Supporting Information for

Correlation of Relaxivity with Coordination Number in Six-, Seven-, and Eight-Coordinate Mn(II) Complexes of Pendant-Arm Cyclen Derivatives

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Contents:

X-Ray Crystallographic Analyses

All data collection and structure solutions were performed by Neil R. Brooks and Victor G. Young, Jr., X-Ray Crystallographic Laboratory, Department of Chemistry, University of Minnesota. The text below has been adapted from reports they provided.

$[Mn(DOTAM)]Cl_2 \cdot 2H_2O$

A crystal of approximate dimensions $0.46 \times 0.38 \times 0.20$ mm^3 was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Siemens CCD area detector diffractometer for data collection at 173(2)K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 115 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 10 seconds and a detector distance of 4.9 cm. The complete sphere of reciprocal space was surveyed to a resolution of 0.77 Å. Three major sections of frames were collected with 0.30° steps in ω at three different ϕ settings and a detector position of -28° in 2θ. The intensity data were corrected for absorption and decay (SADABS).[1] Final cell constants were calculated from the xyz centroids of 3508 strong reflections from the actual data after integration (SAINT 6.01, 1999).[2]

The structure was solved using SIR92[3] and refined using SHELXL-97.[4] The space group *C*2/*c* was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the full 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 ligand hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The hydrogen atoms on the solvent water molecules were found in the difference density map and refined isotropically with no restraints. The final full matrix least squares refinement converged to R1 = 0.0255 and wR2 = 0.0644 (F^2, all data).

Refer to Table S1 for additional data collection and refinement information.

$[Mn(DO3AM)][MnCl_4] \cdot EtOH$

A crystal of approximate dimensions $0.16 \times 0.16 \times 0.06$ mm^3 was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker CCD area detector diffractometer for data collection at 173(2)K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 71 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 60 seconds and a detector distance of 4.9 cm. A randomly oriented region of reciprocal space was

surveyed to the extent of 1.5 hemispheres and to a resolution of 0.84 Å. Three major sections of frames were collected with 0.30° steps in ω at three different ϕ settings and a detector position of -28° in 2θ. The intensity data were corrected for absorption and decay (SADABS).[1] Final cell constants were calculated from the xyz centroids of 2813 strong reflections from the actual data after integration (SAINT 6.01, 1999).[2]

The structure was solved using SIR92[3] and refined using SHELXL-97.[4] The space group $P2_1/n$ 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. The structure contains disorder for which the model was not immediately apparent. The structure is essentially that of the tri-amide substituted cyclen complex. There is, however, residual difference electron density on the order of 0.9 $eÅ^{-3}$ around the area where a fourth amide arm would be located. There is also a solvent ethanol molecule in this vicinity. Modeling this residual difference electron density as an amide arm seems to agree with the X-ray data. The amide arm was refined as a minor component with the ethanol molecule as the major component (88.5(7)% of the total). There are two possibilities consistent with this model: 1) that the crystal is contaminated with [Mn(DOTAM)], or 2) that the disorder arises from 90° rotations of [Mn(DO3AM)] in the site about an axis perpendicular to the plane of the ring nitrogens. For case 2, disorder at the other amide arms would be expected. Such disorder was not observed, but it is reasonable to assume that the disorder of the other three amide arms would be small and would not be detectable within the experimental error of the data. As a result, the molecular formula was taken as [Mn(DO3AM)][$MnCl_4$]·EtOH. All non-hydrogen atoms except those of the minor components in the disorder model were refined with anisotropic displacement parameters. Most hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The exceptions were: 1) the non-disordered NH_2 groups for which the hydrogen atoms were found in the difference electron density map and were refined with the constraint of equal N-H bond distances and 2) The hydrogen atom on the oxygen of the ethanol molecule was found in the difference electron density map and was refined with the constraint of a 0.84 Å O-H bond distance. There is also additional disorder in one of the amide arms. There are two positions of the arms with the major component comprising 75.9(8)% of the total. Restraints were applied to keep the bond distances and angles in both of the components the same. The final full matrix least squares refinement converged to R1 = 0.0536 and wR2 = 0.1230 (F^2, all data). The program PLATON[5] was used to check the structure.

Refer to Table S1 for additional data collection and refinement information.

Mn(H_2DOTA)

A crystal of approximate dimensions 0.26 × 0.10 × 0.10 mm^3 was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker CCD area

detector diffractometer for data collection at 173(2)K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 41 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 60 seconds and a detector distance of 4.9 cm. The complete sphere of reciprocal space was surveyed to a resolution of 0.84 Å. Three major sections of frames were collected with 0.30° steps in ω at three different ϕ settings and a detector position of -28° in 2θ. The intensity data were corrected for absorption and decay (SADABS).[1] Final cell constants were calculated from the xyz centroids of 2827 strong reflections from the actual data after integration (SAINT 6.01, 1999).[2]

The structure was solved and refined using SHELXL-97.[4] The space group *C*2/*c* was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the full 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 attached to carbon were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The hydrogen atoms attached to oxygen were found in the difference density map and allowed to refine freely. The final full matrix least squares refinement converged to R1 = 0.0314 and wR2 = 0.0840 (F^2, all data). The program PLATON[5] was used to check the structure.

Refer to Table S1 for additional data collection and refinement information.

1) An empirical correction for absorption anisotropy, Blessing R. *Acta Cryst.* **1995**, *A51*, 33-38.
2) SAINT V6.1, Bruker Analytical X-Ray Systems, Madison, WI.
3) SIR92. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Gualardi, A. *J. Appl. Cryst.* **1993**, *26*, 343-350.
4) SHELXTL-Plus V5.10, **1998**, Bruker Analytical X-Ray Systems, Madison, WI.
5) Spek, A. L. *J.Appl.Cryst.* **1990**, A*46*, C34. PLATON, A Multipurpose Crystallographic Tool, **2000**, Utrecht University, Utrecht, The Netherlands, A.L. Spek.

Table S1. Crystal Data and Refinement Parameters for [Mn(DOTAM)]Cl_2·$2H_2O$, [Mn(DO3AM)][$MnCl_4$]·EtOH, and Mn(H_2DOTA)·$2H_2O$.

	[Mn(DOTAM)]Cl_2·$2H_2O$	[Mn(DO3AM)][$MnCl_4$]·EtOH	Mn(H_2DOTA)
Formula	$C_{16}H_{36}Cl_2MnN_8O_6$	$C_{16}H_{35}Cl_4Mn_2N_7O_4$	$C_{16}H_{26}MnN_4O_8$
FW (g mol^{-1})	562.37	641.19	457.35
T (K)	173(2)	173(2)	173(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	*C*2/*c*	$P2_1/n$	*C*2/*c*
a (Å)	18.5798(15)	8.3646(8)	16.374(3)
b (Å)	13.6006(11)	19.483(2)	6.6559(13)
c (Å)	10.5800(8)	16.3627(16)	16.750(3)
α (°)	90	90	90
β (°)	110.490(1)	99.254(2)	98.381(3)
γ (°)	90	90	90
Volume ($Å^3$)	2504.4(3)	2631.9(5)	1806.0(6)
Z	4	4	4
Density (calc.)	1.492	1.622	1.682
Theta Range for Collection	1.90°-27.49°	1.64°-25.03°	2.46°-25.04°
Reflections Collected	10845	13095	6602
Independent Reflections	2853	4626	1598
Observed Reflections	2568	3850	1381
Data/Restraints /Parameters	2853 / 0 /158	4626 / 21 / 336	1598 / 0 / 136
R indices [$I>2\sigma(I)$]	*R*1 = 0.0255 *wR*2 = 0.0629	*R*1 = 0.0536 *wR*2 = 0.1177	*R*1 = 0.0314 *wR*2 = 0.0782
R indices (all data)	*R*1 = 0.0296 *wR*2 = 0.0644	*R*1 = 0.0673 *wR*2 = 0.1230	*R*1 = 0.0392 *wR*2 = 0.0840

Figure S1. Molecular Structure of $[Mn(DOTAM)]Cl_2 \cdot 2H_2O$.

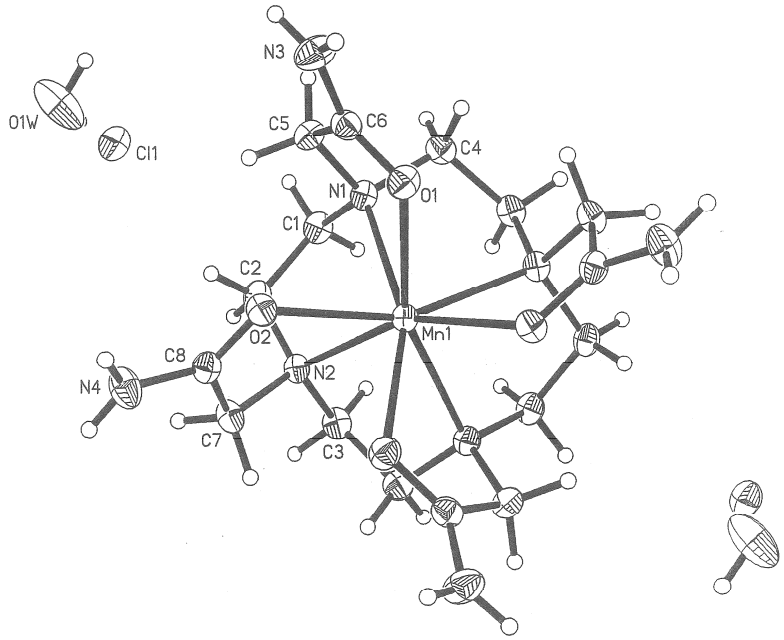


Figure S2. Crystal Structure of $[Mn(DOTAM)]Cl_2 \cdot 2H_2O$.

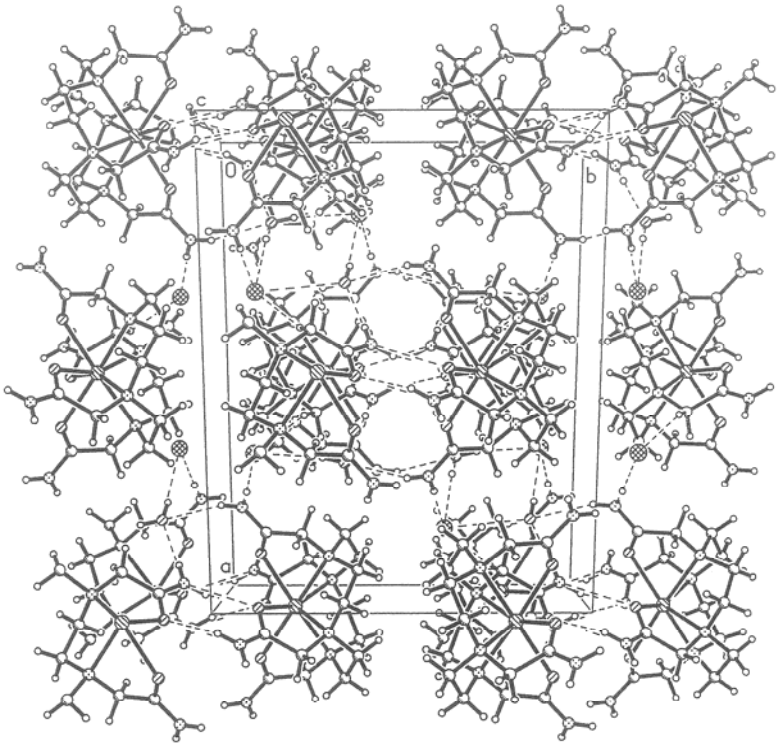


Table S2a. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Mn(DOTAM)]Cl_2 \cdot 2H_2O$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Mn1	5000	2917(1)	2500	16(1)
N1	3899(1)	1983(1)	2580(1)	20(1)
N2	5452(1)	1962(1)	4561(1)	19(1)
O1	3884(1)	3835(1)	1679(1)	23(1)
O2	4925(1)	3809(1)	4306(1)	21(1)
N3	2842(1)	4294(1)	2149(1)	31(1)
N4	5564(1)	4202(1)	6485(1)	28(1)
C1	4156(1)	1190(1)	3599(1)	23(1)
C2	4791(1)	1544(1)	4861(1)	23(1)
C3	5975(1)	1180(1)	4440(1)	22(1)
C4	3478(1)	1557(1)	1230(1)	22(1)
C5	3404(1)	2698(1)	2932(2)	23(1)
C6	3392(1)	3660(1)	2194(1)	22(1)
C7	5855(1)	2658(1)	5644(1)	23(1)
C8	5408(1)	3612(1)	5439(1)	21(1)
Cl1	3343(1)	1151(1)	6317(1)	31(1)
O1W	3158(1)	3493(1)	6184(1)	51(1)

Table S2b. Bond lengths (Å) and bond angles (°) for $[Mn(DOTAM)]Cl_2 \cdot 2H_2O$.

Mn(1)-O(2)	2.3080(9)	N(2)-C(3)	1.4771(17)
Mn(1)-O(2)#1	2.3080(10)	N(2)-C(2)	1.4840(17)
Mn(1)-O(1)#1	2.3128(10)	O(1)-C(6)	1.2402(17)
Mn(1)-O(1)	2.3128(10)	O(2)-C(8)	1.2494(16)
Mn(1)-N(2)#1	2.4218(11)	N(3)-C(6)	1.3255(18)
Mn(1)-N(2)	2.4218(11)	N(4)-C(8)	1.3144(18)
Mn(1)-N(1)	2.4351(11)	C(1)-C(2)	1.518(2)
Mn(1)-N(1)#1	2.4351(11)	C(3)-C(4)#1	1.518(2)
N(1)-C(5)	1.4734(17)	C(4)-C(3)#1	1.518(2)
N(1)-C(1)	1.4815(17)	C(5)-C(6)	1.5207(19)
N(1)-C(4)	1.4847(17)	C(7)-C(8)	1.5150(19)
N(2)-C(7)	1.4722(17)		

O(2)-Mn(1)-O(2)#1	116.60(5)	O(2)-Mn(1)-N(1)#1	126.71(4)
O(2)-Mn(1)-O(1)#1	73.22(4)	O(2)#1-Mn(1)-N(1)#1	87.16(4)
O(2)#1-Mn(1)-O(1)#1	73.83(3)	O(1)#1-Mn(1)-N(1)#1	68.96(4)
O(2)-Mn(1)-O(1)	73.83(3)	O(1)-Mn(1)-N(1)#1	157.24(4)
O(2)#1-Mn(1)-O(1)	73.22(3)	N(2)#1-Mn(1)-N(1)#1	73.73(4)
O(1)#1-Mn(1)-O(1)	114.67(5)	N(2)-Mn(1)-N(1)#1	73.79(4)
O(2)-Mn(1)-N(2)#1	157.64(4)	N(1)-Mn(1)-N(1)#1	117.11(5)
O(2)#1-Mn(1)-N(2)#1	68.82(4)	C(5)-N(1)-C(1)	111.56(11)
O(1)#1-Mn(1)-N(2)#1	127.61(4)	C(5)-N(1)-C(4)	109.60(11)
O(1)-Mn(1)-N(2)#1	88.19(4)	C(1)-N(1)-C(4)	110.10(10)
O(2)-Mn(1)-N(2)	68.82(4)	C(5)-N(1)-Mn(1)	105.72(8)
O(2)#1-Mn(1)-N(2)	157.64(4)	C(1)-N(1)-Mn(1)	110.10(8)
O(1)#1-Mn(1)-N(2)	88.19(4)	C(4)-N(1)-Mn(1)	109.64(8)
O(1)-Mn(1)-N(2)	127.61(4)	C(7)-N(2)-C(3)	111.07(11)
N(2)#1-Mn(1)-N(2)	115.16(5)	C(7)-N(2)-C(2)	108.26(11)
O(2)-Mn(1)-N(1)	87.16(4)	C(3)-N(2)-C(2)	111.16(10)
O(2)#1-Mn(1)-N(1)	126.71(4)	C(7)-N(2)-Mn(1)	106.14(8)
O(1)#1-Mn(1)-N(1)	157.24(4)	C(3)-N(2)-Mn(1)	109.84(8)
O(1)-Mn(1)-N(1)	68.96(4)	C(2)-N(2)-Mn(1)	110.25(8)
N(2)#1-Mn(1)-N(1)	73.79(4)	C(6)-O(1)-Mn(1)	115.68(9)
N(2)-Mn(1)-N(1)	73.73(4)	C(8)-O(2)-Mn(1)	116.78(9)

Table S2b.(cont.) Bond lengths (Å) and bond angles (°) for [Mn(DOTAM)]$Cl_2 \cdot 2H_2O$.

N(1)-C(1)-C(2)	111.27(11)	O(1)-C(6)-C(5)	120.70(12)
N(2)-C(2)-C(1)	112.34(11)	N(3)-C(6)-C(5)	116.70(12)
N(2)-C(3)-C(4)#1	111.44(11)	N(2)-C(7)-C(8)	109.56(11)
N(1)-C(4)-C(3)#1	111.56(11)	O(2)-C(8)-N(4)	123.38(13)
N(1)-C(5)-C(6)	109.62(11)	O(2)-C(8)-C(7)	119.64(12)
O(1)-C(6)-N(3)	122.60(13)	N(4)-C(8)-C(7)	116.98(12)

Symmetry transformations used to generate equivalent atoms:

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

Table S2c. Anisotropic displacement parameters ($Å^2 \times 10^3$) for [Mn(DOTAM)]$Cl_2 \cdot 2H_2O$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + \ldots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	19(1)	15(1)	16(1)	0	7(1)	0
N1	22(1)	17(1)	20(1)	1(1)	9(1)	0(1)
N2	23(1)	16(1)	19(1)	0(1)	7(1)	1(1)
O1	24(1)	22(1)	25(1)	3(1)	11(1)	2(1)
O2	24(1)	19(1)	21(1)	-1(1)	6(1)	3(1)
N3	28(1)	28(1)	42(1)	8(1)	18(1)	7(1)
N4	37(1)	21(1)	22(1)	-3(1)	5(1)	5(1)
C1	28(1)	18(1)	25(1)	4(1)	12(1)	-1(1)
C2	29(1)	19(1)	22(1)	4(1)	12(1)	1(1)
C3	27(1)	17(1)	22(1)	2(1)	7(1)	4(1)
C4	22(1)	20(1)	23(1)	0(1)	7(1)	-4(1)
C5	23(1)	23(1)	26(1)	1(1)	12(1)	1(1)
C6	21(1)	22(1)	21(1)	-1(1)	5(1)	0(1)
C7	27(1)	20(1)	18(1)	-1(1)	4(1)	3(1)
C8	24(1)	19(1)	21(1)	0(1)	10(1)	-2(1)
Cl1	34(1)	30(1)	33(1)	0(1)	16(1)	3(1)
O1W	60(1)	35(1)	36(1)	1(1)	-10(1)	-10(1)

Table S2d. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $[Mn(DOTAM)]Cl_2 \cdot 2H_2O$.

	x	y	z	U(eq)
H3C	2815	4864	1742	37
H3D	2502	4144	2526	37
H4C	5323	4768	6407	34
H4D	5909	4030	7263	34
H1A	4345	627	3210	27
H1B	3715	960	3841	27
H2A	4582	2051	5309	27
H2B	4973	987	5495	27
H3A	5669	630	3902	27
H3B	6275	925	5349	27
H4A	3139	2066	649	27
H4B	3149	1010	1325	27
H5A	3601	2814	3918	28
H5B	2875	2434	2676	28
H7A	6377	2786	5634	27
H7B	5905	2371	6531	27
H1W	2796(14)	3614(17)	5530(20)	52(7)
H2W	3262(14)	2910(20)	6180(30)	64(8)

Table S2e. Hydrogen bonds and close contacts for $[Mn(DOTAM)]Cl_2 \cdot 2H_2O$. (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N3-H3C...O1W#2	0.88	2.45	3.297(2)	161.1
N3-H3D...Cl1#3	0.88	2.34	3.2155(14)	174.8
N4-H4C...O2#4	0.88	2.07	2.8837(16)	153.3
N4-H4D...O1W#5	0.88	2.06	2.9243(19)	167.1
O1W-H1W...Cl1#3	0.79(2)	2.35(2)	3.1378(16)	174(2)
O1W-H2W...Cl1	0.82(3)	2.39(3)	3.2018(16)	168(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2 #2 x,-y+1,z-1/2 #3 -x+1/2,-y+1/2,-z+1 #4 -x+1,-y+1,-z+1 #5 -x+1,y,-z+3/2

Figure S3. Molecular Structure of [Mn(DO3AM)][$MnCl_4$]·EtOH.

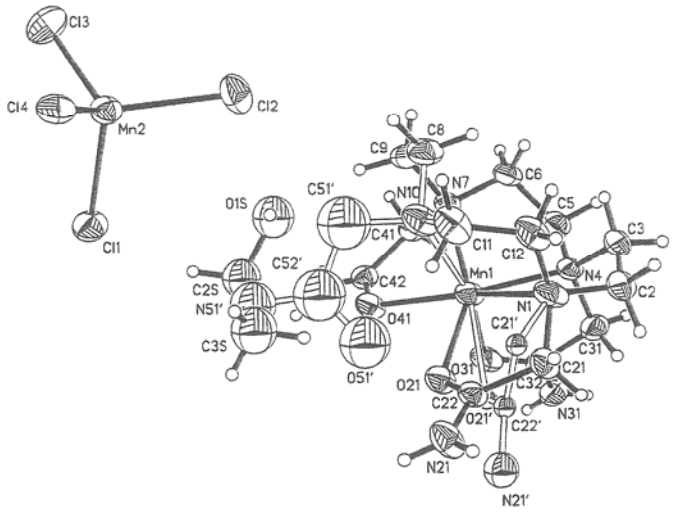


Figure S4. Crystal Structure of [Mn(DO3AM)][$MnCl_4$]·EtOH.

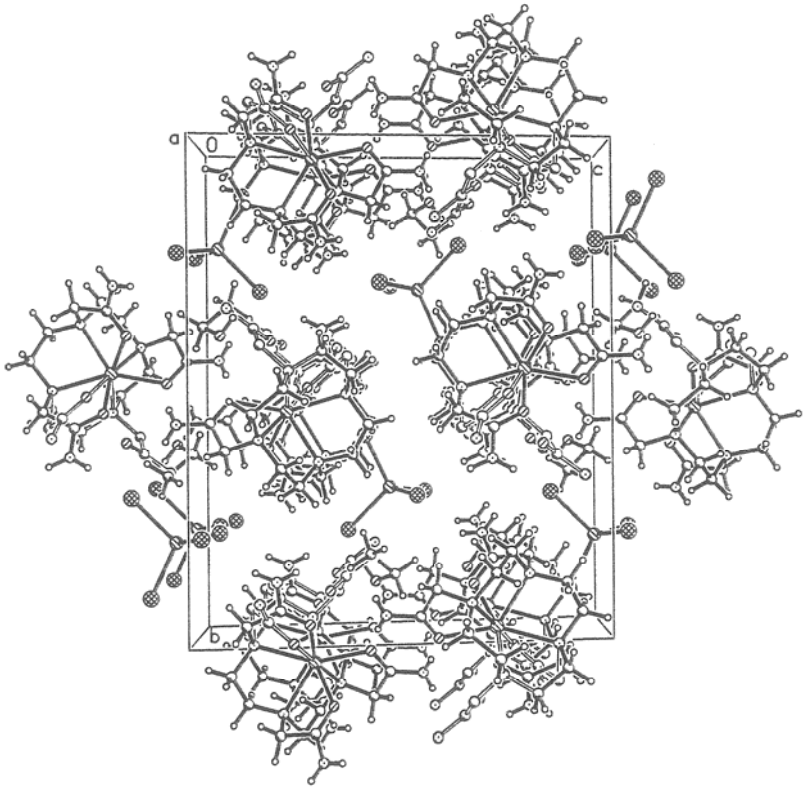


Table S3a. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for [Mn(DO3AM)][$MnCl_4$]·EtOH. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Mn1	2981(1)	4607(1)	7828(1)	34(1)
N1	2575(5)	4947(2)	6385(2)	39(1)
C2	2492(6)	4334(3)	5847(3)	39(1)
C3	1700(6)	3738(3)	6224(3)	38(1)
C5	1594(6)	3115(3)	7514(3)	37(1)
C6	288(5)	3483(3)	7894(3)	35(1)
N7	958(4)	4059(2)	8434(2)	31(1)
C8	-326(6)	4562(3)	8545(3)	38(1)
C9	-619(6)	5057(3)	7825(3)	43(1)
O1S	872(8)	6103(3)	9299(4)	83(2)
C2S	2396(11)	6291(5)	9757(5)	72(1)
C3S	3310(13)	6723(6)	9197(7)	82(1)
N10	908(5)	5403(2)	7726(3)	43(1)
C51'	910(4)	5930(2)	8390(3)	107(2)
C52'	2570(3)	6262(15)	8585(18)	57(1)
O51'	3680(3)	6025(12)	8236(14)	57(1)
N51'	2690(5)	6680(2)	9210(2)	82(1)
C11	799(7)	5799(3)	6948(3)	48(1)
C12	1016(6)	5331(3)	6240(3)	43(1)
C21	3997(8)	5369(3)	6269(3)	30(1)
C22	4750(8)	5709(3)	7079(4)	29(2)
O21	4709(5)	5421(2)	7754(2)	32(1)
N21	5515(6)	6291(3)	7021(3)	40(1)
C21'	3470(3)	5658(16)	6324(17)	32(1)
C22'	5070(3)	5533(13)	6869(16)	23(1)
O21'	5210(3)	5107(11)	7434(14)	49(1)
N21'	6240(4)	5939(18)	6710(2)	85(1)
N4	2553(4)	3583(2)	7070(2)	33(1)
C31	4148(6)	3263(3)	7043(3)	40(1)
C32	5195(6)	3349(3)	7879(3)	36(1)
O31	5006(4)	3847(2)	8321(2)	43(1)
N31	6299(5)	2870(2)	8097(3)	45(1)
C41	1805(5)	3828(2)	9248(3)	31(1)
C42	2973(5)	4379(3)	9631(3)	32(1)
N41	3422(5)	4356(2)	10438(2)	38(1)
O41	3474(4)	4820(2)	9190(2)	36(1)
Mn2	8052(1)	7975(1)	9633(4)	34(0)
Cl1	10769(2)	7843(1)	10323(8)	44(0)
Cl2	7737(2)	7086(1)	8596(1)	48(0)
Cl3	6210(2)	7852(1)	10547(1)	51(0)
Cl4	7818(1)	9080(1)	9032(1)	37(0)

Table S3b. Bond lengths (Å) and bond angles (°) for [Mn(DO3AM)][$MnCl_4$]·EtOH.

Mn(1)-O(21)	2.162(4)	N(10)-C(51')	1.49(2)
Mn(1)-O(41)	2.238(3)	N(10)-C(11)	1.479(6)
Mn(1)-O(31)	2.297(4)	C(51')-C(52')	1.519(19)
Mn(1)-N(10)	2.312(5)	C(52')-O(51')	1.252(18)
Mn(1)-O(21')	2.28(2)	C(52')-N(51')	1.297(19)
Mn(1)-N(4)	2.348(4)	C(11)-C(12)	1.507(8)
Mn(1)-N(7)	2.351(4)	C(21)-C(22)	1.524(8)
Mn(1)-N(1)	2.423(4)	C(22)-O(21)	1.245(6)
N(1)-C(2)	1.478(7)	C(22)-N(21)	1.313(7)
N(1)-C(21)	1.483(7)	C(21)'-C(22)'	1.503(18)
N(1)-C(12)	1.490(7)	C(22)'-O(21)'	1.235(17)
N(1)-C(21)'	1.59(3)	C(22)'-N(21')	1.321(18)
C(2)-C(3)	1.516(7)	N(4)-C(31)	1.480(6)
C(3)-N(4)	1.482(5)	C(31)-C(32)	1.510(6)
C(5)-N(4)	1.481(6)	C(32)-O(31)	1.236(6)
C(5)-C(6)	1.521(7)	C(32)-N(31)	1.320(6)
C(6)-N(7)	1.480(6)	C(41)-C(42)	1.517(6)
N(7)-C(41)	1.475(6)	C(42)-O(41)	1.239(6)
N(7)-C(8)	1.487(6)	C(42)-N(4)1	1.314(6)
C(8)-C(9)	1.512(7)	Mn(2)-Cl(3)	2.3260(15)
C(9)-N(10)	1.476(7)	Mn(2)-Cl(4)	2.3624(15)
O(1S)-C((2S)	1.419(10)	Mn(2)-Cl(1)	2.3831(14)
C((2S)-C(3S)	1.535(14)	Mn(2)-Cl(2)	2.4085(15)

O(21)-Mn(1)-O(41)	84.38(13)	N(10)-Mn(1)-N(4)	118.89(14)
O(21)-Mn(1)-O(21')	24.4(6)	O(21)-Mn(1)-N(7)	152.90(15)
O(41)-Mn(1)-O(21')	100.0(6)	O(41)-Mn(1)-N(7)	72.22(12)
O(21)-Mn(1)-O(31)	91.73(14)	O(21')-Mn(1)-N(7)	170.9(5)
O(41)-Mn(1)-O(31)	76.28(13)	O(31)-Mn(1)-N(7)	95.70(13)
O(21')-Mn(1)-O(31)	77.6(5)	N(10)-Mn(1)-N(7)	75.71(15)
O(21)-Mn(1)-N(10)	90.28(16)	N(4)-Mn(1)-N(7)	77.12(13)
O(41)-Mn(1)-N(10)	87.91(14)	O(21)-Mn(1)-N(1)	74.66(13)
O(21')-Mn(1)-N(10)	109.3(6)	O(41)-Mn(1)-N(1)	153.39(14)
O(31)-Mn(1)-N(10)	163.79(14)	O(21')-Mn(1)-N(1)	66.5(5)
O(21)-Mn(1)-N(4)	129.82(15)	O(31)-Mn(1)-N(1)	119.85(14)
O(41)-Mn(1)-N(4)	132.21(13)	N(10)-Mn(1)-N(1)	76.16(15)
O(21')-Mn(1)-N(4)	105.9(7)	N(4)-Mn(1)-N(1)	74.40(14)
O(31)-Mn(1)-N(4)	71.24(13)	N(7)-Mn(1)-N(1)	122.50(13)
C(2)-N(1)-C(21)	109.5(4)	N(1)-C(12)-C(11)	113.1(4)
C(2)-N(1)-C(12)	110.8(4)	N(1)-C(21)-C(22)	111.0(4)
C(21)-N(1)-C(12)	113.6(4)	O(21)-C(22)-N(21)	122.4(5)
C(2)-N(1)-C(21')	130.3(13)	O(21)-C(22)-C(21)	120.6(5)
C(21)-N(1)-C(21')	27.3(10)	N(21)-C(22)-C(21)	116.8(5)
C(12)-N(1)-C(21')	87.7(10)	C(22)-O(21)-Mn(1)	119.6(3)

Table S3b.(cont.) Bond angles (°) for [Mn(DO3AM)][$MnCl_4$]·EtOH.

C(2)-N(1)-Mn(1)	110.2(3)	C(22')-C(21')-N(1)	101.8(18)
C(21)-N(1)-Mn(1)	106.6(3)	O(21')-C(22')-N(21')	125(2)
C(12)-N(1)-Mn(1)	105.9(3)	O(21')-C(22')-C(21')	121(2)
C(21')-N(1)-Mn(1)	107.8(10)	N(21')-C(22')-C(21')	114(2)
N(1)-C(2)-C(3)	111.1(4)	C(22')-O(21')-Mn(1)	121.0(16)
N(4)-C(3)-C(2)	111.1(4)	C(31)-N(4)-C(5)	108.5(4)
N(4)-C(5)-C(6)	113.0(4)	C(31)-N(4)-C(3)	111.1(4)
N(7)-C(6)-C(5)	111.9(4)	C(5)-N(4)-C(3)	111.5(4)
C(41)-N(7)-C(6)	112.8(4)	C(31)-N(4)-Mn(1)	108.2(3)
C(41)-N(7)-C(8)	110.0(4)	C(5)-N(4)-Mn(1)	108.2(3)
C(6)-N(7)-C(8)	111.2(4)	C(3)-N(4)-Mn(1)	109.3(3)
C(41)-N(7)-Mn(1)	104.2(3)	N(4)-C(31)-C(32)	108.8(4)
C(6)-N(7)-Mn(1)	108.8(3)	O(31)-C(32)-N(31)	123.1(4)
C(8)-N(7)-Mn(1)	109.5(3)	O(31)-C(32)-C(31)	120.4(5)
N(7)-C(8)-C(9)	110.8(4)	N(31)-C(32)-C(31)	116.5(5)
N(10)-C(9)-C(8)	110.0(4)	C(32)-O(31)-Mn(1)	117.3(3)
O(1S)-C(2S)-C(3S)	108.5(8)	N(7)-C(41)-C(42)	110.0(4)
C(9)-N(10)-C(11)	113.4(4)	O(41)-C(42)-N(41)	122.7(4)
C(9)-N(10)-C(51')	97.8(12)	O(41)-C(42)-C(41)	120.4(4)
C(11)-N(10)-C(51')	105(2)	N(41)-C(42)-C(41)	116.9(4)
C(9)-N(10)-Mn(1)	109.7(3)	C(42)-O(41)-Mn(1)	115.2(3)
C(11)-N(10)-Mn(1)	110.7(3)	Cl(3)-Mn(2)-Cl(4)	110.04(5)
C(51')-N(10)-Mn(1)	119.8(18)	Cl(3)-Mn(2)-Cl(1)	111.34(6)
N(10)-C(51')-C(52')	109.8(18)	Cl(4)-Mn(2)-Cl(1)	107.71(5)
O(51')-C(52')-N(51')	129(2)	Cl(3)-Mn(2)-Cl(2)	111.75(6)
O(51')-C(52')-C(51')	118(2)	Cl(4)-Mn(2)-Cl(2)	111.66(5)
N(51')-C(52')-C(51')	112(2)	Cl(1)-Mn(2)-Cl(2)	104.16(6)
N(10)-C(11)-C(12)	110.4(4)	Cl(1)-Mn(2)-Cl(2)	104.16(6)

Table S3c. Anisotropic displacement parameters ($Å^2 \times 10^3$) for [Mn(DO3AM)][$MnCl_4$]·EtOH. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + \ldots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	24(1)	56(1)	22(4)	6(1)	0(1)	-6(3)
N1	29(2)	55(3)	30(2)	10(2)	-4(2)	-10(2)
C2	33(3)	61(3)	21(2)	3(2)	-3(2)	-1(2)
C3	29(3)	57(3)	24(2)	-2(2)	-5(2)	1(2)
C5	30(3)	50(3)	29(2)	1(2)	-1(2)	-6(2)
C6	24(2)	48(3)	29(2)	3(2)	0(2)	-8(2)
N7	25(2)	45(2)	23(2)	2(2)	2(2)	-5(2)
C8	26(2)	48(3)	39(3)	0(2)	5(2)	0(2)
C9	28(3)	56(3)	44(3)	6(3)	-2(2)	4(2)
N10	43(3)	49(3)	34(2)	4(2)	-5(19)	-8(2)
C11	55(4)	46(3)	39(3)	11(2)	-4(3)	-9(3)
C12	45(3)	48(3)	31(3)	10(2)	-7(2)	-8(3)
C21	32(3)	35(4)	22(3)	4(2)	1(2)	-2(3)
C22	25(3)	39(4)	23(3)	0(3)	3(3)	-2(3)
O21	31(2)	46(3)	19(2)	0(2)	3(16)	-10(2)
N21	49(3)	44(3)	24(2)	3(2)	-2(2)	-14(3)
N4	20(2)	54(3)	23(2)	1(2)	-2(2)	0(2)
C31	25(2)	64(4)	30(3)	1(2)	2(2)	7(2)
C32	25(2)	54(3)	30(2)	6(2)	7(2)	-4(2)
O31	28(2)	54(2)	41(2)	4(2)	-8(2)	-3(16)
N31	30(2)	70(3)	32(2)	0(2)	-1(2)	9(2)
C41	27(2)	41(3)	25(2)	3(2)	4(2)	-5(2)
C42	25(2)	43(3)	28(2)	4(2)	2(2)	2(2)
N41	41(2)	50(3)	23(2)	4(2)	2(2)	-13(2)
O41	34(2)	46(2)	26(2)	6(2)	1(14)	-12(2)
Mn2	29(1)	43(1)	29(1)	2(1)	2(1)	1(1)
Cl1	32(1)	62(9)	34(1)	0(1)	-2(1)	8(1)
Cl2	60(9)	52(1)	32(1)	-6(1)	6(1)	-16(1)
Cl3	51(1)	54(1)	51(1)	12(7)	22(1)	11(1)
Cl4	27(1)	47(1)	36(1)	7(1)	-1(1)	1(1)

Table S3d. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for [Mn(DO3AM)][$MnCl_4$]·EtOH.

	x	y	z	U(eq)
H2A	3599	4202	5768	47
H2B	1862	4445	5298	47
H3A	555	3852	6247	45
H3B	1718	3327	5869	45
H5A	2333	2877	7958	45
H5B	1078	2761	7123	45
H6A	-545	3662	7446	41
H6B	-243	3152	8223	41
H8A	5	4821	9065	45
H8B	-1343	4315	8589	45
H9A	-1048	4805	7311	52
H9B	-1433	5403	7923	52
H1S	512	6427	8983	124
H2S1	3028	5875	9945	86
H2S2	2239	6560	10251	86
H3S1	4368	6856	9505	124
H3S2	2681	7136	9018	124
H3S3	3464	6452	8711	124
H10A	1129	5699	8139	52
H51A	625	5716	8892	129
H51B	87	6288	8198	129
H11A	1646	6158	7011	58
H11B	-270	6027	6827	58
H12A	109	4999	6150	51
H12B	968	5609	5729	51
H21A	3657	5726	5847	36
H21B	4814	5074	6066	36
H21C	6024	6492	7471	48
H21D	5520	6480	6533	48
H21E	3612	5760	5747	39
H21F	2871	6040	6537	39
H21G	7207	5916	7013	102
H21H	6059	6232	6294	102
H31A	4671	3485	6611	48
H31B	4008	2769	6908	48
H31	6943	2897	8577	53
H32	6389	2524	7762	53
H41A	2407	3399	9181	37
H41B	1005	3730	9618	37
H41	4106	4663	10686	46
H42	3040	4034	10731	46

Table S3e. Hydrogen bonds for [Mn(DO3AM)][$MnCl_4$]·EtOH. (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D..A)	<DHA)
O1S-H1S...Cl2	0.84	2.64	3.301(7)	136.6
N21-H21C...Cl2#1	0.88	2.44	3.309(5)	171.7
N21-H21D...Cl1#2	0.88	2.42	3.287(5)	170.4
N21'-H21H...Cl1	0.88	2.39	3.26(3)	171.0
N31-H32...Cl2#4	0.88	2.59	3.373(5)	148.2
N31-H31...Cl1#3	0.88	2.81	3.549(4)	143.0
N41-H41...O41#4	0.88	2.24	3.030(5)	149.1
N41-H42...Cl2#5	0.88	2.57	3.439(4)	167.4
N10-H10A...O1S	0.88	2.10	2.917(8)	153.6

Symmetry tranformations used to generate equivalent atoms:
#1 x+1, y, z #2 x+1/2, -y+3/2, z-1/2 #3 -x+1/2, -y-1/2, -z+3/2 #4 -x+1, -y+1, -z+2
#5 -x,-y+1,-z+2

Figure S5. Molecular Structure of Mn(H_2DOTA).

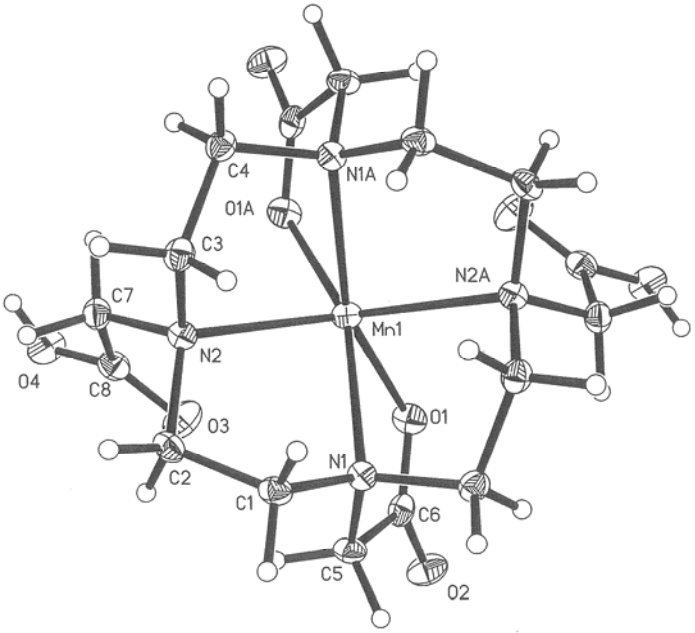


Figure S6. Crystal Structure of Mn(H_2DOTA).

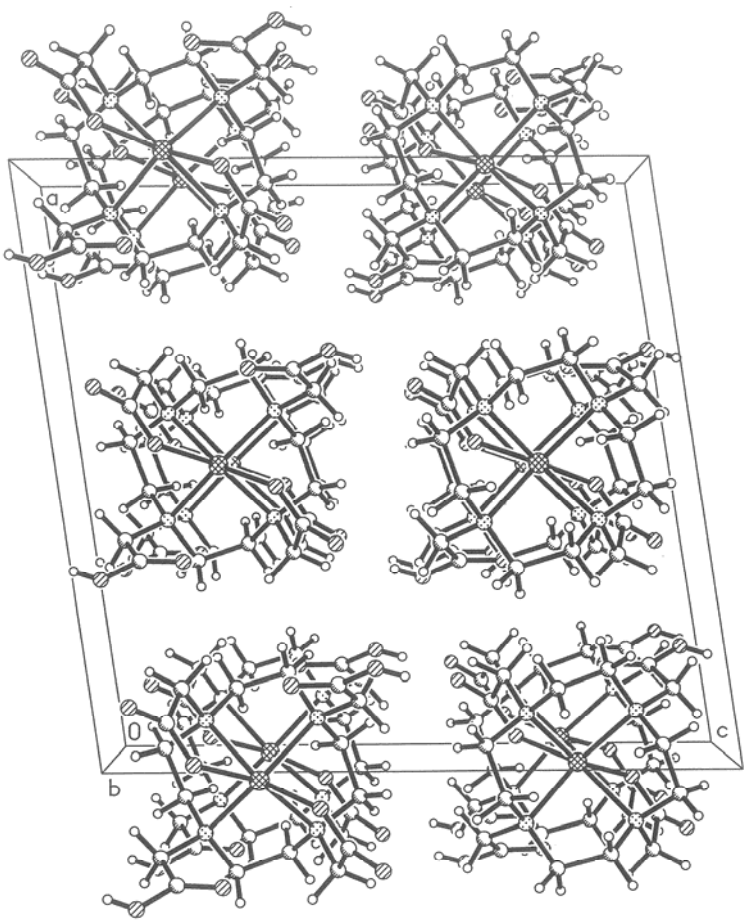


Table S4a. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for Mn(H_2DOTA). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Mn1	5000	2917(1)	2500	16(1)
N1	3899(1)	1983(1)	2580(1)	20(1)
N2	5452(1)	1962(1)	4561(1)	19(1)
O1	3884(1)	3835(1)	1679(1)	23(1)
O2	4925(1)	3809(1)	4306(1)	21(1)
N3	2842(1)	4294(1)	2149(1)	31(1)
N4	5564(1)	4202(1)	6485(1)	28(1)
C1	4156(1)	1190(1)	3599(1)	23(1)
C2	4791(1)	1544(1)	4861(1)	23(1)
C3	5975(1)	1180(1)	4440(1)	22(1)
C4	3478(1)	1557(1)	1230(1)	22(1)
C5	3404(1)	2698(1)	2932(2)	23(1)
C6	3392(1)	3660(1)	2194(1)	22(1)
C7	5855(1)	2658(1)	5644(1)	23(1)
C8	5408(1)	3612(1)	5439(1)	21(1)
Cl1	3343(1)	1151(1)	6317(1)	31(1)
O1W	3158(1)	3493(1)	6184(1)	51(1)

Table S4b. Bond lengths (Å) and bond angles (°) for Mn(H_2DOTA).

Mn(1)-O(1)	2.1601(16)	N(2)-C(3)	1.490(3)
Mn(1)-O(1)#1	2.1601(16)	O(1)-C(6)	1.265(3)
Mn(1)-N(1)	2.3481(19)	O(2)-C(6)	1.252(3)
Mn(1)-N(1)#1	2.3481(18)	O(3)-C(8)	1.210(3)
Mn(1)-N(2)	2.3803(18)	O(4)-C(8)	1.327(3)
Mn(1)-N(2)#1	2.3803(18)	C(1)-C(2)	1.512(3)
N(1)-C(5)	1.472(3)	C(3)-C(4)	1.516(3)
N(1)-C(4)#1	1.482(3)	C(4)-N(1)#1	1.482(3)
N(1)-C(1)	1.485(3)	C(5)-C(6)	1.530(3)
N(2)-C(7)	1.472(3)	C(7)-C(8)	1.514(3)
N(2)-C(2)	1.488(3)		

O(1)-Mn(1)-O(1)#1	101.03(9)	C(1)-N(1)-Mn(1)	111.06(13)
O(1)-Mn(1)-N(1)	73.81(6)	C(7)-N(2)-C(2)	109.78(17)
O(1)#1-Mn(1)-N(1)	157.21(6)	C(7)-N(2)-C(3)	109.60(17)
O(1)-Mn(1)-N(1)#1	157.21(6)	C(2)-N(2)-C(3)	108.72(17)
O(1)#1-Mn(1)-N(1)#1	73.81(6)	C(7)-N(2)-Mn(1)	112.68(13)
N(1)-Mn(1)-N(1)#1	119.25(9)	C(2)-N(2)-Mn(1)	110.69(13)
O(1)-Mn(1)-N(2)	125.72(6)	C(3)-N(2)-Mn(1)	105.22(13)
O(1)#1-Mn(1)-N(2)	91.76(6)	C(6)-O(1)-Mn(1)	119.20(14)
N(1)-Mn(1)-N(2)	74.72(6)	N(1)-C(1)-C(2)	111.07(18)
N(1)#1-Mn(1)-N(2)	76.99(6)	N(2)-C(2)-C(1)	111.55(18)
O(1)-Mn(1)-N(2)#1	91.76(6)	N(2)-C(3)-C(4)	111.76(18)
O(1)#1-Mn(1)-N(2)#1	125.72(6)	N(1)#1-C(4)-C(3)	111.32(18)
N(1)-Mn(1)-N(2)#1	76.99(6)	N(1)-C(5)-C(6)	110.69(18)
N(1)#1-Mn(1)-N(2)#1	74.72(6)	O(2)-C(6)-O(1)	125.0(2)
N(2)-Mn(1)-N(2)#1	122.21(9)	O(2)-C(6)-C(5)	117.4(2)
C(5)-N(1)-C(4)#1	109.23(18)	O(1)-C(6)-C(5)	117.6(2)
C(5)-N(1)-C(1)	111.80(17)	N(2)-C(7)-C(8)	112.93(19)
C(4)#1-N(1)-C(1)	110.71(17)	O(3)-C(8)-O(4)	121.2(2)
C(5)-N(1)-Mn(1)	104.83(13)	O(3)-C(8)-C(7)	123.9(2)
C(4)#1-N(1)-Mn(1)	109.01(13)	O(4)-C(8)-C(7)	114.9(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+3/2

Table S4c. Anisotropic displacement parameters ($Å^2 \times 10^3$) for Mn(H_2DOTA). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + \ldots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	15(1)	14(1)	16(1)	0	4(1)	0
N1	14(1)	11(1)	15(1)	-1(1)	2(1)	0(1)
N2	14(1)	13(1)	15(1)	0(1)	2(1)	0(1)
O1	19(1)	15(1)	24(1)	-2(1)	5(1)	-2(1)
O2	32(1)	20(1)	24(1)	-5(1)	12(1)	-1(1)
O3	39(1)	21(1)	20(1)	-1(1)	8(1)	3(1)
O4	29(1)	21(1)	22(1)	5(1)	7(1)	9(1)
C1	14(1)	15(1)	18(1)	-2(1)	5(1)	-4(1)
C2	12(1)	15(1)	20(1)	-2(1)	2(1)	-3(1)
C3	18(1)	14(1)	15(1)	-2(1)	2(1)	1(1)
C4	17(1)	15(1)	14(1)	-1(1)	3(1)	1(1)
C5	14(1)	17(1)	19(1)	-2(1)	6(1)	1(1)
C6	21(1)	16(1)	13(1)	2(1)	0(1)	3(1)
C7	16(1)	18(1)	15(1)	-1(1)	0(1)	2(1)
C8	16(1)	16(1)	21(1)	2(1)	3(1)	-1(1)

Table S4d. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $Mn(H_2DOTA)$.

	x	y	z	U(eq)
H1A	5985	6788	7310	19
H1B	6834	6030	7044	19
H2A	7056	3807	8122	19
H2B	6869	5965	8477	19
H3A	5352	6698	8358	19
H3B	5740	6232	9273	19
H4A	4676	3906	9387	18
H4B	4289	6065	9136	18
H5A	6902	2227	6979	19
H5B	6703	2999	6065	19
H7A	5802	2438	9516	20
H7B	6701	3389	9526	20
H1	6710(20)	-220(50)	9950(20)	41(10)

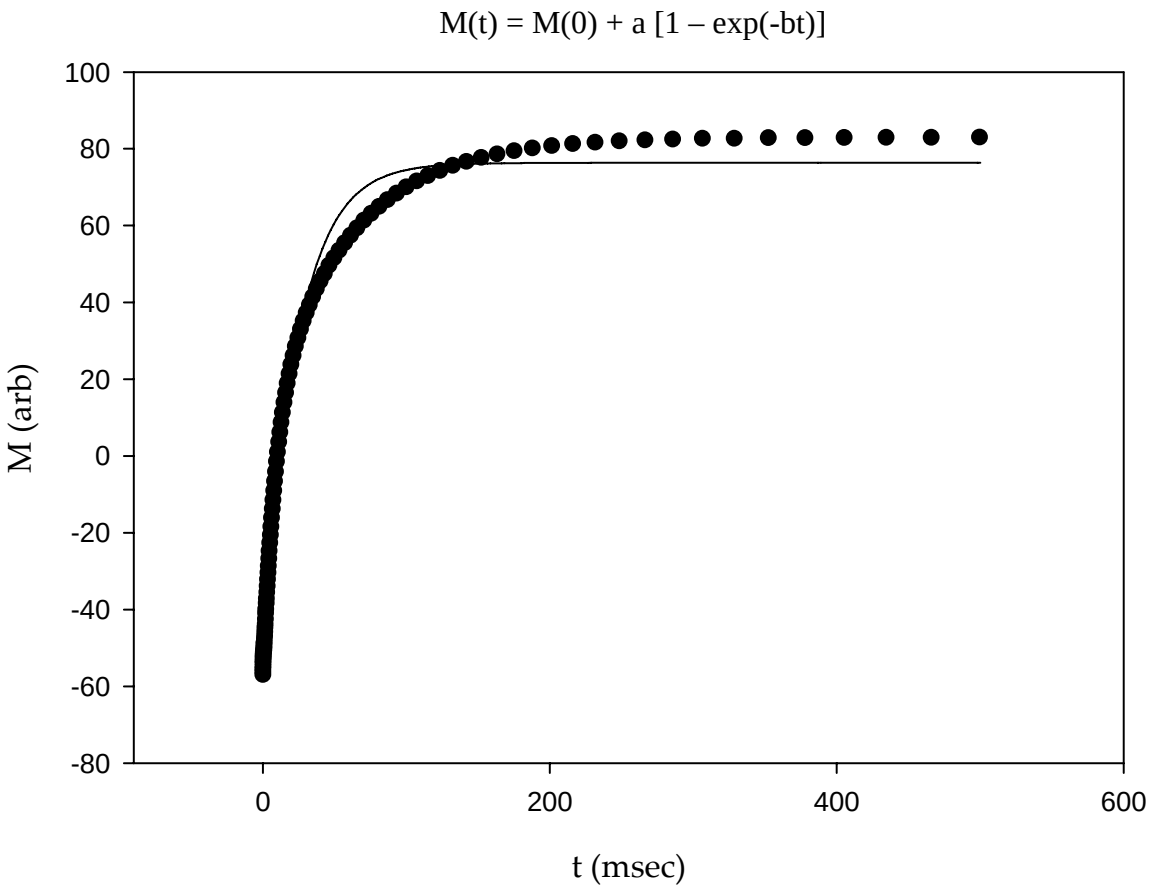
Table S4e. Hydrogen bond for $Mn(H_2DOTA)$. (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O4-H1...O2#2	0.80(3)	1.79(4)	2.577(3)	172(3)

Symmetry transformations used to generate equivalent atoms:

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

Figure S7. Fit of Magnetization *vs* time curve of Mn^{2+} in 1:1 MeOH:H_2O to a single exponential decay.

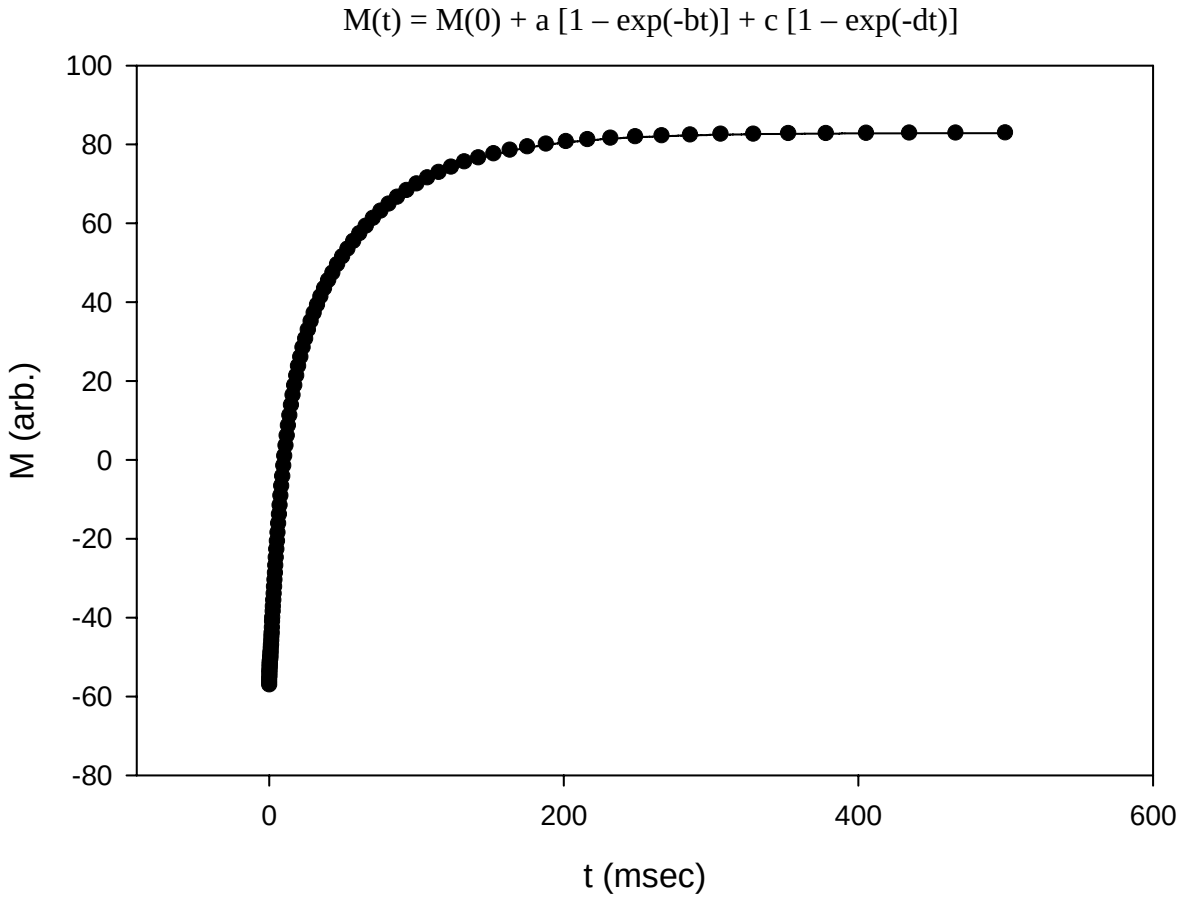


Best Fit Parameters:
M(0) = -54.1666 ± 1.0652
a = 130.5173 ± 1.3350
b = 0.0424 ± 0.0013

R^2 = 0.9900

T_1 = 1/b, thus T_1 = 23.58 ± 0.72 msec

Figure S8. Fit of Magnetization *vs* time curve of Mn^{2+} in 1:1 MeOH:H_2O to a double exponential decay.



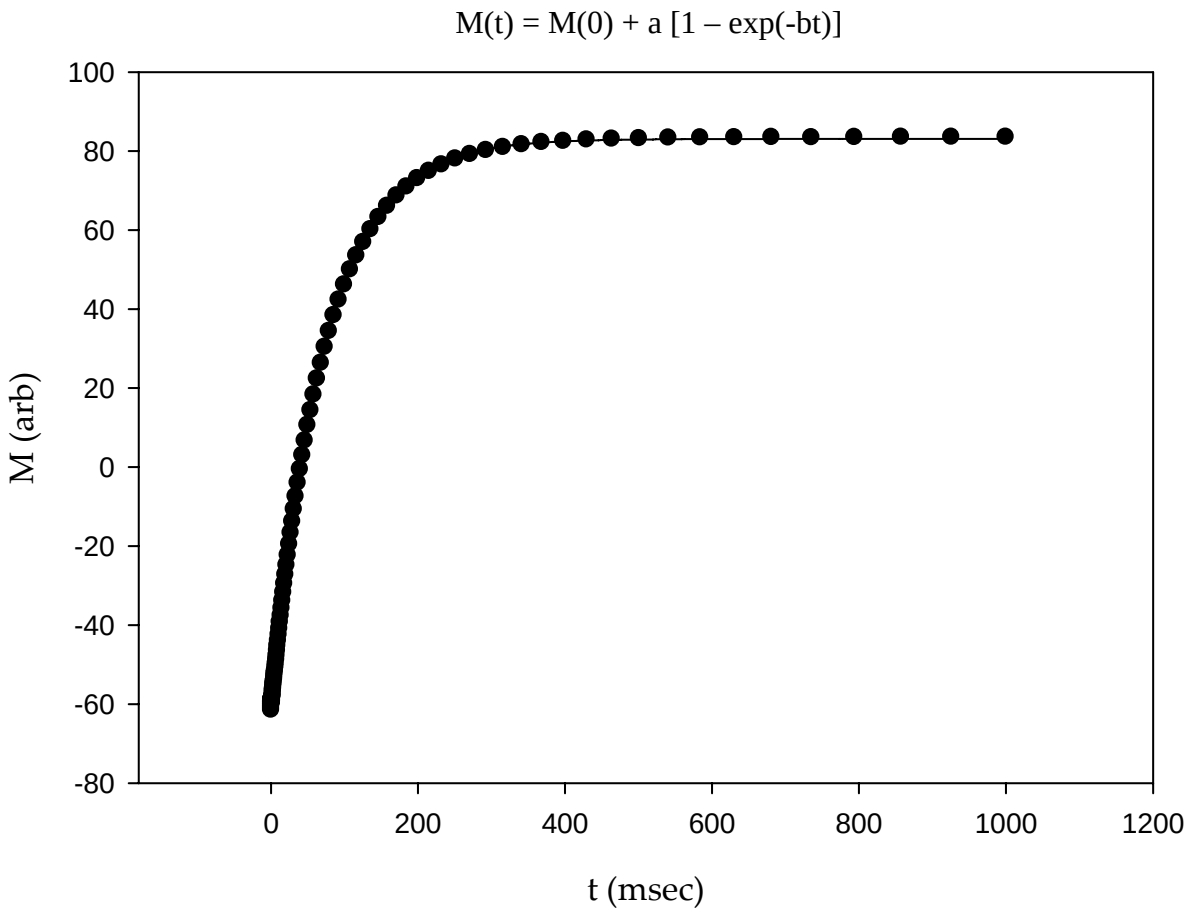
Best Fit Parameters:
M(0) = -61.3217 ± 0.1272
a = 71.4374 ± 0.6675
b = 0.1095 ± 0.0013
c = 72.7559 ± 0.6626
d = 0.0170 ± 0.0002

R^2 = 0.9999

T_1^{fast} = 1/b, thus T_1^{fast} = 9.13 ± 0.11 msec with a relative weight of 49.5%

T_1^{slow} = 1/d, thus T_1^{slow} = 58.52 ± 0.69 msec with a relative weight of 51.5%.

Figure S9. Fit of Magnetization *vs* time curve of $[Mn(DOTAM)]^{2+}$ in 1:1 MeOH:H_2O to a single exponential decay.



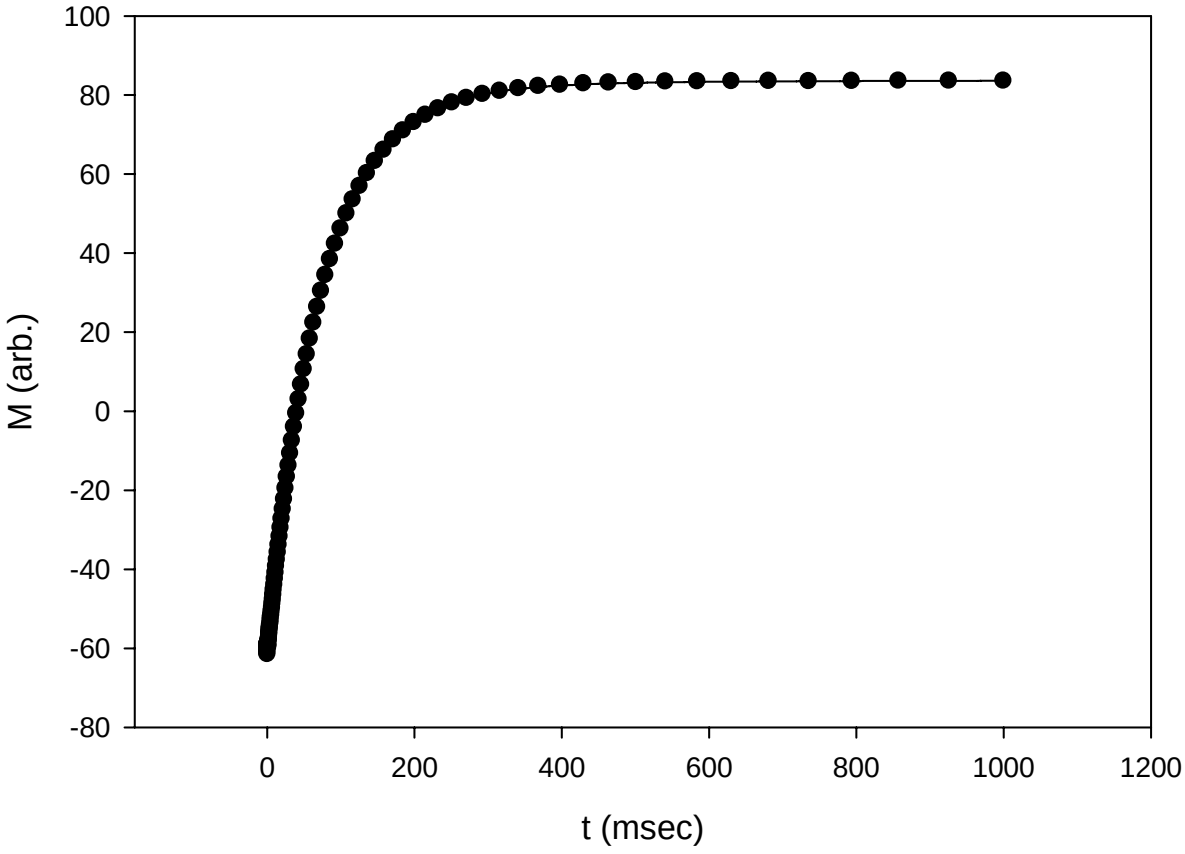
Best Fit Parameters:
M(0) = -62.2335 ± 0.0913
a = 145.3273 ± 0.1416
b = 0.0137 ± 4.1740×10^{-5}

R^2 = 0.9999

T_1 = 1/b, thus T_1 = 72.99 ± 0.22 msec

Figure S10. Fit of Magnetization *vs* time curve of $[Mn(DOTAM)]^{2+}$ in 1:1 MeOH:H_2O to a double exponential decay.

$$M(t) = M(0) + a\,[1 - \exp(-bt)] + c\,[1 - \exp(-dt)]$$



Best Fit Parameters:
M(0) = -62.3392 ± 0.0936
a = 140.3313 ± 6.3414
b = 0.0141 ± 0.0003
c = 5.6410 ± 6.1386
d = 0.0052 ± 0.0037

R^2 = 0.9999.

T_1^{fast} = 1/b, thus T_1^{fast} = 70.92 ± 1.51 msec with a relative weight of 96.1 ± 4.3%

T_1^{slow} = 1/d, thus T_1^{slow} = 192.3 ± 136.8 msec with a relative weight of 3.9 ± 4.2%.

Table S5. Summary of Electrochemical Results.[a]

Complex	E_p^{anodic} (V)	$E_p^{cathodic}$ (V)
Mn(DO2A)	+1.0345	+0.723
Mn(H_2DOTA)	+0.828	+0.521
[Mn(DO3AM)]Cl_2	+0.965	+0.861
[Mn(DO3AM-CyOH)]Cl_2	+0.902	+0.728
[Mn(DOTAM)]Cl_2	+0.984	+0.744

a) Cyclic voltammetry at glassy carbon in 0.1M aqueous $NaNO_3$, scan rate = 100 mV s^{-1}. All potentials are reported *vs* SCE.