

Supporting Information

The Effects of Non-Redox Active Metal Ions on the Activation of Dioxygen: Isolation and Characterization of a Heterobimetallic Complex Containing a Mn^{III}– (μ -OH)–Ca^{II} core.

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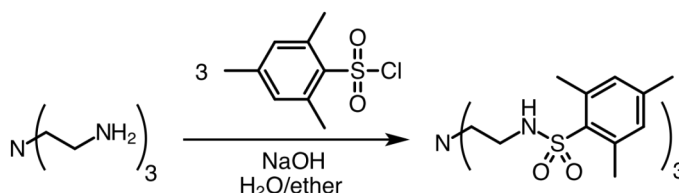
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General Methods

All reagents were purchased from commercial sources and used as received, unless otherwise noted. Solvents were sparged with argon and dried over columns containing Q-5 and molecular sieves. Sodium hydride (NaH) as a 30% dispersion in mineral oil was filtered with a medium porosity glass frit and washed 5 times each with pentane and Et₂O. Solid NaH was dried under a vacuum and stored under an inert

atmosphere. Elemental analyses were performed on a Perkin-Elmer 2400 CHNS analyzer. The synthesis of ligands was carried out under a dinitrogen atmosphere. The syntheses of metal complexes were conducted in a Vacuum Atmospheres, Co. drybox under an argon atmosphere. Dioxygen was dried on a Drierite gas purifier purchased from Fischer Scientific. $^{18}\text{O}_2$ was obtained from ICON Isotopes (Summit, NJ). Electronic absorbance spectra were recorded with a Cary 50 spectrophotometer using a 1.00 cm quartz cuvette. Fourier transform infrared spectra were collected on a Varian 800 Scimitar Series FTIR spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX500 spectrometer.

Ligands Synthesis



Preparation of N,N',N'' -(2,2',2''-nitrilotris(ethane-2,1-diyl))tris(2,4,6-trimethylbenzenesulfonamide) (H_3MST). To a 250 mL round-bottom flask containing tren (1.2 g, 8.2 mmol) and NaOH (1.5 g, 38 mmol) in water (40 mL), 2,4,6-trimethylsulfonyl chloride (5.4 g, 25 mmol) dissolved in ether (20 mL) was added drop wise at room temperature with vigorous stirring. After allowing the reaction mixture to stir overnight, ether was removed under reduced pressure and the resulting white precipitate was collected on a glass frit, which was washed with copious amount of water and dried under reduced pressure. The resulting white solid was redissolved in chloroform (100 mL) and dried again with anhydrous sodium sulfate. After filtering off the insoluble species, the solvent was removed and the residue was dried under vacuum at 80 °C for 4 h. The residue was redissolved in dichloromethane (DCM) (20 mL) in the dry box and precipitated with pentane to give an ivory powder. Yield: 82~87%. ^1H NMR (500 MHz, CDCl_3 , ppm): 2.27 (s, 3H), 2.61 (br s, 8H), 3.06 (d, 2H), 5.91 (br t, 1H, NH), 6.91 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): 20.8, 22.9, 40.4, 53.8, 131.8, 134.4, 138.9, 141.8. FTIR (KBr disc, cm^{-1} , selected bands): 3274, 3025, 2973, 2936, 2826, 1604, 1565, 1440, 1303, 1154, 1137, 1097, 1051, 966, 852, 803, 654, 576, 536. HRMS (ES+): Exact mass calcd for $\text{C}_{33}\text{H}_{48}\text{N}_4\text{O}_6\text{S}_3\text{Na}$ [M + Na], 715.2634. Found 715.2626.

Complex Synthesis

Preparation of $[\text{NMe}_4][\text{Mn}^{\text{II}}\text{MST}]$. A solution of H_3MST (400 mg, 0.58 mmol) dissolved in 6 mL of anhydrous DMA was treated with solid NaH (42 mg, 1.8 mmol). The mixture was stirred until gas evolution ceased. $\text{Mn}(\text{OAc})_2$ (99.8 mg, 0.576 mmol) and NMe_4OAc (76.8 mg, 0.576 mmol) were added to the pale yellow solution, after which the mixture was stirred overnight. Diethyl ether (10 mL) was added to precipitate NaOAc and the pale yellow mixture was filtered to remove insoluble species. The

filtrate was concentrated under vacuum to ca. 1 mL and triturated with Et₂O (10 mL) until a solid began to form. Pentane (20 mL) was added to complete the precipitation of a white solid, which was collected on glass frit, redissolved in THF (15 mL), and filtered again to remove any insoluble materials. The filtrate was concentrated under vacuum to ca. 1 mL and treated with pentane (20 mL) to precipitate a white solid. The white solid was collected on glass frit and dried under a vacuum to give 425 mg of product (90%). Elemental analysis calcd for [NMe₄][Mn^{II}MST], C₃₇H₅₇MnN₅O₆S₃: C, 54.25; H, 7.01; N, 8.55%, found: C, 53.91; H, 7.19; N, 8.30%. FTIR (KBr disc, cm⁻¹, selected bands): 3528, 3029, 2967, 2932, 2848, 1635, 1604, 1490, 1457, 1407, 1257, 1233, 1135, 1100, 1055, 977, 953, 848, 809, 653, 604, 577, 541.

Preparation of Ca(OTf)₂/15-Crown-5-Ether Complex. This complex was synthesized according to the literature method for Mg(15-crown-5)(OTf)₂ with minor modifications.¹ In a Ar-filled drybox, calcium trifluoromethanesulfonate (1.00 g, 2.96 mmol) and 15-crown-5 (0.66 g, 3.0 mmol) were suspended in MeCN (10 mL) and heated at 50°C (heating mantle) for 2 h. The initial suspension became clear during the reaction. The solution was cooled and filtered to remove any insoluble materials. The filtrate was concentrated under vacuum to ca. 4 mL and Et₂O (10 mL) was added to precipitate the product. The white solid was filtered and washed twice with Et₂O (10 mL). Drying in vacuo gave 1.57 g of Ca(OTf)₂/15-crown-5 ether adduct as a cotton-like white solid in 94% yield: this complex was used without further purification. Elemental analysis confirmed 1:1 adduct. Elemental analysis calcd for Ca(OTf)₂/15-crown-5, C₁₂H₂₀CaF₆O₁₁S₂: C, 25.81; H, 3.61%, found: C, 26.09; H, 3.38%.

Preparation of Ba(OTf)₂/18-crown-6-Ether adduct. This complex was prepared as above for Ca(OTf)₂/15-crown-5 using barium trifluoromethanesulfonate (1 g, 2.3 mmol) and 18-Crown-6 (0.61 g, 2.3 mmol) to afford 1.56 g of Ba(OTf)₂/15-crown-5 ether adduct as a cotton-like white solid in 96% yield and it was used without further purification. Elemental analysis confirmed 1:1 adduct. Elemental analysis calcd for Ba(OTf)₂/18-crown-6, C₁₄H₂₄BaF₆O₁₂S₂: C, 24.03; H, 3.46, found: C, 24.04; H, 3.02%.

Preparation of [15-crown-5]Ca^{II}-(μ-OH)-Mn^{III}MST]OTf. A Schlenk flask was charged with a solution of [NMe₄][Mn^{II}MST] (100 mg, 0.12 mmol) and Ca(OTf)₂/15-crown-5 adduct (68.3 mg, 0.122 mmol) in 5 mL of anhydrous DCM. The flask was sealed with a rubber septum and brought out from the dry box, after which excess O₂ (10 mL, T = 298 K, P = 1 atm, 0.4 mmol) was injected to the headspace via syringe and the mixture was stirred overnight at room temperature. During the reaction, the initial colorless solution became blue-green in color and produced a white precipitate. After the reaction was stopped, all volatiles were removed under vacuum and the reaction flask was brought into the box. The dark green residue was redissolved in DCM (5 mL) and filtered to remove any insoluble materials. The filtrate was layered with pentane and after 2 d, dark green crystals and a white precipitate ([NMe₄]OTf) appeared. This heterogeneous mixture was vigorously shaken to suspend the white solid and the supernatant was carefully decanted (which also removed most of the white solid). This process was repeated twice to ensure all the

white solid was removed. The remained green solid was redissolved in DCM and recrystallization twice from DMC/pentane. The resulting dark green crystals were collected on glass frit and dried under vacuum, affording the produce in yields that ranged between 50~60%. Elemental analysis calcd for [15-crown-5 \supset Ca^{II}-(μ -OH)-Mn^{III}MST]OTf·0.5CH₂Cl₂, C_{44.5}H₆₇CaClF₃MnN₄O₁₅S₄: C, 44.04; H, 5.56; N, 4.62%, found: C, 43.94; H, 5.67; N, 4.59%. FTIR (KBr disc, cm⁻¹, selected bands): 3313, 2972, 2934, 2887, 1603, 1564, 1469, 1458, 1403, 1383, 1355, 1275, 1223, 1144, 1087, 1030, 971, 958, 931, 872, 817, 750, 722, 660, 637, 611, 572, 541, 516. $\mu_{\text{eff}} = 4.72 \mu\text{B}$ in DMSO (Evans method).

Preparation of [18-crown-6 \supset Ba^{II}-(μ -OH)-Mn^{III}MST]OTf. This salt was prepared using the method described above for the Mn/Ca system with [NMe₄][Mn^{III}MST] (100 mg, 0.12 mmol) and Ba(OTf)₂/18-crown-6 adduct (87.6 mg, 0.122 mmol) to produce desired salt in yields that were less than 30%. ESI-MS (ES+): Exact mass calcd for C₄₅H₇₀BaMnN₄O₁₃S₃⁺ [M - CF₃SO₃⁻], 1163.21. Found 1163.25 (For the isotope distribution and its simulation, see Figure S4). FTIR (KBr disc, cm⁻¹, selected bands): 3339, 2971, 2921, 2867, 1603, 1563, 1468, 1455, 1404, 1382, 1352, 1281, 1261, 1224, 1146, 1097, 1033, 965, 931, 827, 745, 723, 659, 636, 609, 575, 542, 517. $\mu_{\text{eff}} = 4.74 \mu\text{B}$ in DMSO (Evans method).

Crystallography

Structure of [15-crown-5 \supset Ca^{II}-(μ -OH)-Mn^{III}MST]OTf. A green crystal of approximate dimensions 0.13 x 0.19 x 0.28 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2² program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT³ and SADABS⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵ program. There were neither systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors⁶ for neutral atoms were used throughout the analysis. Hydrogen atom H(7A) was located from a difference-Fourier map and refined (*x,y,z* and *U*_{iso}) with d(O-H) fixed at 0.85Å. The remaining hydrogen atoms were included using a riding model. The fluorine atoms and oxygen atoms O(13), O(14) and O(15) were disordered and included using multiple components, partial site-occupancy-factors and equivalent thermal parameters (isotropic for fluorine, anisotropic for oxygen). There was one molecule of dichloromethane solvent present. Least-squares analysis yielded wR2 = 0.1404 and Goof = 1.039 for 679 variables (4 restraints) refined against 13214 data (0.76Å), R1 = 0.0515 for those 10795 data with I > 2.0σ(I).

Structure of [18-crown-6]Ba^{II}-(μ -OH)-Mn^{III}MST]OTf. A blue crystal of approximate dimensions 0.08 x 0.18 x 0.33 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2² program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT³ and SADABS⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵ program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors⁶ for neutral atoms were used throughout the analysis. Hydrogen atom H(7A) was located from a difference-Fourier map and refined (x,y,z and fixed U_{iso}). The remaining hydrogen atoms were included using a riding model. There was one molecule of THF solvent present. The solvent was disordered and included using multiple components, partial site-occupancy-factors and geometric restraints. At convergence, wR2 = 0.1035 and Goof = 1.030 for 716 variables (30 restraints) refined against 15047 data (0.73 Å), R1 = 0.0373 for those 12382 data with I > 2.0σ(I).

Definitions:

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

Goof = S = $[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

References

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Table S1. Crystal data and structure refinement for [15-crown-5 \supset Ca^{II}-(μ -OH)-Mn^{III}MST]OTf (CaMnOH).

Empirical formula	C ₄₄ H ₆₆ Ca F ₃ Mn N ₄ O ₁₅ S ₄ • CH ₂ Cl ₂	
Formula weight	1256.19	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 14.4165(7) Å	a = 112.4295(6)°.
	b = 14.7066(7) Å	b = 97.6849(6)°.
	c = 15.7017(8) Å	g = 106.5477(6)°.
Volume	2837.2(2) Å ³	
Z	2	
Density (calculated)	1.470 Mg/m ³	
Absorption coefficient	0.640 mm ⁻¹	
F(000)	1312	
Crystal color	green	
Crystal size	0.28 x 0.19 x 0.13 mm ³	
Theta range for data collection	1.61 to 27.88°	
Index ranges	-18 ≤ h ≤ 18, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20	
Reflections collected	33863	
Independent reflections	13214 [R(int) = 0.0224]	
Completeness to theta = 25.50°	99.8 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9237 and 0.8397	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13214 / 4 / 679	
Goodness-of-fit on F ²	1.039	
Final R indices [I > 2σ(I) = 10795 data]	R1 = 0.0515, wR2 = 0.1314	
R indices (all data, 0.76Å)	R1 = 0.0635, wR2 = 0.1404	
Largest diff. peak and hole	1.369 and -1.581 e.Å ⁻³	

Table S2. Crystal data and structure refinement for [18-crown-6 \supset Ba^{II}-(μ -OH)-Mn^{III}MST]OTf (BaMnOH).

Empirical formula	C ₄₆ H ₆₉ Ba F ₃ Mn N ₄ O ₁₆ S ₄ • C ₄ H ₈ O	
Formula weight	1383.68	
Temperature	198(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 13.0048(5) Å	a = 110.5560(4)°.
	b = 14.7028(5) Å	b = 92.2863(4)°.
	c = 18.2798(7) Å	g = 105.8019(4)°.
Volume	3113.2(2) Å ³	
Z	2	
Density (calculated)	1.476 Mg/m ³	
Absorption coefficient	1.041 mm ⁻¹	
F(000)	1426	
Crystal color	blue	
Crystal size	0.33 x 0.18 x 0.08 mm ³	
Theta range for data collection	1.89 to 28.94°	
Index ranges	-16 ≤ h ≤ 17, -19 ≤ k ≤ 19, -24 ≤ l ≤ 24	
Reflections collected	38065	
Independent reflections	15047 [R(int) = 0.0254]	
Completeness to theta = 25.50°	99.7 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9232 and 0.7237	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	15047 / 30 / 716	
Goodness-of-fit on F ²	1.030	
Final R indices [I > 2σ(I) = 12382 data]	R1 = 0.0373, wR2 = 0.0968	
R indices (all data, 0.73 Å)	R1 = 0.0486, wR2 = 0.1035	
Largest diff. peak and hole	0.795 and -0.665 e.Å ⁻³	

Table S3. Selected interatomic distances (Å) and angles (°)

CaMnOH		BaMnOH	
Mn(1)-O(7)	1.8290(18)	Mn(1)-O(7)	1.8235(18)
Mn(1)-N(1)	2.075(2)	Mn(1)-N(1)	2.096(2)
Mn(1)-N(2)	2.019(2)	Mn(1)-N(2)	2.065(2)
Mn(1)-N(3)	2.107(2)	Mn(1)-N(3)	2.068(2)
Mn(1)-N(4)	2.029(2)	Mn(1)-N(4)	2.027(2)
Mn(1)-Ca(1)	3.7478(6)	Mn(1)-Ba(1)	4.2394(4)
Ca(1)-O(1)	2.3328(19)	Ba(1)-O(1)	2.7452(19)
Ca(1)-O(3)	2.3693(18)	Ba(1)-O(3)	2.727(2)
Ca(1)-O(7)	2.3422(19)	Ba(1)-O(7)	2.7401(18)
Ca(1)-O(8)	2.490(3)	Ba(1)-O(8)	2.888(3)
Ca(1)-O(9)	2.508(2)	Ba(1)-O(9)	2.878(2)
Ca(1)-O(10)	2.4921(19)	Ba(1)-O(10)	2.822(3)
Ca(1)-O(11)	2.486(2)	Ba(1)-O(11)	2.907(3)
Ca(1)-O(12)	2.453(2)	Ba(1)-O(12)	2.910(3)
		Ba(1)-O(13)	2.859(3)
O(7)-Mn(1)-N(2)	96.95(8)	O(7)-Mn(1)-N(2)	102.02(9)
O(7)-Mn(1)-N(4)	96.58(8)	O(7)-Mn(1)-N(4)	95.74(9)
N(2)-Mn(1)-N(4)	131.81(10)	N(2)-Mn(1)-N(4)	124.27(10)
O(7)-Mn(1)-N(1)	176.94(9)	O(7)-Mn(1)-N(1)	176.43(9)
N(2)-Mn(1)-N(1)	81.83(9)	N(2)-Mn(1)-N(1)	80.89(10)
N(4)-Mn(1)-N(1)	82.25(9)	N(4)-Mn(1)-N(1)	80.84(9)
O(7)-Mn(1)-N(3)	101.09(8)	O(7)-Mn(1)-N(3)	100.27(9)
N(2)-Mn(1)-N(3)	109.38(9)	N(2)-Mn(1)-N(3)	106.69(10)
N(4)-Mn(1)-N(3)	112.93(9)	N(4)-Mn(1)-N(3)	121.44(10)
N(1)-Mn(1)-N(3)	81.97(9)	N(1)-Mn(1)-N(3)	80.74(9)
Mn(1)-O(7)-Ca(1)	127.49(9)	Mn(1)-O(7)-Ba(1)	135.60(9)

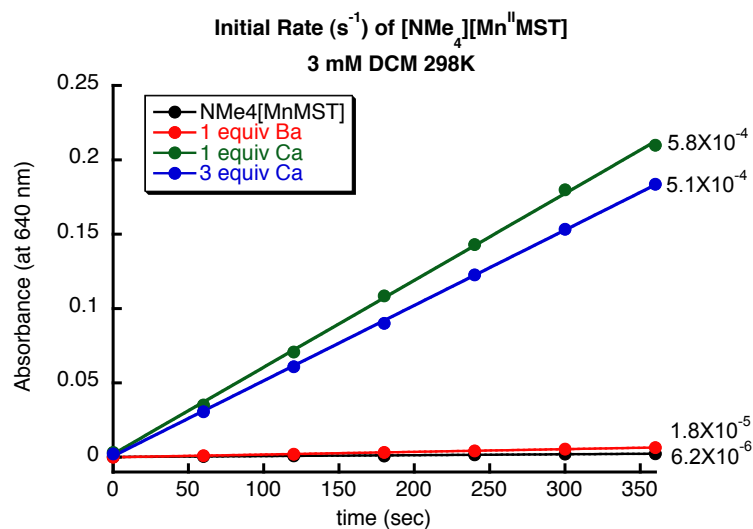


Figure S1. Initial rates of reactions between [NMe₄][Mn^{II}MST] and excess O₂ in the absence or presence of Group II metal crown ether adduct (Ca(OTf)₂/15-crown-5 or Ba(OTf)₂/18-crown-6). The absorbance changes at 640 nm were recorded every 60 s at 298K (collection began 30 sec after injection of O₂ (5 mL)).

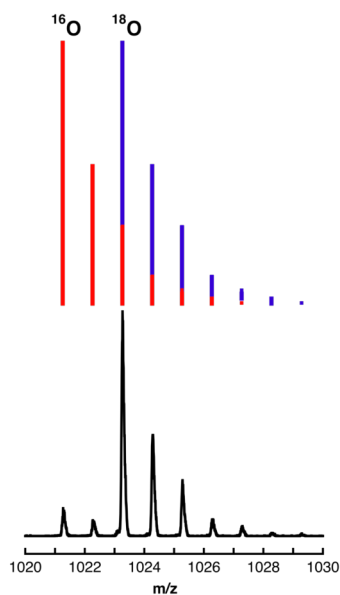


Figure S2. ESI-MS spectrum of [15-crown-5]Ca^{II}-(μ-O¹⁸H)-Mn^{III}MST]⁺ monocation generated from the reaction between equimolar amount of [NMe₄][Mn^{II}MST] and Ca(OTf)₂/15-crown-5 adduct under ¹⁸O₂ in DCM and the simulated isotope distribution patterns. Red and blue lines denote species from ¹⁶O and ¹⁸O respectively.

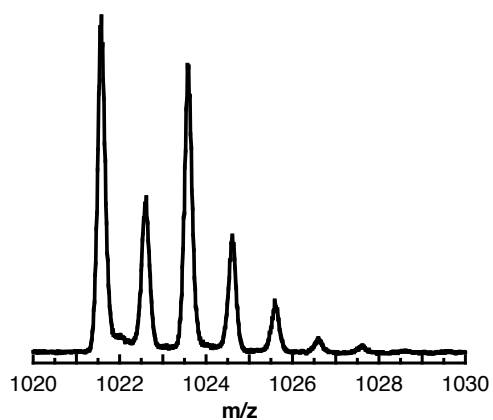


Figure S3. ESI-MS spectrum of [15-crown-5Ca^{II}-(μ -OH)-Mn^{III}MST]⁺ monocation after addition of 10 equiv of H₂¹⁸O in MeCN.

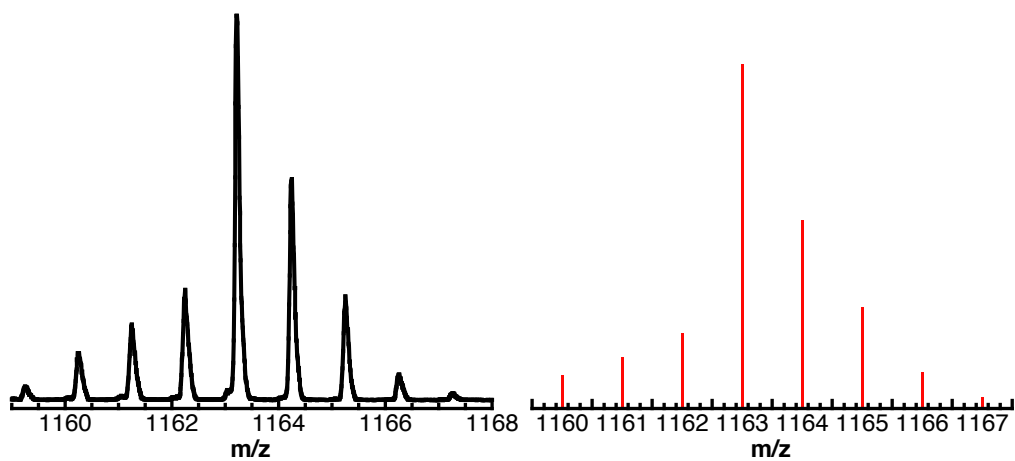


Figure S4. ESI-MS spectrum of [18-crown-6Ba^{II}-(μ -OH)-Mn^{III}MST]⁺ monocation in DCM (left) and the simulated spectrum (right) showing the isotope distribution pattern.

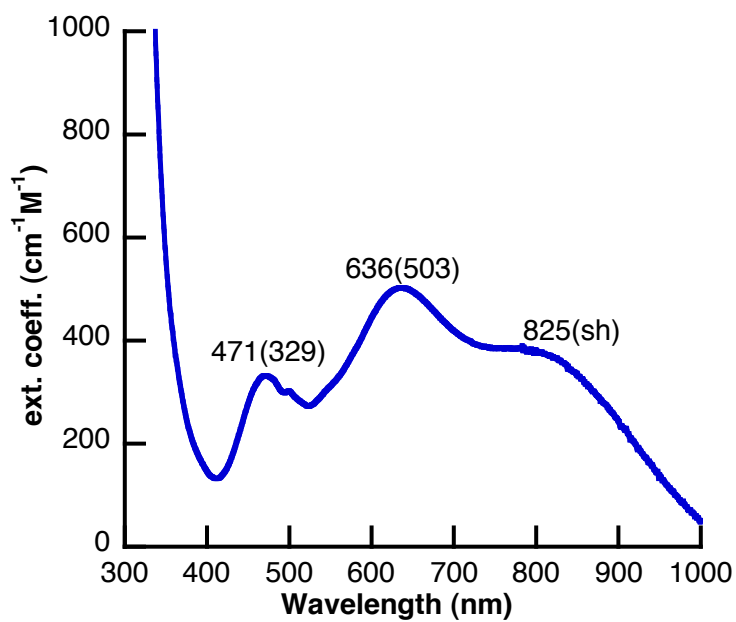


Figure S5. UV/Vis spectrum of [18-crown-6⊃Ba^{II}-(μ -OH)-Mn^{III}MST]OTf (0.43 mM) in DCM.

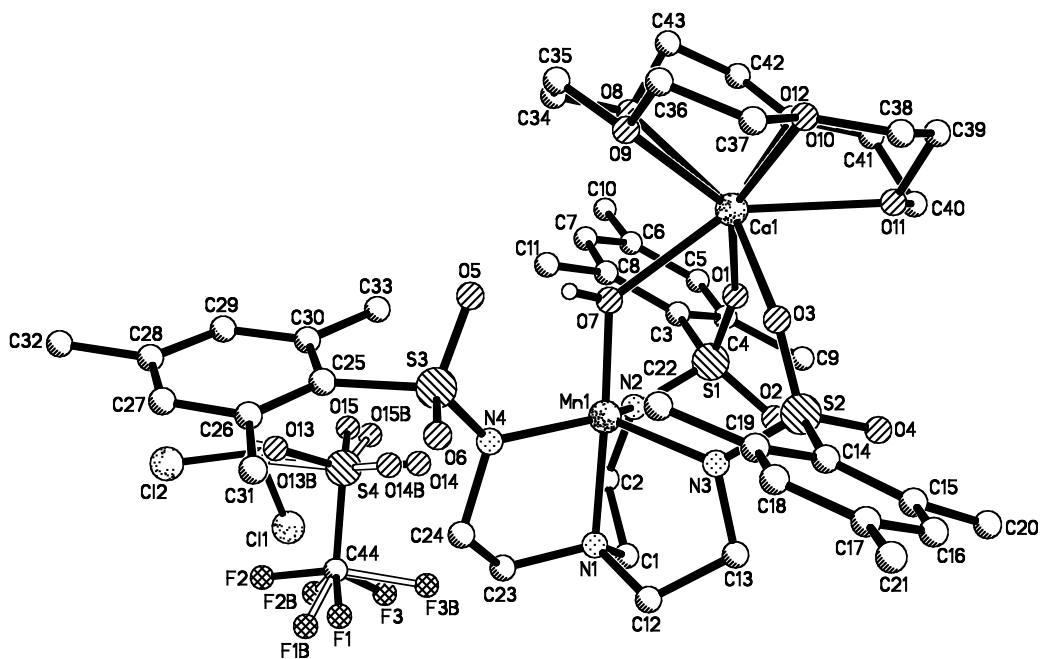


Figure S6. Numbering schemes for [15-crown-5⊃Ca^{II}-(μ -OH)-Mn^{III}MST]OTf.

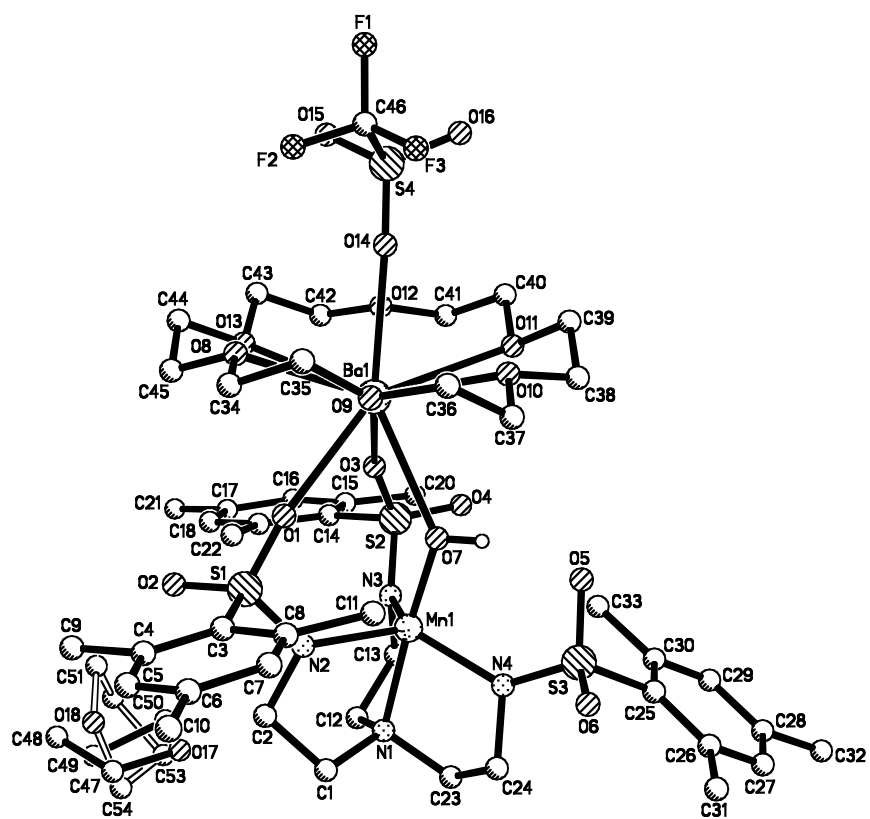


Figure S7. Numbering schemes for [18-crown-6]Ba^{II}-(μ -OH)-Mn^{III}[MST]OTf.