp}), and bandwidths (fwhm; cm^{-1}) from Gaussian deconvolutions of 298 K absorption and 2 K, 7 T MCD data of $[Mn^{III}(O_2)(Tp^{Ph2})(THF)]^{\cdot}$

band	energy	$f_{exp} \times 10^3$	fwhm
1	Abs: 19 000	0.083	Abs: 2248
	MCD: 19 000		MCD: 1998
2	Abs: 20 890	0.135	Abs: 2248
	MCD: 21 455		MCD: 1665
3	Abs: 22 600	0.290	Abs: 2248
	MCD: 22 325		MCD: 1665
4	Abs: NA		Abs: NA
	MCD: 23 675		MCD: 500
5	Abs: 24 350	0.342	Abs: 2248
	MCD: 24 800		MCD: 1832
6	Abs: NA		Abs: NA
	MCD: 25 150		MCD: 666
7	Abs: 26 300	167.64	Abs: 2331
	MCD: 26 060		MCD: 1832
8	Abs: 28 400	83.28	Abs: 2331
	MCD: 27 609		MCD: 1832
9	Abs: NA		Abs: NA
	MCD: 28 350		MCD: 999

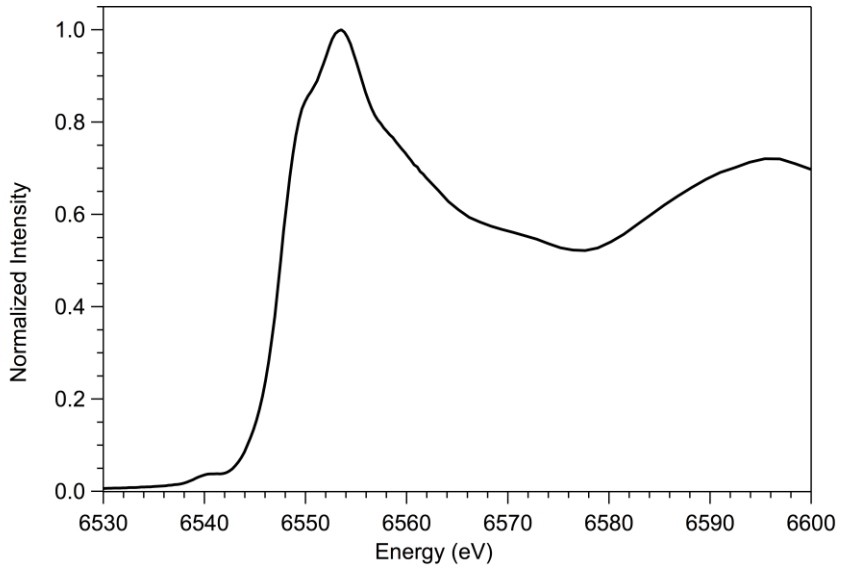


Figure S6. Mn K-edge X-ray Absorption data of $[Mn^{II}(Tp^{Ph2})(DMF)_3](OTf)$ with an edge at 6547.5 eV and a pre-edge feature at 6540.6 eV.

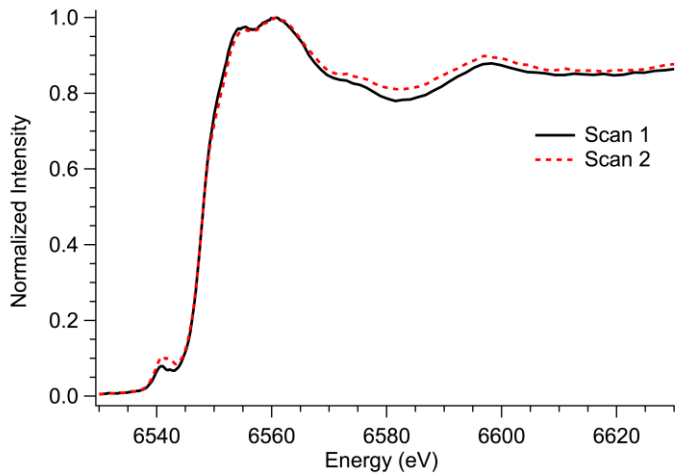


Figure S7. Mn K-edge X-ray Absorption data of $[Mn^{III}(O_2)(Tp^{Ph2})(THF)]$ with change in pre-edge feature from scan 1 to scan 2.

Table S10. Comparison of Mn-Ligand Bond Lengths from X-ray Diffraction (XRD) and EXAFS fits for $[Mn^{II}(Tp^{Ph2})(DMF)_3](OTf)$.

	XRD (Å)	EXAFS (Å)
Mn-N(1)	2.286(1)	2.28
Mn-N(2)	2.250(3)	2.28
Mn-N(3)	2.319(1)	2.28
Mn-O(1)	2.157(3)	2.14
Mn-O(2)	2.141(6)	2.14
Mn-O(3)	2.191(1)	2.14

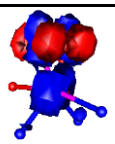
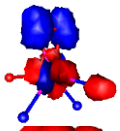
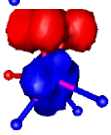
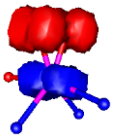
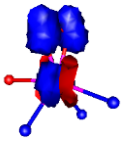
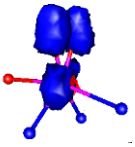
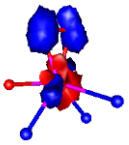
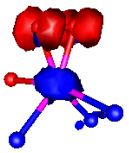
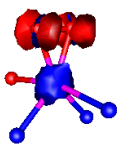
Table S11. All EXAFS Fitting Results for $[Mn^{II}(Tp^{Ph2})(DMF)_3](OTf)$.

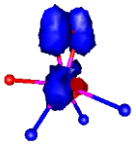
fit	Mn-O			Mn-N			Mn-N/C			Mn-B			Mn-C			F-factor
	n	r(Å)	σ^2	n	r(Å)	σ^2	n	r(Å)	σ^2	n	r(Å)	σ^2	n	r(Å)	σ^2	
1	6	2.18	7.41													0.612
2	3	2.14	3.29	3	2.26	2.58										0.598
3	3	2.14	3.53	3	2.26	2.84	5	3.10	3.14							0.552
4	3	2.14	3.44	3	2.26	2.87	6	3.10	4.72							0.558
5	3	2.14	3.44	3	2.27	2.26	5	3.18	8.15	1	3.11	-4.40				0.520
6	3	2.17	7.16	3	2.23	5.20	5	3.19	8.63	1	3.08	-3.80				0.526
7	3	2.14	3.86	3	2.26	2.78	5	3.09					6	3.18	-2.90	0.536
8	3	2.14	3.68	3	2.26	2.69	5	3.09	2.95				6	3.70	15.78	0.549
9	3	2.16	3.75	3	2.27	3.68	5	3.08	3.32	1	3.33	4.54				0.551
10	3	2.16	3.88	3	2.27	3.53	3	3.08	0.60	1	3.30	6.05				0.535
11	3	2.15	3.48	3	2.28	3.09	3	3.08	1.15	1	3.33	7.59	1	3.53	-1.70	0.528
12	3	2.16	3.62	3	2.28	3.59	3	3.08	0.67	1	3.31	5.03	6	3.54	22.79	0.532
13	3	2.15	3.39	3	2.28	2.98	3	3.09	0.61	1	3.31	3.69	6	3.50	7.43	0.531
14	3	2.16	3.31	3	2.28	3.17	6	3.10	5.11	1	3.35	1.61	6	3.51	2.66	0.540
15	*3*	*2.16*	*3.42*	*3*	*2.28*	*3.17*	*4*	*3.09*	*2.09*	*1*	*3.33*	*2.40*	*6*	*3.49*	*5.51*	*0.534*

Table S12. Energies (eV) and Compositions (%) of the O 2p-based MOs and the Mn 3d-based MOs Based on Spin-Unrestricted B3LYP DFT Computations for [$Mn^{III}(O_2)(Tp^{Ph2})(THF)$].

orbital	occup	spin	energy	Mn 3d	O_2 2p	N 2p	O_{THF} 2p
193 (Mn xz)	1.0	↑	-8.662	71.2	2.0	5.4	1.0
195 (Mn xy/x^2-y^2)	1.0	↑	-7.942	23.3	8.6	11.9	0.5
197 (Mn x^2-y^2/ Tp^{Ph2})	1.0	↑	-7.630	12.8	3.4	17.5	0.2
199 (Mn yz/O_2 π_{op}*)	1.0	↑	-7.512	53.4	26.1	4.6	4.3
200 (Mn x^2-y^2/ Tp^{Ph2})	1.0	↑	-7.403	12.2	4.3	14.3	0.0
201 (Mn xy/x^2-y^2/O_2 π_{op}*)	1.0	↑	-7.265	21.8	16.7	9.0	12.0
213 (Tp^{Ph2})	1.0	↑	-6.297	2.1	0.9	24.9	0.2
214 (Mn z^2/Tp^{Ph2})	1.0	↑	-6.149	18.5	3.7	17.8	1.5
215 (Mn z^2/Tp^{Ph2})	1.0	↑	-6.059	21.4	3.0	22.5	1.6
216 (Tp^{Ph2})	1.0	↑	-5.803	0.4	0.2	22.2	0.0
217 (O_2 π_{op}*)	1.0	↑	-5.018	4.0	92.9	0.0	0.0
218 (Mn xy/O_2 π_{op}*)	0.0	↑	-1.582	34.0	52.1	4.7	0.0
213 (O_2 π^*)	1.0	↓	-5.141	5.4	88.8	0.7	0.2
214 (Mn yz/xy)	0.0	↓	-1.295	17.7	0.8	20.5	0.0
215 (Mn xz)	0.0	↓	-1.236	19.0	2.0	18.8	0.2
218 (Tp^{Ph2})	0.0	↓	-0.654	1.5	0.0	10.0	0.0
219 (Mn x^2-y^2/xy)	0.0	↓	-0.614	51.9	2.7	2.7	0.0
221 (Mn xz/Tp^{Ph2})	0.0	↓	-0.406	24.0	2.0	19.0	0.1
224 (Mn yz)	0.0	↓	-0.239	24.0	0.7	2.6	0.0
225 (Mn z^2)	0.0	↓	-0.180	48.6	1.7	2.5	0.0

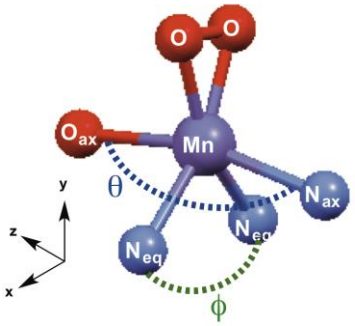
Table S13. TD-DFT Calculated Energies, Percent Contributions from Dominant One-electron Excitations, and Oscillator Strengths for the Major Electronic Transitions of $[Mn^{III}(O_2)(Tp^{Ph2})]$.

region	state	energy (cm^{-1})	f_{osc}	transition	%	donor MO	acceptor MO	comments	EDDM
A	1	10 000	0.000011	217α⟶218α	96	O_2 π*	O_2 π* / Mn d_{xy}	O_2 ⟶Mn CT	
	2	20 500	0.000326	215α⟶218α	41	Mn d_{z^2}	O_2 π* / Mn d_{xy}	Mn d⟶d	
				214α⟶218α	32	Mn d_{z^2}	O_2 π* / Mn d_{xy}		
	3	23 000	0.000251	213β⟶214β	58	O_2 π*	Mn d_{xy} / d_{yz}	O_2 ⟶Mn CT	
	4	23 300	0.000841	213β⟶215β	58	O_2 π*	Mn d_{xz}	O_2 ⟶Mn CT	
	5	25 500	0.000497	213β⟶219β	46	O_2 π*	Mn x^2-y^2/xy	O_2 ⟶Mn CT	
B	8	27 200	0.000193	199α⟶218α	41	Mn d_{yz}	O_2 π* / Mn d_{xy}	Mn d⟶d	
				201α⟶218α	11	Mn $d_{x^2-y^2}$/d_{yz}	O_2 π* / Mn d_{xy}		
				195α⟶218α	3	Mn $d_{x^2-y^2}$/d_{yz}	O_2 π* / Mn d_{xy}		
B	10	28 400	0.003914	216α⟶218α	61	Tp^{Ph2}	O_2 π* / Mn d_{xy}	Tp^{Ph2}⟶Mn CT	
				195α⟶218α	5	Mn $d_{x^2-y^2}$/d_{yz}	O_2 π* / Mn d_{xy}	Mn d⟶d	
B	12	28 800	0.005577	215α⟶218α	8	Mn d_{z^2}	O_2 π* / Mn d_{xy}	Mn d⟶d	
				200α⟶218α	8	Mn $d_{x^2-y^2}$	O_2 π* / Mn d_{xy}		
				199α⟶218α	8	Mn d_{yz}	O_2 π* / Mn d_{xy}		
				197α⟶218α	8	Mn $d_{x^2-y^2}$	O_2 π* / Mn d_{xy}		
				195α⟶218α	6	Mn $d_{x^2-y^2}$/d_{yz}	O_2 π* / Mn d_{xy}		
C	14	29 500	0.003044	213β⟶221β	16	O_2 π_{op}*	Mn d_{xz}	O_2⟶ Mn CT	
				213β⟶215β	16	O_2 π_{op}*	Mn d_{xz}	O_2⟶Mn CT	
				213β⟶218β	9	O_2 π_{op}*	Tp^{Ph2}		
				199α⟶218α	5	Mn d_{yz}	O_2 π*/Mn d_{xy}	Mn d⟶d	
C	15	29 800	0.003648	213β⟶224β	18	O_2 π_{op}*	Mn d_{yz}	O_2⟶ Mn CT	

				213β⟶225β	17	O_2 π_{op}*	Mn d_{z^2}	O_2⟶Mn CT	
				213β⟶218β	8	O_2 π_{op}*	Tp^{Ph2}	O_2⟶Tp^{Ph2} CT	
B	17	30 600	0.001215	215α⟶218α	16	Mn d_{z^2}	O_2 π*/Mn d_{xy}	Mn d⟶d/ O_2	
				214α⟶218α	8	Mn d_{z^2}	O_2 π*/Mn d_{xy}		
				193α⟶218α	6	Mn d_{xz}	O_2 π*/Mn d_{xy}		

[a]Electronic transition energies have been rounded to the nearest 100 cm^{-1}. Included in this table are all Mn d-d transitions, as well as charge-transfer (CT) transitions, with $f_{osc} > 0.003$. [b]Composition of molecular orbitals (MOs) involved in these electronic transitions are listed in Table S5. Spin-up and spin-down MOs are designated by ↑ and ↓, respectively. [c]Electron density difference maps (EDDMs) showing surface contour plots of loss (red) and gain (blue) of electron density for a given electronic transition. For clarity, only the Mn, N, and O atoms are shown in these plots.

Figure S8. Calculation of τ parameter for $[Mn^{III}(O_2)(Tp^{Ph2})]$. For clarity, only the primary coordination sphere of Mn, N, and O is shown.



θ = 93.1(3)
ϕ = 163.0(9)

τ = | (θ - ϕ) / 60° |
τ = 1.17

Table S14. Band comparison of the experimental absorption and MCD transition energies, TD-DFT and NEVPT2 calculated transition energies in wavenumbers.

Band	Exp. Absorption		MCD	TD-DFT		CASSCF/NEVPT2		Assignment
	cm^{-1}	f_{exp} x 10^3	cm^{-1}	cm^{-1}	f_{osc} x 10^3	cm^{-1}	f_{osc} x 10^3	
1	19 000	0.083	19 000	20 500	0.326	25 700	0.164	d_z^2 - d_{xy}
2	20 890	0.135	21 455	23 300	0.841	-		CT
3	22 600	0.290	22 325	27 200	0.193	29 500	0.448	d_{yz} - d_{xy}
4	[b]	-	23 675	[c]	-	26 800[a]	0.000	SF[c]
5	24 350	34.20	24 800	28 800	5.577	31 600	0.198	$d_{x^2-y^2}$ - d_{xy}
6	[b]	-	25 150	[c]	-	30 500[a]	-	SF[c]
7	26 300	167.64	26 060	30 600	1.215	32 000	0.005	d_{xz} - d_{xy}
8	28 400	83.28	27 609	29 500	3.044	-	-	O_2-Mn CT
9	28 350		-	29 800	3.648	-	-	O_2-Mn CT

[a]Indicates spin-forbidden states calculated by NEVPT2 with negligible contribution to the absorption spectrum. [b]Band only apparent in low-temperature, 7 T MCD spectrum. [c]Mn^{III} spin-forbidden *d-d* transitions to triplet excited states.

Table S15. CASSCF/NEVPT2 calculated individual contributions to zero field splitting parameters. (D = -2.905 cm^{-1}, E/D = 0.275)

Multiplicity	Root	Energy (cm^{-1})	D (cm^{-1})	E
5	1	25688.2	-0.368	0.006
5	2	29493.3	-0.489	-0.005
5	3	32046.6	0.001	-0.037
5	4	31593.8	0.095	0.030
3	0	18355.4	-0.473	-0.035
3	1	19212.3	-0.337	0.017
3	2	20430.1	-0.014	0.002
3	3	22931.6	0.000	0.000
3	4	23652.4	-0.264	-0.006
3	5	23690.7	-0.011	0.005
3	6	25183.4	-0.113	0.037
3	7	24935.5	-0.145	-0.023
3	8	26826.9	-0.003	-0.002
3	9	30521.8	-0.784	-0.788

Table S16. Energies (eV) and Compositions (%) of the O 2p-based MOs and the Mn 3d-based MOs Based on Spin-Unrestricted B3LYP DFT Computations for [$Mn^{III}(O_2)(Ph^{iPr2})(pz^{iPr2}H)$] (193 K) from XRD coordinates.

orbital	occupancy	spin	energy (eV)	Mn 3d	O (2p)
186	1.0	↑	-6.4209	6.6	3.7
187	1.0	↑	-6.3665	12.1	4.6
188	1.0	↑	-6.1353	1.0	0.6
189	1.0	↑	-6.0422	0.7	0.3
190	1.0	↑	-5.4246	51.6	6.8
191	1.0	↑	-5.0085	5.8	65.2
192	0.0	↑	-1.0234	45.5	44.5
186	1.0	↓	-6.0434	0.2	0.4
187	1.0	↓	-5.1158	5.2	88.6
188	0.0	↓	-0.6623	56.8	3.4
189	0.0	↓	-0.6169	61.3	2.9
190	0.0	↓	-0.2795	75.1	3.1
191	0.0	↓	0.3637	0.7	0.6

Table S17. Energies (eV) and Compositions (%) of the O 2p-based MOs and the Mn 3d-based MOs Based on Spin-Unrestricted B3LYP DFT Computations for [$Mn^{III}(O_2)(Ph^{iPr2})(pz^{iPr2}H)$] (193 K) from hydrogen optimized DFT structures.

orbital	occupancy	spin	energy (eV)	Mn 3d	O (2p)
186	1.0	↑	-6.5581	3.9	3.1
187	1.0	↑	-6.5183	9.9	4.3
188	1.0	↑	-6.2916	1.0	0.5
189	1.0	↑	-6.1642	0.6	0.2
190	1.0	↑	-5.6258	49.4	6.8
191	1.0	↑	-5.2261	5.4	90.6
192	0.0	↑	-1.2706	43.3	46.5
186	1.0	↓	-6.1651	0.1	0.6
187	1.0	↓	-5.3378	4.5	88.2
188	0.0	↓	-0.8139	62.6	2.6
189	0.0	↓	-0.7628	61.0	4.2
190	0.0	↓	-0.4787	73.9	4.0
191	0.0	↓	0.2707	2.6	0.6

Table S18. Energies (eV) and Compositions (%) of the O 2p-based MOs and the Mn 3d-based MOs Based on Spin-Unrestricted B3LYP DFT Computations for [$Mn^{III}(O_2)(Ph^{iPr2})(pz^{iPr2}H)$] (253 K) from XRD coordinates.

orbital	occupancy	spin	energy (eV)	Mn 3d	O 2p
186	1.0	↑	-6.3618	13.4	5.1
187	1.0	↑	-6.2663	6.4	3.8
188	1.0	↑	-5.9808	1.0	0.3
189	1.0	↑	-5.9184	0.8	0.3
190	1.0	↑	-5.3902	51.3	6.5
191	1.0	↑	-4.8770	6.2	91.9
192	0.0	↑	-0.8555	45.0	44.4
186	1.0	↓	-5.9202	0.1	0.5
187	1.0	↓	-4.9824	5.9	89.0
188	0.0	↓	-0.5594	52.5	4.9
189	0.0	↓	-0.4820	61.5	3.4
190	0.0	↓	-0.1782	70.6	4.1
191	0.0	↓	0.4323	1.9	0.5
192	0.0	↓	0.6041	38.2	0.7

Table S19. Energies (eV) and Compositions (%) of the O 2p-based MOs and the Mn 3d-based MOs Based on Spin-Unrestricted B3LYP DFT Computations for [$Mn^{III}(O_2)(Ph^{iPr2})(pz^{iPr2}H)$] (253 K) from hydrogen optimized DFT structures.

orbital	occupancy	spin	energy (eV)	Mn 3d	O 2p
186	1.0	↑	-6.5267	11.8	5.0
187	1.0	↑	-6.4220	5.7	3.7
188	1.0	↑	-6.1397	1.4	0.6
189	1.0	↑	-6.1062	0.5	0.2
190	1.0	↑	-5.5686	50.0	6.5
191	1.0	↑	-4.9866	5.4	92.1
192	0.0	↑	-1.0412	42.4	46.6
187	1.0	↓	-5.0910	5.5	89.4
188	0.0	↓	-0.6845	51.8	4.2
189	0.0	↓	-0.6208	59.9	3.3
190	0.0	↓	-0.3412	70.0	3.8
191	0.0	↓	0.2922	2.2	0.6

Table S20. TD-DFT Calculated Energies, Percent Contributions from Dominant One-electron Excitations, and Oscillator Strengths for the Major Electronic Transitions of $[Mn^{III}(O_2)(Ph^{iPr2})(pz^{iPr2}H)]$ (193 K) from XRD coordinates.

band	state	energy (cm^{-1})	f_{osc}	transition	%	donor MO	acceptor MO	comments
i	1	14969.5	0.000049	191α ⟶ 192α	98	O_2	Mn d / O_2	LMCT
ii	2	17339.6	0.000664	190α⟶192α	96%	Mn d	Mn d / O_2	d ⟶ d
iii	3	24912.4	0.000093	187β ⟶ 188β	31	O_2	Mn d / O_2	LMCT
				187β ⟶ 189β	52	O_2	Mn d / O_2	LMCT
				187β ⟶ 190β	12	O_2	Mn d / O_2	LMCT
	4	25450.6	0.000505	187β ⟶ 188β	50	O_2	Mn d / O_2	LMCT
				187β ⟶ 189β	26	O_2	Mn d / O_2	LMCT

Table S21. TD-DFT Calculated Energies, Percent Contributions from Dominant One-electron Excitations, and Oscillator Strengths for the Major Electronic Transitions of $[Mn^{III}(O_2)(Ph^{iPr2})(pz^{iPr2}H)]$ (193 K) from hydrogen optimized DFT structures.

band	state	energy (cm^{-1})	f_{osc}	transition	%	donor MO	acceptor MO	comments
i	1	14583.9	0.000053	191α ⟶ 192α	98	O_2	Mn d / O_2	LMCT
ii	2	17466.1	0.000808	190α ⟶192α	95	Mn d	Mn d / O_2	d ⟶ d
iii	3	25165.9	0.000022	187β ⟶188β	58	O_2	Mn d	LMCT
				187β ⟶ 189β	26	O_2	Mn d	LMCT
				187β ⟶ 190β	11	O_2	Mn d	LMCT
	4	25939.3	0.000191	187β ⟶ 188β	23	O_2	Mn d	LMCT
				187β ⟶ 189β	50	O_2	Mn d	LMCT

Table S22. TD-DFT Calculated Energies, Percent Contributions from Dominant One-electron Excitations, and Oscillator Strengths for the Major Electronic Transitions of $[Mn^{III}(O_2)(Ph^{iPr2})(pz^{iPr2}H)]$ (253 K) from XRD coordinates.

band	state	energy (cm^{-1})	f_{osc}	transition	%	donor MO	acceptor MO	comments
i	1	15091.5	0.000032	191α ⟶ 192α	98	O_2	Mn d / O_2	LMCT
ii	2	18475.4	0.000670	190α ⟶192α	95	Mn d	Mn d / O_2	d ⟶ d
iii	3	24717.0	0.000170	187β ⟶ 188β	26	O_2	Mn d / O_2	LMCT
				187β ⟶ 189β	54	O_2	Mn d / O_2	LMCT
				187β ⟶ 190β	1	O_2	Mn d / O_2	LMCT
	4	25274.5	0.000989	187β ⟶ 188β	53	O_2	Mn d / O_2	LMCT
				187β ⟶ 189β	25	O_2	Mn d / O_2	LMCT

Table S23. TD-DFT Calculated Energies, Percent Contributions from Dominant One-electron Excitations, and Oscillator Strengths for the Major Electronic Transitions of $[Mn^{III}(O_2)(Ph^{iPr2})(pz^{iPr2}H)]$ (253 K) from hydrogen optimized DFT structures.

band	state	energy (cm^{-1})	f_{osc}	transition	%	donor MO	acceptor MO	comments
i	1	14321.4	0.000023	191α ⟶ 192α	98	O_2	Mn d / O_2	LMCT
ii	2	18891.6	0.000724	190α ⟶ 192α	95	Mn d	Mn d / O_2	d ⟶ d
iii	3	24355.1	0.000061	187β ⟶ 188β	30	O_2	Mn d	LMCT
				187β ⟶ 189β	47	O_2	Mn d	LMCT
				187β ⟶ 190β	18	O_2	Mn d	LMCT
	4	25119.5	0.000522	187β ⟶ 188β	47	O_2	Mn d	LMCT
				187β ⟶ 189β	30	O_2	Mn d	LMCT