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SUPPORTING INFORMATION

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Title: Oxalate Oxidase Model Studies – Substrate Reactivity
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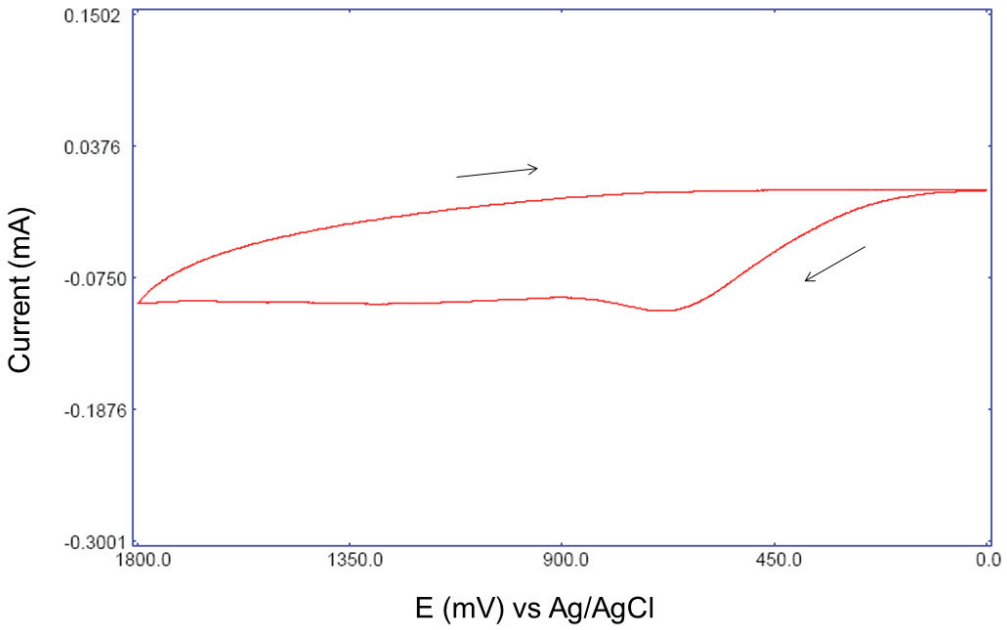


Figure S1. Cyclic voltammogram for **1** in acetonitrile in the presence of 2 equiv TBAO at 25°C. Supporting electrolyte: $TBAPF_6$, 30 mM; working electrode: Pt; reference electrode: Ag/AgCl; auxiliary electrode: Pt wire; [1]: 2×10^{-4} M; Scan Rate: 50 mV s^{-1}.

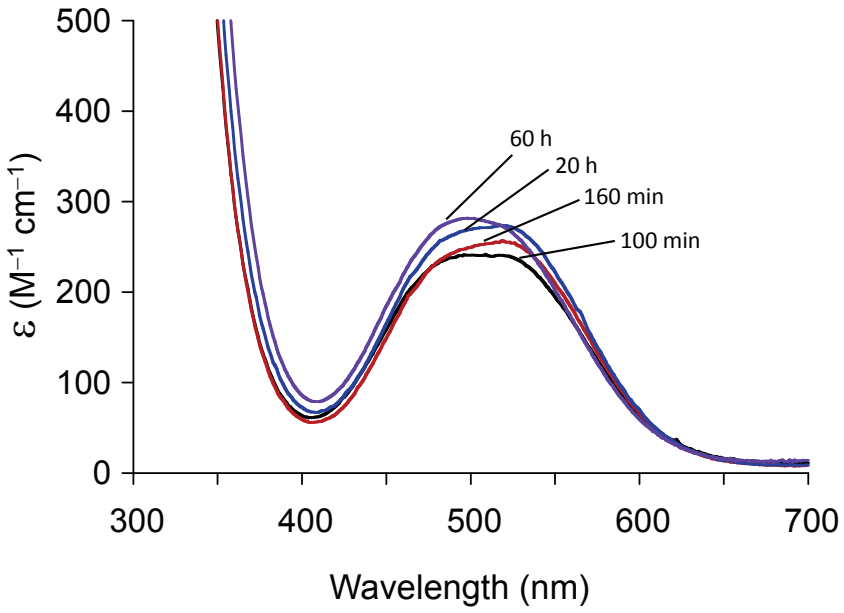


Figure S2. UV-vis spectrum for the oxygenation of **1** in acetonitrile (1.5 mM) in the presence of 20 equiv TBAO. Elapsed time indicated for each trace.

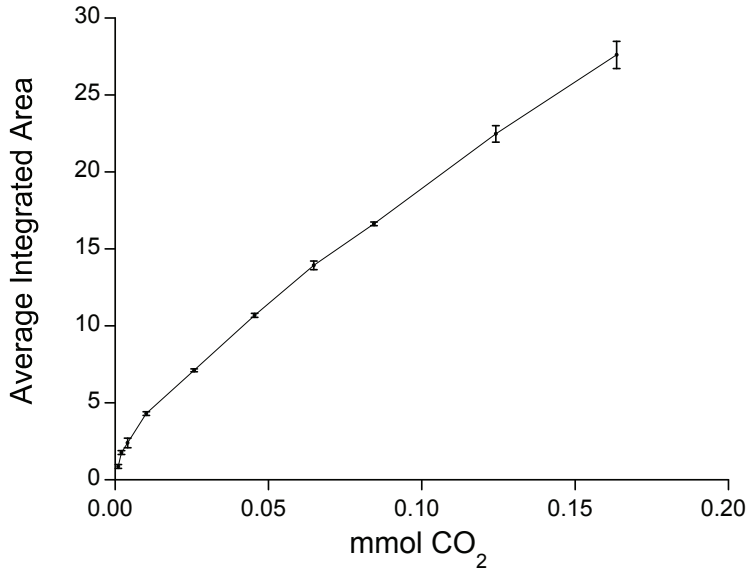
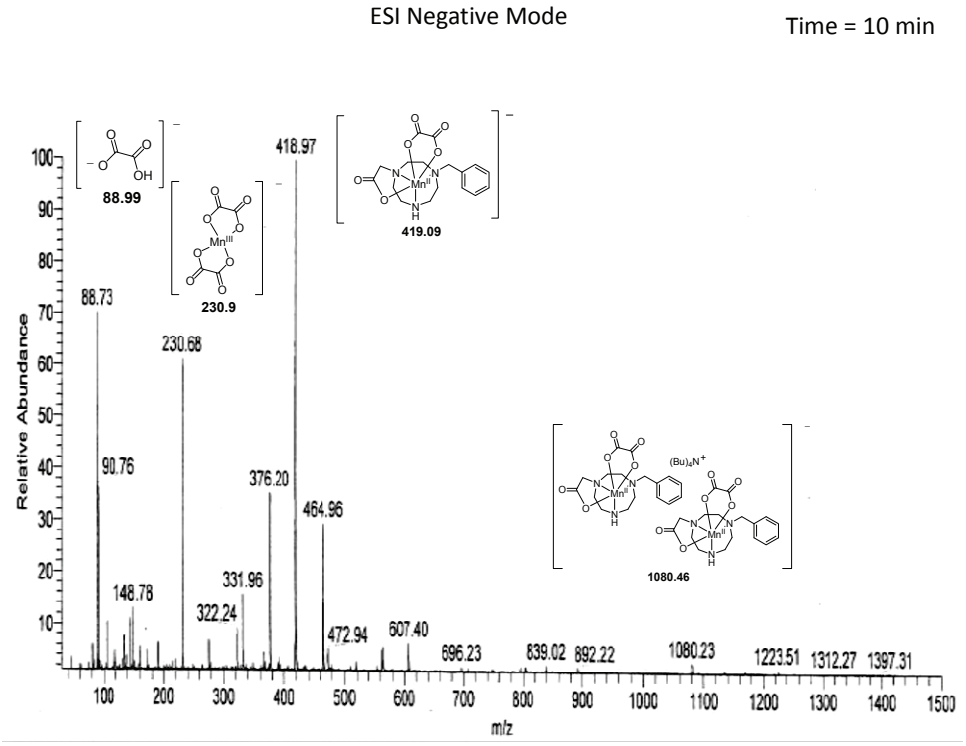


Figure S3. Standard curve for CO_2 measured by FTIR. The average integrated Area (n = 3) for ν_{CO} vs mmol CO_2 with the standard error for each measurement given.



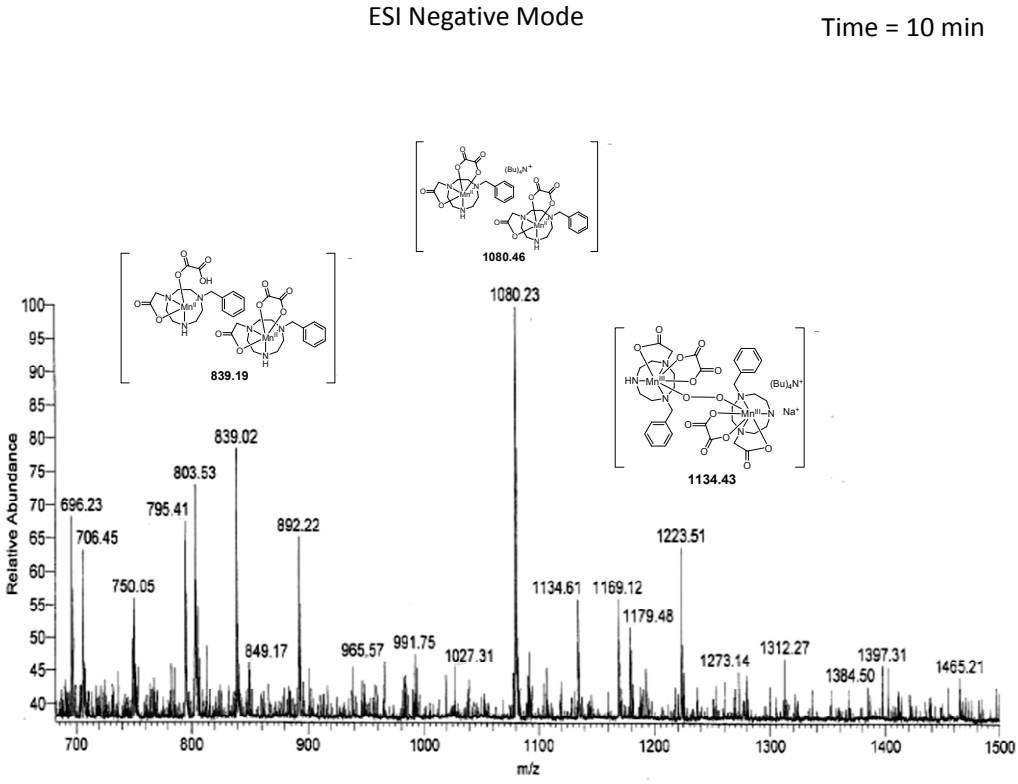


Figure S4. ESI-MS (Negative Mode) of **1** in the presence of 4 equiv TBAO in acetonitrile 10 min after oxygenation.

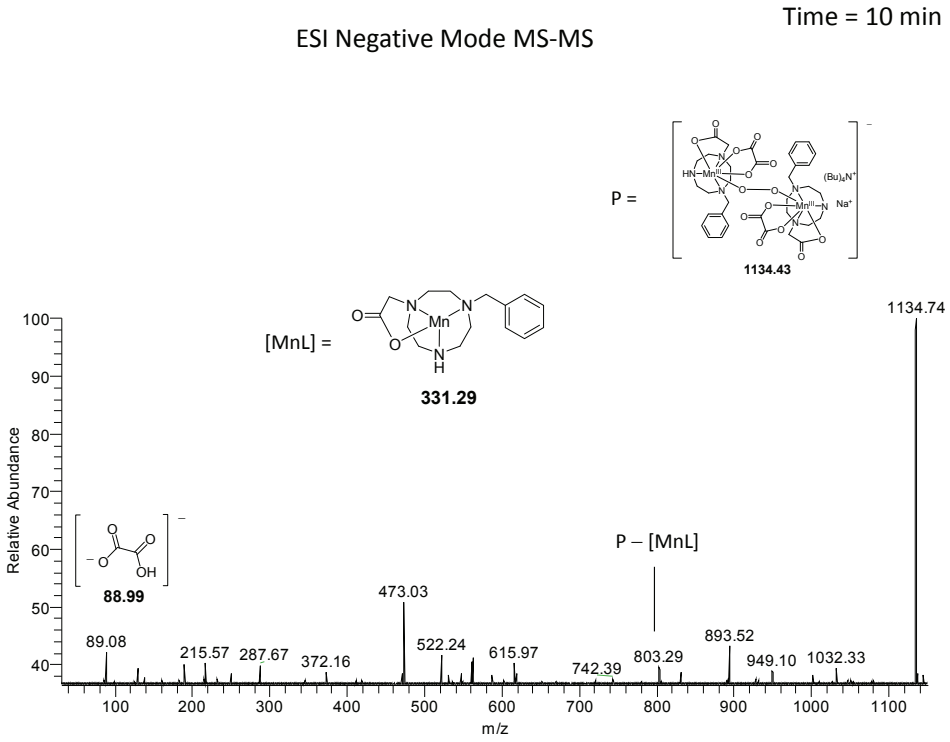


Figure S5. ESI-MS-MS spectrum (Negative Mode) of **1** in the presence of 4 equiv TBAO in acetonitrile 10 min after oxygenation.

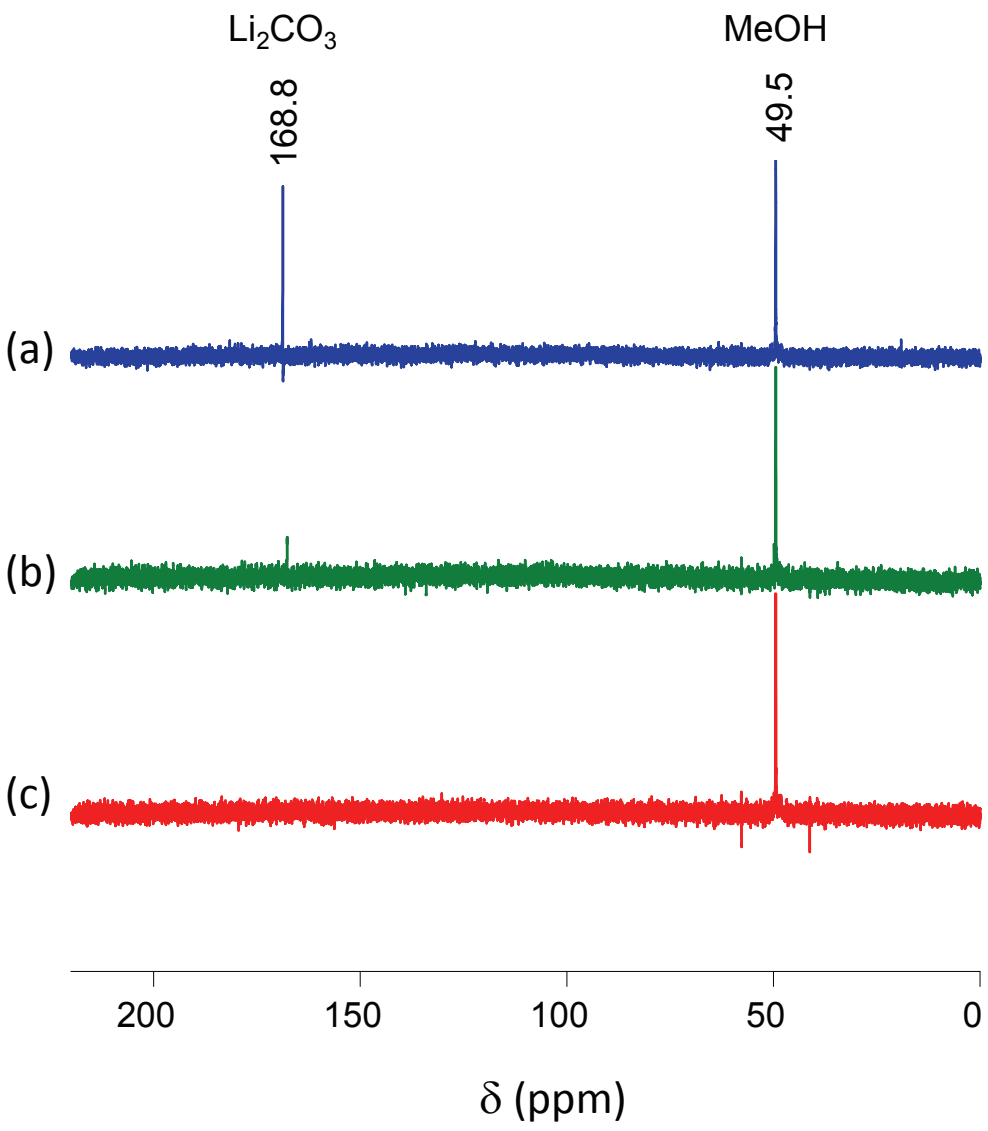


Figure S6. (a) ^{13}C NMR of authentic Li_2CO_3, (b), solid derived from LiBr induced precipitation of a reaction mixture (**1** plus 20 equiv TBAO in 10 mL acetonitrile stiring under oxygen for 3 d), and (c) sample shown in (b) plus 1 drop of conc. DCl. All samples were monitored in D_2O at 25 ºC with methanol as the internal standard.

ESI Negative Mode Time = 24 h

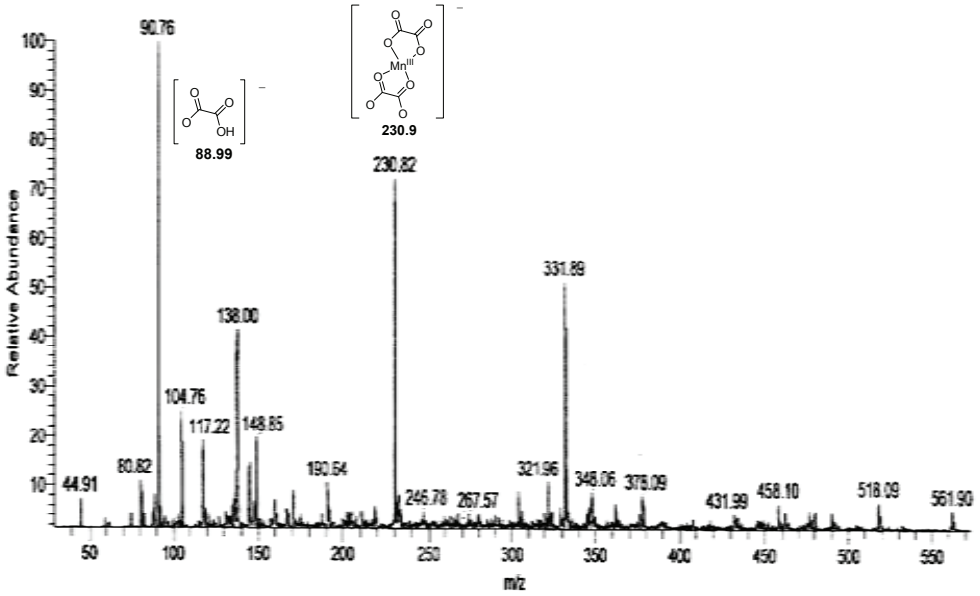


Figure S7. ESI-MS (Negative Mode) of **1** in the presence of 4 equiv TBAO in acetonitrile 24 h after oxygenation.

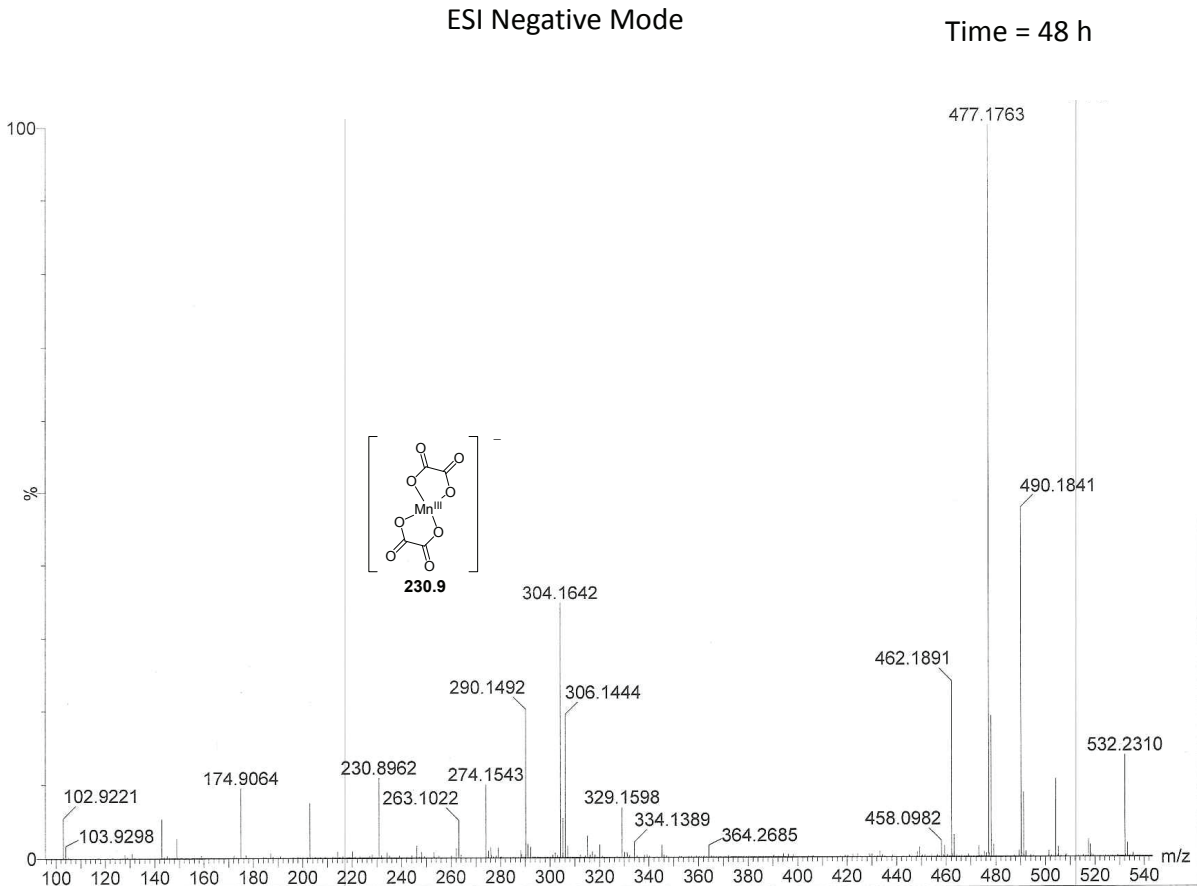


Figure S8. ESI-MS (Negative Mode) of **1** in the presence of 4 equiv TBAO in acetonitrile 48 h after oxygenation.

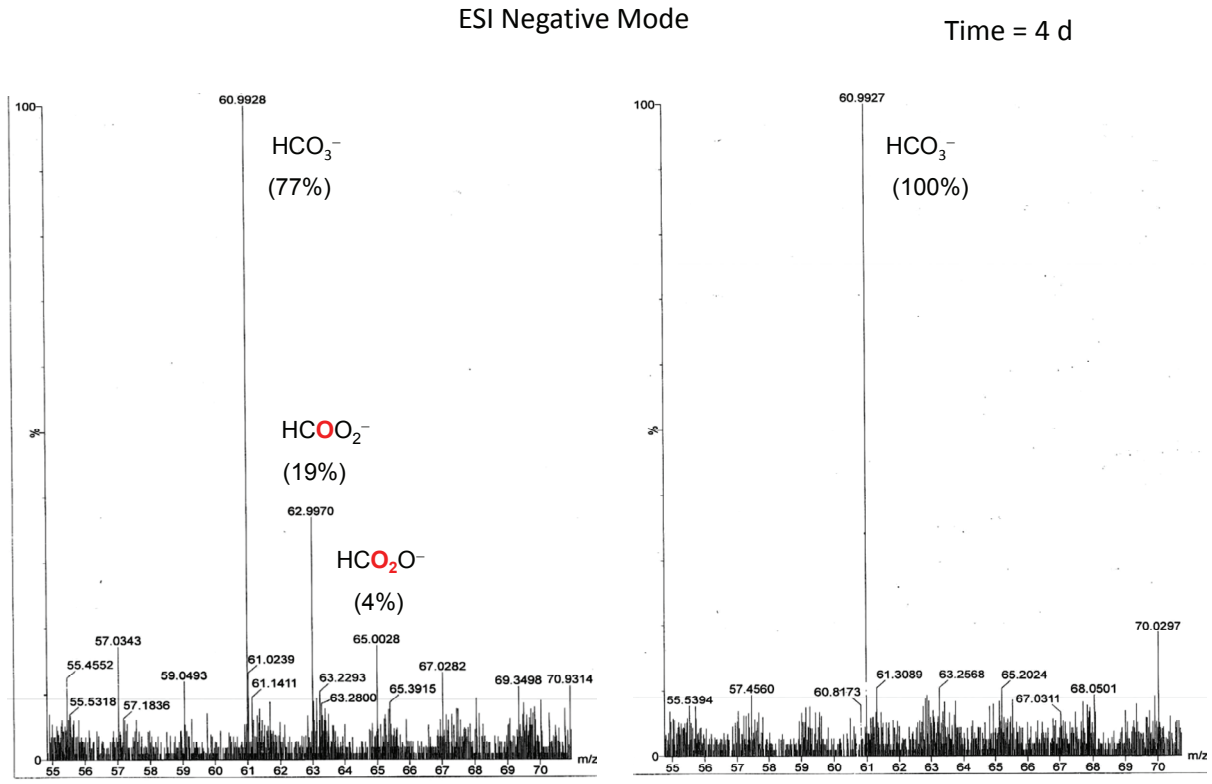


Figure S9. ESI-MS (Negative Mode) of **1** in the presence of 4 equiv TBAO in acetonitrile 4 d after oxygenation. O-16 is shown in black while O-18 is shown in bold red.

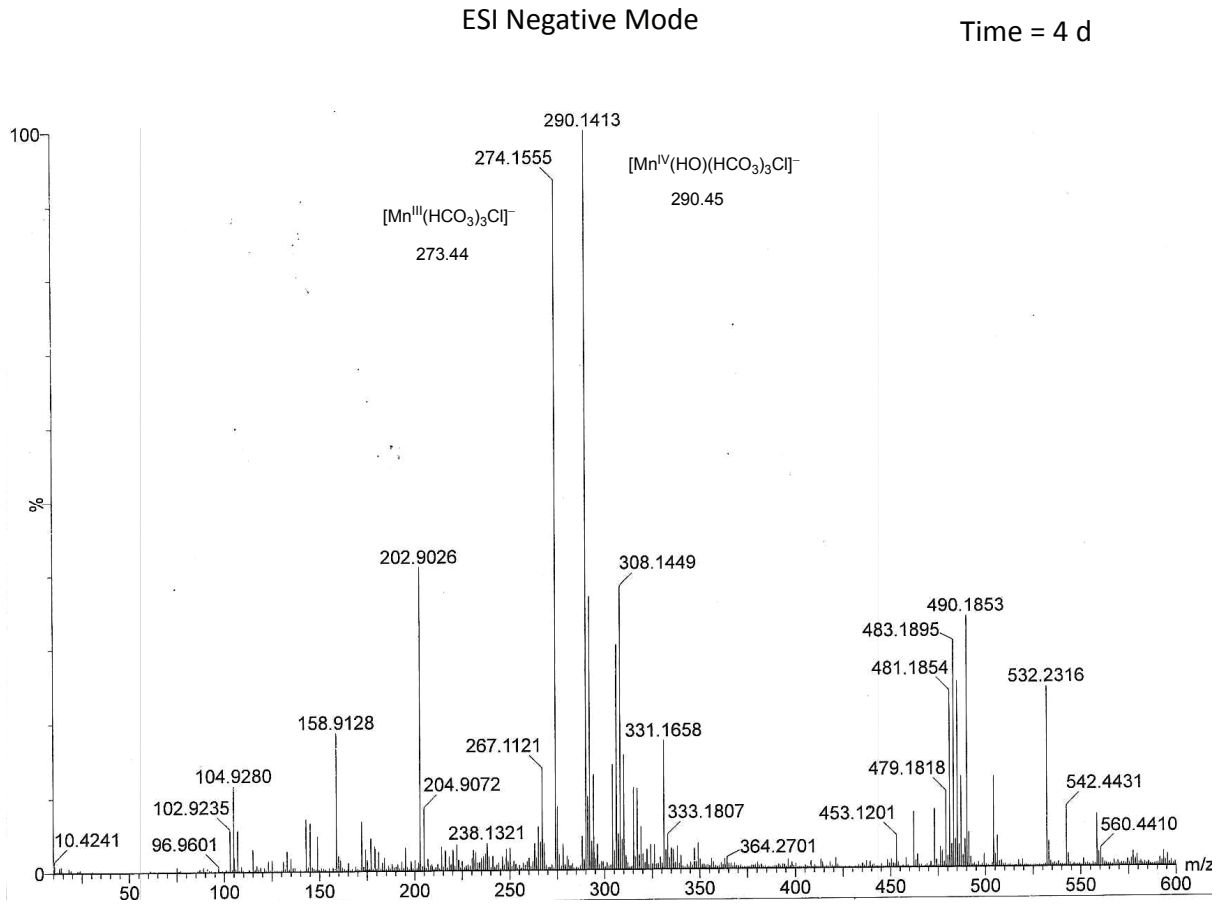


Figure S10. ESI-MS (Negative Mode) of **1** in the presence of 4 equiv TBAO in acetonitrile 4 d after oxygenation.

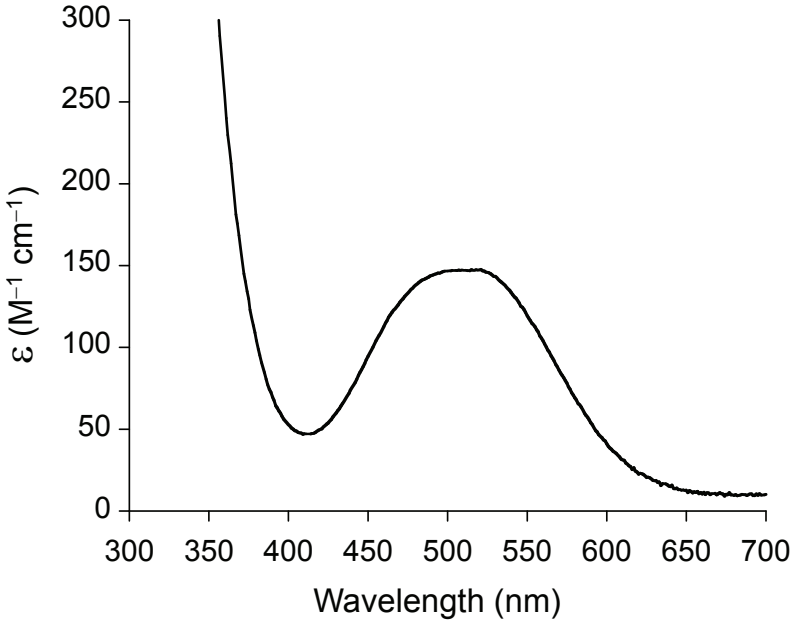


Figure S11. UV-vis spectrum for the oxygenation of $MnCl_2$ in acetonitrile (1.5 mM) in the presence of 20 equiv TBAO. Elapsed time indicated for each trace = 100 min. *Note: A pink precipitate formed during oxygenation.*

Crystallographic Data for [MnLCl]·0.5H_2O (1·0.5H_2O)

Data collection

A crystal (0.28 x 0.26 x 0.05 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 100.0(1) K.[1] A preliminary set of cell constants and an orientation matrix were calculated from 148 reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 45 seconds and a detector distance of 5.00 cm. A randomly oriented region of reciprocal space was surveyed: four major sections of frames were collected with 0.50º steps in ω at four different ϕ settings and a detector position of -33º in 2θ. The intensity data were corrected for absorption.[2] Final cell constants were calculated from the xyz centroids of 4063 strong reflections from the actual data collection after integration.[3] See Table S1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR97[4] and refined using SHELXL-97.[5] The space group $P2_12_12_1$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The structure refined as an inversion twin (53:47). The final full matrix least squares refinement converged to $R1 = 0.0646$ (F^2, $I > 2\sigma(I)$) and $wR2 = 0.1594$ (F^2, all data). *Due to the severe disorder, this report is intended for proof of connectivity; bond lengths and angles are provided for advice only.*

Structure description

The structure is the one suggested. The molecules align as one dimensional chains parallel to the *a*-axis, with all atoms in general positions. There is a co-crystallized water molecule that was given half occupancy as an approximation. The triamine ligand is modeled as disordered over two positions (58:42) and the benzyl group is modeled as disordered over three positions (39:35:26). Hydrogen bonding is observed (see Table S7).

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

[1] *APEX2*, version 2.1-0; Bruker AXS: Madison, WI, 2006.

[2] Sheldrick, G. M. *SADABS*, version 2007/2; University of Göttingen: Göttingen, Germany, 2004.

[3] *SAINT*, version 7.34A; Bruker AXS: Madison, WI, 2006.

[4] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR97: A new program for solving and refining crystal structures*; Istituto di Cristallografia, CNR: Bari, Italy, 1999.

[5] Sheldrick, G. M. *Acta. Cryst.* **2008***, A64*, 112-122.

Some equations of interest:

$$R_{int} = \Sigma|F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma|F_o^2|$$

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

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

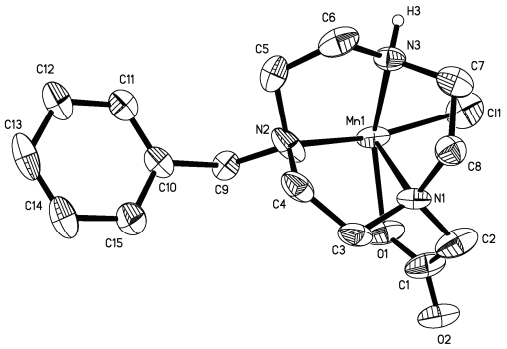
where $w = 1 \,/\, [\sigma^2(F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max(0, F_o^2) + 2/3\, F_c^2$$

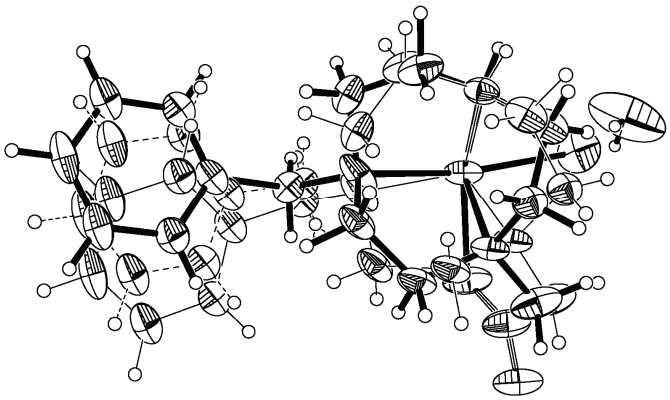
$$\text{GOF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters

(a)



(b)



(c)

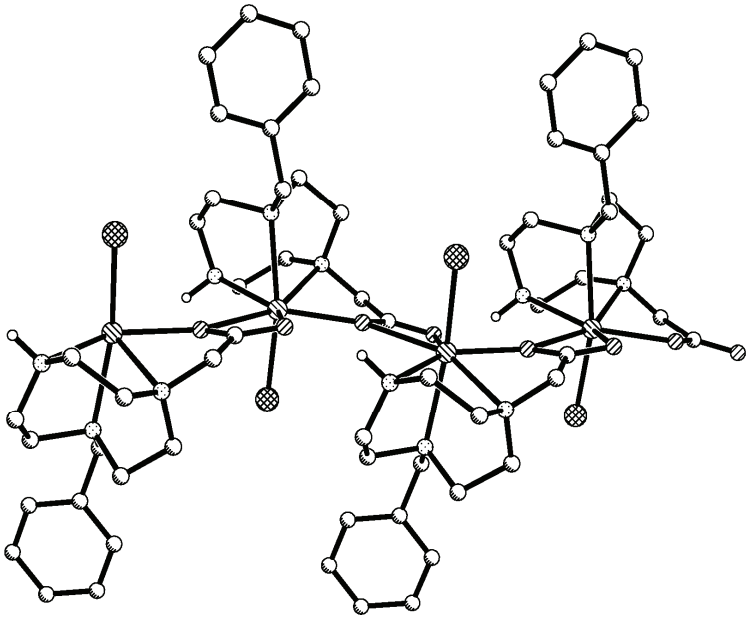


Figure S12. (a) ORTEP diagram of [MnLCl] (**1**), (b) Modeling of disorder in **1**, and (c) connectivity for the extended solid state structure of **1**. Thermal ellipsoids are shown at 50% probability and H atoms (except for H3) have been removed for clarity.

Table S1 Crystal data and structure refinement for [MnLCl]·0.5H_2O (**1**·0.5H_2O).

Identification code	oakfc01	
Empirical formula	$C_{15}H_{23}ClMnN_3O_{2.5}$	
Formula weight	375.75	
Temperature	100.0(1) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.2740(16) Å	α = 90°
	b = 10.472(2) Å	β = 90°
	c = 19.088(4) Å	γ = 90°
Volume	1654.0(6) $Å^3$	
Z	4	
Density (calculated)	1.509 Mg/m^3	
Absorption coefficient	0.973 mm^{-1}	
F(000)	784	
Crystal color, morphology	colorless, plate	
Crystal size	0.28 x 0.26 x 0.05 mm^3	
Theta range for data collection	2.13 to 30.51°	
Index ranges	$-11 \le h \le 11, -14 \le k \le 14, -27 \le l \le 27$	
Reflections collected	26950	
Independent reflections	5031 [R(int) = 0.0556]	
Observed reflections	3907	
Completeness to theta = 30.51°	100.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9529 and 0.7722	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5031 / 76 / 242	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	$R1$ = 0.0646, $wR2$ = 0.1459	
R indices (all data)	$R1$ = 0.0877, $wR2$ = 0.1594	
Absolute structure parameter	0.47(4)	
Largest diff. peak and hole	0.976 and -0.606 e.$Å^{-3}$	

Table S2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) For [MnLCl]·0.5H_2O (**1**·0.5H_2O). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Mn1	9695(1)	1854(1)	4640(1)	34(1)
Cl1	9763(2)	3572(1)	3740(1)	58(1)
O1	7085(4)	2165(3)	4807(2)	52(1)
O2	4668(4)	2054(3)	4348(2)	50(1)
C1	6129(5)	1772(5)	4336(3)	50(1)
C2	6800(30)	860(30)	3794(10)	53(3)
N1	8196(16)	192(14)	4054(7)	34(2)
C3	7752(12)	-783(12)	4601(7)	39(2)
C4	9204(13)	-1319(10)	5003(6)	40(2)
N2	10102(16)	-140(7)	5259(6)	46(2)
C5	11890(14)	-493(10)	5166(5)	37(1)
C6	12265(16)	-450(10)	4396(6)	43(2)
N3	11607(4)	695(3)	4074(2)	32(1)
C7	10735(13)	455(11)	3399(6)	40(2)
C8	9236(12)	-310(11)	3493(6)	36(2)
C1'	6129(5)	1772(5)	4336(3)	50(1)
C2'	6810(20)	1090(20)	3697(7)	53(3)
N1'	8296(11)	446(10)	3870(5)	34(2)
C3'	7977(10)	-771(8)	4247(5)	39(2)
C4'	8124(10)	-668(8)	5051(4)	40(2)
N2'	9690(11)	-146(6)	5269(4)	46(2)
C5'	11105(10)	-841(7)	5019(4)	37(1)
C6'	12330(10)	-57(7)	4650(5)	43(2)
N3'	11607(4)	695(3)	4074(2)	32(1)
C7'	11066(10)	-99(8)	3482(5)	40(2)
C8'	9383(9)	277(8)	3264(4)	36(2)
C9	9910(19)	-131(10)	6048(5)	28(2)
C10	10411(9)	-1215(6)	6542(4)	33(2)
C11	11980(8)	-1257(6)	6802(4)	35(2)
C12	12429(8)	-2216(7)	7266(4)	43(2)

C13	11310(10)	-3134(6)	7470(3)	48(3)
C14	9742(9)	-3091(6)	7211(4)	45(2)
C15	9292(8)	-2132(7)	6747(4)	41(2)
C9'	9500(20)	261(11)	6023(7)	28(2)
C10'	9223(11)	-866(7)	6519(4)	33(2)
C11'	7655(9)	-1226(8)	6689(4)	35(2)
C12'	7391(10)	-2255(8)	7135(5)	43(2)
C13'	8695(13)	-2924(7)	7410(4)	48(3)
C14'	10264(11)	-2564(8)	7239(5)	45(2)
C15'	10528(9)	-1535(8)	6794(5)	41(2)
C9"	9910(30)	284(14)	6007(5)	28(2)
C10"	9961(11)	-829(6)	6511(4)	33(2)
C11"	8526(12)	-1444(8)	6682(5)	35(2)
C12"	8549(13)	-2501(9)	7123(5)	43(2)
C13"	10006(14)	-2942(7)	7392(4)	48(3)
C14"	11441(13)	-2326(9)	7221(6)	45(2)
C15"	11419(12)	-1270(9)	6781(6)	41(2)
O3	10202(17)	6460(7)	3712(6)	146(6)

Table S3 Bond lengths [Å] and angles [°] for [MnLCl]·0.5H_2O (**1**·0.5H_2O).

Mn(1)-O(1)	2.207(3)	C(6)-H(6B)	0.9900
Mn(1)-O(2)#1	2.245(3)	N(3)-C(7)	1.497(11)
Mn(1)-N(3)	2.268(3)	N(3)-H(3)	0.9300
Mn(1)-N(1')	2.382(12)	C(7)-C(8)	1.487(13)
Mn(1)-N(1)	2.412(18)	C(7)-H(7A)	0.9900
Mn(1)-N(2')	2.415(5)	C(7)-H(7B)	0.9900
Mn(1)-N(2)	2.423(5)	C(8)-H(8A)	0.9900
Mn(1)-O(1)#1	2.466(3)	C(8)-H(8B)	0.9900
Mn(1)-Cl(1)	2.4885(15)	C(2')-N(1')	1.443(10)
O(1)-C(1)	1.266(6)	C(2')-H(2C)	0.9900
O(1)-Mn(1)#2	2.466(3)	C(2')-H(2D)	0.9900
O(2)-C(1)	1.245(6)	N(1')-C(8')	1.475(9)
O(2)-Mn(1)#2	2.245(3)	N(1')-C(3')	1.488(10)
C(1)-C(2)	1.517(14)	C(3')-C(4')	1.542(10)
C(2)-N(1)	1.437(13)	C(3')-H(3C)	0.9900
C(2)-H(2A)	0.9900	C(3')-H(3D)	0.9900
C(2)-H(2B)	0.9900	C(4')-N(2')	1.467(10)
N(1)-C(8)	1.470(13)	C(4')-H(4C)	0.9900
N(1)-C(3)	1.506(13)	C(4')-H(4D)	0.9900
C(3)-C(4)	1.531(14)	N(2')-C(5')	1.459(10)
C(3)-H(3A)	0.9900	N(2')-C(9')	1.509(8)
C(3)-H(3B)	0.9900	C(5')-C(6')	1.482(10)
C(4)-N(2)	1.521(12)	C(5')-H(5C)	0.9900
C(4)-H(4A)	0.9900	C(5')-H(5D)	0.9900
C(4)-H(4B)	0.9900	C(6')-H(6C)	0.9900
N(2)-C(9")	1.504(9)	C(6')-H(6D)	0.9900
N(2)-C(9)	1.514(9)	C(7')-C(8')	1.506(10)
N(2)-C(5)	1.535(14)	C(7')-H(7C)	0.9900
C(5)-C(6)	1.502(13)	C(7')-H(7D)	0.9900
C(5)-H(5A)	0.9900	C(8')-H(8C)	0.9900
C(5)-H(5B)	0.9900	C(8')-H(8D)	0.9900
C(6)-N(3)	1.453(11)	C(9)-C(10)	1.534(10)
C(6)-H(6A)	0.9900	C(9)-H(9A)	0.9900

C(9)-H(9B)	0.9900	C(13")-C(14")	1.3900
C(10)-C(11)	1.3900	C(13")-H(13")	0.9500
C(10)-C(15)	1.3900	C(14")-C(15")	1.3900
C(11)-C(12)	1.3900	C(14")-H(14")	0.9500
C(11)-H(11)	0.9500	C(15")-H(15")	0.9500
C(12)-C(13)	1.3900	O(3)-H(3E)	0.8501
C(12)-H(12)	0.9500	O(3)-H(3F)	0.8501
C(13)-C(14)	1.3900	O(1)-Mn(1)-O(2)#1	77.90(12)
C(13)-H(13)	0.9500	O(1)-Mn(1)-N(3)	146.13(13)
C(14)-C(15)	1.3900	O(2)#1-Mn(1)-N(3)	133.61(13)
C(14)-H(14)	0.9500	O(1)-Mn(1)-N(1')	72.9(2)
C(15)-H(15)	0.9500	O(2)#1-Mn(1)-N(1')	147.3(2)
C(9')-C(10')	1.530(10)	N(3)-Mn(1)-N(1')	73.3(2)
C(9')-H(9C)	0.9900	O(1)-Mn(1)-N(1)	70.8(3)
C(9')-H(9D)	0.9900	O(2)#1-Mn(1)-N(1)	139.6(3)
C(10')-C(11')	1.3900	N(3)-Mn(1)-N(1)	75.6(3)
C(10')-C(15')	1.3900	N(1')-Mn(1)-N(1)	10.7(4)
C(11')-C(12')	1.3900	O(1)-Mn(1)-N(2')	93.1(2)
C(11')-H(11')	0.9500	O(2)#1-Mn(1)-N(2')	90.8(2)
C(12')-C(13')	1.3900	N(3)-Mn(1)-N(2')	76.9(2)
C(12')-H(12')	0.9500	N(1')-Mn(1)-N(2')	76.7(3)
C(13')-C(14')	1.3900	N(1)-Mn(1)-N(2')	66.7(4)
C(13')-H(13')	0.9500	O(1)-Mn(1)-N(2)	101.1(3)
C(14')-C(15')	1.3900	O(2)#1-Mn(1)-N(2)	91.2(3)
C(14')-H(14')	0.9500	N(3)-Mn(1)-N(2)	71.0(3)
C(15')-H(15')	0.9500	N(1')-Mn(1)-N(2)	80.5(4)
C(9")-C(10")	1.512(12)	N(1)-Mn(1)-N(2)	71.1(4)
C(9")-H(9E)	0.9900	N(2')-Mn(1)-N(2)	8.1(4)
C(9")-H(9F)	0.9900	O(1)-Mn(1)-O(1)#1	131.40(4)
C(10")-C(11")	1.3900	O(2)#1-Mn(1)-O(1)#1	55.08(12)
C(10")-C(15")	1.3900	N(3)-Mn(1)-O(1)#1	82.40(12)
C(11")-C(12")	1.3900	N(1')-Mn(1)-O(1)#1	155.7(2)
C(11")-H(11")	0.9500	N(1)-Mn(1)-O(1)#1	155.7(3)
C(12")-C(13")	1.3900	N(2')-Mn(1)-O(1)#1	98.6(2)
C(12")-H(12")	0.9500	N(2)-Mn(1)-O(1)#1	92.2(3)

O(1)-Mn(1)-Cl(1)	90.90(12)	C(3)-C(4)-H(4A)	110.9
O(2)#1-Mn(1)-Cl(1)	103.08(11)	N(2)-C(4)-H(4B)	110.9
N(3)-Mn(1)-Cl(1)	92.40(10)	C(3)-C(4)-H(4B)	110.9
N(1')-Mn(1)-Cl(1)	91.84(19)	H(4A)-C(4)-H(4B)	108.9
N(1)-Mn(1)-Cl(1)	102.3(3)	C(9")-N(2)-C(4)	119.6(11)
N(2')-Mn(1)-Cl(1)	166.1(2)	C(9)-N(2)-C(4)	105.9(8)
N(2)-Mn(1)-Cl(1)	163.1(3)	C(9")-N(2)-C(5)	106.3(11)
O(1)#1-Mn(1)-Cl(1)	88.63(11)	C(9)-N(2)-C(5)	102.6(10)
C(1)-O(1)-Mn(1)	117.4(3)	C(4)-N(2)-C(5)	103.8(9)
C(1)-O(1)-Mn(1)#2	86.4(3)	C(9")-N(2)-Mn(1)	101.2(6)
Mn(1)-O(1)-Mn(1)#2	155.24(15)	C(9)-N(2)-Mn(1)	117.7(6)
C(1)-O(2)-Mn(1)#2	97.3(3)	C(4)-N(2)-Mn(1)	118.4(7)
O(2)-C(1)-O(1)	121.1(4)	C(5)-N(2)-Mn(1)	106.6(6)
O(2)-C(1)-C(2)	121.2(11)	C(6)-C(5)-N(2)	107.7(9)
O(1)-C(1)-C(2)	117.5(11)	C(6)-C(5)-H(5A)	110.2
N(1)-C(2)-C(1)	111.4(13)	N(2)-C(5)-H(5A)	110.2
N(1)-C(2)-H(2A)	109.4	C(6)-C(5)-H(5B)	110.2
C(1)-C(2)-H(2A)	109.4	N(2)-C(5)-H(5B)	110.2
N(1)-C(2)-H(2B)	109.4	H(5A)-C(5)-H(5B)	108.5
C(1)-C(2)-H(2B)	109.4	N(3)-C(6)-C(5)	111.2(8)
H(2A)-C(2)-H(2B)	108.0	N(3)-C(6)-H(6A)	109.4
C(2)-N(1)-C(8)	113.1(12)	C(5)-C(6)-H(6A)	109.4
C(2)-N(1)-C(3)	111.8(16)	N(3)-C(6)-H(6B)	109.4
C(8)-N(1)-C(3)	113.9(11)	C(5)-C(6)-H(6B)	109.4
C(2)-N(1)-Mn(1)	102.9(16)	H(6A)-C(6)-H(6B)	108.0
C(8)-N(1)-Mn(1)	107.1(8)	C(6)-N(3)-C(7)	114.0(7)
C(3)-N(1)-Mn(1)	107.0(9)	C(6)-N(3)-Mn(1)	120.1(5)
N(1)-C(3)-C(4)	113.8(9)	C(7)-N(3)-Mn(1)	99.4(5)
N(1)-C(3)-H(3A)	108.8	C(6)-N(3)-H(3)	107.5
C(4)-C(3)-H(3A)	108.8	C(7)-N(3)-H(3)	107.5
N(1)-C(3)-H(3B)	108.8	Mn(1)-N(3)-H(3)	107.5
C(4)-C(3)-H(3B)	108.8	C(8)-C(7)-N(3)	112.8(9)
H(3A)-C(3)-H(3B)	107.7	C(8)-C(7)-H(7A)	109.0
N(2)-C(4)-C(3)	104.3(9)	N(3)-C(7)-H(7A)	109.0
N(2)-C(4)-H(4A)	110.9	C(8)-C(7)-H(7B)	109.0

N(3)-C(7)-H(7B)	109.0	N(2')-C(5')-C(6')	115.4(6)
H(7A)-C(7)-H(7B)	107.8	N(2')-C(5')-H(5C)	108.4
N(1)-C(8)-C(7)	112.5(10)	C(6')-C(5')-H(5C)	108.4
N(1)-C(8)-H(8A)	109.1	N(2')-C(5')-H(5D)	108.4
C(7)-C(8)-H(8A)	109.1	C(6')-C(5')-H(5D)	108.4
N(1)-C(8)-H(8B)	109.1	H(5C)-C(5')-H(5D)	107.5
C(7)-C(8)-H(8B)	109.1	C(5')-C(6')-H(6C)	109.3
H(8A)-C(8)-H(8B)	107.8	C(5')-C(6')-H(6D)	109.3
N(1')-C(2')-H(2C)	109.5	H(6C)-C(6')-H(6D)	107.9
N(1')-C(2')-H(2D)	109.5	C(8')-C(7')-H(7C)	109.6
H(2C)-C(2')-H(2D)	108.1	C(8')-C(7')-H(7D)	109.6
C(2')-N(1')-C(8')	113.5(9)	H(7C)-C(7')-H(7D)	108.1
C(2')-N(1')-C(3')	111.0(12)	N(1')-C(8')-C(7')	112.3(7)
C(8')-N(1')-C(3')	112.6(8)	N(1')-C(8')-H(8C)	109.1
C(2')-N(1')-Mn(1)	105.5(10)	C(7')-C(8')-H(8C)	109.1
C(8')-N(1')-Mn(1)	105.2(6)	N(1')-C(8')-H(8D)	109.1
C(3')-N(1')-Mn(1)	108.5(6)	C(7')-C(8')-H(8D)	109.1
N(1')-C(3')-C(4')	114.1(7)	H(8C)-C(8')-H(8D)	107.9
N(1')-C(3')-H(3C)	108.7	N(2)-C(9)-C(10)	125.4(8)
C(4')-C(3')-H(3C)	108.7	N(2)-C(9)-H(9A)	106.0
N(1')-C(3')-H(3D)	108.7	C(10)-C(9)-H(9A)	106.0
C(4')-C(3')-H(3D)	108.7	N(2)-C(9)-H(9B)	106.0
H(3C)-C(3')-H(3D)	107.6	C(10)-C(9)-H(9B)	106.0
N(2')-C(4')-C(3')	112.2(6)	H(9A)-C(9)-H(9B)	106.3
N(2')-C(4')-H(4C)	109.2	C(11)-C(10)-C(15)	120.0
C(3')-C(4')-H(4C)	109.2	C(11)-C(10)-C(9)	119.7(7)
N(2')-C(4')-H(4D)	109.2	C(15)-C(10)-C(9)	120.3(7)
C(3')-C(4')-H(4D)	109.2	C(12)-C(11)-C(10)	120.0
H(4C)-C(4')-H(4D)	107.9	C(12)-C(11)-H(11)	120.0
C(5')-N(2')-C(4')	115.5(7)	C(10)-C(11)-H(11)	120.0
C(5')-N(2')-C(9')	122.4(9)	C(11)-C(12)-C(13)	120.0
C(4')-N(2')-C(9')	106.6(10)	C(11)-C(12)-H(12)	120.0
C(5')-N(2')-Mn(1)	105.6(4)	C(13)-C(12)-H(12)	120.0
C(4')-N(2')-Mn(1)	100.6(5)	C(12)-C(13)-C(14)	120.0
C(9')-N(2')-Mn(1)	103.3(5)	C(12)-C(13)-H(13)	120.0

C(14)-C(13)-H(13)	120.0	C(14')-C(15')-C(10')	120.0
C(15)-C(14)-C(13)	120.0	C(14')-C(15')-H(15')	120.0
C(15)-C(14)-H(14)	120.0	C(10')-C(15')-H(15')	120.0
C(13)-C(14)-H(14)	120.0	N(2)-C(9")-C(10")	111.9(9)
C(14)-C(15)-C(10)	120.0	N(2)-C(9")-H(9E)	109.2
C(14)-C(15)-H(15)	120.0	C(10")-C(9")-H(9E)	109.2
C(10)-C(15)-H(15)	120.0	N(2)-C(9")-H(9F)	109.2
N(2')-C(9')-C(10')	112.8(8)	C(10")-C(9")-H(9F)	109.2
N(2')-C(9')-H(9C)	109.0	H(9E)-C(9")-H(9F)	107.9
C(10')-C(9')-H(9C)	109.0	C(11")-C(10")-C(15")	120.0
N(2')-C(9')-H(9D)	109.0	C(11")-C(10")-C(9")	119.0(9)
C(10')-C(9')-H(9D)	109.0	C(15")-C(10")-C(9")	120.9(9)
H(9C)-C(9')-H(9D)	107.8	C(10")-C(11")-C(12")	120.0
C(11')-C(10')-C(15')	120.0	C(10")-C(11")-H(11")	120.0
C(11')-C(10')-C(9')	119.7(8)	C(12")-C(11")-H(11")	120.0
C(15')-C(10')-C(9')	120.3(8)	C(13")-C(12")-C(11")	120.0
C(12')-C(11')-C(10')	120.0	C(13")-C(12")-H(12")	120.0
C(12')-C(11')-H(11')	120.0	C(11")-C(12")-H(12")	120.0
C(10')-C(11')-H(11')	120.0	C(14")-C(13")-C(12")	120.0
C(11')-C(12')-C(13')	120.0	C(14")-C(13")-H(13")	120.0
C(11')-C(12')-H(12')	120.0	C(12")-C(13")-H(13")	120.0
C(13')-C(12')-H(12')	120.0	C(13")-C(14")-C(15")	120.0
C(14')-C(13')-C(12')	120.0	C(13")-C(14")-H(14")	120.0
C(14')-C(13')-H(13')	120.0	C(15")-C(14")-H(14")	120.0
C(12')-C(13')-H(13')	120.0	C(14")-C(15")-C(10")	120.0
C(15')-C(14')-C(13')	120.0	C(14")-C(15")-H(15")	120.0
C(15')-C(14')-H(14')	120.0	C(10")-C(15")-H(15")	120.0
C(13')-C(14')-H(14')	120.0	H(3E)-O(3)-H(3F)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,-z+1 #2 x-1/2,-y+1/2,-z+1

Table S4 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for [MnLCl]·0.5H_2O (**1**·0.5H_2O). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	22(1)	27(1)	53(1)	-16(1)	4(1)	-2(1)
Cl1	68(1)	23(1)	85(1)	0(1)	-6(1)	12(1)
O1	28(2)	51(2)	78(3)	-35(2)	2(2)	0(1)
O2	26(1)	41(2)	81(2)	-34(2)	5(2)	-2(2)
C1	31(2)	40(2)	77(3)	-28(3)	-3(2)	-8(2)
C2	30(2)	54(8)	74(5)	-37(5)	-5(3)	12(4)
N1	20(2)	34(5)	50(6)	-3(3)	8(3)	-2(3)
C3	29(3)	42(3)	45(5)	-5(4)	7(4)	-15(2)
C4	48(4)	40(4)	32(3)	-5(3)	9(3)	-23(3)
N2	67(5)	39(2)	31(2)	-11(2)	13(3)	-41(3)
C5	48(4)	22(3)	40(4)	-2(3)	-13(3)	4(3)
C6	31(2)	24(4)	73(6)	-9(4)	-5(4)	8(3)
N3	25(2)	24(2)	46(2)	0(2)	6(1)	2(1)
C7	42(4)	31(4)	49(4)	-12(4)	15(3)	7(3)
C8	35(3)	38(4)	36(4)	-6(3)	3(3)	3(3)
C1'	31(2)	40(2)	77(3)	-28(3)	-3(2)	-8(2)
C2'	30(2)	54(8)	74(5)	-37(5)	-5(3)	12(4)
N1'	20(2)	34(5)	50(6)	-3(3)	8(3)	-2(3)
C3'	29(3)	42(3)	45(5)	-5(4)	7(4)	-15(2)
C4'	48(4)	40(4)	32(3)	-5(3)	9(3)	-23(3)
N2'	67(5)	39(2)	31(2)	-11(2)	13(3)	-41(3)
C5'	48(4)	22(3)	40(4)	-2(3)	-13(3)	4(3)
C6'	31(2)	24(4)	73(6)	-9(4)	-5(4)	8(3)
N3'	25(2)	24(2)	46(2)	0(2)	6(1)	2(1)
C7'	42(4)	31(4)	49(4)	-12(4)	15(3)	7(3)
C8'	35(3)	38(4)	36(4)	-6(3)	3(3)	3(3)
C9	37(6)	11(4)	37(2)	-7(3)	-3(3)	4(4)
C10	46(5)	21(3)	32(3)	-6(3)	9(5)	-6(4)
C11	45(4)	30(3)	30(3)	-7(3)	4(4)	-5(4)
C12	66(6)	33(3)	28(4)	-3(3)	3(4)	-17(4)

C13	94(8)	25(3)	24(3)	1(2)	11(4)	-2(5)
C14	76(7)	32(5)	28(3)	1(4)	9(5)	-3(5)
C15	46(5)	41(5)	37(4)	1(4)	2(4)	-2(3)
C9'	37(6)	11(4)	37(2)	-7(3)	-3(3)	4(4)
C10'	46(5)	21(3)	32(3)	-6(3)	9(5)	-6(4)
C11'	45(4)	30(3)	30(3)	-7(3)	4(4)	-5(4)
C12'	66(6)	33(3)	28(4)	-3(3)	3(4)	-17(4)
C13'	94(8)	25(3)	24(3)	1(2)	11(4)	-2(5)
C14'	76(7)	32(5)	28(3)	1(4)	9(5)	-3(5)
C15'	46(5)	41(5)	37(4)	1(4)	2(4)	-2(3)
C9"	37(6)	11(4)	37(2)	-7(3)	-3(3)	4(4)
C10"	46(5)	21(3)	32(3)	-6(3)	9(5)	-6(4)
C11"	45(4)	30(3)	30(3)	-7(3)	4(4)	-5(4)
C12"	66(6)	33(3)	28(4)	-3(3)	3(4)	-17(4)
C13"	94(8)	25(3)	24(3)	1(2)	11(4)	-2(5)
C14"	76(7)	32(5)	28(3)	1(4)	9(5)	-3(5)
C15"	46(5)	41(5)	37(4)	1(4)	2(4)	-2(3)
O3	132(11)	52(5)	254(17)	-43(8)	87(12)	-29(7)

Table S5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for [MnLCl]·0.5H_2O (**1**·0.5H_2O).

	x	y	z	U(eq)
H2A	5957	229	3664	63
H2B	7099	1339	3367	63
H3A	7177	-1498	4371	46
H3B	6996	-387	4939	46
H4A	8845	-1852	5402	48
H4B	9898	-1840	4692	48
H5A	12583	120	5422	44
H5B	12096	-1360	5353	44
H6A	13451	-468	4328	51
H6B	11802	-1213	4165	51
H3	12468	1238	3977	38
H7A	10452	1284	3182	48
H7B	11467	-1	3074	48
H8A	8623	-316	3048	44
H8B	9534	-1203	3604	44
H2C	6008	459	3524	63
H2D	7004	1717	3319	63
H3C	8747	-1425	4078	46
H3D	6873	-1066	4129	46
H4C	7249	-113	5231	48
H4D	7983	-1526	5260	48
H5C	10737	-1523	4697	44
H5D	11630	-1260	5424	44
H6C	12847	530	4989	51
H6D	13180	-623	4458	51
H3'	12388	1257	3908	38
H7C	11080	-1010	3620	48
H7D	11815	13	3082	48
H8C	9432	1084	2996	44

H8D	8935	-391	2952	44
H9A	8748	22	6138	34
H9B	10486	640	6215	34
H11	12744	-630	6662	42
H12	13501	-2245	7443	51
H13	11618	-3789	7787	57
H14	8977	-3718	7350	54
H15	8220	-2103	6569	49
H9C	8581	859	6061	34
H9D	10490	724	6171	34
H11'	6763	-768	6501	42
H12'	6319	-2500	7251	51
H13'	8515	-3627	7714	57
H14'	11155	-3021	7428	54
H15'	11600	-1289	6678	49
H9E	8872	740	6060	34
H9F	10792	889	6125	34
H11"	7530	-1143	6498	42
H12"	7568	-2922	7240	51
H13"	10021	-3664	7693	57
H14"	12437	-2628	7405	54
H15"	12399	-849	6664	49
H3E	9454	6805	3951	175
H3F	10082	5654	3715	175

Table S6 Torsion angles [°] for [MnLCl]·0.5H_2O (**1**·0.5H_2O).

O2#1-Mn1-O1-C1	176.9(4)	O1#1-Mn1-N1-C2	-164.6(12)
N3-Mn1-O1-C1	-21.9(6)	Cl1-Mn1-N1-C2	-49.5(13)
N1'-Mn1-O1-C1	-17.9(4)	O1-Mn1-N1-C8	156.5(9)
N1-Mn1-O1-C1	-29.0(5)	O2#1-Mn1-N1-C8	-162.2(6)
N2'-Mn1-O1-C1	-92.9(5)	N3-Mn1-N1-C8	-19.4(7)
N2-Mn1-O1-C1	-94.2(5)	N1'-Mn1-N1-C8	57(2)
O1#1-Mn1-O1-C1	162.7(4)	N2'-Mn1-N1-C8	-101.2(8)
Cl1-Mn1-O1-C1	73.8(4)	N2-Mn1-N1-C8	-93.9(8)
O2#1-Mn1-O1-Mn1#2	13.4(5)	O1#1-Mn1-N1-C8	-45.1(12)
N3-Mn1-O1-Mn1#2	174.6(4)	Cl1-Mn1-N1-C8	69.9(8)
N1'-Mn1-O1-Mn1#2	178.6(5)	O1-Mn1-N1-C3	-80.9(7)
N1-Mn1-O1-Mn1#2	167.5(6)	O2#1-Mn1-N1-C3	-39.7(10)
N2'-Mn1-O1-Mn1#2	103.5(5)	N3-Mn1-N1-C3	103.2(7)
N2-Mn1-O1-Mn1#2	102.2(6)	N1'-Mn1-N1-C3	180(3)
O1#1-Mn1-O1-Mn1#2	-0.8(4)	N2'-Mn1-N1-C3	21.4(7)
Cl1-Mn1-O1-Mn1#2	-89.8(5)	N2-Mn1-N1-C3	28.7(7)
Mn1#2-O2-C1-O1	-2.8(6)	O1#1-Mn1-N1-C3	77.4(10)
Mn1#2-O2-C1-C2	172.1(16)	Cl1-Mn1-N1-C3	-167.5(7)
Mn1-O1-C1-O2	-170.7(4)	C2-N1-C3-C4	-168.0(14)
Mn1#2-O1-C1-O2	2.5(6)	C8-N1-C3-C4	62.3(16)
Mn1-O1-C1-C2	14.3(17)	Mn1-N1-C3-C4	-56.0(11)
Mn1#2-O1-C1-C2	-172.5(17)	N1-C3-C4-N2	52.0(14)
O2-C1-C2-N1	-151.6(17)	C3-C4-N2-C9"	101.2(12)
O1-C1-C2-N1	23(3)	C3-C4-N2-C9	111.8(10)
C1-C2-N1-C8	-158.0(19)	C3-C4-N2-C5	-140.6(9)
C1-C2-N1-C3	72(3)	C3-C4-N2-Mn1	-22.8(11)
C1-C2-N1-Mn1	-43(3)	O1-Mn1-N2-C9"	-70.6(11)
O1-Mn1-N1-C2	37.1(12)	O2#1-Mn1-N2-C9"	7.3(11)
O2#1-Mn1-N1-C2	78.3(14)	N3-Mn1-N2-C9"	143.6(11)
N3-Mn1-N1-C2	-138.9(13)	N1'-Mn1-N2-C9"	-140.9(11)
N1'-Mn1-N1-C2	-62(3)	N1-Mn1-N2-C9"	-135.6(11)
N2'-Mn1-N1-C2	139.4(13)	N2'-Mn1-N2-C9"	-80(4)
N2-Mn1-N1-C2	146.7(13)	O1#1-Mn1-N2-C9"	62.4(11)

Cl1-Mn1-N2-C9"	155.1(11)	N1-Mn1-N3-C6	-84.4(7)
O1-Mn1-N2-C9	-67.2(10)	N2'-Mn1-N3-C6	-15.5(7)
O2#1-Mn1-N2-C9	10.7(10)	N2-Mn1-N3-C6	-9.8(7)
N3-Mn1-N2-C9	147.0(11)	O1#1-Mn1-N3-C6	85.2(7)
N1'-Mn1-N2-C9	-137.5(10)	Cl1-Mn1-N3-C6	173.5(7)
N1-Mn1-N2-C9	-132.2(11)	O1-Mn1-N3-C7	33.6(6)
N2'-Mn1-N2-C9	-76(3)	O2#1-Mn1-N3-C7	-172.3(5)
O1#1-Mn1-N2-C9	65.8(10)	N1'-Mn1-N3-C7	29.6(5)
Cl1-Mn1-N2-C9	158.5(8)	N1-Mn1-N3-C7	40.5(6)
O1-Mn1-N2-C4	62.2(9)	N2'-Mn1-N3-C7	109.4(5)
O2#1-Mn1-N2-C4	140.1(9)	N2-Mn1-N3-C7	115.1(6)
N3-Mn1-N2-C4	-83.7(9)	O1#1-Mn1-N3-C7	-149.9(5)
N1'-Mn1-N2-C4	-8.1(8)	Cl1-Mn1-N3-C7	-61.6(5)
N1-Mn1-N2-C4	-2.9(8)	C6-N3-C7-C8	66.1(11)
N2'-Mn1-N2-C4	53(3)	Mn1-N3-C7-C8	-62.9(9)
O1#1-Mn1-N2-C4	-164.8(8)	C2-N1-C8-C7	105(2)
Cl1-Mn1-N2-C4	-72.2(15)	C3-N1-C8-C7	-126.1(13)
O1-Mn1-N2-C5	178.5(7)	Mn1-N1-C8-C7	-7.9(12)
O2#1-Mn1-N2-C5	-103.6(7)	N3-C7-C8-N1	49.5(13)
N3-Mn1-N2-C5	32.6(6)	O1-Mn1-N1'-C2'	30.6(10)
N1'-Mn1-N2-C5	108.2(7)	O2#1-Mn1-N1'-C2'	58.2(11)
N1-Mn1-N2-C5	113.4(8)	N3-Mn1-N1'-C2'	-151.8(10)
N2'-Mn1-N2-C5	169(4)	N1-Mn1-N1'-C2'	108(3)
O1#1-Mn1-N2-C5	-48.5(7)	N2'-Mn1-N1'-C2'	128.1(10)
Cl1-Mn1-N2-C5	44.1(15)	N2-Mn1-N1'-C2'	135.4(10)
C9"-N2-C5-C6	-159.4(10)	O1#1-Mn1-N1'-C2'	-150.6(10)
C9-N2-C5-C6	-176.3(9)	Cl1-Mn1-N1'-C2'	-59.8(10)
C4-N2-C5-C6	73.6(10)	O1-Mn1-N1'-C8'	150.8(6)
Mn1-N2-C5-C6	-52.1(10)	O2#1-Mn1-N1'-C8'	178.4(4)
N2-C5-C6-N3	45.6(12)	N3-Mn1-N1'-C8'	-31.6(5)
C5-C6-N3-C7	-133.8(9)	N1-Mn1-N1'-C8'	-132(3)
C5-C6-N3-Mn1	-16.1(12)	N2'-Mn1-N1'-C8'	-111.7(6)
O1-Mn1-N3-C6	-91.3(7)	N2-Mn1-N1'-C8'	-104.4(6)
O2#1-Mn1-N3-C6	62.8(7)	O1#1-Mn1-N1'-C8'	-30.4(9)
N1'-Mn1-N3-C6	-95.3(7)	Cl1-Mn1-N1'-C8'	60.4(5)

O1-Mn1-N1'-C3'	-88.5(5)	N1-Mn1-N2'-C9'	-140.0(9)
O2#1-Mn1-N1'-C3'	-60.9(7)	N2-Mn1-N2'-C9'	98(3)
N3-Mn1-N1'-C3'	89.2(5)	O1#1-Mn1-N2'-C9'	60.2(9)
N1-Mn1-N1'-C3'	-11(2)	Cl1-Mn1-N2'-C9'	-179.1(9)
N2'-Mn1-N1'-C3'	9.1(5)	C4'-N2'-C5'-C6'	127.1(7)
N2-Mn1-N1'-C3'	16.4(6)	C9'-N2'-C5'-C6'	-100.3(9)
O1#1-Mn1-N1'-C3'	90.4(7)	Mn1-N2'-C5'-C6'	17.0(9)
Cl1-Mn1-N1'-C3'	-178.8(5)	C2'-N1'-C8'-C7'	166.2(13)
C2'-N1'-C3'-C4'	-97.8(11)	C3'-N1'-C8'-C7'	-66.6(11)
C8'-N1'-C3'-C4'	133.7(9)	Mn1-N1'-C8'-C7'	51.4(8)
Mn1-N1'-C3'-C4'	17.7(9)	C4-N2-C9-C10	56.8(16)
N1'-C3'-C4'-N2'	-54.3(11)	C5-N2-C9-C10	-51.7(15)
C3'-C4'-N2'-C5'	-56.6(9)	Mn1-N2-C9-C10	-168.2(9)
C3'-C4'-N2'-C9'	163.8(8)	N2-C9-C10-C11	87.6(14)
C3'-C4'-N2'-Mn1	56.4(8)	N2-C9-C10-C15	-94.3(14)
O1-Mn1-N2'-C5'	157.9(5)	C15-C10-C11-C12	0.0
O2#1-Mn1-N2'-C5'	-124.1(5)	C9-C10-C11-C12	178.2(7)
N3-Mn1-N2'-C5'	10.7(5)	C10-C11-C12-C13	0.0
N1'-Mn1-N2'-C5'	86.4(6)	C11-C12-C13-C14	0.0
N1-Mn1-N2'-C5'	90.4(6)	C12-C13-C14-C15	0.0
N2-Mn1-N2'-C5'	-31(3)	C13-C14-C15-C10	0.0
O1#1-Mn1-N2'-C5'	-69.4(5)	C11-C10-C15-C14	0.0
Cl1-Mn1-N2'-C5'	51.4(12)	C9-C10-C15-C14	-178.2(7)
O1-Mn1-N2'-C4'	37.6(5)	C5'-N2'-C9'-C10'	-69.9(14)
O2#1-Mn1-N2'-C4'	115.5(5)	C4'-N2'-C9'-C10'	66.2(13)
N3-Mn1-N2'-C4'	-109.7(5)	Mn1-N2'-C9'-C10'	171.7(9)
N1'-Mn1-N2'-C4'	-34.0(5)	N2'-C9'-C10'-C11'	-93.6(12)
N1-Mn1-N2'-C4'	-29.9(5)	N2'-C9'-C10'-C15'	85.9(13)
N2-Mn1-N2'-C4'	-152(4)	C15'-C10'-C11'-C12'	0.0
O1#1-Mn1-N2'-C4'	170.2(5)	C9'-C10'-C11'-C12'	179.5(9)
Cl1-Mn1-N2'-C4'	-69.0(11)	C10'-C11'-C12'-C13'	0.0
O1-Mn1-N2'-C9'	-72.5(8)	C11'-C12'-C13'-C14'	0.0
O2#1-Mn1-N2'-C9'	5.4(8)	C12'-C13'-C14'-C15'	0.0
N3-Mn1-N2'-C9'	140.2(9)	C13'-C14'-C15'-C10'	0.0
N1'-Mn1-N2'-C9'	-144.1(9)	C11'-C10'-C15'-C14'	0.0

C9'-C10'-C15'-C14'	-179.5(9)
C4-N2-C9"-C10"	42.6(19)
C5-N2-C9"-C10"	-74.2(15)
Mn1-N2-C9"-C10"	174.6(12)
N2-C9"-C10"-C11"	-89.5(15)
N2-C9"-C10"-C15"	87.9(16)
C15"-C10"-C11"-C12"	0.0
C9"-C10"-C11"-C12"	177.5(6)
C10"-C11"-C12"-C13"	0.0
C11"-C12"-C13"-C14"	0.0
C12"-C13"-C14"-C15"	0.0
C13"-C14"-C15"-C10"	0.0
C11"-C10"-C15"-C14"	0.0
C9"-C10"-C15"-C14"	-177.4(6)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,-z+1 #2 x-1/2,-y+1/2,-z+1

Table S7 Hydrogen bonds and close contacts for [MnLCl]·0.5H_2O (**1**·0.5H_2O) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N3-H3...O2#3	0.93	2.13	2.952(5)	146.5
N3'-H3'...O2#3	0.93	2.23	2.952(5)	134.3
O3-H3F...Cl1	0.85	2.20	3.047(8)	179.1

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,-z+1 #2 x-1/2,-y+1/2,-z+1 #3 x+1,y,z