Supplementary Information

for

Mn(II) betadiketonates: structural diversity from deceptively minor alterations to synthetic protocols

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1. Summary Table of Crystal Data and Structure Refinement with Acquisition Codes

Table S1. Crystal Data and Structure Refinement with Acquisition Codes

Compound	**1**-K[Mn(tfac)$_3$]	**2**-Mn(tfac)$_2$(OH)$_2$.H$_2$O	**3**-Mn$_3$(tfac)$_6$(OH$_2$)	**4**-Mn(tfac)$_2$DME
Empirical formula	$C_{15}H_{12}F_9KMnO_6$	$C_{10}H_{14}O_7F_6Mn$	$C_{30}H_{28}F_{18}Mn_3O_{14}$	$C_{14}H_{18}F_6MnO_6$
Formula weight	553.29	415.15	1119.34	451.22
Temperature/K	100.01(10)	100.00(10)	100.01(10)	150.15
Crystal system	orthorhombic	monoclinic	triclinic	orthorhombic
Space group	*Pnma*	$P2_1/c$	$P\bar{1}$	*Pbca*
a/Å	13.4514(3)	10.9445(8)	10.7690(2)	12.4430(6)
b/Å	13.7819(3)	6.9902(5)	11.5144(3)	13.5342(6)
c/Å	10.8398(2)	21.9193(19)	16.9696(4)	21.9592(12)
α/°	90	90	85.497(2)	90
β/°	90	102.495(8)	76.820(2)	90
γ/°	90	90	84.015(2)	90
Volume/Å^3	2009.55(7)	1637.2(2)	2034.35(8)	3698.1(3)
Z	4	4	2	8
ρ_{calc}g/cm^3	1.829	1.684	1.827	1.621
μ/mm^{-1}	8.293	7.482	8.822	0.800
F(000)	1100.0	836.0	1114.0	1832.0
Crystal size/mm^3	0.264 × 0.051 × 0.033	0.453 × 0.118 × 0.046	0.175 × 0.106 × 0.07	0.27 × 0.22 × 0.06
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	MoKα (λ = 0.71073)
2Θ range for data collection/°	10.382 to 160.454	8.264 to 135.49	5.358 to 160.618	3.71 to 50.49
Index ranges	$-17 \le h \le 16$, $-17 \le k \le 12$, $-10 \le l \le 13$	$-12 \le h \le 13$, $-7 \le k \le 8$, $-26 \le l \le 26$	$-13 \le h \le 12$, $-14 \le k \le 14$, $-21 \le l \le 19$	$-14 \le h \le 14$, $-16 \le k \le 16$, $-26 \le l \le 26$
Reflections collected	10677	13185	44915	38776
Independent reflections	2268 [R_{int} = 0.0440, R_{sigma} = 0.0316]	2937 [R_{int} = 0.1096, R_{sigma} = 0.0685]	8821 [R_{int} = 0.0320, R_{sigma} = 0.0252]	3345 [R_{int} = 0.0564, R_{sigma} = 0.0312]
Data/restraints/parameters	2268/30/162	2937/7/237	8821/235/761	3345/0/249
Goodness-of-fit on F^2	1.064	1.073	1.054	1.031
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0378, wR_2 = 0.1019	R1 = 0.0891, wR2 = 0.2354	R_1 = 0.0339, wR_2 = 0.0915	R_1 = 0.0295, wR_2 = 0.0626
Final *R* indexes [all data]	R_1 = 0.0396, wR_2 = 0.1032	R1 = 0.1140, wR2 = 0.2524	R_1 = 0.0374, wR_2 = 0.0940	R_1 = 0.0443, wR_2 = 0.0660
Largest diff. peak/hole / e Å^{-3}	0.51/-0.45	1.60/-1.27	0.49/-0.43	0.29/-0.26
CCDC Acquisition Code	2441294	2441295	2441296	2441638

Compound	**5**-Mn(hfac)$_2$DME	**6**-Mn(hfac)$_2$THF(OH$_2$)	**7**-Mn(hfac)$_2$(THF)$_2$	**8**-Mn(hfac)$_2$NCCH$_3$(OH$_2$)
Empirical formula	$C_{14}H_{12}F_{12}MnO_6$	$C_{14}H_{12}F_{12}MnO_6$	$C_{18}H_{18}O_6F_{12}Mn$	$C_{12}H_7NO_5F_{12}Mn$
Formula weight	559.18	559.18	613.26	528.13
Temperature/K	200.00	99.99(10)	150.03	100.0(2)
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/n$	C2/c	*Pnma*	*Pnma*
a/Å	11.9426(3)	21.5361(3)	15.4825(8)	9.1029(3)
b/Å	12.8936(3)	6.81320(10)	19.6279(8)	21.7344(6)
c/Å	14.0015(3)	27.8521(5)	7.7219(4)	9.0051(3)
α/°	90	90	90	90
β/°	100.799(2)	104.621(2)	90	90
γ/°	90	90	90	90
Volume/Å^3	2117.81(9)	3954.39(11)	2346.6(2)	1781.62(10)
Z	4	8	4	4
ρ_{calc}g/cm^3	1.754	1.878	1.736	1.969
μ/mm^{-1}	6.359	6.811	0.691	7.488
F(000)	1108.0	2216.0	1228.0	1036.0
Crystal size/mm^3	0.147 × 0.138 × 0.093	0.505 × 0.074 × 0.048	0.3 × 0.23 × 0.17	0.199 × 0.174 × 0.157
Radiation	CuKα (λ = 1.54184)	Cu Kα (λ = 1.54184)	MoKα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.944 to 150.016	6.56 to 160.85	4.15 to 54.932	8.136 to 149.832
Index ranges	$-12 \le h \le 14$, $-12 \le k \le 15$, $-16 \le l \le 17$	$-27 \le h \le 21$, $-8 \le k \le 8$, $-34 \le l \le 35$	$-20 \le h \le 20$, $-23 \le k \le 25$, $-10 \le l \le 9$	$-8 \le h \le 11$, $-23 \le k \le 26$, $-11 \le l \le 10$
Reflections collected	20736	40093	40469	7617
Independent reflections	4248 [R_{int} = 0.0348, R_{sigma} = 0.0251]	4294 [R_{int} = 0.0672, R_{sigma} = 0.0304]	2764 [R_{int} = 0.0278, R_{sigma} = 0.0128]	1770 [R_{int} = 0.0406, R_{sigma} = 0.0239]
Data/restraints/parameters	4248/128/390	4294/12/321	2764/79/212	1770/1/152
Goodness-of-fit on F^2	1.034	1.095	1.027	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0391, wR_2 = 0.1016	R_1 = 0.0941, wR_2 = 0.2397	R_1 = 0.0308, wR_2 = 0.0768	R_1 = 0.0766, wR_2 = 0.1784
Final R indexes [all data]	R_1 = 0.0445, wR_2 = 0.1056	R_1 = 0.0977, wR_2 = 0.2417	R_1 = 0.0374, wR_2 = 0.0812	R_1 = 0.0842, wR_2 = 0.1821
Largest diff. peak/hole / e Å^{-3}	0.51/-0.41	1.20/-1.71	0.36/-0.30	1.13/-0.90
CCDC Acquisition Code	2441639	2441297	2441640	2441298

2. Detailed Crystal Structure Report for 1, K[Mn(tfac)$_3$]

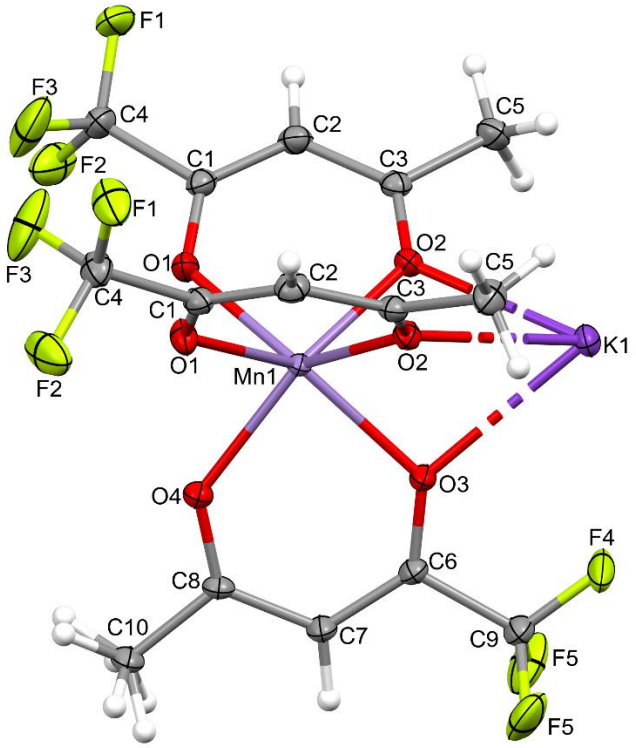


Fig. S1. Displacement ellipsoids plot (40% probability) depicting one ion pair of the complex salt in structure **1** (two asymmetric units). The atom numbering scheme used in the Tables is shown. There is rotational positional disorder in methyl group hydrogen atoms of C10 (shown).

The ion pair (Fig. S1) is found at Wyckoff position 4*c* in *Pnma*, No. 62, with the Mn^{2+} (fractional coordinates: 0.71602(3), 0.75, 0.26992(4)) and K^+ (fractional coordinates: 0.46122(4), 0.75, 0.38646(6)) ions, the O3,4, C6-10 and H7 atoms located on a mirror symmetry plane. Hence, the other atoms that are off-plane (F5, the H atoms on C10, and the whole of the O1,2 tfac ligands are duplicated by symmetry and are identical to their mirror image (as viewed, all the rear atoms are described by the x, 1.5-y, z symmetry operation.) Consequently, the C10 methyl H atoms are each at half occupancy and the ensemble is 50:50 disordered by symmetry. Fig. 1 in the main article depicts three of these ion pairs, plus one extra K^+ to emphasize the polymeric chain formed in the lattice. This whole chain sits on the *m* planes that are ⊥ to *a* and intercept this axis at 0.25 and 0.75 (Fig. S2).

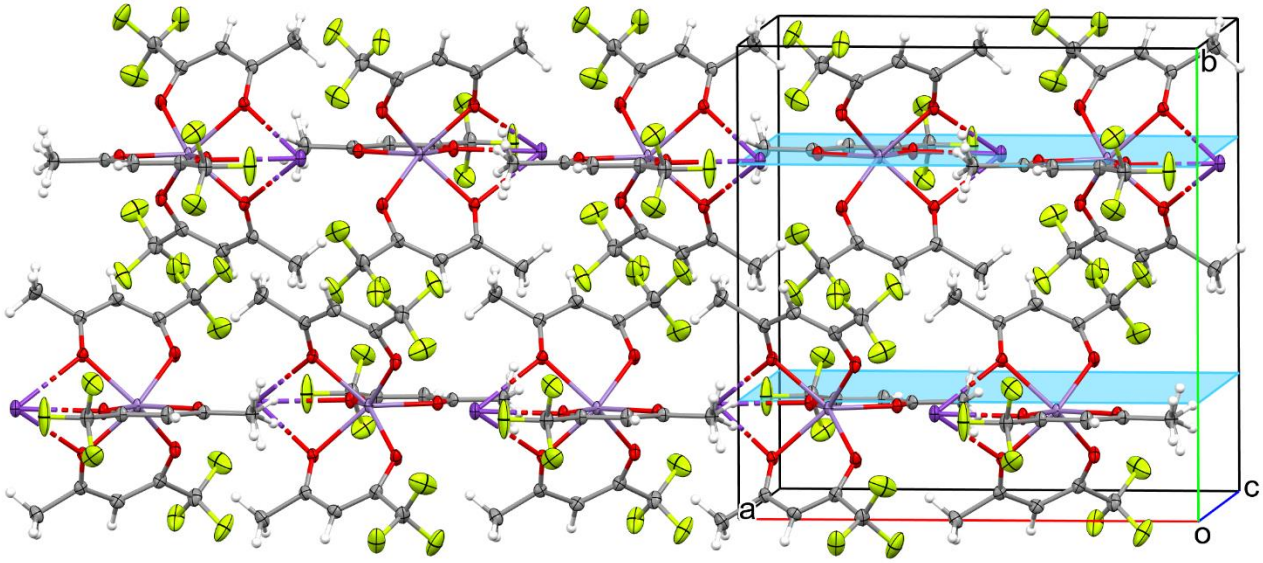


Fig. S2. Displacement ellipsoids plot (40%) two offset polymeric chains in **1** with the two *m* in blue.

Table S2 Crystal data and structure refinement for 1-K[Mn(tfac)$_3$].

Identification code	RB23048f
Empirical formula	$C_{15}H_{12}F_9KMnO_6$
Formula weight	553.29
Temperature/K	100.01(10)
Crystal system	orthorhombic
Space group	Pnma
a/Å	13.4514(3)
b/Å	13.7819(3)
c/Å	10.8398(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2009.55(7)
Z	4
ρ_{calc}g/cm^3	1.829
μ/mm^{-1}	8.293
F(000)	1100.0
Crystal size/mm^3	0.264 × 0.051 × 0.033
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.382 to 160.454
Index ranges	-17 ≤ h ≤ 16, -17 ≤ k ≤ 12, -10 ≤ l ≤ 13
Reflections collected	10677
Independent reflections	2268 [R_{int} = 0.0440, R_{sigma} = 0.0316]
Data/restraints/parameters	2268/30/162
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0378, wR_2 = 0.1019
Final R indexes [all data]	R_1 = 0.0396, wR_2 = 0.1032
Largest diff. peak/hole / e Å^{-3}	0.51/-0.45

Table S3 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1-K[Mn(tfac)$_3$]. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mn1	7160.2(3)	7500	2699.2(4)	14.52(14)
K1	9612.2(4)	7500	1135.4(6)	22.84(17)
F1	7656.0(12)	4888.3(15)	-1039.7(15)	46.9(5)
F2	8817.4(13)	4767.3(15)	280.1(16)	54.0(5)
F3	8641.8(17)	6079.1(14)	-746.2(19)	64.4(6)
F4	5478.3(17)	7500	6493(2)	70.6(11)
F5	6613.6(15)	8267.4(14)	7450.5(17)	52.8(5)
O1	7865.1(10)	6490.2(12)	1430.5(14)	23.4(3)
O2	5957.5(10)	6450.7(11)	2507.7(13)	18.9(3)
O3	6594.7(15)	7500	4572.3(18)	20.3(4)
O4	8573.3(15)	7500	3640.9(19)	19.1(4)
C1	7475.5(16)	5794.5(15)	838.8(18)	20.7(4)
C2	6561.5(16)	5367.6(15)	991.3(19)	22.7(4)

Table S3 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 1-K[Mn(tfac)$_3$]. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C3	5846.9(15)	5704.1(15)	1858.6(18)	19.6(4)
C4	8145.0(17)	5380.0(18)	-181(2)	27.2(5)
C5	4893.7(17)	5145.9(18)	1999(2)	27.5(5)
C6	7074(2)	7500	5564(3)	19.5(6)
C7	8095(2)	7500	5745(3)	23.5(6)
C8	8794(2)	7500	4771(2)	18.2(5)
C9	6429(2)	7500	6748(3)	27.3(7)
C10	9875(2)	7500	5122(3)	24.6(6)

Table S4 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 1-K[Mn(tfac)$_3$] The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	11.1(2)	21.3(2)	11.1(2)	0	-0.78(14)	0
K1	13.2(3)	32.8(3)	22.5(3)	0	-1.4(2)	0
F1	32.7(8)	75.7(12)	32.3(8)	-29.4(8)	-1.1(6)	3.9(8)
F2	42.3(9)	80.0(13)	39.7(9)	-18.7(9)	-6.0(7)	33.3(9)
F3	80.0(14)	55.5(11)	57.8(11)	-18.1(9)	48.5(11)	-16.5(10)
F4	18.0(10)	171(3)	22.7(11)	0	5.5(8)	0
F5	62.5(12)	56.4(10)	39.6(8)	-20.9(8)	28.3(8)	-10.6(9)
O1	15.1(7)	31.9(8)	23.3(7)	-9.2(6)	1.5(5)	-0.9(6)
O2	15.5(6)	23.1(7)	18.0(6)	-2.2(5)	-0.8(5)	-2.0(5)
O3	14.5(9)	31.9(10)	14.4(9)	0	0.4(7)	0
O4	17.1(7)	23.6(7)	16.8(7)	0	-1.7(6)	0
C1	20.8(10)	25.7(10)	15.4(8)	-2.0(7)	-1.2(8)	3.8(8)
C2	25.5(10)	23.9(9)	18.9(9)	-3.9(8)	-2.4(8)	-1.6(8)
C3	19.5(9)	23.2(9)	16.1(9)	1.4(7)	-3.7(7)	-0.4(7)
C4	23.7(10)	35.1(11)	22.9(10)	-8.6(9)	1.9(8)	0.9(9)
C5	25.1(11)	32.2(11)	25.1(10)	-3.5(9)	-1.1(9)	-8.9(9)
C6	19.1(13)	26.3(13)	13.1(12)	0	0.8(10)	0
C7	19.0(13)	37.9(16)	13.6(13)	0	-1.4(11)	0
C8	18.8(13)	21.9(12)	14.0(12)	0	-4.7(10)	0
C9	21.4(14)	43.7(18)	16.7(13)	0	1.5(11)	0
C10	18.8(13)	37.3(16)	17.8(13)	0	-5.1(11)	0

Table S5 Bond Lengths for 1-K[Mn(tfac)$_3$].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	K1	3.7084(7)	F5	C9	1.327(3)
Mn1	K1^1	3.6528(7)	O1	C1	1.267(3)
Mn1	O1	2.1742(15)	O2	C3	1.255(2)
Mn1	O1^2	2.1742(15)	O3	C6	1.254(4)
Mn1	O2^2	2.1797(14)	O4	C8	1.261(3)
Mn1	O2	2.1797(14)	C1	C2	1.373(3)
Mn1	O3	2.168(2)	C1	C4	1.536(3)
Mn1	O4	2.158(2)	C2	H2	0.9500

Table S5 Bond Lengths for 1-K[Mn(tfac)$_3$].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
K1	F3	3.114(2)	C2	C3	1.422(3)
K1	F3^2	3.114(2)	C3	C5	1.503(3)
K1	F4^3	3.078(2)	C5	H5A	0.9800
K1	O1^2	2.7499(15)	C5	H5B	0.9800
K1	O1	2.7499(15)	C5	H5C	0.9800
K1	O2^4	2.7440(15)	C6	C7	1.386(4)
K1	O2^3	2.7440(15)	C6	C9	1.549(4)
K1	O3^3	2.775(2)	C7	H7	0.9500
K1	O4	3.054(2)	C7	C8	1.413(4)
F1	C4	1.326(3)	C8	C10	1.503(4)
F2	C4	1.334(3)	C10	H10A	0.9800
F3	C4	1.323(3)	C10	H10B	0.9800
F4	C9	1.308(4)	C10	H10C	0.9800

[1]-1/2+X,+Y,1/2-Z; [2]+X,3/2-Y,+Z; [3]1/2+X,+Y,1/2-Z; [4]1/2+X,3/2-Y,1/2-Z

Table S6 Bond Angles for 1-K[Mn(tfac)$_3$].

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
K1^1	Mn1	K1	173.031(15)	O2^3	K1	F4^3	104.27(5)
O1^2	Mn1	K1^1	128.90(4)	O2^4	K1	O1^2	103.57(5)
O1^2	Mn1	K1	47.39(4)	O2^3	K1	O1	103.57(5)
O1	Mn1	K1	47.39(4)	O2^4	K1	O1	140.17(5)
O1	Mn1	K1^1	128.90(4)	O2^3	K1	O1^2	140.17(5)
O1^2	Mn1	O1	79.59(9)	O2^4	K1	O2^3	63.60(6)
O1^2	Mn1	O2	133.48(6)	O2^4	K1	O3^3	60.95(5)
O1	Mn1	O2	80.72(6)	O2^3	K1	O3^3	60.95(5)
O1	Mn1	O2^2	133.48(6)	O2^4	K1	O4	79.93(5)
O1^2	Mn1	O2^2	80.72(6)	O2^3	K1	O4	79.93(5)
O2^2	Mn1	K1	128.07(4)	O3^3	K1	Mn1^3	36.28(4)
O2	Mn1	K1^1	48.44(4)	O3^3	K1	Mn1	168.85(5)
O2^2	Mn1	K1^1	48.44(4)	O3^3	K1	F3^2	102.81(5)
O2	Mn1	K1	128.06(4)	O3^3	K1	F3	102.81(5)
O2^2	Mn1	O2	83.12(8)	O3^3	K1	F4^3	51.71(6)
O3	Mn1	K1	137.74(6)	O3^3	K1	O4	133.28(6)
O3	Mn1	K1^1	49.23(5)	O4	K1	Mn1	35.57(4)
O3	Mn1	O1	138.19(5)	O4	K1	Mn1^3	97.00(4)
O3	Mn1	O1^2	138.19(5)	O4	K1	F3^2	112.99(4)
O3	Mn1	O2^2	80.14(5)	O4	K1	F3	112.99(4)
O3	Mn1	O2	80.14(5)	O4	K1	F4^3	175.01(6)
O4	Mn1	K1^1	131.53(6)	C4	F3	K1	111.48(15)
O4	Mn1	K1	55.44(6)	C9	F4	K1^1	124.40(18)
O4	Mn1	O1^2	85.12(6)	Mn1	O1	K1	97.03(6)
O4	Mn1	O1	85.12(6)	C1	O1	Mn1	128.62(13)
O4	Mn1	O2	134.34(4)	C1	O1	K1	132.65(13)
O4	Mn1	O2^2	134.34(4)	Mn1	O2	K1^1	95.09(5)

Table S6 Bond Angles for 1-K[Mn(tfac)$_3$].

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O4	Mn1	O3	82.30(8)	C3	O2	Mn1	133.25(13)
Mn1^3	K1	Mn1	132.566(18)	C3	O2	K1^1	130.86(13)
F3^2	K1	Mn1	85.79(3)	Mn1	O3	K1^1	94.49(7)
F3	K1	Mn1	85.79(3)	C6	O3	Mn1	128.49(18)
F3^2	K1	Mn1^3	128.30(4)	C6	O3	K1^1	137.02(18)
F3	K1	Mn1^3	128.30(4)	Mn1	O4	K1	88.99(7)
F3	K1	F3^2	77.92(9)	C8	O4	Mn1	131.83(19)
F4^3	K1	Mn1^3	87.99(4)	C8	O4	K1	139.17(18)
F4^3	K1	Mn1	139.44(5)	O1	C1	C2	129.32(19)
F4^3	K1	F3	63.41(4)	O1	C1	C4	113.78(18)
F4^3	K1	F3^2	63.41(4)	C2	C1	C4	116.89(19)
O1^2	K1	Mn1^3	139.61(4)	C1	C2	C3	123.03(19)
O1	K1	Mn1^3	139.61(4)	O2	C3	C2	123.89(19)
O1	K1	Mn1	35.58(3)	O2	C3	C5	117.64(18)
O1^2	K1	Mn1	35.58(3)	C2	C3	C5	118.47(19)
O1	K1	F3^2	92.08(6)	F1	C4	F2	106.0(2)
O1^2	K1	F3^2	53.12(4)	F1	C4	C1	113.86(18)
O1	K1	F3	53.11(4)	F2	C4	C1	111.31(18)
O1^2	K1	F3	92.08(6)	F3	C4	F1	107.3(2)
O1^2	K1	F4^3	115.54(5)	F3	C4	F2	107.0(2)
O1	K1	F4^3	115.54(5)	F3	C4	C1	111.02(19)
O1	K1	O1^2	60.81(7)	O3	C6	C7	129.1(3)
O1	K1	O3^3	148.59(3)	O3	C6	C9	115.0(3)
O1^2	K1	O3^3	148.59(3)	C7	C6	C9	116.0(3)
O1	K1	O4	60.36(5)	C6	C7	C8	123.6(3)
O1^2	K1	O4	60.36(5)	O4	C8	C7	124.7(3)
O2^3	K1	Mn1^3	36.47(3)	O4	C8	C10	118.2(3)
O2^3	K1	Mn1	109.97(3)	C7	C8	C10	117.1(2)
O2^4	K1	Mn1	109.97(3)	F4	C9	F5	107.68(19)
O2^4	K1	Mn1^3	36.47(3)	F4	C9	F5^2	107.69(19)
O2^3	K1	F3^2	163.51(5)	F4	C9	C6	111.9(3)
O2^3	K1	F3	107.22(5)	F5^2	C9	F5	105.7(3)
O2^4	K1	F3^2	107.22(6)	F5^2	C9	C6	111.77(18)
O2^4	K1	F3	163.51(5)	F5	C9	C6	111.77(18)
O2^4	K1	F4^3	104.27(5)				

[1]-1/2+X,+Y,1/2-Z; [2]+X,3/2-Y,+Z; [3]1/2+X,+Y,1/2-Z; [4]1/2+X,3/2-Y,1/2-Z

Table S7 Torsion Angles for 1-K[Mn(tfac)$_3$].

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Mn1	O1	C1	C2	-13.4(3)	K1	O4	C8	C10	0.000(1)
Mn1	O1	C1	C4	167.24(14)	O1	C1	C2	C3	3.7(4)
Mn1	O2	C3	C2	-1.9(3)	O1	C1	C4	F1	-159.5(2)
Mn1	O2	C3	C5	179.09(14)	O1	C1	C4	F2	80.7(3)
Mn1	O3	C6	C7	0.000(1)	O1	C1	C4	F3	-38.3(3)

Table S7 Torsion Angles for 1-K[Mn(tfac)$_3$].

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Mn1	O3	C6	C9	180.000(0)	O3	C6	C7	C8	0.000(1)
Mn1	O4	C8	C7	0.000(0)	O3	C6	C9	F4	0.000(0)
Mn1	O4	C8	C10	180.000(0)	O3	C6	C9	F5	-120.9(2)
K1	F3	C4	F1	172.14(14)	O3	C6	C9	F5^2	120.9(2)
K1	F3	C4	F2	-74.47(18)	C1	C2	C3	O2	4.5(3)
K1	F3	C4	C1	47.1(2)	C1	C2	C3	C5	-176.5(2)
K1^1	F4	C9	F5^2	123.22(18)	C2	C1	C4	F1	21.0(3)
K1^1	F4	C9	F5	123.21(18)	C2	C1	C4	F2	-98.7(2)
K1^1	F4	C9	C6	0.000(1)	C2	C1	C4	F3	142.2(2)
K1	O1	C1	C2	175.00(16)	C4	C1	C2	C3	176.96(19)
K1	O1	C1	C4	5.6(3)	C6	C7	C8	O4	0.000(1)
K1^1	O2	C3	C2	165.23(14)	C6	C7	C8	C10	180.000(0)
K1^1	O2	C3	C5	-13.8(3)	C7	C6	C9	F4	180.000(0)
K1^1	O3	C6	C7	180.000(0)	C7	C6	C9	F5^2	-59.1(2)
K1^1	O3	C6	C9	0.000(1)	C7	C6	C9	F5	59.1(2)
K1	O4	C8	C7	180.000(0)	C9	C6	C7	C8	180.000(0)

[1]-1/2+X,+Y,1/2-Z; [2]+X,3/2-Y,+Z

Table S8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1-K[Mn(tfac)$_3$].

Atom	*x*	*y*	*z*	U(eq)
H2	6398.89	4822.28	494.68	27
H5A	4897.31	4799.92	2788.91	41
H5B	4832.21	4677.58	1323	41
H5C	4330.1	5596.11	1976.86	41
H7	8337.09	7500	6567.82	28
H10A	9974.46	7079.15	5840.15	37
H10B	10082.86	8162.37	5325.59	37
H10C	10271.75	7258.49	4428.94	37

Table S9 Atomic Occupancy for 1-K[Mn(tfac)$_3$].

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
H10A	0.5	H10B	0.5	H10C	0.5

Experimental

Single crystals of $C_{15}H_{12}F_9KMnO_6$ **1-K[Mn(tfac)$_3$]** were grown from methanol by slow evaporation to dryness. A suitable crystal was selected and mounted in Paratone™ oil on a 100 μm MiTeGen loop on a SuperNova, Dual, Cu at home/near, Pilatus 200K diffractometer. The crystal was kept at 100.01(10) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

3. Detailed Crystal Structure Report for 2, $Mn(tfac)_2(OH)_2.H_2O$

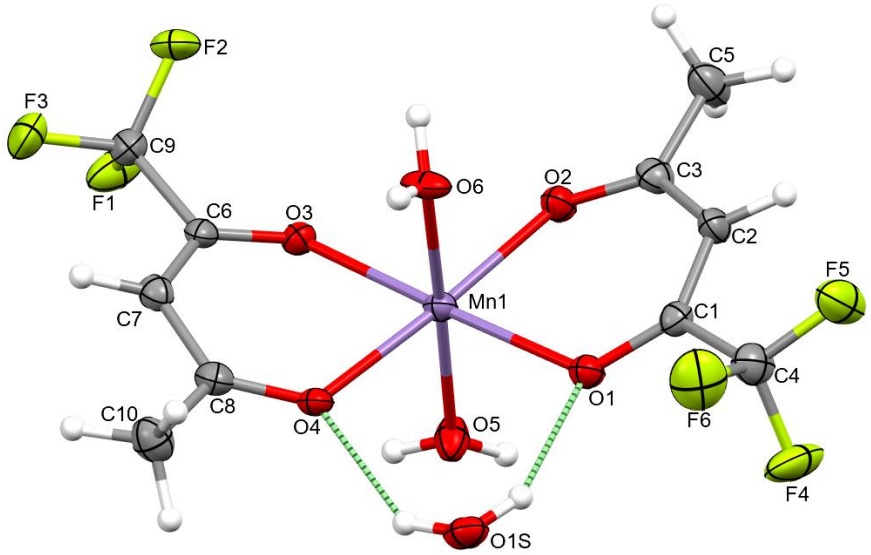


Fig. S3. Displacement ellipsoids plot (40% probability) depicting the asymmetric unit in structure **2**, consisting of the neutral $[Mn(tfac)_2(OH)_2]$ complex and the H-bonded water of crystallization. The atom numbering scheme used in the Tables is shown.

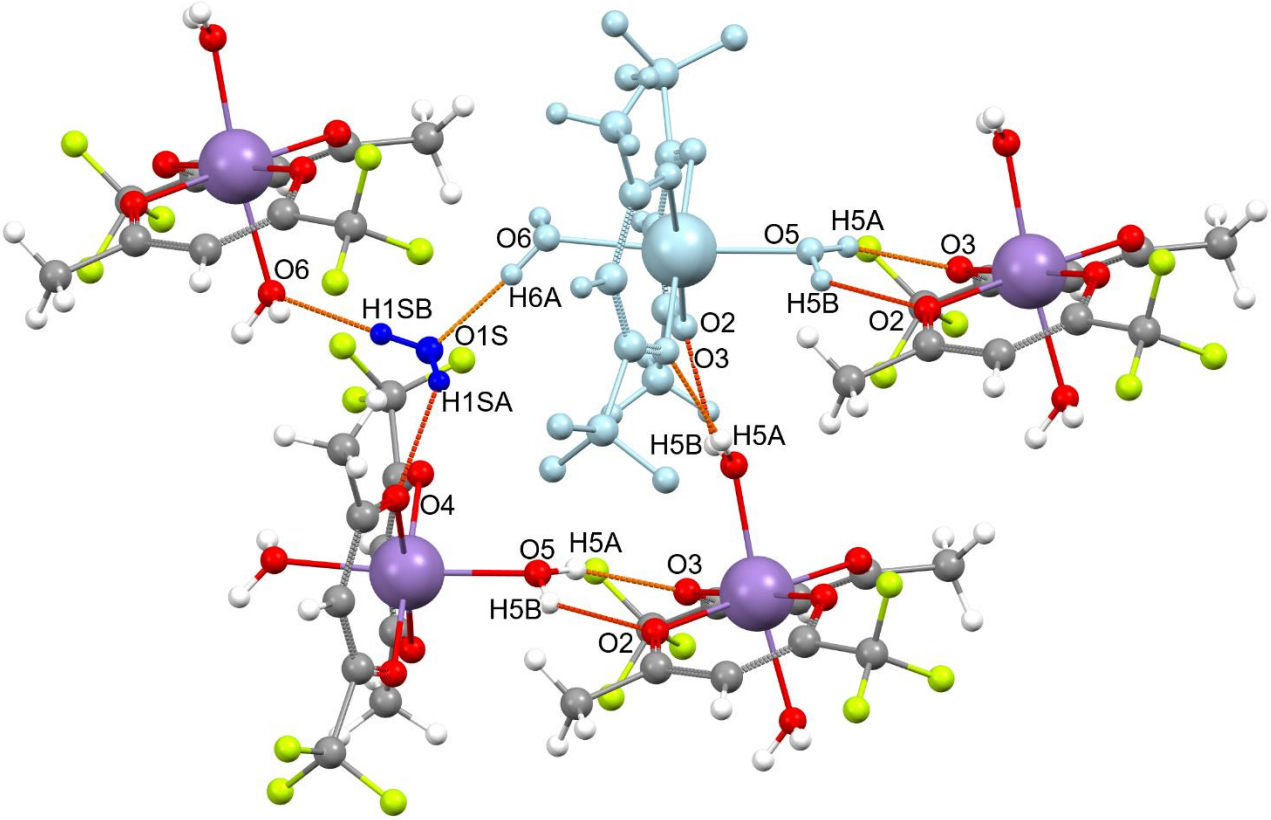


Fig. S4. Ball and stick plot showing the asymmetric unit light blue for $[Mn(tfac)_2(OH)_2]$ and dark blue for water. The strongest H-bond is from the donor aqua to the acceptor water (orange dashed line) and the remaining slightly longer H-bonds) red dashed lines.

Table S10 Crystal data and structure refinement for 2-Mn(tfac)$_2$(OH)$_2$.H$_2$O.

Identification code	RB24064-Rev2b
Empirical formula	$C_{10}H_{14}O_7F_6Mn$
Formula weight	415.15
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.9445(8)
b/Å	6.9902(5)
c/Å	21.9193(19)
α/°	90
β/°	102.495(8)
γ/°	90
Volume/Å^3	1637.2(2)
Z	4
ρ_{calc}g/cm^3	1.684
μ/mm^{-1}	7.482
F(000)	836.0
Crystal size/mm^3	0.453 × 0.118 × 0.046
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.264 to 135.49
Index ranges	$-12 \le h \le 13$, $-7 \le k \le 8$, $-26 \le l \le 26$
Reflections collected	13112
Independent reflections	2937 [R_{int} = 0.1096, R_{sigma} = 0.0685]
Data/restraints/parameters	2937/7/237
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0891, wR_2 = 0.2354
Final R indexes [all data]	R_1 = 0.1140, wR_2 = 0.2524
Largest diff. peak/hole / e Å^{-3}	1.60/-1.27

Table S11 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2-Mn(tfac)$_2$(OH)$_2$.H$_2$O. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mn1	2968.9(9)	4134.9(13)	2596.9(5)	21.3(4)
F1	3960(4)	7351(7)	768(2)	47.8(12)
O1	2646(4)	2659(6)	3413(2)	25.5(10)
C1	2759(6)	3416(9)	3941(3)	22.5(13)
F2	2822(5)	9139(6)	1207(2)	47.9(12)
O2	4159(4)	5924(6)	3272(2)	27.5(10)
C2	3425(7)	5085(10)	4175(3)	28.1(15)
F3	2006(5)	7688(7)	352(2)	48.6(12)
O3	3333(4)	5666(6)	1806(2)	24.1(10)
C3	4121(6)	6211(10)	3833(3)	27.7(14)
F4	2700(6)	689(7)	4551(3)	58.8(15)
O4	1720(4)	2479(6)	1888(2)	24.3(10)
C4	2124(7)	2347(11)	4381(4)	35.5(17)

Table S11 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2-Mn(tfac)$_2$(OH)$_2$.H$_2$O. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F5	2075(5)	3240(7)	4906(2)	52.6(14)
O5	4434(5)	2151(8)	2554(2)	34.1(12)
C5	4872(8)	7841(12)	4154(4)	40.5(18)
F6	949(5)	1941(8)	4105(3)	58.0(14)
O6	1356(5)	5923(6)	2625(3)	33.4(12)
C6	2571(6)	5791(9)	1283(3)	24.5(14)
C7	1564(6)	4642(10)	1033(3)	25.8(14)
C8	1206(7)	2971(10)	1342(3)	28.9(15)
C9	2832(6)	7472(10)	894(3)	29.3(15)
C10	136(7)	1810(12)	1003(4)	37.1(17)
O1S	1158(5)	-193(7)	2710(2)	31.7(11)

Table S12 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 2-Mn(tfac)$_2$(OH)$_2$.H$_2$O. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	25.7(6)	16.0(5)	22.7(6)	-0.8(4)	6.1(4)	-1.0(4)
F1	50(3)	37(2)	63(3)	20(2)	27(2)	8(2)
O1	32(2)	21(2)	25(2)	-1.1(18)	8.5(18)	-1.7(18)
C1	23(3)	23(3)	23(3)	3(3)	8(2)	3(2)
F2	80(3)	17(2)	47(3)	-1.4(18)	14(2)	2(2)
O2	36(2)	24(2)	24(2)	-1.4(18)	10.2(19)	-4.3(18)
C2	40(4)	24(3)	21(3)	-3(3)	10(3)	-1(3)
F3	67(3)	40(3)	33(2)	14(2)	-2(2)	2(2)
O3	28(2)	21(2)	22(2)	2.0(17)	5.4(18)	-1.8(17)
C3	32(3)	25(3)	28(4)	-3(3)	11(3)	3(3)
F4	93(4)	28(2)	67(4)	21(2)	44(3)	17(2)
O4	33(2)	14(2)	26(2)	-1.1(17)	8.1(18)	0.3(17)
C4	45(4)	33(4)	34(4)	-1(3)	20(3)	-2(3)
F5	86(4)	36(3)	45(3)	-4(2)	36(3)	-14(2)
O5	35(3)	45(3)	23(3)	2(2)	7(2)	16(2)
C5	56(5)	37(4)	33(4)	-9(3)	18(4)	-13(4)
F6	50(3)	66(4)	61(3)	4(3)	19(2)	-26(3)
O6	32(2)	17(2)	50(3)	-7(2)	7(2)	4.7(19)
C6	36(3)	17(3)	22(3)	-1(2)	9(3)	5(2)
C7	25(3)	26(3)	25(3)	-3(3)	3(3)	3(3)
C8	35(4)	22(3)	28(4)	-3(3)	6(3)	3(3)
C9	36(4)	25(3)	26(3)	2(3)	4(3)	3(3)
C10	36(4)	39(4)	36(4)	-6(3)	6(3)	-8(3)
O1S	35(3)	18(2)	40(3)	2(2)	4(2)	-3.1(18)

Table S13 Bond Lengths for 2-Mn(tfac)$_2$(OH)$_2$.H$_2$O.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	O1	2.160(5)	C4	F5	1.321(9)
Mn1	O2	2.149(5)	C4	F6	1.328(9)
Mn1	O3	2.147(4)	O5	H5A	0.84(2)
Mn1	O4	2.168(4)	O5	H5B	0.84(2)
Mn1	O5	2.137(5)	C5	H5C	0.9800
Mn1	O6	2.175(5)	C5	H5D	0.9800
F1	C9	1.325(9)	C5	H5E	0.9800
O1	C1	1.254(8)	O6	H6A	0.83(2)
C1	C2	1.412(9)	O6	H6B	0.84(2)
C1	C4	1.504(10)	C6	C7	1.378(10)
F2	C9	1.354(8)	C6	C9	1.516(9)
O2	C3	1.255(8)	C7	H7	0.9500
C2	H2	0.9500	C7	C8	1.445(10)
C2	C3	1.418(10)	C8	C10	1.485(9)
F3	C9	1.336(8)	C10	H10A	0.9800
O3	C6	1.266(8)	C10	H10B	0.9800
C3	C5	1.490(10)	C10	H10C	0.9800
F4	C4	1.333(9)	O1S	H1SA	0.84(2)
O4	C8	1.256(8)	O1S	H1SB	0.84(2)

Table S14 Bond Angles for 2-Mn(tfac)$_2$(OH)$_2$.H$_2$O

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Mn1	O4	98.50(17)	O2	C3	C5	116.9(6)
O1	Mn1	O6	88.4(2)	C2	C3	C5	118.6(6)
O2	Mn1	O1	83.74(17)	C8	O4	Mn1	128.3(4)
O2	Mn1	O4	176.67(17)	F4	C4	C1	110.8(6)
O2	Mn1	O6	91.19(19)	F5	C4	C1	115.9(6)
O3	Mn1	O1	178.04(17)	F5	C4	F4	105.9(6)
O3	Mn1	O2	94.30(17)	F5	C4	F6	106.2(6)
O3	Mn1	O4	83.47(17)	F6	C4	C1	110.5(6)
O3	Mn1	O6	91.72(19)	F6	C4	F4	107.1(7)
O4	Mn1	O6	86.42(18)	O3	C6	C7	129.3(6)
O5	Mn1	O1	89.14(19)	O3	C6	C9	113.3(6)
O5	Mn1	O2	93.4(2)	C7	C6	C9	117.4(6)
O5	Mn1	O3	90.92(19)	C6	C7	C8	124.0(6)
O5	Mn1	O4	89.12(19)	O4	C8	C7	123.8(6)
O5	Mn1	O6	174.5(2)	O4	C8	C10	118.0(6)
C1	O1	Mn1	124.2(4)	C7	C8	C10	118.2(6)
O1	C1	C2	128.6(6)	F1	C9	F2	105.7(6)
O1	C1	C4	114.5(6)	F1	C9	F3	107.7(6)
C2	C1	C4	116.8(6)	F1	C9	C6	111.4(5)
C3	O2	Mn1	128.6(4)	F2	C9	C6	111.0(6)
C1	C2	C3	124.1(6)	F3	C9	F2	106.0(6)
C6	O3	Mn1	124.3(4)	F3	C9	C6	114.5(6)
O2	C3	C2	124.4(6)				

Table S15 Hydrogen Bonds for 2-Mn(tfac)$_2$(OH)$_2$.H$_2$O.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O5	H5A	O31	0.84(2)	1.95(5)	2.745(6)	157(10)
O5	H5B	O21	0.84(2)	2.03(6)	2.756(7)	145(9)
O6	H6A	O1S2	0.83(2)	1.91(3)	2.733(7)	169(9)
O6	H6B	O1S3	0.84(2)	1.97(2)	2.801(7)	173(9)
O1S	H1SA	O4	0.84(2)	2.05(7)	2.755(7)	141(10)
O1S	H1SB	O1	0.84(2)	2.05(5)	2.814(7)	152(9)

[1]1-X,-1/2+Y,1/2-Z; [2]+X,1+Y,+Z; [3]-X,1/2+Y,1/2-Z

Table S16 Torsion Angles for 2-Mn(tfac)$_2$(OH)$_2$.H$_2$O.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Mn1	O1	C1	C2	-19.8(9)	C2	C1	C4	F4	-109.7(7)
Mn1	O1	C1	C4	162.2(4)	C2	C1	C4	F5	10.9(10)
Mn1	O2	C3	C2	13.7(10)	C2	C1	C4	F6	131.8(7)
Mn1	O2	C3	C5	-166.8(5)	O3	C6	C7	C8	-1.5(12)
Mn1	O3	C6	C7	-20.3(10)	O3	C6	C9	F1	60.4(8)
Mn1	O3	C6	C9	159.2(4)	O3	C6	C9	F2	-57.1(8)
Mn1	O4	C8	C7	13.7(10)	O3	C6	C9	F3	-177.0(6)
Mn1	O4	C8	C10	-163.9(5)	C4	C1	C2	C3	177.1(7)
O1	C1	C2	C3	-0.9(11)	C6	C7	C8	O4	5.4(11)
O1	C1	C4	F4	68.6(8)	C6	C7	C8	C10	-177.0(7)
O1	C1	C4	F5	-170.8(6)	C7	C6	C9	F1	-120.0(7)
O1	C1	C4	F6	-50.0(8)	C7	C6	C9	F2	122.5(7)
C1	C2	C3	O2	4.7(11)	C7	C6	C9	F3	2.5(9)
C1	C2	C3	C5	-174.7(7)	C9	C6	C7	C8	179.0(6)

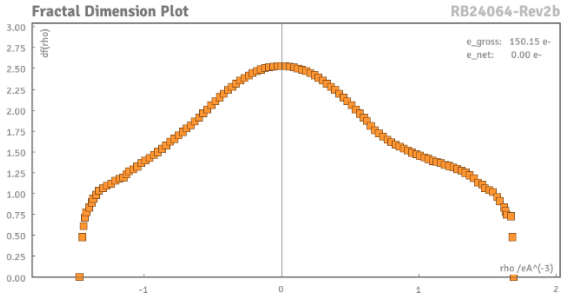
Table S17 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2-Mn(tfac)$_2$(OH)$_2$.H$_2$O

Atom	*x*	*y*	*z*	U(eq)
H2	3405.73	5478.04	4587.91	34
H5A	5080(60)	1910(150)	2830(30)	51
H5B	4630(90)	2090(150)	2210(20)	51
H5C	5756.64	7644.49	4149.25	61
H5D	4773.18	7916.55	4586.78	61
H5E	4580.36	9035.59	3935.98	61
H6A	1340(70)	7110(30)	2610(40)	50
H6B	610(20)	5590(110)	2490(40)	50
H7	1075.22	4966.95	633.57	31
H10A	343.33	447.82	1057.87	56
H10B	-35.17	2130.24	557.49	56
H10C	-606.25	2084.48	1170.58	56
H1SA	1310(90)	130(150)	2360(20)	48
H1SB	1560(80)	400(130)	3020(30)	48

Experimental

Single crystals of $C_{10}H_{14}O_7F_6Mn$ **2-Mn(tfac)$_2$(OH)$_2$.H$_2$O** were isolated from the precipitate formed by slow evaporation of diethyl ether in air. A suitable crystal was selected and mounted in Paratone™ oil on a 100 µm MiTeGen loop on a SuperNova, Dual, Cu at home/near, Pilatus 200K diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

This structure is challenged, with a high R(integration) of 10.96%, although the merging R-factor is only 4.66%. There are large residual peaks in the final difference Fourier of 1.6 and 1.3 e/Å^3 near to Mn (0.93 and 0.94 Å, respectively), which can not be explained merely by the presence of a (moderately) heavy element. The Fractal Dimension Plot is broad and slightly distorted towards positive ED (as discussed in K. Meindl and J. Henn (2008), Acta Cryst. A64, 404-418).



The crystals presented as aggregated plates that could be separated in the Paratone into tabular plates. Data collection was mandated on Cu due to weak diffraction, but this also encountered a significant fluorescence background that further challenged peak integration. The dataset was processed repeatedly to obtain the one used in the refinement as the best of possible options. This structure has excessive R1 and wR2 and does not provide very accurate derived geometric parameters. However, it does provide sufficiently clear structure resolution to show the chemical constituency and the connectivity for a new complex that has proven to be a useful starting material for Mn(tfac)2L2 chemistry. Moreover, it displays a very interesting H-bonding pattern.

4. Detailed Crystal Structure Report for 3, $Mn_3(tfac)_6(OH_2)_2$

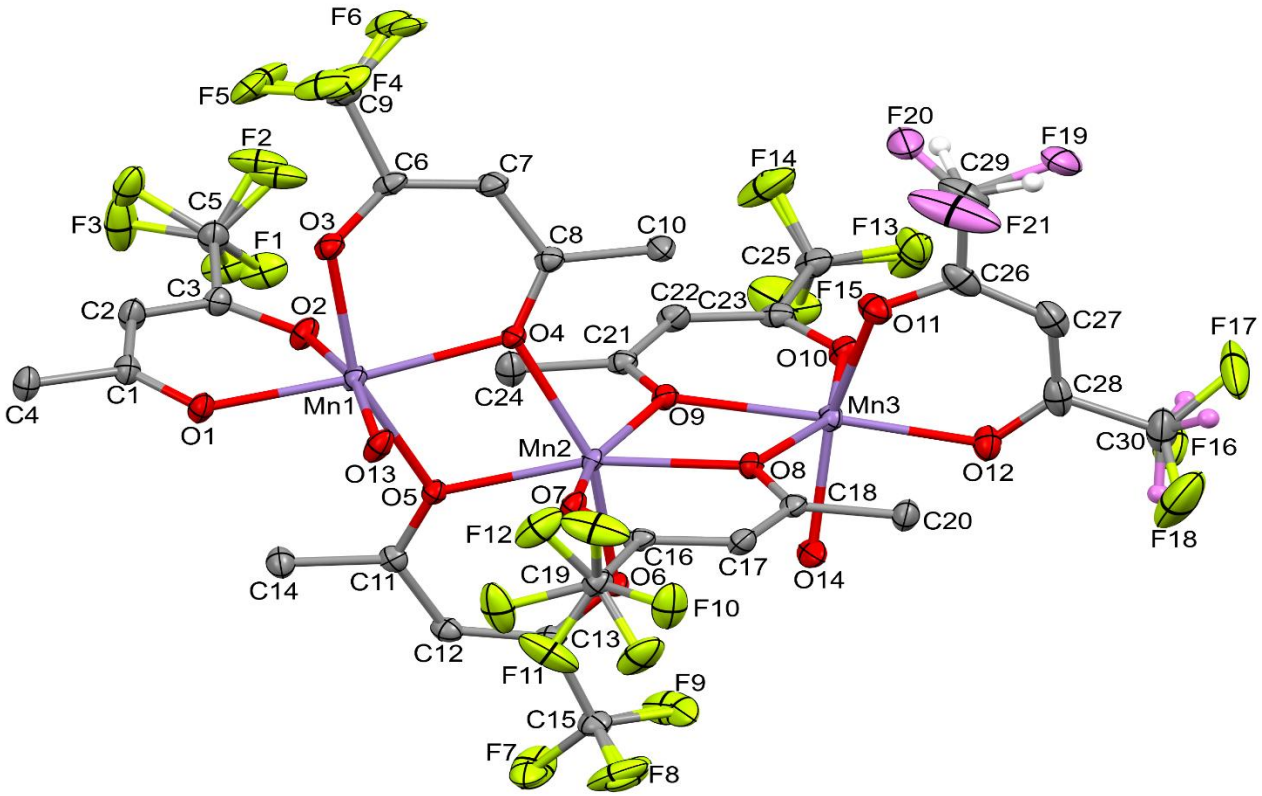


Fig. S5. Displacement ellipsoids plot (40% probability) depicting the asymmetric unit in structure **3**, consisting of discrete trimeric $[Mn_3(tfac)_6(OH_2)_2]$. The atom numbering scheme used in the Tables is shown. H-atoms and labels of the minor F atom components have been omitted for clarity. The 65:35 'left-right' positional disorder of the O11,12 tfac ligand at Mn3 is indicated by rendering the minor component atoms in violet. A second case of such CH_3/CF_3 exchange occurs at the O5,O6 tfac ligand, but is extremely minor (ca. 5%, accounting for the Max Peak in the final difference map).

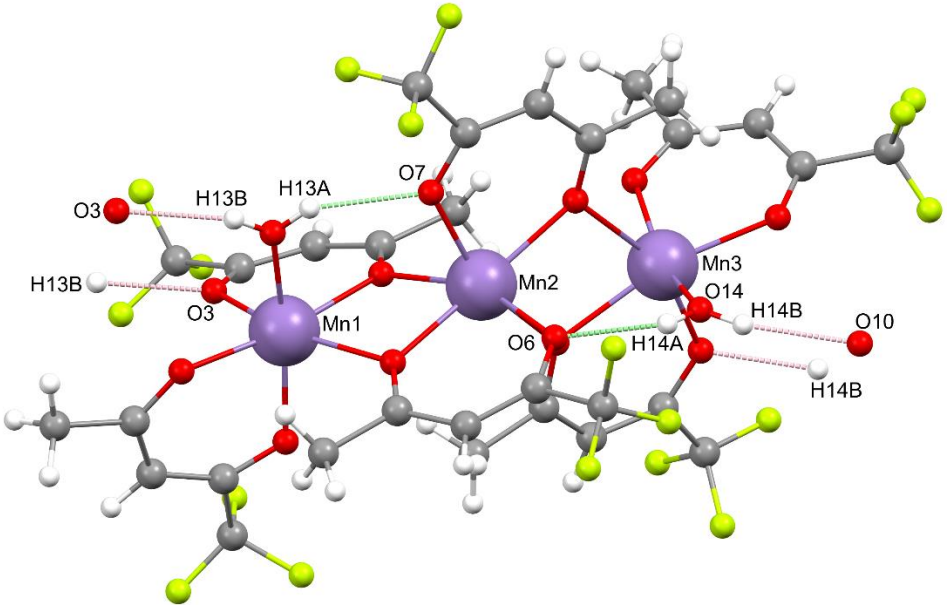


Fig. S6. Ball and stick depiction of intermolecular (green) and intramolecular (pink) H-bonding in the lattice of structure **3**. The intramolecular contacts are necessarily centrosymmetric by space group symmetry and generate infinite chains of centrosymmetric pairs of trimers through the lattice. See Table S23 for the relevant parameters.

Table S18 Crystal data and structure refinement for 3-$Mn_3(tfac)_6(OH_2)_2$.

Identification code	RB24005
Empirical formula	$C_{30}H_{28}F_{18}Mn_3O_{14}$
Formula weight	1119.34
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.7690(2)
b/Å	11.5144(3)
c/Å	16.9696(4)
α/°	85.497(2)
β/°	76.820(2)
γ/°	84.015(2)
Volume/$Å^3$	2034.35(8)
Z	2
$\rho_{calc}g/cm^3$	1.827
μ/mm^{-1}	8.822
F(000)	1114.0
Crystal size/mm^3	0.175 × 0.106 × 0.07
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.358 to 160.618
Index ranges	$-13 \le h \le 12$, $-14 \le k \le 14$, $-21 \le l \le 19$
Reflections collected	44915
Independent reflections	8821 [R_{int} = 0.0320, R_{sigma} = 0.0252]
Data/restraints/parameters	8821/235/761
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0339, wR_2 = 0.0915
Final R indexes [all data]	R_1 = 0.0374, wR_2 = 0.0940
Largest diff. peak/hole / e $Å^{-3}$	0.49/-0.43

Table S19 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for 3-$Mn_3(tfac)_6(OH_2)_2$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mn2	2177.1(3)	2050.2(3)	7694.0(2)	15.41(8)
Mn1	4809.0(3)	1110.3(3)	6211.2(2)	18.83(8)
Mn3	213.4(3)	4461.5(3)	8574.6(2)	19.51(8)
O8	169.1(13)	2723.8(13)	8010.2(8)	18.7(3)
O5	3987.1(13)	952.8(12)	7563.9(8)	18.2(3)
O4	3195.8(13)	2491.6(12)	6423.4(8)	18.2(3)
O3	5180.0(15)	1879.6(13)	4984.4(9)	23.2(3)
O9	2274.5(14)	3832.4(12)	8078.8(8)	18.7(3)
O1	6292.7(14)	-233.0(13)	5845.2(9)	23.4(3)
O6	1958.6(15)	1453.8(13)	8946.2(9)	22.6(3)
O7	1420.7(14)	637.4(13)	7257.5(9)	21.9(3)
F14	3138(8)	7988(8)	8132(5)	30(3)
O10	1032.9(15)	5978.7(14)	8808.8(10)	26.2(3)

Table S19 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3-$Mn_3(tfac)_6(OH_2)_2$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F7	3055(18)	20(30)	10581(13)	51(4)
O2	6282.1(15)	2041.1(14)	6408.5(9)	25.5(3)
O12	-1558.0(16)	5228.2(15)	9255.0(10)	29.7(4)
F8	1338(18)	-337(15)	10242(10)	54(4)
F4	4860(20)	2847(19)	3367(10)	46(3)
F13	1400(13)	8136(13)	9032(17)	57(4)
F6	5320(20)	4448(8)	3750(11)	46(3)
O13	3573.1(16)	-171.5(15)	6105.4(10)	27.0(3)
O11	-432.9(17)	5259.0(14)	7563.5(10)	29.0(3)
O14	224.1(17)	3308.2(15)	9623.5(9)	28.7(3)
F9	1500(30)	1350(18)	10557(15)	47(4)
F1	7930(7)	3424(4)	6692(2)	40.0(10)
F15	3140(30)	7401(17)	9344(14)	73(4)
F2	7752(7)	3826(6)	5463(4)	49.5(12)
F5	6622(9)	2936(13)	3718(8)	42(2)
F3	9412(3)	2762(4)	5735(6)	63.5(18)
F12	630(4)	-916(3)	6381(2)	46.2(10)
C16	271(2)	399.7(18)	7421.8(12)	20.2(4)
C11	4467.3(19)	314.1(18)	8089.1(12)	18.8(4)
C17	-813(2)	1066.6(19)	7793.9(13)	21.9(4)
F10	-1162(2)	-977(3)	7210(3)	42.5(11)
C12	3888(2)	215.7(18)	8921.5(13)	21.2(4)
C7	3709(2)	3598(2)	5166.7(13)	24.6(4)
C6	4729(2)	2871.4(19)	4762.8(12)	21.9(4)
C18	-828.5(19)	2186.6(19)	8075.8(12)	20.0(4)
C13	2707(2)	750.6(18)	9271.4(12)	20.9(4)
C1	7444(2)	-101.1(19)	5544.2(13)	22.8(4)
C19	87(2)	-804(2)	7153.2(13)	24.2(4)
C22	3262(2)	5503.0(19)	8268.6(14)	24.9(4)
C15	2163(2)	444(2)	10173.4(13)	25.4(4)
C3	7414(2)	1896(2)	5991.8(13)	22.7(4)
C21	3281(2)	4344.7(19)	8067.8(12)	21.0(4)
F16	-3137(3)	6803(3)	10206.6(16)	49.4(7)
C2	8030(2)	940(2)	5581.7(15)	27.8(5)
C8	2955(2)	3360.2(18)	5942.9(12)	20.0(4)
C4	8260(2)	-1112(2)	5121.5(15)	27.5(5)
C23	2182(2)	6215.1(19)	8602.5(12)	23.8(4)
C9	5385(2)	3300(2)	3899.1(14)	28.8(5)
C14	5723(2)	-385(2)	7789.9(14)	26.8(5)
C26	-1414(3)	5938(2)	7531.9(17)	32.6(5)
C24	4550(2)	3658(2)	7823.4(16)	30.3(5)
C20	-2088(2)	2788(2)	8486.5(15)	27.2(5)
C25	2428(3)	7457(2)	8779.2(14)	29.8(5)

Table S19 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3-Mn$_3$(tfac)$_6$(OH$_2$)$_2$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C10	1799(2)	4181(2)	6236.2(13)	27.7(5)
C28	-2379(2)	5914(2)	8993.7(18)	33.3(5)
F11	533(5)	-1632(2)	7586(3)	57.6(15)
C5	8146(2)	2980(2)	5945.2(16)	29.0(5)
C27	-2389(3)	6276(2)	8194.7(18)	35.2(6)
C30	-3500(3)	6368(3)	9654(2)	45.2(7)
C29	-1512(3)	6411(2)	6683(2)	45.7(7)
F17	-4272(3)	7227(4)	9341(2)	88.1(15)
F18	-4192(4)	5531(4)	9944(3)	93.4(15)
F10A	-753(7)	-1370(5)	7667(4)	49(3)
F11A	1200(6)	-1551(5)	7100(6)	48(2)
F12A	-124(12)	-720(5)	6445(5)	58(3)
F19	-2418(5)	7399(4)	6811(3)	42.1(12)
F20	-448(5)	6813(5)	6378(3)	51.5(15)
F21	-1930(10)	5704(5)	6375(4)	98(3)
F6A	5020(30)	4418(11)	3735(13)	51(4)
F4A	5120(30)	2700(20)	3340(12)	51(4)
F5A	6638(11)	3210(30)	3825(15)	64(4)
F3A	9240(16)	2944(13)	5347(11)	45(4)
F2A	7500(30)	3820(20)	5618(17)	49.5(12)
F1A	8386(19)	3272(14)	6565(9)	40.0(10)
F9A	1740(30)	1394(14)	10574(14)	50(4)
F7A	3029(13)	-130(20)	10543(10)	43(3)
F8A	1241(11)	-259(11)	10274(7)	43(3)
F14A	3231(17)	7929(13)	8158(8)	73(5)
F13A	1350(12)	8158(13)	8923(12)	40(3)
F15A	2931(13)	7417(14)	9426(6)	39(3)

Table S20 Anisotropic Displacement Parameters (Å^2×10^3) for 3-Mn$_3$(tfac)$_6$(OH$_2$)$_2$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn2	16.22(15)	16.67(15)	11.94(14)	-3.32(11)	-0.15(11)	0.29(11)
Mn1	17.48(15)	19.84(16)	16.52(15)	-4.00(12)	2.20(12)	-0.51(12)
Mn3	21.18(16)	19.64(16)	16.45(15)	-5.88(12)	-1.75(12)	2.26(12)
O8	17.9(6)	19.9(7)	17.1(7)	-4.1(5)	-1.5(5)	0.5(5)
O5	17.7(6)	19.6(7)	16.0(6)	-2.6(5)	-1.4(5)	1.2(5)
O4	20.6(7)	18.3(7)	13.3(6)	-1.7(5)	0.3(5)	0.3(5)
O3	26.7(7)	22.8(7)	17.0(7)	-5.1(6)	2.4(6)	-1.5(6)
O9	21.1(7)	16.9(7)	17.2(7)	-4.4(5)	-1.5(5)	-1.0(5)
O1	19.2(7)	22.9(7)	25.3(8)	-7.1(6)	1.9(6)	-0.1(6)
O6	27.7(8)	22.5(7)	14.3(7)	-1.9(5)	-0.8(6)	4.9(6)
O7	19.2(7)	23.2(7)	21.5(7)	-8.7(6)	2.1(6)	-2.9(6)
F14	42(4)	15(4)	31(4)	-6(2)	1(4)	-10(3)

Table S20 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3-$Mn_3(tfac)_6(OH_2)_2$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O10	29.1(8)	21.4(7)	25.5(8)	-9.1(6)	1.9(6)	-2.4(6)
F7	41(6)	92(11)	24(4)	-4(5)	-15(4)	0(5)
O2	21.9(7)	27.7(8)	24.7(8)	-10.3(6)	2.7(6)	-3.6(6)
O12	25.3(8)	34.3(9)	27.4(8)	-9.5(7)	-3.0(6)	6.5(7)
F8	81(9)	50(6)	28(5)	-2(4)	11(5)	-41(5)
F4	56(5)	66(7)	17(3)	-5(3)	-1(3)	-22(4)
F13	65(6)	31(5)	64(6)	-27(4)	24(5)	-18(4)
F6	65(7)	30(3)	31(3)	-3(2)	19(4)	-16(3)
O13	23.7(7)	26.2(8)	27.9(8)	-12.5(6)	6.9(6)	-6.8(6)
O11	38.0(9)	24.6(8)	23.6(8)	-4.8(6)	-7.9(7)	5.3(7)
O14	37.5(9)	28.1(8)	15.1(7)	-4.7(6)	0.9(6)	9.1(7)
F9	69(7)	43(7)	15(4)	-2(4)	8(4)	24(6)
F1	49(3)	41.1(13)	34.3(13)	-6.7(10)	-11.4(16)	-18.1(17)
F15	120(9)	46(5)	74(7)	-17(5)	-58(7)	-14(6)
F2	78(3)	33.7(9)	41(3)	16.7(16)	-22(2)	-19.5(17)
F5	34(3)	50(4)	29(3)	6(2)	15.6(19)	-1(3)
F3	21.5(11)	37.8(17)	128(5)	-30(2)	1.5(18)	-7.5(10)
F12	57(2)	46.4(18)	32.2(14)	-21.5(12)	12.7(15)	-26.0(17)
C16	25.7(10)	19.8(10)	14.1(9)	-1.2(7)	-1.4(8)	-4.6(8)
C11	20.8(9)	16.7(9)	20.0(9)	-4.0(7)	-5.8(8)	-2.2(7)
C17	19.9(9)	23.6(10)	20.6(10)	-2.1(8)	0.5(8)	-4.7(8)
F10	25.5(12)	35.2(15)	67(3)	-21.1(15)	-1.7(12)	-9.9(10)
C12	27.0(10)	19.0(9)	18.6(9)	-1.0(7)	-7.7(8)	-1.0(8)
C7	31.1(11)	23.1(10)	16.9(10)	0.5(8)	-0.3(8)	-2.1(9)
C6	27.0(10)	22.8(10)	14.8(9)	-3.1(8)	0.7(8)	-7.8(8)
C18	18.3(9)	24.8(10)	15.0(9)	1.3(7)	-1.4(7)	0.1(8)
C13	30.1(11)	19.0(9)	13.7(9)	-2.4(7)	-3.9(8)	-4.3(8)
C1	19.5(9)	24.8(10)	22.7(10)	-4.9(8)	-2.1(8)	1.7(8)
C19	24.7(10)	24.2(11)	22.5(10)	-4.1(8)	-1.0(8)	-4.0(8)
C22	27.5(11)	21.1(10)	24.9(10)	-5.0(8)	-0.5(9)	-6.5(8)
C15	32.8(11)	27.4(11)	14.9(9)	-0.9(8)	-3.8(8)	-0.5(9)
C3	19.5(9)	24.4(10)	24.1(10)	-2.0(8)	-4.4(8)	-2.0(8)
C21	24.5(10)	20.9(10)	16.6(9)	-1.5(7)	-1.9(8)	-3.2(8)
F16	45.3(14)	60.0(18)	36.7(14)	-19.3(12)	0.9(11)	13.6(12)
C2	17.7(10)	26.5(11)	36.6(12)	-6.7(9)	0.7(9)	-1.1(8)
C8	23.0(10)	19.9(9)	16.8(9)	-2.5(7)	-3.0(8)	-2.1(8)
C4	19.8(10)	28.2(11)	32.5(12)	-9.8(9)	-0.7(9)	2.3(8)
C23	35.6(12)	19.1(10)	15.6(9)	-2.8(7)	-1.9(8)	-5.2(9)
C9	37.4(12)	23.9(11)	20.3(10)	-2.4(8)	5.9(9)	-6.8(9)
C14	23.9(10)	30.4(11)	25.1(11)	-4.1(9)	-5.7(9)	5.2(9)
C26	39.3(13)	17.5(10)	46.2(15)	-3.1(10)	-19.5(11)	-2.6(9)
C24	22.9(11)	25.7(11)	41.8(13)	-8.3(10)	-4.5(10)	-1.0(9)
C20	20.1(10)	29.2(11)	29.4(11)	-4.9(9)	0.2(9)	1.4(8)
C25	41.5(13)	23.3(11)	21.9(11)	-7.6(8)	2.2(10)	-6.7(10)

Table S20 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3-$Mn_3(tfac)_6(OH_2)_2$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C10	29.6(11)	28.9(11)	19.6(10)	1.2(8)	-0.2(9)	6.9(9)
C28	23.0(11)	26.0(12)	51.9(15)	-14.5(11)	-8.6(11)	3.5(9)
F11	89(4)	24.0(13)	74(3)	6.1(14)	-53(3)	-2.0(15)
C5	22.9(10)	25.1(11)	37.2(13)	-5.7(9)	-1.7(9)	-1.7(9)
C27	32.2(12)	24.9(11)	50.0(16)	-3.9(11)	-14.9(11)	4.8(10)
C30	26.6(12)	41.2(15)	63.1(19)	-14.7(14)	0.7(12)	4.2(11)
C29	65(2)	24.8(12)	53.1(18)	8.3(12)	-29.9(16)	-2.5(13)
F17	67(2)	129(3)	50.2(18)	-12.1(19)	-9.9(16)	72(2)
F18	70(2)	80(3)	106(3)	-31(2)	50(2)	-30(2)
F10A	55(4)	34(3)	50(4)	-13(3)	19(3)	-24(3)
F11A	35(3)	25(2)	89(6)	-23(3)	-19(3)	3(2)
F12A	118(8)	35(3)	38(4)	1(2)	-49(5)	-19(4)
F19	41(2)	39(3)	45(3)	18(2)	-15(2)	3(2)
F20	54(3)	57(3)	29(2)	10(2)	4(2)	21(3)
F21	221(10)	37(3)	71(4)	6(3)	-104(6)	-25(4)
F6A	71(10)	26(3)	33(4)	13(3)	27(5)	1(4)
F4A	90(11)	40(4)	16(3)	-10(2)	12(5)	-22(6)
F5A	42(4)	97(10)	46(6)	10(6)	11(3)	-29(4)
F3A	28(5)	33(5)	64(8)	-13(5)	16(5)	-10(4)
F2A	78(3)	33.7(9)	41(3)	16.7(16)	-22(2)	-19.5(17)
F1A	49(3)	41.1(13)	34.3(13)	-6.7(10)	-11.4(16)	-18.1(17)
F9A	92(10)	32(4)	21(3)	-10(3)	-1(5)	-1(5)
F7A	38(4)	64(5)	18(4)	15(4)	-1(3)	10(3)
F8A	34(4)	76(6)	20(4)	4(3)	-6(3)	-19(3)
F14A	101(9)	45(6)	52(6)	-21(4)	45(6)	-36(5)
F13A	41(4)	22(4)	53(5)	-11(3)	-1(4)	8(3)
F15A	58(5)	29(4)	31(4)	-11(2)	-8(4)	-12(2)

Table S21 Bond Lengths for 3-$Mn_3(tfac)_6(OH_2)_2$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn2	O8	2.1799(14)	C13	C15	1.536(3)
Mn2	O5	2.1860(14)	C1	C2	1.424(3)
Mn2	O4	2.2308(14)	C1	C4	1.508(3)
Mn2	O9	2.2215(14)	C19	F11	1.278(3)
Mn2	O6	2.1492(14)	C19	F10A	1.296(5)
Mn2	O7	2.1446(15)	C19	F11A	1.390(5)
Mn1	O5	2.2644(14)	C19	F12A	1.267(6)
Mn1	O4	2.2150(14)	C22	H22	0.9500
Mn1	O3	2.1639(15)	C22	C21	1.399(3)
Mn1	O1	2.1246(15)	C22	C23	1.386(3)
Mn1	O2	2.1048(16)	C15	F9A	1.318(10)
Mn1	O13	2.1313(16)	C15	F7A	1.330(8)
Mn3	O8	2.2944(15)	C15	F8A	1.318(8)
Mn3	O9	2.2513(14)	C3	C2	1.376(3)

Table S21 Bond Lengths for 3-$Mn_3(tfac)_6(OH_2)_2$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn3	O10	2.1399(16)	C3	C5	1.532(3)
Mn3	O12	2.1344(16)	C21	C24	1.495(3)
Mn3	O11	2.1061(16)	F16	C30	1.251(4)
Mn3	O14	2.1370(16)	C2	H2	0.9500
O8	C18	1.274(3)	C8	C10	1.496(3)
O5	C11	1.277(2)	C4	H4A	0.9800
O4	C8	1.283(3)	C4	H4B	0.9800
O3	C6	1.258(3)	C4	H4C	0.9800
O9	C21	1.283(3)	C23	C25	1.545(3)
O1	C1	1.249(3)	C9	F6A	1.332(10)
O6	C13	1.268(3)	C9	F4A	1.317(11)
O7	C16	1.260(3)	C9	F5A	1.319(11)
F14	C25	1.332(7)	C14	H14C	0.9800
O10	C23	1.259(3)	C14	H14D	0.9800
F7	C15	1.339(11)	C14	H14E	0.9800
O2	C3	1.264(3)	C26	C27	1.401(4)
O12	C28	1.257(3)	C26	C29	1.522(4)
F8	C15	1.309(9)	C24	H24A	0.9800
F4	C9	1.329(9)	C24	H24B	0.9800
F13	C25	1.294(10)	C24	H24C	0.9800
F6	C9	1.324(10)	C20	H20A	0.9800
O13	H13A	0.833(18)	C20	H20B	0.9800
O13	H13B	0.820(18)	C20	H20C	0.9800
O11	C26	1.256(3)	C25	F14A	1.321(9)
O14	H14A	0.839(18)	C25	F13A	1.328(8)
O14	H14B	0.824(18)	C25	F15A	1.326(10)
F9	C15	1.329(11)	C10	H10A	0.9800
F1	C5	1.365(5)	C10	H10B	0.9800
F15	C25	1.347(11)	C10	H10C	0.9800
F2	C5	1.321(5)	C28	C27	1.389(4)
F5	C9	1.327(8)	C28	C30	1.527(4)
F3	C5	1.330(4)	C5	F3A	1.368(10)
F12	C19	1.318(4)	C5	F2A	1.300(16)
C16	C17	1.380(3)	C5	F1A	1.219(12)
C16	C19	1.538(3)	C27	H27	0.9500
C11	C12	1.409(3)	C30	H30A	0.9800
C11	C14	1.503(3)	C30	H30B	0.9800
C17	H17	0.9500	C30	H30C	0.9800
C17	C18	1.407(3)	C30	F17	1.379(4)
F10	C19	1.360(3)	C30	F18	1.278(5)
C12	H12	0.9500	C29	H29A	0.9800
C12	C13	1.378(3)	C29	H29B	0.9800
C7	H7	0.9500	C29	H29C	0.9800
C7	C6	1.390(3)	C29	F19	1.416(6)
C7	C8	1.404(3)	C29	F20	1.264(7)

Table S21 Bond Lengths for 3-$Mn_3(tfac)_6(OH_2)_2$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C6	C9	1.542(3)	C29	F21	1.179(6)
C18	C20	1.501(3)			

Table S22 Bond Angles for 3-$Mn_3(tfac)_6(OH_2)_2$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O8	Mn2	O5	164.42(6)	F11	C19	C16	111.3(2)
O8	Mn2	O4	115.24(5)	F11	C19	F10	106.5(3)
O8	Mn2	O9	77.14(5)	F10A	C19	C16	114.1(3)
O5	Mn2	O4	76.69(5)	F10A	C19	F11A	102.8(4)
O5	Mn2	O9	113.61(5)	F11A	C19	C16	110.8(3)
O9	Mn2	O4	92.53(5)	F12A	C19	C16	110.9(3)
O6	Mn2	O8	86.62(6)	F12A	C19	F10A	112.5(5)
O6	Mn2	O5	82.80(5)	F12A	C19	F11A	105.1(5)
O6	Mn2	O4	157.57(6)	C23	C22	C21	125.8(2)
O6	Mn2	O9	87.38(6)	F7	C15	C13	113.7(10)
O7	Mn2	O8	83.18(6)	F8	C15	F7	108.2(13)
O7	Mn2	O5	87.29(6)	F8	C15	F9	104.7(15)
O7	Mn2	O4	88.70(6)	F8	C15	C13	109.4(7)
O7	Mn2	O9	158.78(6)	F9	C15	F7	107.8(17)
O7	Mn2	O6	99.41(6)	F9	C15	C13	112.5(12)
O4	Mn1	O5	75.43(5)	F9A	C15	C13	111.2(11)
O3	Mn1	O5	158.65(6)	F9A	C15	F7A	105.9(15)
O3	Mn1	O4	84.09(5)	F9A	C15	F8A	110.0(14)
O1	Mn1	O5	111.40(6)	F7A	C15	C13	112.9(7)
O1	Mn1	O4	171.86(6)	F8A	C15	C13	111.5(5)
O1	Mn1	O3	89.52(6)	F8A	C15	F7A	104.9(10)
O1	Mn1	O13	84.25(6)	O2	C3	C2	129.4(2)
O2	Mn1	O5	90.09(6)	O2	C3	C5	112.33(19)
O2	Mn1	O4	99.78(6)	C2	C3	C5	118.3(2)
O2	Mn1	O3	87.45(6)	O9	C21	C22	124.1(2)
O2	Mn1	O1	84.92(6)	O9	C21	C24	117.68(19)
O2	Mn1	O13	166.75(7)	C22	C21	C24	118.2(2)
O13	Mn1	O5	86.78(6)	C3	C2	C1	124.0(2)
O13	Mn1	O4	91.89(6)	O4	C8	C7	124.50(19)
O13	Mn1	O3	100.06(6)	O4	C8	C10	117.55(18)
O9	Mn3	O8	74.26(5)	C7	C8	C10	117.95(19)
O10	Mn3	O8	156.47(6)	O10	C23	C22	129.1(2)
O10	Mn3	O9	82.96(6)	O10	C23	C25	115.4(2)
O12	Mn3	O8	117.10(6)	C22	C23	C25	115.5(2)
O12	Mn3	O9	166.40(6)	F4	C9	C6	109.1(9)
O12	Mn3	O10	86.28(7)	F6	C9	F4	107.7(13)
O12	Mn3	O14	85.50(7)	F6	C9	F5	105.7(10)
O11	Mn3	O8	85.84(6)	F6	C9	C6	115.8(9)
O11	Mn3	O9	104.65(6)	F5	C9	F4	106.1(10)
O11	Mn3	O10	94.44(7)	F5	C9	C6	111.9(6)

Table S22 Bond Angles for 3-$Mn_3(tfac)_6(OH_2)_2$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O11	Mn3	O12	84.41(7)	F6A	C9	C6	112.0(10)
O11	Mn3	O14	157.69(7)	F4A	C9	C6	112.2(11)
O14	Mn3	O8	81.15(6)	F4A	C9	F6A	106.6(15)
O14	Mn3	O9	89.21(6)	F4A	C9	F5A	108.9(13)
O14	Mn3	O10	104.70(7)	F5A	C9	C6	109.6(9)
Mn2	O8	Mn3	103.78(6)	F5A	C9	F6A	107.3(12)
C18	O8	Mn2	129.07(13)	O11	C26	C27	126.0(2)
C18	O8	Mn3	124.90(13)	O11	C26	C29	114.9(3)
Mn2	O5	Mn1	102.64(6)	C27	C26	C29	119.2(2)
C11	O5	Mn2	130.62(13)	F14	C25	F15	104.1(13)
C11	O5	Mn1	126.63(13)	F14	C25	C23	111.5(4)
Mn1	O4	Mn2	102.80(6)	F13	C25	F14	108.3(10)
C8	O4	Mn2	129.07(13)	F13	C25	F15	107.4(12)
C8	O4	Mn1	128.04(13)	F13	C25	C23	114.5(9)
C6	O3	Mn1	125.66(13)	F15	C25	C23	110.4(8)
Mn2	O9	Mn3	103.86(6)	F14A	C25	C23	110.8(6)
C21	O9	Mn2	127.60(13)	F14A	C25	F13A	108.1(11)
C21	O9	Mn3	128.39(13)	F14A	C25	F15A	108.2(9)
C1	O1	Mn1	126.59(14)	F13A	C25	C23	111.5(8)
C13	O6	Mn2	128.54(14)	F15A	C25	C23	110.4(7)
C16	O7	Mn2	126.80(13)	F15A	C25	F13A	107.8(11)
C23	O10	Mn3	128.60(14)	O12	C28	C27	128.1(2)
C3	O2	Mn1	121.76(14)	O12	C28	C30	114.1(3)
C28	O12	Mn3	127.52(17)	C27	C28	C30	117.8(2)
C26	O11	Mn3	130.00(17)	F1	C5	C3	110.1(3)
O7	C16	C17	129.1(2)	F2	C5	F1	106.1(4)
O7	C16	C19	113.66(18)	F2	C5	F3	110.4(4)
C17	C16	C19	117.26(19)	F2	C5	C3	111.6(4)
O5	C11	C12	124.21(19)	F3	C5	F1	104.1(3)
O5	C11	C14	117.28(18)	F3	C5	C3	113.9(2)
C12	C11	C14	118.50(18)	F3A	C5	C3	112.6(6)
C16	C17	C18	125.1(2)	F2A	C5	C3	106.0(16)
C13	C12	C11	124.74(19)	F2A	C5	F3A	97.7(13)
C6	C7	C8	125.8(2)	F1A	C5	C3	118.4(7)
O3	C6	C7	129.6(2)	F1A	C5	F3A	109.0(8)
O3	C6	C9	113.92(19)	F1A	C5	F2A	111.1(18)
C7	C6	C9	116.47(19)	C28	C27	C26	123.7(2)
O8	C18	C17	123.89(19)	F16	C30	C28	112.2(2)
O8	C18	C20	117.52(19)	F16	C30	F17	107.0(3)
C17	C18	C20	118.59(19)	F16	C30	F18	110.5(4)
O6	C13	C12	128.99(19)	F17	C30	C28	111.0(3)
O6	C13	C15	113.39(19)	F18	C30	C28	109.1(3)
C12	C13	C15	117.58(19)	F18	C30	F17	107.0(4)
O1	C1	C2	124.0(2)	F19	C29	C26	104.4(3)
O1	C1	C4	117.7(2)	F20	C29	C26	105.0(3)

Table S22 Bond Angles for 3-$Mn_3(tfac)_6(OH_2)_2$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C4	118.30(19)	F20	C29	F19	105.6(4)
F12	C19	C16	110.9(2)	F21	C29	C26	108.6(4)
F12	C19	F10	104.5(3)	F21	C29	F19	108.8(5)
F10	C19	C16	113.3(2)	F21	C29	F20	122.9(7)
F11	C19	F12	110.0(3)				

Table S23 Hydrogen Bonds for 3-$Mn_3(tfac)_6(OH_2)_2$.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O13	H13A	O7	0.833(18)	2.11(3)	2.799(2)	140(3)
O13	H13B	O3[1]	0.820(18)	2.05(2)	2.825(2)	157(3)
O14	H14A	O6	0.839(18)	2.05(2)	2.818(2)	153(3)
O14	H14B	O10[2]	0.824(18)	2.04(2)	2.838(2)	164(3)
O14	H14B	F13[2]	0.824(18)	2.56(4)	3.04(2)	118(3)

[1]1-X,-Y,1-Z; [2]-X,1-Y,2-Z

Table S24 Torsion Angles for 3-$Mn_3(tfac)_6(OH_2)_2$.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Mn2	O8	C18	C17	-13.3(3)	O2	C3	C5	F2A	-59.3(14)
Mn2	O8	C18	C20	166.10(14)	O2	C3	C5	F1A	66.2(11)
Mn2	O5	C11	C12	-2.0(3)	O12	C28	C27	C26	-2.2(4)
Mn2	O5	C11	C14	177.17(14)	O12	C28	C30	F16	52.4(4)
Mn2	O4	C8	C7	175.79(16)	O12	C28	C30	F17	172.1(3)
Mn2	O4	C8	C10	-3.4(3)	O12	C28	C30	F18	-70.3(4)
Mn2	O9	C21	C22	175.38(15)	O11	C26	C27	C28	1.7(4)
Mn2	O9	C21	C24	-4.5(3)	O11	C26	C29	F19	-162.0(3)
Mn2	O6	C13	C12	3.1(3)	O11	C26	C29	F20	-51.1(4)
Mn2	O6	C13	C15	-174.49(14)	O11	C26	C29	F21	82.0(6)
Mn2	O7	C16	C17	12.4(3)	C16	C17	C18	O8	0.8(3)
Mn2	O7	C16	C19	-168.29(13)	C16	C17	C18	C20	-178.6(2)
Mn1	O5	C11	C12	-177.45(15)	C11	C12	C13	O6	-3.8(4)
Mn1	O5	C11	C14	1.7(3)	C11	C12	C13	C15	173.8(2)
Mn1	O4	C8	C7	-0.3(3)	C17	C16	C19	F12	126.6(3)
Mn1	O4	C8	C10	-179.56(14)	C17	C16	C19	F10	9.5(3)
Mn1	O3	C6	C7	-15.8(3)	C17	C16	C19	F11	-110.5(4)
Mn1	O3	C6	C9	167.14(14)	C17	C16	C19	F10A	-40.4(5)
Mn1	O1	C1	C2	16.8(3)	C17	C16	C19	F11A	-155.9(5)
Mn1	O1	C1	C4	-163.68(15)	C17	C16	C19	F12A	87.8(7)
Mn1	O2	C3	C2	-25.1(3)	C12	C13	C15	F7	22.0(17)
Mn1	O2	C3	C5	153.46(15)	C12	C13	C15	F8	-99.1(11)
Mn3	O8	C18	C17	-173.39(15)	C12	C13	C15	F9	144.9(18)
Mn3	O8	C18	C20	6.0(2)	C12	C13	C15	F9A	131.9(16)
Mn3	O9	C21	C22	-9.7(3)	C12	C13	C15	F7A	12.9(13)
Mn3	O9	C21	C24	170.39(15)	C12	C13	C15	F8A	-104.9(7)
Mn3	O10	C23	C22	-10.0(3)	C7	C6	C9	F4	-94.0(11)

Table S24 Torsion Angles for 3-$Mn_3(tfac)_6(OH_2)_2$.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Mn3	O10	C23	C25	172.86(14)	C7	C6	C9	F6	27.6(11)
Mn3	O12	C28	C27	5.3(4)	C7	C6	C9	F5	148.8(8)
Mn3	O12	C28	C30	-175.99(17)	C7	C6	C9	F6A	12.4(18)
Mn3	O11	C26	C27	-4.6(4)	C7	C6	C9	F4A	-107.5(16)
Mn3	O11	C26	C29	175.73(17)	C7	C6	C9	F5A	131.3(19)
O5	C11	C12	C13	3.0(3)	C6	C7	C8	O4	8.1(4)
O3	C6	C9	F4	83.5(11)	C6	C7	C8	C10	-172.6(2)
O3	C6	C9	F6	-154.9(11)	C19	C16	C17	C18	-179.76(19)
O3	C6	C9	F5	-33.7(9)	C22	C23	C25	F14	51.6(5)
O3	C6	C9	F6A	-170.2(18)	C22	C23	C25	F13	175.0(14)
O3	C6	C9	F4A	70.0(16)	C22	C23	C25	F15	-63.7(16)
O3	C6	C9	F5A	-51.2(19)	C22	C23	C25	F14A	45.6(11)
O1	C1	C2	C3	3.7(4)	C22	C23	C25	F13A	166.0(10)
O6	C13	C15	F7	-160.1(17)	C22	C23	C25	F15A	-74.2(7)
O6	C13	C15	F8	78.8(11)	C21	C22	C23	O10	1.9(4)
O6	C13	C15	F9	-37.2(18)	C21	C22	C23	C25	179.1(2)
O6	C13	C15	F9A	-50.2(16)	C2	C3	C5	F1	-137.2(4)
O6	C13	C15	F7A	-169.2(13)	C2	C3	C5	F2	105.2(4)
O6	C13	C15	F8A	73.0(7)	C2	C3	C5	F3	-20.7(6)
O7	C16	C17	C18	-0.4(4)	C2	C3	C5	F3A	13.7(12)
O7	C16	C19	F12	-52.8(3)	C2	C3	C5	F2A	119.4(14)
O7	C16	C19	F10	-169.9(3)	C2	C3	C5	F1A	-115.1(11)
O7	C16	C19	F11	70.1(4)	C8	C7	C6	O3	0.8(4)
O7	C16	C19	F10A	140.2(5)	C8	C7	C6	C9	177.8(2)
O7	C16	C19	F11A	24.7(5)	C4	C1	C2	C3	-175.8(2)
O7	C16	C19	F12A	-91.6(7)	C23	C22	C21	O9	8.7(4)
O10	C23	C25	F14	-130.9(4)	C23	C22	C21	C24	-171.4(2)
O10	C23	C25	F13	-7.5(14)	C14	C11	C12	C13	-176.1(2)
O10	C23	C25	F15	113.9(16)	C5	C3	C2	C1	-177.1(2)
O10	C23	C25	F14A	-136.8(11)	C27	C26	C29	F19	18.3(4)
O10	C23	C25	F13A	-16.4(10)	C27	C26	C29	F20	129.2(4)
O10	C23	C25	F15A	103.3(7)	C27	C26	C29	F21	-97.7(6)
O2	C3	C2	C1	1.4(4)	C27	C28	C30	F16	-128.7(3)
O2	C3	C5	F1	44.1(4)	C27	C28	C30	F17	-9.0(4)
O2	C3	C5	F2	-73.5(4)	C27	C28	C30	F18	108.6(4)
O2	C3	C5	F3	160.6(6)	C30	C28	C27	C26	179.1(2)
O2	C3	C5	F3A	-165.1(12)	C29	C26	C27	C28	-178.7(2)

Table S25 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3-$Mn_3(tfac)_6(OH_2)_2$.

Atom	*x*	*y*	*z*	U(eq)
H13A	2850(20)	-260(30)	6404(17)	41
H13B	3760(30)	-770(20)	5861(18)	41
H14A	690(30)	2680(20)	9590(20)	43
H14B	-50(30)	3400(30)	10111(12)	43

Table S25 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3-Mn$_3$(tfac)$_6$(OH$_2$)$_2$.

Atom	*x*	*y*	*z*	U(eq)
H17	-1611.04	744.71	7865.45	26
H12	4344.38	-253.54	9266.51	25
H7	3504.53	4320.23	4893.5	30
H22	4061.19	5830.51	8166.95	30
H2	8899.88	977.06	5306.64	33
H4A	8922.12	-1401.09	5417.92	41
H4B	8665.5	-851.8	4567.51	41
H4C	7721.7	-1741.8	5104.14	41
H14C	5608.48	-965.4	7425.66	40
H14D	6023.28	-785.04	8252.26	40
H14E	6355.53	139.25	7496.56	40
H24A	4572.72	2945.22	8178	45
H24B	5231.75	4131.09	7871.37	45
H24C	4678.34	3445.6	7260.5	45
H20A	-2099.21	2854.34	9060.25	41
H20B	-2784.14	2330.67	8440.2	41
H20C	-2203.2	3570.16	8227.04	41
H10A	1096.02	3734.13	6535.6	42
H10B	1542.47	4618.74	5771.32	42
H10C	2000.32	4727.78	6593.79	42
H27	-3097.36	6780.64	8091.71	42
H30A	-4290.22	6435.67	9453.28	68
H30B	-3343.74	7136.85	9801.48	68
H30C	-3587.19	5821.3	10132.66	68
H29A	-1368.74	5761.91	6322.85	69
H29B	-864.57	6964.25	6478.7	69
H29C	-2366.61	6810.47	6701.1	69

Table S26 Atomic Occupancy for 3-Mn$_3$(tfac)$_6$(OH$_2$)$_2$.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
F14	0.51(8)	F7	0.45(9)	F8	0.45(9)
F4	0.54(6)	F13	0.51(8)	F6	0.54(6)
F9	0.45(9)	F1	0.785(19)	F15	0.51(8)
F2	0.785(19)	F5	0.54(6)	F3	0.785(19)
F12	0.655(8)	F10	0.655(8)	F16	0.656(3)
F11	0.655(8)	H30A	0.344(3)	H30B	0.344(3)
H30C	0.344(3)	H29A	0.656(3)	H29B	0.656(3)
H29C	0.656(3)	F17	0.656(3)	F18	0.656(3)
F10A	0.345(8)	F11A	0.345(8)	F12A	0.345(8)
F19	0.344(3)	F20	0.344(3)	F21	0.344(3)
F6A	0.46(6)	F4A	0.46(6)	F5A	0.46(6)
F3A	0.215(19)	F2A	0.215(19)	F1A	0.215(19)
F9A	0.55(9)	F7A	0.55(9)	F8A	0.55(9)
F14A	0.49(8)	F13A	0.49(8)	F15A	0.49(8)

Experimental

Single crystals of $C_{30}H_{28}F_{18}Mn_3O_{14}$ **3-[$Mn_3(tfac)_6(OH_2)_2$]** were grown by slow evaporation of a diethyl ether solution in air. A suitable crystal was selected and mounted in Paratone™ oil on a 100 μm MiTeGen loop on a SuperNova, Dual, Cu at home/near, Pilatus 200K diffractometer. The crystal was kept at 100.01(10) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

In the final difference map, the max peak of 0.5 e/Å^3, along with peak #3 at 0.4 e/Å^3 are found at the CH_3 group of the O5/O6 tfac ligand, and is very evidently a second example of the of the CF_3/CH_3 ligand reversal that is particularly evident for C29/C30 for the O11/O12 tfac ligand. We have chosen *not* to incorporate this in the model due to the very low fraction of ED relative to F atoms, in an already complex crystallographic model. However, it is evident that all future work with the tfac ligand should take the high likelihood of such methyl/trifluoromethyl positional disorder into account in all structure models.

5. Detailed Crystal Structure Report for 4, Mn(tfac)$_2$DME

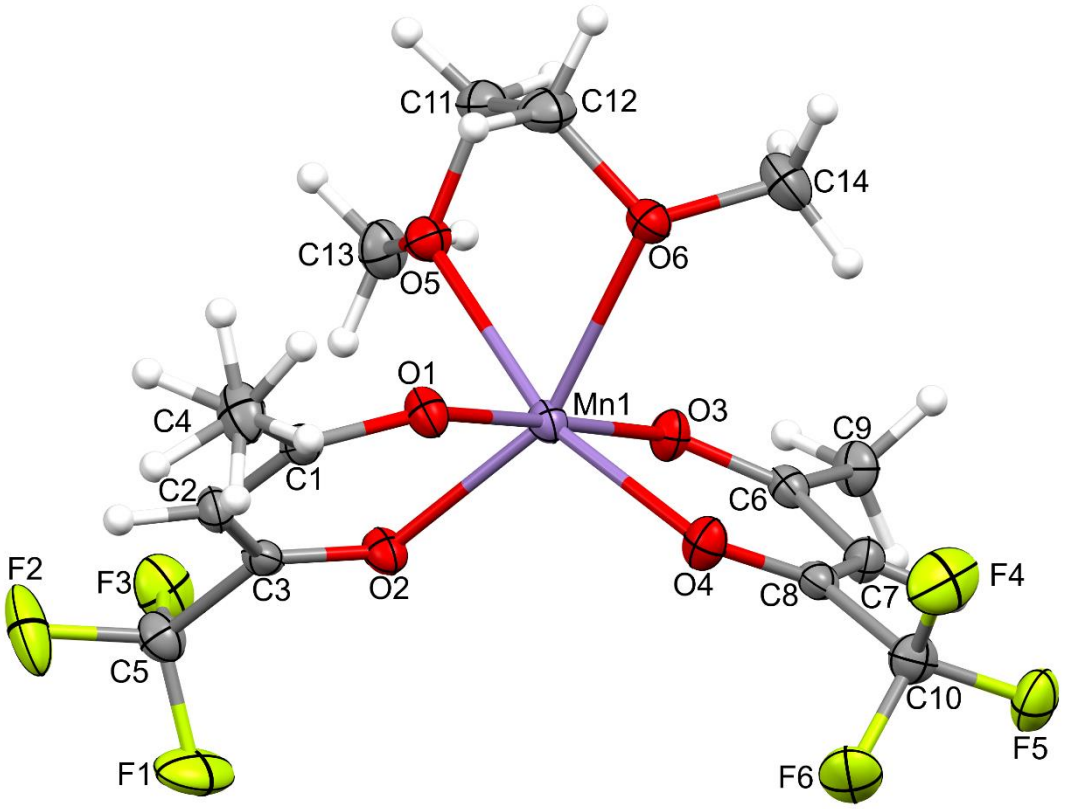


Fig. S7. Displacement ellipsoids plot (40% probability) depicting the asymmetric unit in structure **4**, consisting of discrete neutral [Mn(tfac)$_2$DME]. The atom numbering scheme used in the Tables is shown, as is the constrained rotational disorder of the tfac methyl hydrogens at C4 (62:38 refined occupancies). There is positional disorder of the methyl hydrogen atoms of methyl group C4 (shown).

Table S27 Crystal data and structure refinement for 4-Mn(tfac)$_2$DME

Identification code	d23118_a
Empirical formula	$C_{14}H_{18}F_6MnO_6$
Formula weight	451.22
Temperature/K	150.15
Crystal system	orthorhombic
Space group	Pbca
a/Å	12.4430(6)
b/Å	13.5342(6)
c/Å	21.9592(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3698.1(3)
Z	8
ρ_{calc}g/cm^3	1.621
μ/mm^{-1}	0.800
F(000)	1832.0
Crystal size/mm^3	0.27 × 0.22 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.71 to 50.49
Index ranges	$-14 \le h \le 14$, $-16 \le k \le 16$, $-26 \le l \le 26$
Reflections collected	38776
Independent reflections	3345 [R_{int} = 0.0564, R_{sigma} = 0.0312]
Data/restraints/parameters	3345/0/249
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0295, wR_2 = 0.0626
Final R indexes [all data]	R_1 = 0.0443, wR_2 = 0.0660
Largest diff. peak/hole / e Å^{-3}	0.29/-0.26

Table S28 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 4-Mn(tfac)$_2$DME. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mn1	3427.7(2)	5461.8(2)	6708.3(2)	21.07(9)
F1	5993.8(13)	7816.2(10)	5822.1(7)	57.0(4)
F2	6178.9(13)	6923.2(11)	5026.9(7)	59.4(5)
F3	4679.7(11)	7621.4(10)	5216.3(6)	44.5(4)
F4	3741.0(14)	4823.2(10)	8816.6(6)	53.0(4)
F5	3219.5(11)	6242.9(10)	9133.9(5)	41.2(3)
F6	4764.7(10)	6084.8(11)	8719.9(6)	44.0(4)
O1	4685.5(11)	4456.6(10)	6502.6(6)	26.5(3)
O2	4375.7(11)	6493.6(9)	6220.1(6)	25.6(3)
O3	2190.8(11)	6484.8(10)	6927.3(6)	24.9(3)
O4	3805.3(11)	5517.0(10)	7639.7(6)	27.7(3)
O5	2556.1(12)	5173.9(10)	5795.2(6)	26.6(3)

O6	2375.2(11)	4114.8(10)	6841.8(6)	26.8(3)
C1	5424.7(16)	4525.0(15)	6119.8(9)	23.3(4)
C2	5637.8(16)	5381.5(14)	5766.0(9)	24.3(4)
C3	5127.5(15)	6267.1(14)	5851.2(9)	21.3(4)
C4	6140.4(19)	3639.5(16)	6040.0(11)	36.5(6)
C5	5500.7(18)	7150.1(15)	5476.7(10)	29.9(5)
C6	1884.9(15)	6806.0(14)	7434.7(9)	21.9(4)
C7	2407.4(16)	6579.2(15)	7994.6(9)	24.3(5)
C8	3285.4(16)	5973.6(14)	8047.5(9)	22.0(4)
C9	908.6(16)	7453.0(15)	7456.5(10)	29.1(5)
C10	3741.5(18)	5785.7(16)	8683.8(10)	29.9(5)
C11	1809.1(18)	4366.0(15)	5806.8(10)	32.7(5)
C12	2217.9(19)	3638.8(16)	6261.0(10)	33.8(5)
C13	2153.2(19)	5983.8(17)	5444.8(10)	34.1(5)
C14	1441.7(18)	4139.9(18)	7223.6(11)	39.5(6)

Table S29 Anisotropic Displacement Parameters ($Å^2×10^3$) for 4-Mn(tfac)$_2$DME. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	20.63(16)	20.11(15)	22.48(16)	0.70(13)	3.59(13)	0.44(13)
F1	77.6(11)	35.0(8)	58.5(10)	15.0(7)	-19.2(8)	-31.4(8)
F2	66.2(10)	46.1(9)	65.9(10)	24.5(8)	42.8(9)	10.5(8)
F3	43.7(8)	45.0(8)	45.0(8)	21.0(7)	-2.0(7)	6.2(7)
F4	86.2(11)	31.6(7)	41.1(8)	14.0(6)	-14.9(8)	-1.0(7)
F5	43.1(8)	58.3(9)	22.2(7)	-2.3(6)	-0.7(6)	5.3(7)
F6	28.6(7)	63.6(9)	39.9(8)	2.5(7)	-12.5(6)	-1.5(7)
O1	25.3(8)	21.9(7)	32.2(8)	3.6(6)	8.2(7)	1.8(6)
O2	26.5(8)	19.2(7)	31.0(8)	1.0(6)	6.0(7)	0.3(6)
O3	25.5(8)	27.9(8)	21.3(8)	1.4(6)	1.7(6)	5.8(6)
O4	25.9(7)	32.4(8)	24.9(8)	-1.3(7)	-0.4(6)	8.3(6)
O5	31.7(8)	23.4(8)	24.8(8)	2.8(6)	-2.3(6)	-2.7(6)
O6	27.4(8)	26.0(7)	27.0(8)	1.6(6)	1.1(6)	-5.9(6)
C1	21.4(10)	23.7(10)	24.8(11)	-4.2(9)	-0.3(9)	-0.6(9)
C2	23.6(10)	25.7(11)	23.5(11)	0.0(9)	6.6(9)	-1.5(9)
C3	18.9(10)	23.3(10)	21.8(10)	0.4(9)	-1.9(9)	-5.7(8)
C4	37.9(13)	27.9(12)	43.7(14)	1.4(11)	13.3(11)	6.9(10)
C5	30.8(12)	25.8(11)	33.0(13)	4.9(10)	2.3(10)	-0.3(9)
C6	19.1(10)	19.2(9)	27.4(11)	1.7(9)	4.4(9)	-0.5(8)
C7	24.4(11)	27.2(11)	21.1(11)	-0.8(9)	2.1(9)	1.2(9)
C8	20.9(11)	20.7(10)	24.4(10)	1.9(8)	0.8(9)	-5.0(9)
C9	27.4(11)	29.3(11)	30.6(12)	1.1(10)	2.6(9)	7.0(10)
C10	31.8(13)	30.6(12)	27.3(12)	3.5(10)	-2.8(10)	-0.1(9)
C11	36.0(13)	30.7(12)	31.5(12)	-2.2(10)	-2.4(10)	-7.2(10)
C12	39.4(13)	24.6(11)	37.4(13)	-1.5(10)	-4.1(11)	-6.1(10)
C13	35.6(13)	37.9(13)	28.6(12)	9.2(10)	-0.7(10)	2.6(11)
C14	32.2(13)	42.2(13)	44.0(15)	6.2(11)	9.7(11)	-8.4(11)

Table S30 Bond Lengths for 4-Mn(tfac)$_2$DME.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	O1	2.1223(14)	C4	H4A	0.9800
Mn1	O2	2.1191(14)	C4	H4B	0.9800
Mn1	O3	2.1253(14)	C4	H4C	0.9800
Mn1	O4	2.1000(14)	C4	H4D	0.9800
Mn1	O5	2.3127(14)	C4	H4E	0.9800
Mn1	O6	2.2639(14)	C4	H4F	0.9800
F1	C5	1.328(2)	C6	C7	1.424(3)
F2	C5	1.335(3)	C6	C9	1.498(3)
F3	C5	1.333(2)	C7	H7	0.9500
F4	C10	1.335(2)	C7	C8	1.371(3)
F5	C10	1.335(2)	C8	C10	1.529(3)
F6	C10	1.338(3)	C9	H9A	0.9800
O1	C1	1.250(2)	C9	H9B	0.9800
O2	C3	1.275(2)	C9	H9C	0.9800
O3	C6	1.255(2)	C11	H11A	0.9900
O4	C8	1.266(2)	C11	H11B	0.9900
O5	C11	1.435(2)	C11	C12	1.491(3)
O5	C13	1.430(2)	C12	H12A	0.9900
O6	C12	1.442(3)	C12	H12B	0.9900
O6	C14	1.433(3)	C13	H13A	0.9800
C1	C2	1.420(3)	C13	H13B	0.9800
C1	C4	1.503(3)	C13	H13C	0.9800
C2	H2	0.9500	C14	H14A	0.9800
C2	C3	1.369(3)	C14	H14B	0.9800
C3	C5	1.523(3)	C14	H14C	0.9800

Table S31 Bond Angles for 4-Mn(tfac)$_2$DME.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Mn1	O3	178.76(6)	C2	C1	C4	118.45(18)
O1	Mn1	O5	93.06(5)	C3	C2	C1	123.58(18)
O1	Mn1	O6	86.44(5)	O2	C3	C2	129.62(18)
O2	Mn1	O1	84.51(5)	O2	C3	C5	112.21(17)
O2	Mn1	O3	95.07(5)	C2	C3	C5	118.14(18)
O2	Mn1	O5	86.19(5)	F1	C5	F2	106.66(18)
O2	Mn1	O6	156.67(5)	F1	C5	F3	105.91(17)
O3	Mn1	O5	88.07(5)	F1	C5	C3	111.42(17)
O3	Mn1	O6	94.37(5)	F2	C5	C3	114.31(17)
O4	Mn1	O1	93.73(6)	F3	C5	F2	106.08(17)
O4	Mn1	O2	110.17(6)	F3	C5	C3	111.92(17)
O4	Mn1	O3	85.32(5)	O3	C6	C7	123.59(17)
O4	Mn1	O5	162.82(6)	O3	C6	C9	118.47(18)
O4	Mn1	O6	91.83(5)	C7	C6	C9	117.93(18)
O6	Mn1	O5	72.86(5)	C8	C7	C6	124.47(19)
C1	O1	Mn1	129.68(13)	O4	C8	C7	129.73(19)
C3	O2	Mn1	124.85(12)	O4	C8	C10	112.05(17)

Table S31 Bond Angles for 4-Mn(tfac)$_2$DME.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	O3	Mn1	130.25(12)	C7	C8	C10	118.21(18)
C8	O4	Mn1	126.31(13)	F4	C10	F6	106.42(18)
C11	O5	Mn1	114.62(12)	F4	C10	C8	111.21(17)
C13	O5	Mn1	120.11(12)	F5	C10	F4	106.89(18)
C13	O5	C11	111.50(16)	F5	C10	F6	106.19(17)
C12	O6	Mn1	108.88(12)	F5	C10	C8	114.76(17)
C14	O6	Mn1	121.72(13)	F6	C10	C8	110.90(17)
C14	O6	C12	114.71(17)	O5	C11	C12	107.09(17)
O1	C1	C2	124.46(18)	O6	C12	C11	110.06(17)
O1	C1	C4	117.09(18)				

Table S32 Torsion Angles for 4-Mn(tfac)$_2$DME.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Mn1	O1	C1	C2	6.6(3)	O4	C8	C10	F6	60.2(2)
Mn1	O1	C1	C4	-174.37(14)	O5	C11	C12	O6	55.1(2)
Mn1	O2	C3	C2	-13.8(3)	C1	C2	C3	O2	-3.0(3)
Mn1	O2	C3	C5	168.24(12)	C1	C2	C3	C5	174.81(19)
Mn1	O3	C6	C7	5.3(3)	C2	C3	C5	F1	-110.4(2)
Mn1	O3	C6	C9	-173.89(13)	C2	C3	C5	F2	10.6(3)
Mn1	O4	C8	C7	-4.1(3)	C2	C3	C5	F3	131.3(2)
Mn1	O4	C8	C10	175.52(12)	C4	C1	C2	C3	-171.8(2)
Mn1	O5	C11	C12	-30.2(2)	C6	C7	C8	O4	0.8(3)
Mn1	O6	C12	C11	-53.23(19)	C6	C7	C8	C10	-178.77(18)
O1	C1	C2	C3	7.3(3)	C7	C8	C10	F4	121.6(2)
O2	C3	C5	F1	67.8(2)	C7	C8	C10	F5	0.2(3)
O2	C3	C5	F2	-171.17(18)	C7	C8	C10	F6	-120.2(2)
O2	C3	C5	F3	-50.5(2)	C9	C6	C7	C8	177.83(19)
O3	C6	C7	C8	-1.3(3)	C13	O5	C11	C12	-170.85(17)
O4	C8	C10	F4	-58.0(2)	C14	O6	C12	C11	87.0(2)
O4	C8	C10	F5	-179.51(17)					

Table S33 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4-Mn(tfac)$_2$DME.

Atom	*x*	*y*	*z*	U(eq)
H2	6163.11	5337.54	5453.19	29
H4A	6268.39	3527.26	5605.16	55
H4B	5792.01	3056.85	6216.87	55
H4C	6827.17	3756.98	6246.11	55
H4D	6323.32	3366.8	6440.27	55
H4E	6799.7	3837.21	5828.56	55
H4F	5764.54	3137.08	5799.32	55
H7	2128.36	6867.33	8355.97	29
H9A	1058.28	8034.46	7708.63	44
H9B	306.89	7082.84	7632.19	44
H9C	722.14	7664.91	7043.08	44

Table S33 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4-Mn(tfac)$_2$DME.

Atom	*x*	*y*	*z*	U(eq)
H11A	1759.08	4056.58	5399.28	39
H11B	1086.11	4602.46	5925.8	39
H12A	1696.15	3091.31	6305.35	41
H12B	2907.18	3357.47	6117.25	41
H13A	2691.12	6512.41	5433.85	51
H13B	1491.13	6232.93	5631.57	51
H13C	2001.12	5761.23	5029	51
H14A	1608.7	4497.1	7600.09	59
H14B	1222.18	3463.22	7322.42	59
H14C	855.68	4476.49	7009.42	59

Table S34 Atomic Occupancy for 4-Mn(tfac)$_2$DME.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
H4A	0.62(3)	H4B	0.62(3)	H4C	0.62(3)
H4D	0.38(3)	H4E	0.38(3)	H4F	0.38(3)

Experimental

Single crystals of $C_{14}H_{18}F_6MnO_6$ **4-Mn(tfac)$_2$DME**were grown from a hexane solution by slow cooling to –18 °C for 12 h. A suitable crystal was selected and mounted on a Bruker Kappa APEX-DUO CMOD PHOTON II diffractometer. The crystal was kept at 150.15 K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

6. Detailed Crystal Structure Report for 5, $Mn(hfac)_2DME$

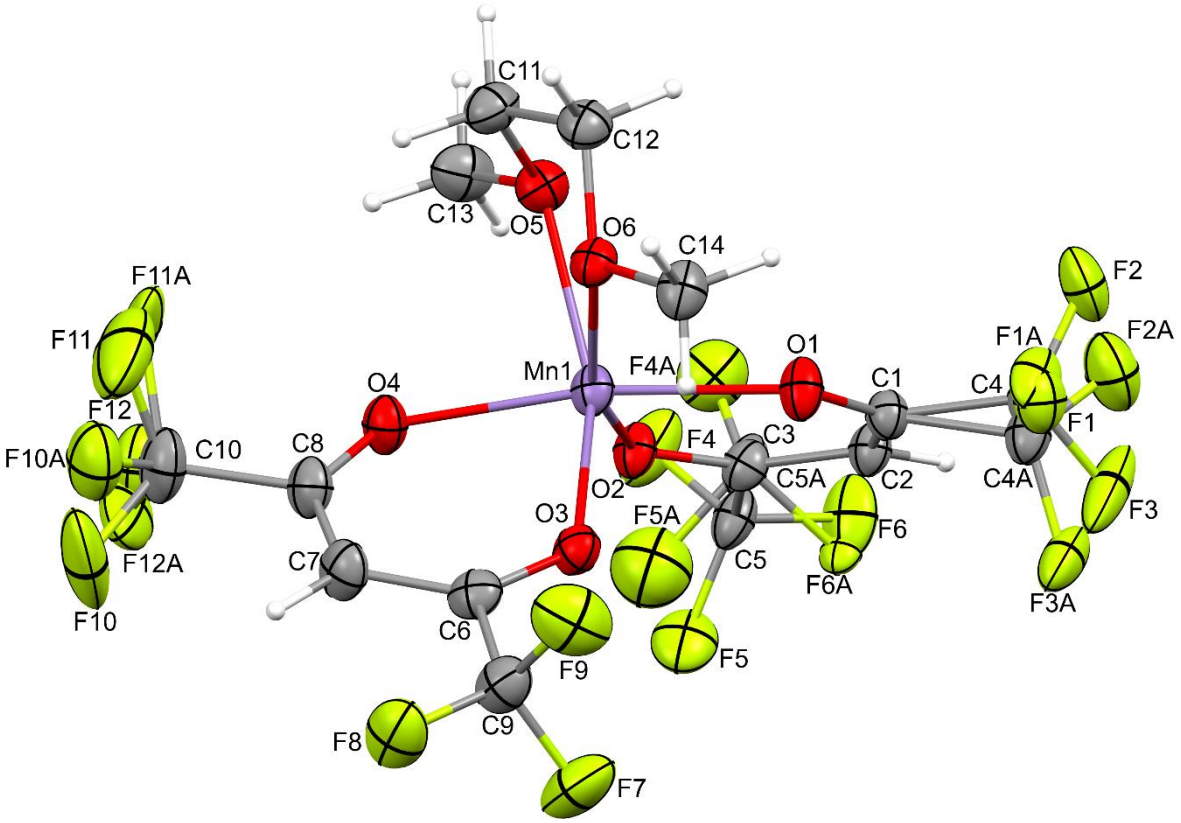


Fig. S8. Displacement ellipsoids plot (40% probability) depicting the asymmetric unit in structure **5**, consisting of discrete neutral [$Mn(hfac)_2DME$]. The atom numbering scheme used in the Tables is shown. There is typical rotational disorder in the CF_3 groups, modelled by two parts as shown for the C4, C5 and C10 trifluoromethyl groups, whereas the C9 group is ordered at 100 K in the lattice.

The complex in structure **5** is in a general position and is generally similar to that of the analogous tfac complex found in structure **4**. There is typical CF_3 rotational disorder, that could be modelled albeit imperfectly as a two-part full group displacement in the case of C4 (70:30 ratio) and C5 (86:14 ratio), but for C10 a simple rotational disorder (80:20 ratio) with a common C atom suffices. Final difference map peaks near the F atoms of the ordered C9 group are significantly smaller than remaining peaks around the disordered moieties, yet the largest final difference peak is only 0.5 e/Å^3.

Mn occupancy. An interesting phenomenon, pointed out by a very thorough reviewer, was observed in a first structure of **5** obtained at 200 K on a crystal obtained by crystallization from solution (i.e. not subsequently vacuum sublimed), which displays significant electron deficiencies around the Mn. A follow up free occupancy refinement of the metal converged to ~0.90. Since there is no possibility of having mixed in a lighter transition metal (i.e. Sc – Cr) as these metals are not used in our synthetic work at all, the most logical explanation for the apparent electron deficiency at the metal is partial incorporation of Mg^{2+}, from exposure to $MgSO_4$ as a drying agent in concentrated aqueous solutions prior to extraction into hexanes. Concerns about this possibility are discussed in the main article. Similar free occupancy refinements for the other structures in this study (excepting that of **6** which has a whole molecule disorder) averaged to 0.98. This corresponds to about 0.5 e deficiency for $_{25}$Mn, which we find reasonable when using neutral atom scattering factors for Mn(II). Moreover, the hfac ligands are expected to be significantly electron withdrawing, with the expectation of partial positive charge at the metal. We also note that in the improved structure determination in the reported structure, a free occupancy refinement comes to 0.96 for **5**, which is the *lowest* of the eight comparable structures in this report. This may indicate that even these crystals further purified by sublimation may retain some mixed Mg/Mn composition.

Table S35 Crystal data and structure refinement for 5-Mn(hfac)$_2$DME.

Identification code	RB25046
Empirical formula	$C_{14}H_{12}F_{12}MnO_6$
Formula weight	559.18
Temperature/K	200.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.9649(3)
b/Å	13.1729(4)
c/Å	14.0648(4)
α/°	90
β/°	100.339(2)
γ/°	90
Volume/Å^3	2180.79(11)
Z	4
ρ_{calc}g/cm^3	1.703
μ/mm^{-1}	6.175
F(000)	1108.0
Crystal size/mm^3	0.14 × 0.14 × 0.04
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.946 to 132.384
Index ranges	-14 ≤ h ≤ 13, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	52817
Independent reflections	3787 [R_{int} = 0.0734, R_{sigma} = 0.0520]
Data/restraints/parameters	3787/267/412
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0654, wR_2 = 0.1777
Final R indexes [all data]	R_1 = 0.0826, wR_2 = 0.1942
Largest diff. peak/hole / e Å^{-3}	0.58/-0.78

Table S36 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 5-Mn(hfac)2DME. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mn1	6482.4(3)	7248.3(3)	6660.2(3)	29.19(12)
F1	2919(11)	8669(9)	5343(6)	44.8(18)
F2	2815(3)	9290(3)	6738.8(19)	53.6(11)
F3	1981(2)	7889(4)	6300(4)	81(2)
F4	5550.3(17)	6132(2)	9635.6(13)	53.7(8)
F5	4722(2)	4991.0(17)	8666.9(18)	55.1(7)
F6	3732(4)	6219(4)	9212(3)	59.0(11)
F7	5553.6(16)	4924.0(17)	3884.7(14)	65.8(5)
F8	7236.3(15)	4959.5(16)	3565.3(12)	59.7(5)
F9	6199.6(19)	6326.5(15)	3389.1(12)	66.8(5)
F10	10359(9)	5584(13)	6159(8)	66(4)
F11	10317(9)	6455(11)	7268(9)	64(4)
F12	9800(20)	4878(12)	7515(14)	74(6)

Table S36 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 5-Mn(hfac)2DME. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	4815.5(14)	7890.9(14)	6281.8(12)	36.6(4)
O2	5832.0(13)	6573.5(13)	7815.8(11)	31.4(4)
O3	6205.6(13)	6331.0(13)	5373.0(12)	33.2(4)
O4	8032.1(14)	6371.5(14)	6973.1(12)	35.9(4)
O5	7468.8(14)	8412.3(13)	7676.8(12)	35.5(4)
O6	6975.3(13)	8494.9(12)	5725.1(11)	30.4(3)
C1	3989.8(19)	7790.4(18)	6703.3(17)	29.9(5)
C2	3939.9(19)	7248.3(18)	7553.4(17)	30.6(5)
C3	4860.9(19)	6680.0(19)	8026.1(16)	30.6(5)
C4	2922(4)	8415(4)	6264(4)	36.1(12)
C5	4699(3)	6000(3)	8893(2)	36.5(8)
C6	6922(2)	5833.1(19)	5007.8(17)	34.3(5)
C7	8033(2)	5568(2)	5443.6(19)	40.1(6)
C8	8492(2)	5857(2)	6397.4(18)	37.6(5)
C9	6488(2)	5499(2)	3954.2(19)	42.5(6)
C10	9727(2)	5538(3)	6813(2)	51.6(7)
C11	8184(2)	9029(2)	7173.4(19)	40.5(6)
C12	7453(2)	9392.8(19)	6244.5(19)	37.7(5)
C13	8076(3)	8061(2)	8607.6(19)	45.7(6)
C14	6246(2)	8754(2)	4818.0(17)	36.9(5)
F3A	2172(5)	7402(6)	5702(6)	50(2)
C4A	2832(11)	8158(11)	6102(11)	36.1(12)
F2A	2305(8)	8706(8)	6665(5)	64(3)
F1A	3020(20)	8800(20)	5410(15)	46(5)
F10A	10100(3)	4756(4)	6335(2)	92.2(18)
F11A	10415(3)	6303(4)	6807(5)	99.3(15)
F12A	9852(5)	5223(4)	7716(3)	60.9(11)
F5A	5190(20)	5346(18)	9145(17)	89(7)
F4A	5269(14)	6817(16)	9746(11)	63(5)
F6A	3700(20)	5962(15)	9064(18)	25(4)
C5A	4770(20)	6390(20)	9104(13)	36.5(8)

Table S37 Anisotropic Displacement Parameters (Å^2×10^3) for 5-Mn(hfac)2DME. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	26.9(2)	33.9(2)	29.1(2)	4.50(15)	11.30(14)	0.60(14)
F1	42(3)	56(4)	34(2)	7.2(19)	2.1(19)	9(3)
F2	53.3(18)	59(2)	50.4(14)	2.0(12)	13.6(12)	29.5(15)
F3	24.4(13)	89(3)	121(4)	70(3)	-6.1(17)	-10.0(15)
F4	39.3(11)	92(2)	28.7(9)	19.3(10)	2.0(7)	-12.8(11)
F5	57.0(13)	46.5(12)	63.6(15)	24.0(10)	15.8(11)	-6.7(10)

Table S37 Anisotropic Displacement Parameters ($Å^2×10^3$) for 5-Mn(hfac)2DME. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F6	42.9(14)	88(3)	52(2)	26.2(19)	26.7(14)	8(2)
F7	52.6(10)	90.1(14)	56.7(10)	-25.1(10)	15.3(8)	-31.3(10)
F8	52.1(10)	83.5(13)	46.1(9)	-24.4(9)	15.7(8)	1.8(9)
F9	96.2(15)	66.5(12)	34.7(8)	2.4(8)	4.9(9)	5.2(11)
F10	48(4)	87(5)	64(5)	-9(4)	16(3)	15(3)
F11	20(4)	113(9)	54(6)	-40(6)	-5(4)	6(5)
F12	52(7)	44(7)	119(14)	30(8)	2(9)	17(6)
O1	28.8(8)	46.8(10)	36.5(9)	15.2(7)	12.5(7)	6.6(7)
O2	24.8(8)	39.1(9)	32.4(8)	10.3(7)	10.6(6)	0.9(6)
O3	28.2(8)	38.1(9)	34.7(8)	-1.4(7)	9.5(6)	-2.5(7)
O4	30.3(8)	46.6(10)	32.2(8)	0.4(7)	9.9(7)	6.2(7)
O5	38.4(9)	36.9(9)	30.9(8)	4.2(7)	5.5(7)	-1.0(7)
O6	28.3(8)	32.6(8)	30.8(8)	6.4(6)	7.4(6)	-2.0(6)
C1	26.2(11)	32.2(12)	32.4(11)	3.4(9)	8.1(9)	1.6(9)
C2	24.7(11)	38.0(13)	31.1(11)	4.6(9)	10.2(9)	0.7(9)
C3	28.6(11)	37.3(12)	27.4(11)	4.2(9)	9.2(9)	-3.1(9)
C4	28.2(15)	43(3)	39(3)	11(2)	9.9(15)	1.5(18)
C5	23.9(12)	51(2)	34.8(16)	11.4(14)	6.5(12)	-3.4(16)
C6	35.5(12)	37.4(13)	33.4(12)	1.2(10)	15.0(10)	-7.5(10)
C7	33.8(13)	52.9(16)	37.5(13)	-4.6(11)	16.3(10)	3.0(11)
C8	29.7(12)	48.9(14)	37.1(13)	3.6(11)	13.8(10)	4.2(10)
C9	39.7(14)	52.4(16)	37.3(13)	-6.4(12)	12.2(11)	-6.7(12)
C10	33.0(14)	78(2)	46.7(16)	-0.1(15)	14.4(12)	10.7(14)
C11	38.4(13)	38.9(13)	42.6(14)	3.1(11)	3.7(11)	-8.0(11)
C12	39.6(13)	33.6(13)	40.0(13)	5.1(10)	8.2(10)	-2.8(10)
C13	57.7(17)	44.8(15)	31.2(12)	3.2(11)	-0.4(12)	0.1(13)
C14	33.9(12)	44.8(14)	32.8(12)	12.6(10)	8.2(10)	0.9(10)
F3A	27(3)	58(4)	63(4)	26(3)	-4(3)	-8(2)
C4A	28.2(15)	43(3)	39(3)	11(2)	9.9(15)	1.5(18)
F2A	61(4)	73(4)	60(3)	-3(3)	17(3)	26(3)
F1A	37(6)	43(6)	56(9)	30(7)	2(6)	1(4)
F10A	69.6(19)	133(4)	65.5(17)	-31.6(19)	-8.2(13)	68(2)
F11A	40.4(15)	106(3)	150(3)	44(3)	14(2)	-7.1(17)
F12A	41.9(14)	92(3)	47.2(13)	5.5(16)	4.5(10)	16(2)
F5A	90(7)	90(7)	87(7)	6(4)	18(4)	-1(4)
F4A	65(6)	72(6)	53(5)	4(4)	11(4)	-4(4)
F6A	22(5)	25(4)	29(5)	8(3)	7(3)	-4(3)
C5A	23.9(12)	51(2)	34.8(16)	11.4(14)	6.5(12)	-3.4(16)

Table S38 Bond Lengths for 5-Mn(hfac)2DME.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	O1	2.1296(17)	C2	H2	0.9500

Table S38 Bond Lengths for 5-Mn(hfac)2DME.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	O2	2.1092(15)	C2	C3	1.383(3)
Mn1	O3	2.1291(17)	C3	C5	1.539(4)
Mn1	O4	2.1427(17)	C3	C5A	1.579(16)
Mn1	O5	2.2446(17)	C6	C7	1.395(4)
Mn1	O6	2.2211(15)	C6	C9	1.531(3)
F1	C4	1.330(7)	C7	H7	0.9500
F2	C4	1.328(5)	C7	C8	1.396(4)
F3	C4	1.322(6)	C8	C10	1.536(4)
F4	C5	1.322(4)	C10	F10A	1.333(4)
F5	C5	1.340(4)	C10	F11A	1.284(5)
F6	C5	1.344(6)	C10	F12A	1.310(5)
F7	C9	1.328(3)	C11	H11A	0.9900
F8	C9	1.327(3)	C11	H11B	0.9900
F9	C9	1.334(3)	C11	C12	1.499(4)
F10	C10	1.293(10)	C12	H12A	0.9900
F11	C10	1.460(12)	C12	H12B	0.9900
F12	C10	1.290(14)	C13	H13A	0.9800
O1	C1	1.247(3)	C13	H13B	0.9800
O2	C3	1.256(3)	C13	H13C	0.9800
O3	C6	1.253(3)	C14	H14A	0.9800
O4	C8	1.248(3)	C14	H14B	0.9800
O5	C11	1.444(3)	C14	H14C	0.9800
O5	C13	1.440(3)	F3A	C4A	1.311(13)
O6	C12	1.428(3)	C4A	F2A	1.305(14)
O6	C14	1.438(3)	C4A	F1A	1.328(14)
C1	C2	1.391(3)	F5A	C5A	1.43(4)
C1	C4	1.536(6)	F4A	C5A	1.13(3)
C1	C4A	1.552(13)	F6A	C5A	1.39(4)

Table S39 Bond Angles for 5-Mn(hfac)2DME.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Mn1	O4	170.93(7)	F4	C5	C3	110.8(2)
O1	Mn1	O5	104.64(7)	F5	C5	F6	109.8(3)
O1	Mn1	O6	84.86(6)	F5	C5	C3	110.8(3)
O2	Mn1	O1	83.68(6)	F6	C5	C3	112.6(3)
O2	Mn1	O3	113.52(7)	O3	C6	C7	127.8(2)
O2	Mn1	O4	93.08(6)	O3	C6	C9	113.8(2)
O2	Mn1	O5	90.82(6)	C7	C6	C9	118.4(2)
O2	Mn1	O6	157.98(6)	C6	C7	C8	121.6(2)
O3	Mn1	O1	90.91(7)	O4	C8	C7	128.2(2)
O3	Mn1	O4	82.60(6)	O4	C8	C10	113.9(2)
O3	Mn1	O5	152.63(6)	C7	C8	C10	117.9(2)
O3	Mn1	O6	85.37(6)	F7	C9	F9	106.4(2)

Table S39 Bond Angles for 5-Mn(hfac)2DME.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O4	Mn1	O5	83.83(6)	F7	C9	C6	110.8(2)
O4	Mn1	O6	100.85(6)	F8	C9	F7	107.3(2)
O6	Mn1	O5	74.00(6)	F8	C9	F9	107.1(2)
C1	O1	Mn1	128.82(15)	F8	C9	C6	114.2(2)
C3	O2	Mn1	128.57(14)	F9	C9	C6	110.5(2)
C6	O3	Mn1	128.35(15)	F10	C10	F11	88.5(8)
C8	O4	Mn1	128.05(16)	F10	C10	C8	111.5(6)
C11	O5	Mn1	110.31(14)	F11	C10	C8	107.4(5)
C13	O5	Mn1	118.62(15)	F12	C10	F10	127.1(12)
C13	O5	C11	111.8(2)	F12	C10	F11	104.0(11)
C12	O6	Mn1	114.29(13)	F12	C10	C8	112.9(12)
C12	O6	C14	112.32(18)	F10A	C10	C8	113.6(3)
C14	O6	Mn1	120.33(13)	F11A	C10	C8	111.2(3)
O1	C1	C2	128.4(2)	F11A	C10	F10A	107.7(3)
O1	C1	C4	115.2(3)	F11A	C10	F12A	106.7(4)
O1	C1	C4A	114.5(6)	F12A	C10	C8	112.1(3)
C2	C1	C4	116.2(3)	F12A	C10	F10A	105.2(3)
C2	C1	C4A	116.2(6)	O5	C11	C12	107.1(2)
C3	C2	C1	121.2(2)	O6	C12	C11	107.5(2)
O2	C3	C2	129.2(2)	F3A	C4A	C1	114.1(10)
O2	C3	C5	112.4(2)	F3A	C4A	F1A	109.0(17)
O2	C3	C5A	115.3(10)	F2A	C4A	C1	108.6(10)
C2	C3	C5	118.3(2)	F2A	C4A	F3A	109.9(11)
C2	C3	C5A	113.3(10)	F2A	C4A	F1A	105.4(16)
F1	C4	C1	111.7(6)	F1A	C4A	C1	109.5(15)
F2	C4	F1	107.0(6)	F5A	C5A	C3	100.3(17)
F2	C4	C1	113.3(4)	F4A	C5A	C3	122(2)
F3	C4	F1	108.4(7)	F4A	C5A	F5A	108(2)
F3	C4	F2	104.7(5)	F4A	C5A	F6A	125(2)
F3	C4	C1	111.3(4)	F6A	C5A	C3	106.4(18)
F4	C5	F5	105.3(3)	F6A	C5A	F5A	87(2)
F4	C5	F6	107.1(4)				

Table S40 Torsion Angles for 5-Mn(hfac)2DME.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Mn1	O1	C1	C2	1.7(4)	O4	C8	C10	F12A	42.3(4)
Mn1	O1	C1	C4	176.7(2)	O5	C11	C12	O6	-56.5(3)
Mn1	O1	C1	C4A	-166.8(6)	C1	C2	C3	O2	1.8(4)
Mn1	O2	C3	C2	1.4(4)	C1	C2	C3	C5	-173.0(3)
Mn1	O2	C3	C5	176.5(2)	C1	C2	C3	C5A	163.9(12)
Mn1	O2	C3	C5A	-160.4(12)	C2	C1	C4	F1	-163.1(7)
Mn1	O3	C6	C7	14.8(4)	C2	C1	C4	F2	76.0(5)

Table S40 Torsion Angles for 5-Mn(hfac)2DME.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Mn1	O3	C6	C9	164.78(16)	C2	C1	C4	F3	-41.7(5)
Mn1	O4	C8	C7	-12.1(4)	C2	C1	C4A	F3A	-68.0(13)
Mn1	O4	C8	C10	166.42(18)	C2	C1	C4A	F2A	55.0(11)
Mn1	O5	C11	C12	48.5(2)	C2	C1	C4A	F1A	169.6(15)
Mn1	O6	C12	C11	37.9(2)	C2	C3	C5	F4	-133.4(3)
O1	C1	C2	C3	-3.5(4)	C2	C3	C5	F5	110.1(3)
O1	C1	C4	F1	21.3(8)	C2	C3	C5	F6	-13.4(5)
O1	C1	C4	F2	-99.6(5)	C2	C3	C5A	F5A	139.5(14)
O1	C1	C4	F3	142.7(4)	C2	C3	C5A	F4A	-102(3)
O1	C1	C4A	F3A	101.9(12)	C2	C3	C5A	F6A	50(2)
O1	C1	C4A	F2A	-135.1(9)	C4	C1	C2	C3	-178.4(3)
O1	C1	C4A	F1A	-20.5(17)	C6	C7	C8	O4	-1.0(5)
O2	C3	C5	F4	51.0(4)	C6	C7	C8	C10	-179.5(3)
O2	C3	C5	F5	-65.6(3)	C7	C6	C9	F7	122.6(3)
O2	C3	C5	F6	170.9(4)	C7	C6	C9	F8	1.2(4)
O2	C3	C5A	F5A	-55.7(18)	C7	C6	C9	F9	-119.6(3)
O2	C3	C5A	F4A	63(3)	C7	C8	C10	F10	36.6(9)
O2	C3	C5A	F6A	-145.5(15)	C7	C8	C10	F11	132.0(6)
O3	C6	C7	C8	-0.4(4)	C7	C8	C10	F12	-113.9(11)
O3	C6	C9	F7	-57.8(3)	C7	C8	C10	F10A	-20.0(4)
O3	C6	C9	F8	-179.1(2)	C7	C8	C10	F11A	101.7(4)
O3	C6	C9	F9	60.0(3)	C7	C8	C10	F12A	-139.0(3)
O4	C8	C10	F10	-142.0(8)	C9	C6	C7	C8	179.2(2)
O4	C8	C10	F11	-46.7(7)	C13	O5	C11	C12	-177.3(2)
O4	C8	C10	F12	67.5(11)	C14	O6	C12	C11	179.5(2)
O4	C8	C10	F10A	161.3(3)	C4A	C1	C2	C3	164.8(6)
O4	C8	C10	F11A	-77.0(4)					

Table S41 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 5-Mn(hfac)2DME.

Atom	*x*	*y*	*z*	U(eq)
H2	3260.67	7268.92	7813.9	37
H7	8488.15	5181.77	5082.47	48
H11A	8827.64	8608.45	7033.36	49
H11B	8496.94	9630.16	7577.13	49
H12A	6839.79	9851.28	6385.91	45
H12B	7917.85	9786.46	5852.73	45
H13A	7562.45	7652.1	8929.41	69
H13B	8353.93	8661.9	9012.12	69
H13C	8723.1	7631.13	8514.59	69
H14A	5931.04	8116.96	4491.39	55
H14B	6687.2	9124.54	4402.23	55

Table S41 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 5-Mn(hfac)2DME.

Atom	*x*	*y*	*z*	U(eq)
H14C	5621.59	9196.7	4942.46	55

Table S42 Atomic Occupancy for 5-Mn(hfac)2DME.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
F1	0.700(8)	F2	0.700(8)	F3	0.700(8)
F4	0.864(6)	F5	0.864(6)	F6	0.864(6)
F10	0.194(8)	F11	0.194(8)	F12	0.194(8)
C4	0.700(8)	C5	0.864(6)	F3A	0.300(8)
C4A	0.300(8)	F2A	0.300(8)	F1A	0.300(8)
F10A	0.806(8)	F11A	0.806(8)	F12A	0.806(8)
F5A	0.136(6)	F4A	0.136(6)	F6A	0.136(6)
C5A	0.136(6)				

Experimental

Single crystals of $C_{14}H_{12}F_{12}MnO_6$ **5-Mn(hfac)$_2$DME** were grown by vacuum sublimation, in a three-zone furnace under vacuum (10^{-2} mbar) @ 55 °C to give yellow block crystals. A suitable crystal was selected and mounted on a SuperNova, Dual, Cu at home/near, Pilatus 200K diffractometer. The crystal was kept at 100.00(15) K during data collection. The crystal was kept at 200.00 K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

7. Detailed Crystal Structure Report for 6, $Mn(hfac)_2THF(OH_2)$

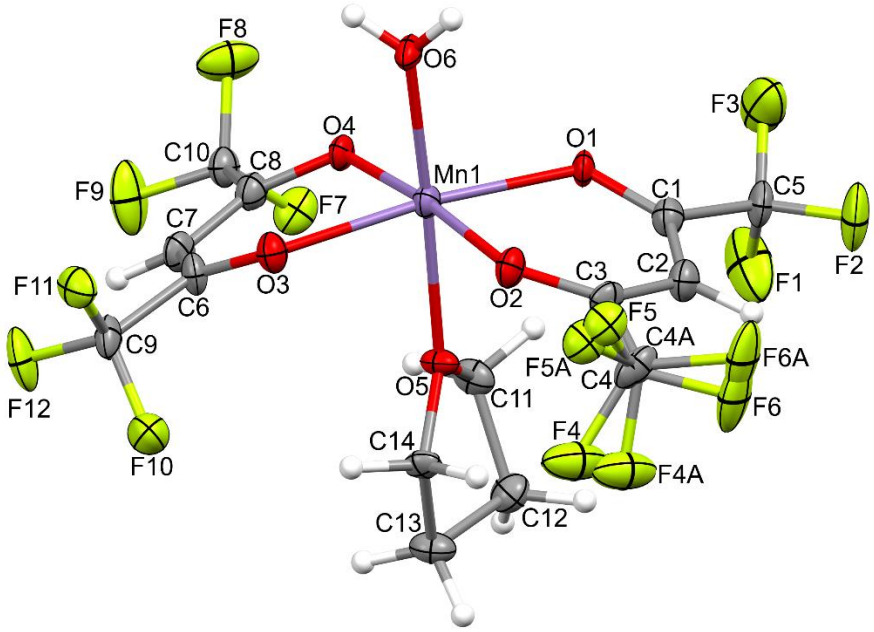


Fig. S9. Displacement ellipsoids plot (40% probability) depicting the asymmetric unit in structure **6**, consisting of discrete neutral *trans* [$Mn(hfac)_2thf(OH_2)$]. The atom numbering scheme used in the Tables is shown. A 10% whole molecule disorder was modelled only by Mn1A (omitted from view).

A persistent, large residual peak in the final difference map occurs at 2.23 Å from Mn and at an unusual angle of about 43° from the MnO_4 coordination plane of the $Mn(hfac)_2$ moiety. A reviewer suggested this to be from *whole molecule disorder* and indeed refining the two Mn sites as disordered produced the second metal at ~10% occupancy. This is too low to necessitate modelling the remaining atoms (though that is the reason for the max peak of 1.2 e/Å^3 in the final difference map).

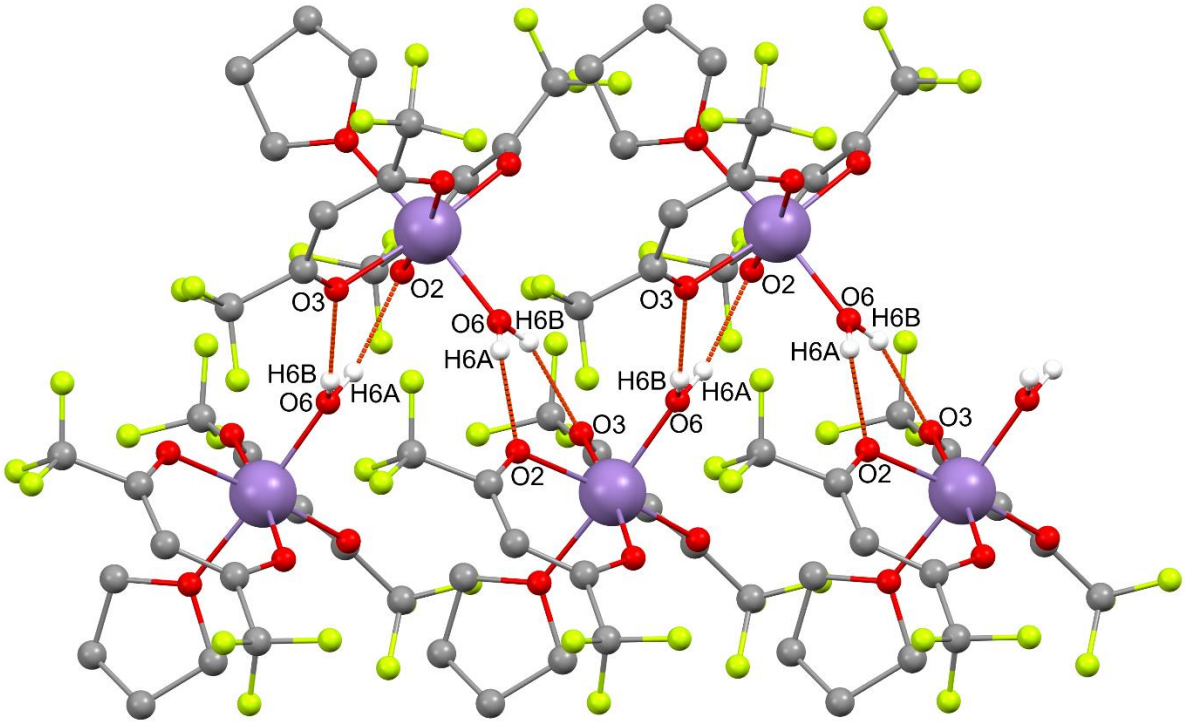


Fig. S10. Ball and stick representation of a portion of the infinite H-bonded chain that connects O6 aqua H-atoms to hfac O atoms on the neighbouring molecule. See Table S48 for relevant parameters.

Table S43 Crystal data and structure refinement for 6-Mn(hfac)$_2$THF(OH$_2$).

Identification code	RB23008i2f2
Empirical formula	C14H12F12MnO6
Formula weight	559.18
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	21.5361(3)
b/Å	6.81320(10)
c/Å	27.8521(5)
α/°	90
β/°	104.621(2)
γ/°	90
Volume/Å3	3954.39(11)
Z	8
ρcalcg/cm3	1.878
μ/mm 1	6.811
F(000)	2216.0
Crystal size/mm3	0.505 × 0.074 × 0.048
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.56 to 160.85
Index ranges	-27 ≤ h ≤ 21, -8 ≤ k ≤ 8, -34 ≤ l ≤ 35
Reflections collected	40093
Independent reflections	4294 [Rint = 0.0672, Rsigma = 0.0304]
Data/restraints/parameters	4294/12/321
Goodness-of-fit on F2	1.095
Final R indexes [I>=2σ (I)]	R1 = 0.0941, wR2 = 0.2397
Final R indexes [all data]	R1 = 0.0977, wR2 = 0.2417
Largest diff. peak/hole / e Å-3	1.20/-1.71

Table S44 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 6-Mn(hfac)$_2$THF(OH$_2$). U$_{eq}$ is defined as 1/3 of the trace of the orthogonalized U$_{IJ}$ tensor.

Atom	*x*	*y*	*z*	U(eq)
Mn1	7230.5(4)	4160.2(15)	6614.6(4)	18.8(3)
F7	8223(2)	2524(7)	5354.6(15)	39.5(10)
F8	8731(3)	514(7)	5906.9(19)	54.2(13)
F9	9196(2)	3079(10)	5746(2)	63.9(17)
F10	8609(2)	9580(7)	6932.1(19)	47.8(12)
F11	9129(2)	7691(6)	7520.5(15)	37.6(10)
F12	9479(2)	8147(9)	6868.2(19)	53.7(14)
F1	5386(3)	2948(12)	5283.5(19)	80(2)
F2	4726(2)	2596(9)	5743(2)	59.3(16)
F3	5425(3)	452(9)	5718(3)	72.9(18)
O1	6373.7(19)	2701(7)	6215.0(17)	25.4(9)
O2	6590(2)	5877(7)	6937.9(17)	30.4(10)
O3	8062(2)	5909(7)	6967.3(17)	30.3(10)

Table S44 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 6-Mn(hfac)$_2$THF(OH$_2$). U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O4	7868.9(19)	2727(7)	6248.6(17)	25.1(9)
O5	7055(2)	6368(7)	6004.8(16)	27.2(10)
O6	7424(2)	2202(8)	7230.7(17)	31.1(11)
C1	5811(3)	3431(11)	6133(3)	30.8(14)
C2	5602(3)	5031(11)	6367(3)	32.6(14)
C3	5994(3)	6069(10)	6749(2)	26.9(13)
C5	5326(3)	2407(11)	5717(3)	33.3(15)
C6	8541(3)	6160(10)	6800(2)	27.5(13)
C7	8720(3)	5139(11)	6418(3)	30.2(14)
C8	8384(3)	3501(11)	6186(3)	30.3(14)
C9	8954(3)	7872(12)	7033(2)	31.7(15)
C10	8644(3)	2437(10)	5795(3)	30.1(14)
C11	6911(4)	5807(10)	5486(2)	31.5(14)
C12	6595(4)	7624(11)	5208(3)	36.6(16)
C13	6951(4)	9291(10)	5530(3)	34.3(15)
C14	7030(3)	8470(9)	6047(2)	26.3(13)
F4	5966(11)	9494(16)	6843(7)	63(4)
F5	5868(12)	7720(30)	7462(5)	41(4)
F6	5081(7)	7930(30)	6824(10)	70(6)
C4	5720(8)	7796(19)	6974(6)	31.1(16)
F4A	5670(17)	9390(30)	6712(12)	63(4)
F5A	5970(20)	8040(60)	7434(10)	41(4)
F6A	5060(13)	7340(60)	6946(18)	70(6)
C4A	5674(13)	7700(30)	6969(10)	31.1(16)
Mn1A	7223(4)	881(15)	6621(4)	18.8(3)

Table S45 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 6-Mn(hfac)$_2$THF(OH$_2$). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	12.8(5)	19.7(5)	25.1(5)	-0.1(4)	6.7(4)	0.2(4)
F7	40(2)	54(3)	26.2(19)	-3.8(18)	11.7(17)	7(2)
F8	75(3)	41(3)	55(3)	4(2)	31(3)	24(3)
F9	35(2)	100(5)	66(3)	-36(3)	31(2)	-15(3)
F10	39(2)	39(3)	63(3)	3(2)	7(2)	-2(2)
F11	40(2)	37(2)	30(2)	-2.6(17)	-0.5(17)	-8.6(18)
F12	29(2)	76(4)	63(3)	-21(3)	25(2)	-22(2)
F1	71(4)	132(6)	31(2)	-7(3)	0(2)	-44(4)
F2	16.9(19)	85(4)	71(3)	-33(3)	2(2)	-3(2)
F3	53(3)	48(3)	103(5)	-22(3)	-8(3)	-2(3)
O1	12.7(19)	30(2)	32(2)	-2.3(18)	3.0(16)	-1.7(16)
O2	21(2)	38(3)	34(2)	-2(2)	9.9(18)	2.9(19)
O3	23(2)	36(3)	33(2)	-3(2)	10.2(18)	-3.2(19)
O4	15.1(19)	29(2)	33(2)	-0.3(18)	9.8(17)	2.0(17)
O5	36(2)	19(2)	26(2)	4.4(17)	6.3(18)	0.5(18)
O6	18(2)	47(3)	29(2)	13(2)	8.0(18)	2(2)
C1	23(3)	36(4)	34(3)	0(3)	8(3)	-2(3)
C2	22(3)	39(4)	37(4)	-1(3)	8(3)	0(3)
C3	24(3)	27(3)	33(3)	0(3)	11(2)	9(3)
C5	17(3)	45(4)	34(3)	-6(3)	1(3)	-3(3)
C6	17(3)	34(3)	32(3)	-7(3)	7(2)	-8(3)
C7	22(3)	34(4)	39(4)	-3(3)	14(3)	2(3)
C8	24(3)	34(4)	33(3)	1(3)	8(3)	2(3)
C9	17(3)	48(4)	30(3)	3(3)	7(2)	-4(3)
C10	22(3)	37(4)	34(3)	-1(3)	12(3)	0(3)
C11	41(4)	28(3)	27(3)	-3(3)	10(3)	-4(3)
C12	35(4)	42(4)	31(3)	2(3)	3(3)	3(3)
C13	47(4)	26(3)	31(3)	5(3)	12(3)	1(3)
C14	32(3)	17(3)	29(3)	-4(2)	6(3)	2(2)
F4	90(12)	39(3)	78(9)	16(4)	53(9)	20(6)
F5	45(8)	45(7)	34(3)	-3(3)	16(3)	9(6)
F6	22(3)	99(13)	84(13)	-43(10)	5(4)	16(5)
C4	24(4)	39(4)	31(3)	0(3)	8(3)	9(3)
F4A	90(12)	39(3)	78(9)	16(4)	53(9)	20(6)
F5A	45(8)	45(7)	34(3)	-3(3)	16(3)	9(6)
F6A	22(3)	99(13)	84(13)	-43(10)	5(4)	16(5)
C4A	24(4)	39(4)	31(3)	0(3)	8(3)	9(3)
Mn1A	12.8(5)	19.7(5)	25.1(5)	-0.1(4)	6.7(4)	0.2(4)

Table S46 Bond Lengths for 6-Mn(hfac)$_2$THF(OH$_2$).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	O1	2.144(4)	C6	C9	1.511(9)
Mn1	O2	2.170(5)	C7	H7	0.9500
Mn1	O3	2.169(5)	C7	C8	1.396(10)

Table S46 Bond Lengths for 6-Mn(hfac)$_2$THF(OH$_2$).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	O4	2.143(4)	C8	C10	1.527(9)
Mn1	O5	2.229(4)	C11	H11A	0.9900
Mn1	O6	2.130(5)	C11	H11B	0.9900
F7	C10	1.331(8)	C11	C12	1.527(10)
F8	C10	1.348(8)	C12	H12A	0.9900
F9	C10	1.306(8)	C12	H12B	0.9900
F10	C9	1.371(9)	C12	C13	1.529(10)
F11	C9	1.320(8)	C13	H13A	0.9900
F12	C9	1.338(7)	C13	H13B	0.9900
F1	C5	1.299(9)	C13	C14	1.514(9)
F2	C5	1.320(8)	C14	H14A	0.9900
F3	C5	1.348(9)	C14	H14B	0.9900
O1	C1	1.277(8)	F4	C4	1.360(13)
O2	C3	1.265(8)	F4	F4A	0.65(3)
O3	C6	1.246(8)	F4	C4A	1.46(3)
O4	C8	1.280(8)	F5	C4	1.316(12)
O5	C11	1.452(8)	F5	C4A	1.33(4)
O5	C14	1.439(8)	F6	C4	1.336(12)
O6	H6A	0.84(2)	F6	F4A	1.70(3)
O6	H6B	0.84(2)	F6	F6A	0.54(5)
C1	C2	1.400(10)	F6	C4A	1.25(4)
C1	C5	1.520(9)	C4	F4A	1.30(3)
C2	H2	0.9500	C4	F5A	1.27(4)

Table S47 Bond Angles for 6-Mn(hfac)$_2$THF(OH$_2$).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Mn1	O2	84.92(17)	F4A	F4	C4	71(3)
O1	Mn1	O3	173.78(19)	F4A	F4	C4A	68(3)
O1	Mn1	O5	87.66(17)	C4	F5	C4A	5.0(17)
O2	Mn1	O5	87.08(18)	C4	F6	F4A	48.8(12)
O3	Mn1	O2	93.14(18)	F6A	F6	C4	90(5)
O3	Mn1	O5	86.35(18)	F6A	F6	F4A	138(6)
O4	Mn1	O1	96.50(17)	F6A	F6	C4A	87(5)
O4	Mn1	O2	174.04(19)	C4A	F6	C4	3.4(15)
O4	Mn1	O3	84.84(17)	C4A	F6	F4A	52.0(13)
O4	Mn1	O5	87.19(17)	F4	C4	C3	109.2(10)
O6	Mn1	O1	95.48(19)	F4	C4	F6A	128(2)
O6	Mn1	O2	91.09(19)	F5	C4	C3	112.1(11)
O6	Mn1	O3	90.46(19)	F5	C4	F4	107.6(12)
O6	Mn1	O4	94.53(18)	F5	C4	F6	106.8(11)
O6	Mn1	O5	176.2(2)	F5	C4	F6A	91(3)
C1	O1	Mn1	124.5(4)	F6	C4	C3	113.5(12)
C3	O2	Mn1	124.5(4)	F6	C4	F4	107.4(12)
C6	O3	Mn1	124.9(4)	F6	C4	F6A	22(2)
C8	O4	Mn1	124.0(4)	F4A	C4	C3	113.7(17)

Table S47 Bond Angles for 6-Mn(hfac)$_2$THF(OH$_2$).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	O5	Mn1	122.3(4)	F4A	C4	F4	28.3(13)
C14	O5	Mn1	127.7(4)	F4A	C4	F5	125(2)
C14	O5	C11	109.9(5)	F4A	C4	F6	80.5(16)
O1	C1	C2	128.5(6)	F4A	C4	F6A	102(2)
O1	C1	C5	113.3(6)	F5A	C4	C3	114(2)
C2	C1	C5	118.2(6)	F5A	C4	F4	94(3)
C3	C2	C1	123.5(6)	F5A	C4	F5	15(3)
O2	C3	C2	129.0(6)	F5A	C4	F6	117(3)
O2	C3	C4	111.5(8)	F5A	C4	F4A	114(2)
O2	C3	C4A	115.1(13)	F5A	C4	F6A	104(2)
C2	C3	C4	119.4(8)	F6A	C4	C3	107(2)
C2	C3	C4A	115.9(13)	F4	F4A	F6	129(4)
C4A	C3	C4	4.4(15)	F4	F4A	C4	81(3)
F1	C5	F2	110.6(6)	F4	F4A	C4A	85(3)
F1	C5	F3	103.2(7)	C4	F4A	F6	50.7(12)
F1	C5	C1	111.6(6)	C4	F4A	C4A	4.4(19)
F2	C5	F3	104.7(6)	C4A	F4A	F6	46.4(16)
F2	C5	C1	114.0(6)	C4	F5A	C4A	4.8(17)
F3	C5	C1	112.0(6)	F6	F6A	C4	68(4)
O3	C6	C7	128.9(6)	F6	F6A	C4A	69(4)
C4	F4	C4A	2.6(18)				

Table S48 Hydrogen Bonds for 6-Mn(hfac)$_2$THF(OH$_2$).

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O6	H6A	O21	0.84(2)	2.09(5)	2.864(7)	152(8)
O6	H6B	O31	0.84(2)	2.03(4)	2.836(6)	161(9)

[1]3/2-X,-1/2+Y,3/2-Z

Table S49 Torsion Angles for 6-Mn(hfac)$_2$THF(OH$_2$).

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Mn1	O1	C1	C2	-16.4(10)	C4	F4	C4A	F6	166(25)
Mn1	O1	C1	C5	162.1(4)	C4	F4	C4A	F4A	-174(23)
Mn1	O2	C3	C2	12.6(10)	C4	F4	C4A	F5A	45(23)
Mn1	O2	C3	C4	-163.3(7)	C4	F4	C4A	F6A	157(25)
Mn1	O2	C3	C4A	-166.0(11)	C4	F5	C4A	C3	86(12)
Mn1	O3	C6	C7	-13.5(11)	C4	F5	C4A	F4	-25(11)
Mn1	O3	C6	C9	163.3(4)	C4	F5	C4A	F6	-138(13)
Mn1	O4	C8	C7	15.6(10)	C4	F5	C4A	F4A	-45(11)
Mn1	O4	C8	C10	-163.7(4)	C4	F5	C4A	F5A	-7(18)
Mn1	O5	C11	C12	160.1(4)	C4	F5	C4A	F6A	-156(13)
Mn1	O5	C14	C13	175.5(4)	C4	F6	F4A	F4	-24(4)
O1	C1	C2	C3	-1.8(12)	C4	F6	F4A	C4A	1.5(18)
O1	C1	C5	F1	-77.7(8)	C4	F6	F6A	C4A	-1.6(12)
O1	C1	C5	F2	156.1(7)	C4	F6	C4A	C3	-129(28)

Table S49 Torsion Angles for 6-Mn(hfac)$_2$THF(OH$_2$).

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C1	C5	F3	37.4(9)	C4	F6	C4A	F4	-11(26)
O2	C3	C4	F4	66.9(16)	C4	F6	C4A	F5	99(27)
O2	C3	C4	F5	-52.2(16)	C4	F6	C4A	F4A	-20(27)
O2	C3	C4	F6	-173.3(13)	C4	F6	C4A	F5A	86(27)
O2	C3	C4	F4A	97(2)	C4	F6	C4A	F6A	151(25)
O2	C3	C4	F5A	-36(3)	C4	F4A	C4A	C3	-77(14)
O2	C3	C4	F6A	-151(2)	C4	F4A	C4A	F4	4(14)
O2	C3	C4A	F4	65(2)	C4	F4A	C4A	F5	55(15)
O2	C3	C4A	F5	-44(3)	C4	F4A	C4A	F6	165(15)
O2	C3	C4A	F6	-176(2)	C4	F4A	C4A	F5A	46(14)
O2	C3	C4A	F4A	92(2)	C4	F4A	C4A	F6A	161(15)
O2	C3	C4A	F5A	-28(2)	C4	F5A	C4A	C3	80(13)
O2	C3	C4A	F6A	-151(2)	C4	F5A	C4A	F4	-25(13)
O3	C6	C7	C8	-5.3(12)	C4	F5A	C4A	F5	172(20)
O3	C6	C9	F10	-62.6(8)	C4	F5A	C4A	F6	-133(14)
O3	C6	C9	F11	55.1(8)	C4	F5A	C4A	F4A	-42(13)
O3	C6	C9	F12	178.5(6)	C4	F5A	C4A	F6A	-155(14)
O4	C8	C10	F7	62.1(8)	C4	F6A	C4A	C3	-165(54)
O4	C8	C10	F8	-55.1(8)	C4	F6A	C4A	F4	-31(51)
O4	C8	C10	F9	-174.9(6)	C4	F6A	C4A	F5	79(52)
O5	C11	C12	C13	34.4(7)	C4	F6A	C4A	F6	-54(51)
C1	C2	C3	O2	3.9(12)	C4	F6A	C4A	F4A	-44(52)
C1	C2	C3	C4	179.5(9)	C4	F6A	C4A	F5A	71(53)
C1	C2	C3	C4A	-177.5(12)	F4A	F4	C4	C3	104(4)
C2	C1	C5	F1	101.0(8)	F4A	F4	C4	F5	-134(4)
C2	C1	C5	F2	-25.2(10)	F4A	F4	C4	F6	-19(4)
C2	C1	C5	F3	-143.9(7)	F4A	F4	C4	F5A	-139(4)
C2	C3	C4	F4	-109.4(15)	F4A	F4	C4	F6A	-27(5)
C2	C3	C4	F5	131.4(13)	F4A	F4	C4A	C3	107(4)
C2	C3	C4	F6	10.4(16)	F4A	F4	C4A	F5	-137(4)
C2	C3	C4	F4A	-79(2)	F4A	F4	C4A	F6	-20(4)
C2	C3	C4	F5A	147(3)	F4A	F4	C4A	F5A	-141(4)
C2	C3	C4	F6A	33(3)	F4A	F4	C4A	F6A	-29(5)
C2	C3	C4A	F4	-114.0(17)	F4A	F6	C4	C3	-112(2)
C2	C3	C4A	F5	137(2)	F4A	F6	C4	F4	9.0(19)
C2	C3	C4A	F6	5(3)	F4A	F6	C4	F5	124(2)
C2	C3	C4A	F4A	-87(2)	F4A	F6	C4	F5A	113(2)
C2	C3	C4A	F5A	153(2)	F4A	F6	C4	F6A	172(7)
C2	C3	C4A	F6A	31(2)	F4A	F6	F6A	C4	-9(8)
C3	C4	F4A	F4	-87(4)	F4A	F6	F6A	C4A	-11(7)
C3	C4	F4A	F6	111.6(15)	F4A	F6	C4A	C3	-109(2)
C3	C4	F4A	C4A	97(15)	F4A	F6	C4A	F4	9(2)
C3	C4	F5A	C4A	-94(13)	F4A	F6	C4A	F5	119(3)
C3	C4	F6A	F6	-111(6)	F4A	F6	C4A	F5A	106(2)
C3	C4	F6A	C4A	14(52)	F4A	F6	C4A	F6A	171(7)

Table S49 Torsion Angles for 6-Mn(hfac)$_2$THF(OH$_2$).

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C5	C1	C2	C3	179.7(7)	F4A	C4	F5A	C4A	133(14)
C6	C7	C8	O4	4.1(12)	F4A	C4	F6A	F6	8(7)
C6	C7	C8	C10	-176.6(6)	F4A	C4	F6A	C4A	134(54)
C7	C6	C9	F10	114.6(7)	F5A	C4	F4A	F4	46(4)
C7	C6	C9	F11	-127.8(7)	F5A	C4	F4A	F6	-115(3)
C7	C6	C9	F12	-4.3(10)	F5A	C4	F4A	C4A	-130(14)
C7	C8	C10	F7	-117.3(7)	F5A	C4	F6A	F6	128(7)
C7	C8	C10	F8	125.5(7)	F5A	C4	F6A	C4A	-107(54)
C7	C8	C10	F9	5.7(10)	F6A	F6	C4	C3	77(7)
C9	C6	C7	C8	178.1(6)	F6A	F6	C4	F4	-163(7)
C11	O5	C14	C13	-7.7(7)	F6A	F6	C4	F5	-47(7)
C11	C12	C13	C14	-38.2(7)	F6A	F6	C4	F4A	-172(7)
C12	C13	C14	O5	28.9(7)	F6A	F6	C4	F5A	-59(7)
C14	O5	C11	C12	-17.0(7)	F6A	F6	F4A	F4	-11(12)
F4	C4	F4A	F6	-162(4)	F6A	F6	F4A	C4	13(10)
F4	C4	F4A	C4A	-176(14)	F6A	F6	F4A	C4A	14(9)
F4	C4	F5A	C4A	153(14)	F6A	F6	C4A	C3	80(7)
F4	C4	F6A	F6	21(8)	F6A	F6	C4A	F4	-162(6)
F4	C4	F6A	C4A	147(54)	F6A	F6	C4A	F5	-52(7)
F4	F4A	C4A	C3	-81(4)	F6A	F6	C4A	F4A	-171(7)
F4	F4A	C4A	F5	51(5)	F6A	F6	C4A	F5A	-65(7)
F4	F4A	C4A	F6	161(4)	F6A	C4	F4A	F4	158(4)
F4	F4A	C4A	F5A	42(4)	F6A	C4	F4A	F6	-3(3)
F4	F4A	C4A	F6A	157(4)	F6A	C4	F4A	C4A	-18(13)
F5	C4	F4A	F4	58(4)	F6A	C4	F5A	C4A	22(13)
F5	C4	F4A	F6	-103.9(17)	C4A	C3	C4	F4	-147(22)
F5	C4	F4A	C4A	-118(15)	C4A	C3	C4	F5	93(21)
F5	C4	F5A	C4A	-8(20)	C4A	C3	C4	F6	-28(21)
F5	C4	F6A	F6	135(6)	C4A	C3	C4	F4A	-117(22)
F5	C4	F6A	C4A	-99(53)	C4A	C3	C4	F5A	109(21)
F6	C4	F4A	F4	162(4)	C4A	C3	C4	F6A	-5(19)
F6	C4	F4A	C4A	-14(14)	C4A	F4	C4	C3	111(24)
F6	C4	F5A	C4A	42(13)	C4A	F4	C4	F5	-128(24)
F6	C4	F6A	C4A	125(51)	C4A	F4	C4	F6	-13(23)
F6	F4A	C4A	C3	118(3)	C4A	F4	C4	F4A	6(23)
F6	F4A	C4A	F4	-161(4)	C4A	F4	C4	F5A	-132(23)
F6	F4A	C4A	F5	-110(2)	C4A	F4	C4	F6A	-21(22)
F6	F4A	C4A	F5A	-119(3)	C4A	F4	F4A	F6	18(3)
F6	F4A	C4A	F6A	-4(3)	C4A	F4	F4A	C4	-0.3(10)
F6	F6A	C4A	C3	-111(7)	C4A	F5	C4	C3	-87(12)
F6	F6A	C4A	F4	23(8)	C4A	F5	C4	F4	153(12)
F6	F6A	C4A	F5	132(7)	C4A	F5	C4	F6	38(12)
F6	F6A	C4A	F4A	10(7)	C4A	F5	C4	F4A	128(13)
F6	F6A	C4A	F5A	125(7)	C4A	F5	C4	F5A	173(19)
C4	C3	C4A	F4	29(20)	C4A	F5	C4	F6A	22(12)

Table S49 Torsion Angles for 6-Mn(hfac)$_2$THF(OH$_2$).

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C4	C3	C4A	F5	-79(21)	C4A	F6	C4	C3	47(26)
C4	C3	C4A	F6	148(23)	C4A	F6	C4	F4	168(27)
C4	C3	C4A	F4A	56(20)	C4A	F6	C4	F5	-77(27)
C4	C3	C4A	F5A	-64(21)	C4A	F6	C4	F4A	159(28)
C4	C3	C4A	F6A	174(22)	C4A	F6	C4	F5A	-88(28)
C4	F4	F4A	F6	18(3)	C4A	F6	C4	F6A	-29(25)
C4	F4	F4A	C4A	0.3(10)	C4A	F6	F4A	F4	-25(5)
C4	F4	C4A	C3	-66(23)	C4A	F6	F4A	C4	-1.5(18)
C4	F4	C4A	F5	50(24)	C4A	F6	F6A	C4	1.6(12)

Table S50 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 6-Mn(hfac)$_2$THF(OH$_2$).

Atom	*x*	*y*	*z*	U(eq)
H6A	7790(20)	1870(140)	7400(30)	47
H6B	7200(40)	1770(130)	7420(30)	47
H2	5165.16	5419.43	6255.3	39
H7	9082.75	5580.82	6312.83	36
H11A	6615.09	4669.86	5419.57	38
H11B	7307.88	5463.94	5386.7	38
H12A	6129.47	7661.76	5189.08	44
H12B	6657.23	7678.78	4867.94	44
H13A	7372.51	9548.28	5460.09	41
H13B	6695.52	10515.3	5481.63	41
H14A	7429.5	8967.57	6273.34	32
H14B	6662.35	8859.81	6179.82	32

Table S51 Atomic Occupancy for 6-Mn(hfac)$_2$THF(OH$_2$).

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
Mn1	0.905(2)	F4	0.64(3)	F5	0.64(3)
F6	0.64(3)	C4	0.64(3)	F4A	0.36(3)
F5A	0.36(3)	F6A	0.36(3)	C4A	0.36(3)
Mn1A	0.095(2)				

Experimental

Single crystals of $C_{14}H_{12}F_{12}MnO_{6.31}$ **6-Mn(hfac)$_2$THF(OH$_2$)** were grown from a concentrated solution in THF at –18 °C for 12 h. A suitable crystal was selected and mounted in Paratone™ oil on a 100 μm MiTeGen loop on a SuperNova, Dual, Cu at home/near, Pilatus 200K diffractometer. The crystal was kept at 99.99(10) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

8. Detailed Crystal Structure Report for 7, $Mn(hfac)_2(THF)_2$

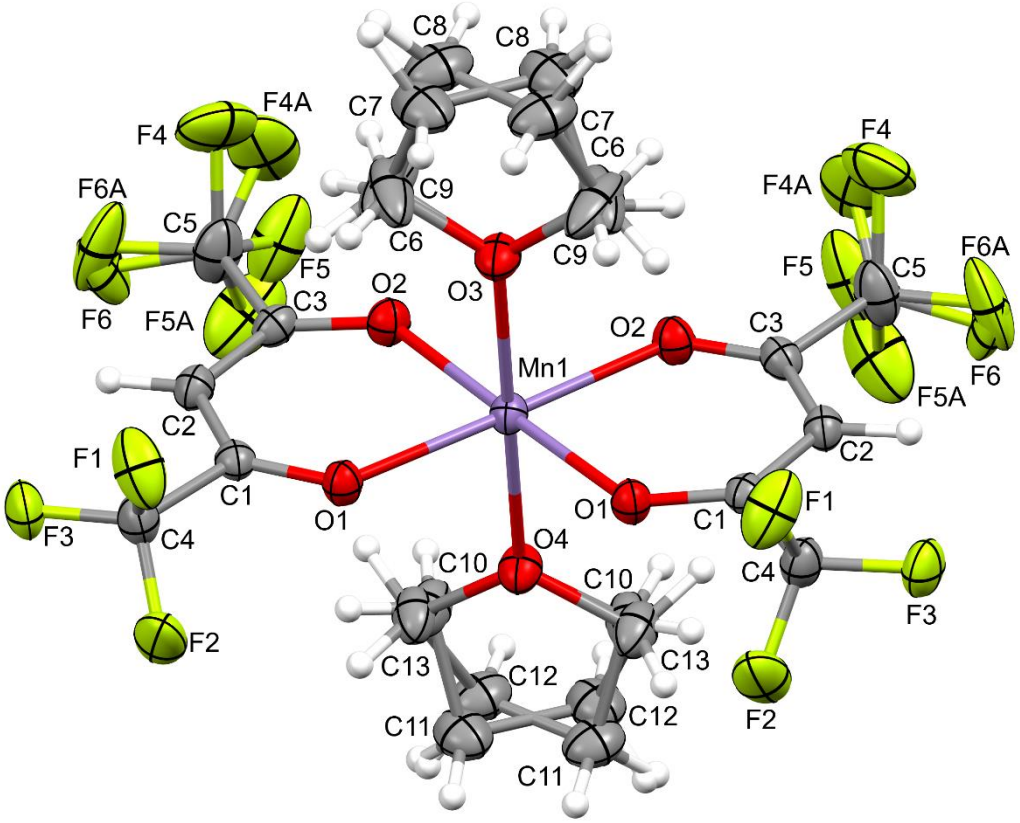


Fig. S11. Displacement ellipsoids plot (40% probability) depicting the asymmetric unit in structure **7**, consisting of discrete neutral *trans* $[Mn(hfac)_2(THF)_2]$. The atom numbering scheme used in the Tables is shown. The hfac ligands are symmetry equivalent (left←→right) as are the puckered THF. For a description of the positional disorder (shown) see the text following.

The monomeric complex in **7** crystallizes on a mirror plane that contains the Mn ion and the oxygen atoms O3,4 of the THF ligand. Consequently, the two hfac ligands are mirror images of each other, with an ordered C4 CF_3 and a rotationally disordered C5 CF_3. Each are mirror imaged. The puckered thf ligands therefore also are reflection disordered and show rather larger displacement ellipsoids.

Table S52 Crystal data and structure refinement for 7-Mn(hfac)$_2$(THF)$_2$.

Identification code	d23116a_c
Empirical formula	$C_{18}H_{18}O_6F_{12}Mn$
Formula weight	613.26
Temperature/K	150.03
Crystal system	orthorhombic
Space group	Pnma
a/Å	15.4825(8)
b/Å	19.6279(8)
c/Å	7.7219(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2346.6(2)
Z	4
ρ_{calc}g/cm^3	1.736
μ/mm^{-1}	0.691
F(000)	1228.0
Crystal size/mm^3	0.3 × 0.23 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.15 to 54.932
Index ranges	-20 ≤ h ≤ 20, -23 ≤ k ≤ 25, -10 ≤ l ≤ 9
Reflections collected	40469
Independent reflections	2764 [R_{int} = 0.0278, R_{sigma} = 0.0128]
Data/restraints/parameters	2764/79/212
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0308, wR_2 = 0.0768
Final R indexes [all data]	R_1 = 0.0374, wR_2 = 0.0812
Largest diff. peak/hole / e Å^{-3}	0.36/-0.30

Table S53 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 7-Mn(hfac)$_2$(THF)$_2$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mn1	3730.5(2)	2500	4775.2(4)	25.38(10)
F1	4623.1(10)	4291.1(6)	848.2(15)	62.6(4)
F2	5675.4(7)	4203.5(6)	2644(2)	66.0(4)
F3	4807.9(7)	5046.0(5)	2812.8(15)	45.1(3)
F4	1714(3)	4378(5)	5974(14)	79(2)
F5	2297(8)	4123(3)	8342(10)	77(3)
F6	2696(6)	5009(3)	6984(12)	67(2)
F4A	1760(3)	4169(3)	6983(14)	89(3)
F5A	2828(7)	4297(3)	8655(4)	87(2)
F6A	2562(5)	5021(3)	6691(9)	77.7(18)
O1	4409.0(7)	3317.8(5)	3532.2(14)	30.0(2)
O2	3029.1(7)	3308.5(5)	6017.0(15)	32.6(3)
O3	2796.6(11)	2500	2625(2)	37.4(4)

Table S53 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 7-Mn(hfac)$_2$(THF)$_2$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O4	4652.5(11)	2500	6953(2)	35.2(4)
C1	4282.0(10)	3944.5(8)	3682(2)	26.7(3)
C2	3693.4(10)	4283.1(8)	4741(2)	29.8(3)
C3	3123.5(10)	3935.3(8)	5820(2)	29.6(3)
C4	4852.2(12)	4379.0(8)	2493(2)	37.0(4)
C5	2517.3(15)	4369.0(10)	6935(3)	50.5(5)
C6	2399(7)	1896(3)	1913(12)	70.7(13)
C7	1964(3)	2162(2)	223(6)	54.8(9)
C8	1613(3)	2819(2)	916(6)	54.8(9)
C9	2462(6)	3075(3)	1726(13)	70.7(13)
C10	4887(6)	1938(3)	8012(11)	45.7(9)
C11	5696(3)	2130(2)	8971(7)	48.9(10)
C12	5374(3)	2828(2)	9497(7)	48.9(10)
C13	4967(7)	3129(3)	7779(11)	45.7(9)

Table S54 Anisotropic Displacement Parameters (Å^2×10^3) for 7-Mn(hfac)$_2$(THF)$_2$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	29.16(18)	21.98(16)	25.01(17)	0	-0.50(13)	0
F1	101.3(10)	53.7(7)	32.8(6)	1.9(5)	11.9(6)	-25.5(7)
F2	35.2(6)	48.4(7)	114.4(12)	16.3(7)	21.4(7)	-2.3(5)
F3	54.5(7)	26.5(5)	54.4(7)	3.9(4)	5.1(5)	-8.4(5)
F4	38.9(19)	99(4)	99(5)	-15(3)	7(2)	25(2)
F5	125(7)	62(3)	45(3)	15(2)	45(4)	41(4)
F6	65(3)	38(3)	98(5)	-40(3)	34(3)	-16(3)
F4A	52.0(19)	74(2)	141(7)	-25(3)	47(3)	7.0(17)
F5A	130(5)	97(3)	32.7(13)	-15.2(15)	9(2)	47(3)
F6A	117(4)	43(3)	73(3)	16(2)	46(2)	45(2)
O1	32.2(6)	25.5(5)	32.2(6)	-0.7(4)	5.0(5)	0.6(4)
O2	35.5(6)	30.0(6)	32.3(6)	-0.7(5)	5.9(5)	2.0(5)
O3	42.2(10)	32.8(8)	37.2(9)	0	-13.7(8)	0
O4	46.3(10)	30.0(8)	29.4(8)	0	-10.5(7)	0
C1	27.9(7)	26.3(7)	25.7(7)	0.9(6)	-3.6(6)	-1.6(6)
C2	35.3(8)	24.6(7)	29.6(8)	-1.2(6)	-2.7(6)	2.7(6)
C3	31.9(8)	30.1(8)	26.9(7)	-2.2(6)	-1.4(6)	6.4(6)
C4	40.4(9)	28.5(8)	42.0(9)	0.2(7)	5.7(7)	-4.4(7)
C5	60.8(13)	38.4(10)	52.3(12)	-0.5(9)	23.3(10)	11.1(9)
C6	95(2)	44.5(14)	72(2)	21(3)	-53(2)	-32(4)
C7	50(3)	69.9(17)	44(2)	-13.0(14)	-17.0(15)	13.9(14)
C8	50(3)	69.9(17)	44(2)	-13.0(14)	-17.0(15)	13.9(14)
C9	95(2)	44.5(14)	72(2)	21(3)	-53(2)	-32(4)
C10	62.3(18)	31.8(13)	43.0(19)	6(2)	-20.0(16)	-6(3)
C11	48(3)	59.0(14)	40(3)	-5.5(13)	-12.6(16)	8.5(13)

Table S54 Anisotropic Displacement Parameters ($Å^2×10^3$) for 7-Mn(hfac)$_2$(THF)$_2$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C12	48(3)	59.0(14)	40(3)	-5.5(13)	-12.6(16)	8.5(13)
C13	62.3(18)	31.8(13)	43.0(19)	6(2)	-20.0(16)	-6(3)

Table S55 Bond Lengths for 7-Mn(hfac)$_2$(THF)$_2$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	O1	2.1450(11)	C2	C3	1.392(2)
Mn1	O1[1]	2.1451(11)	C3	C5	1.532(2)
Mn1	O2[1]	2.1487(11)	C6	H6A	0.9900
Mn1	O2	2.1487(11)	C6	H6B	0.9900
Mn1	O3	2.2014(16)	C6	C7	1.558(7)
Mn1	O4	2.2057(16)	C7	H7A	0.9900
F1	C4	1.330(2)	C7	H7B	0.9900
F2	C4	1.326(2)	C7	C8	1.498(5)
F3	C4	1.3338(19)	C8	H8A	0.9900
F4	C5	1.449(6)	C8	H8B	0.9900
F5	C5	1.237(4)	C8	C9	1.541(7)
F6	C5	1.286(6)	C9	H9A	0.9900
F4A	C5	1.238(4)	C9	H9B	0.9900
F5A	C5	1.420(5)	C10	H10A	0.9900
F6A	C5	1.295(5)	C10	H10B	0.9900
O1	C1	1.2512(18)	C10	C11	1.502(6)
O2	C3	1.2483(19)	C11	H11A	0.9900
O3	C6	1.445(6)	C11	H11B	0.9900
O3	C9	1.423(6)	C11	C12	1.513(5)
O4	C10	1.420(7)	C12	H12A	0.9900
O4	C13	1.473(7)	C12	H12B	0.9900
C1	C2	1.393(2)	C12	C13	1.583(6)
C1	C4	1.533(2)	C13	H13A	0.9900
C2	H2	0.9500	C13	H13B	0.9900

[1]+X,1/2-Y,+Z

Table S56 Bond Angles for 7-Mn(hfac)$_2$(THF)$_2$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Mn1	O1[1]	96.89(6)	O2	C3	C5	114.06(15)
O1	Mn1	O2[1]	178.94(4)	C2	C3	C5	116.88(15)
O1	Mn1	O2	83.94(4)	F1	C4	F3	106.87(15)
O1[1]	Mn1	O2[1]	83.95(4)	F1	C4	C1	110.26(14)
O1[1]	Mn1	O2	178.94(4)	F2	C4	F1	107.85(16)
O1[1]	Mn1	O3	89.10(5)	F2	C4	F3	106.76(14)
O1	Mn1	O3	89.10(5)	F2	C4	C1	110.88(14)
O1	Mn1	O4	91.39(4)	F3	C4	C1	113.94(15)
O1[1]	Mn1	O4	91.39(4)	F4	C5	C3	104.2(3)
O2[1]	Mn1	O2	95.22(6)	F5	C5	F4	102.6(4)

Table S56 Bond Angles for 7-Mn(hfac)$_2$(THF)$_2$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	Mn1	O3	90.26(5)	F5	C5	F6	114.4(5)
O2[1]	Mn1	O3	90.26(5)	F5	C5	C3	116.5(3)
O2	Mn1	O4	89.25(5)	F6	C5	F4	100.8(4)
O2[1]	Mn1	O4	89.25(5)	F6	C5	C3	115.3(4)
O3	Mn1	O4	179.27(7)	F4A	C5	F5A	105.1(3)
C1	O1	Mn1	128.12(10)	F4A	C5	F6A	111.7(4)
C3	O2	Mn1	127.91(11)	F4A	C5	C3	114.9(3)
C6	O3	Mn1	124.6(3)	F5A	C5	C3	105.2(3)
C9	O3	Mn1	127.4(3)	F6A	C5	F5A	102.5(3)
C9	O3	C6	108.0(2)	F6A	C5	C3	115.7(4)
C10	O4	Mn1	127.2(3)	O3	C6	C7	103.2(4)
C10	O4	C13	108.5(2)	C8	C7	C6	98.3(5)
C13	O4	Mn1	123.0(3)	C7	C8	C9	96.7(5)
O1	C1	C2	128.77(15)	O3	C9	C8	104.4(4)
O1	C1	C4	113.65(14)	O4	C10	C11	107.6(6)
C2	C1	C4	117.57(14)	C10	C11	C12	94.9(5)
C3	C2	C1	122.13(15)	C11	C12	C13	104.1(6)
O2	C3	C2	129.07(15)	O4	C13	C12	100.5(4)

[1]+X,1/2-Y,+Z

Table S57 Torsion Angles for 7-Mn(hfac)$_2$(THF)$_2$.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Mn1	O1	C1	C2	2.8(2)	C1	C2	C3	O2	-0.9(3)
Mn1	O1	C1	C4	-175.89(10)	C1	C2	C3	C5	179.26(16)
Mn1	O2	C3	C2	0.9(3)	C2	C1	C4	F1	-110.24(17)
Mn1	O2	C3	C5	-179.29(12)	C2	C1	C4	F2	130.38(16)
Mn1	O3	C6	C7	-168.5(3)	C2	C1	C4	F3	9.9(2)
Mn1	O3	C9	C8	-158.4(3)	C2	C3	C5	F4	98.0(5)
Mn1	O4	C10	C11	164.7(3)	C2	C3	C5	F5	-149.8(8)
Mn1	O4	C13	C12	165.2(3)	C2	C3	C5	F6	-11.5(5)
O1	C1	C2	C3	-1.1(3)	C2	C3	C5	F4A	136.2(6)
O1	C1	C4	F1	68.63(19)	C2	C3	C5	F5A	-108.7(5)
O1	C1	C4	F2	-50.8(2)	C2	C3	C5	F6A	3.7(5)
O1	C1	C4	F3	-171.22(15)	C4	C1	C2	C3	177.54(15)
O2	C3	C5	F4	-81.8(5)	C6	O3	C9	C8	20.2(5)
O2	C3	C5	F5	30.3(8)	C6	C7	C8	C9	51.1(7)
O2	C3	C5	F6	168.7(5)	C7	C8	C9	O3	-45.9(7)
O2	C3	C5	F4A	-43.6(6)	C9	O3	C6	C7	12.9(5)
O2	C3	C5	F5A	71.5(5)	C10	O4	C13	C12	-2.4(4)
O2	C3	C5	F6A	-176.2(4)	C10	C11	C12	C13	-45.9(7)
O3	C6	C7	C8	-41.6(7)	C11	C12	C13	O4	31.8(7)
O4	C10	C11	C12	46.1(6)	C13	O4	C10	C11	-28.4(4)

Table S58 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 7-Mn(hfac)$_2$(THF)$_2$.

Atom	*x*	*y*	*z*	U(eq)
H2	3680.48	4766.99	4726.59	36
H6A	1964.3	1705.58	2719.23	85
H6B	2835.93	1542.74	1653.44	85
H7A	2389.07	2235.77	-716.81	66
H7B	1500.54	1853.83	-186.23	66
H8A	1154.73	2746.77	1790.19	66
H8B	1400.38	3122.87	-13.51	66
H9A	2869.68	3229.61	819.23	85
H9B	2351.83	3457.16	2533.9	85
H10A	4991.88	1530.2	7287.86	55
H10B	4417.64	1833.67	8839.91	55
H11A	6209.41	2150.78	8210.11	59
H11B	5810.06	1830.34	9976.17	59
H12A	5855.64	3117.07	9912.15	59
H12B	4933.77	2793.24	10423.03	59
H13A	4488.72	3449.16	8030.85	55
H13B	5406.47	3361.45	7058.02	55

Table S59 Atomic Occupancy for 7-Mn(hfac)$_2$(THF)$_2$.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
F4	0.430(15)	F5	0.430(15)	F6	0.430(15)
F4A	0.570(15)	F5A	0.570(15)	F6A	0.570(15)
C6	0.5	H6A	0.5	H6B	0.5
C7	0.5	H7A	0.5	H7B	0.5
C8	0.5	H8A	0.5	H8B	0.5
C9	0.5	H9A	0.5	H9B	0.5
C10	0.5	H10A	0.5	H10B	0.5
C11	0.5	H11A	0.5	H11B	0.5
C12	0.5	H12A	0.5	H12B	0.5
C13	0.5	H13A	0.5	H13B	0.5

Experimental

Single crystals of $C_{18}H_{18}O_6F_{12}Mn$ **7-Mn(hfac)$_2$(THF)$_2$** were grown from a concentrated THF solution of **7**. A suitable crystal was selected and mounted on a Bruker Kappa APEX-DUO CMOS PHOTON II diffractometer. The crystal was kept at 150.03 K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

9. Detailed Crystal Structure Report for 8, $Mn(hfac)_2NCCH_3(OH_2)$.

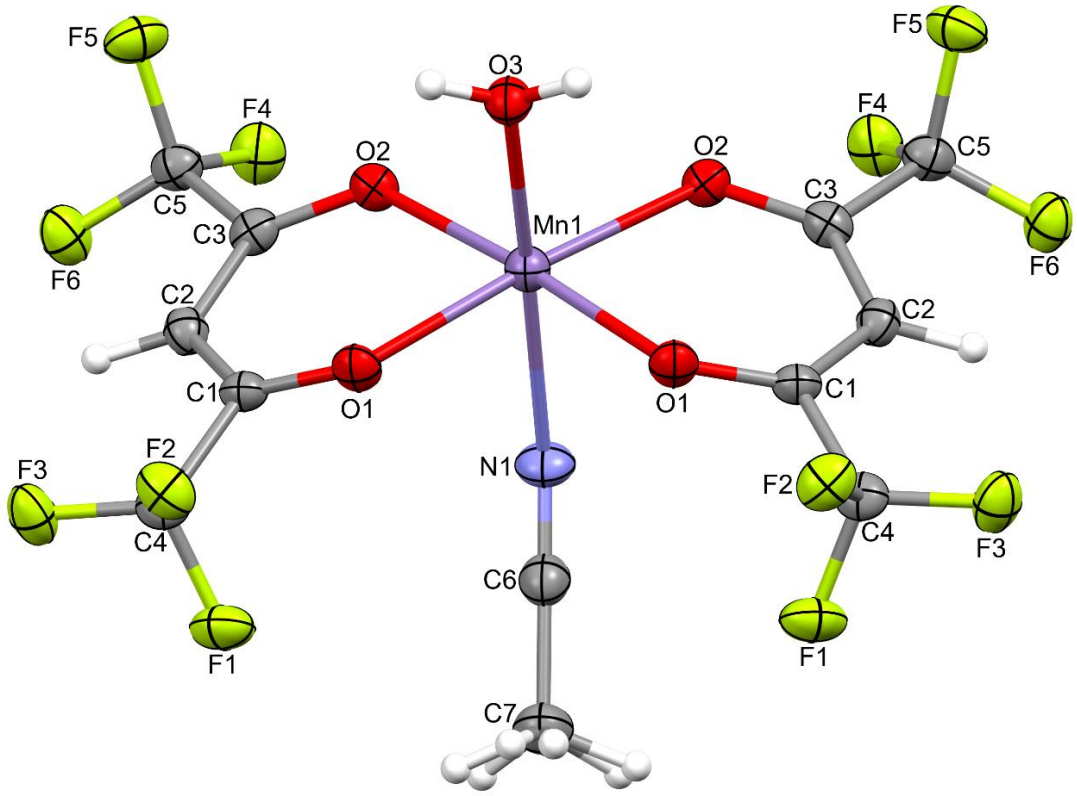


Fig. S12. Displacement ellipsoids plot (40% probability) depicting the asymmetric unit in structure **8**, consisting of discrete neutral *trans*-[$Mn(hfac)_2NCCH_3(OH_2)$]. The atom numbering scheme used in the Tables is shown. The complex crystallises with mirror symmetry (through the CH_3CN and H_2O ligands and the Mn atom. The two hfac groups are symmetry equivalent and the CH_3 group is reflection-disordered (shown).

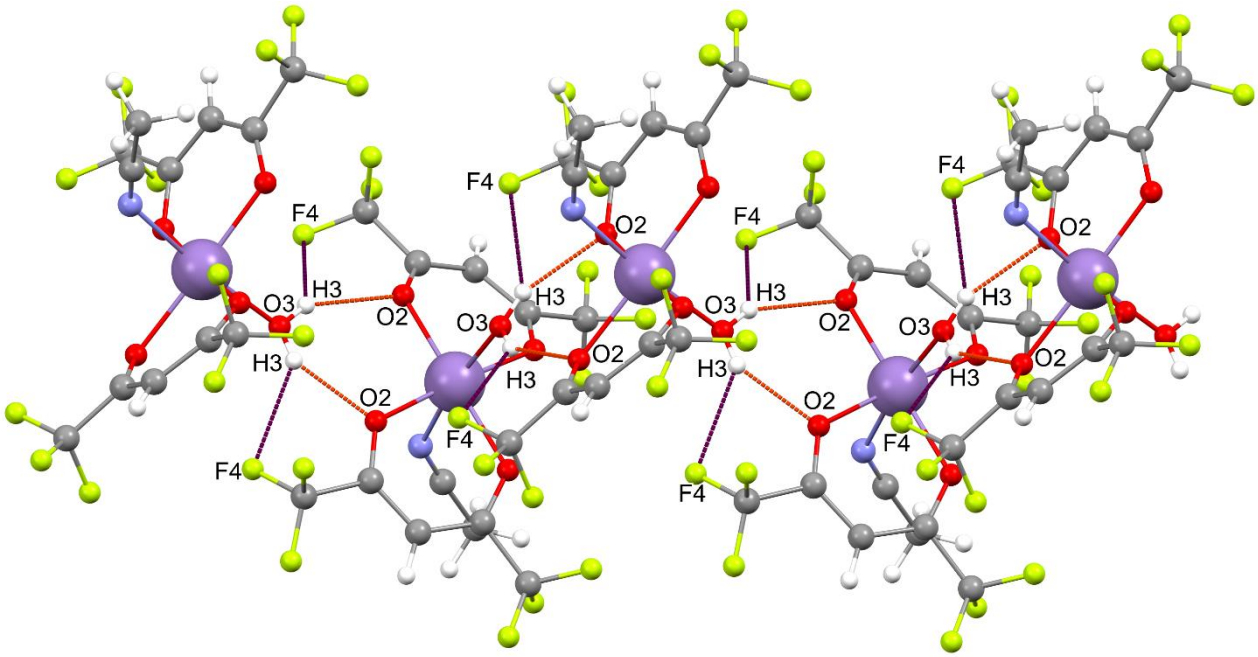


Fig. S13. Ball and sticks plot showing the double H-bond strand in structure **8**, consisting of aqua ligand H atoms donating to both one F atom of an hfac CF_3 group (weakly) and to the O of the hfac ligands (stronger). The infinite chain zig-zags along the unit cell *a* direction.

Table S60 Crystal data and structure refinement for 8-Mn(hfac)$_2$NCCH$_3$(OH$_2$).

Identification code	RB25004iPt75fF
Empirical formula	$C_{12}H_7NO_5F_{12}Mn$
Formula weight	528.13
Temperature/K	100.0(2)
Crystal system	orthorhombic
Space group	Pnma
a/Å	9.1029(3)
b/Å	21.7344(6)
c/Å	9.0051(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1781.62(10)
Z	4
ρ_{calc}g/cm^3	1.969
μ/mm^{-1}	7.488
F(000)	1036.0
Crystal size/mm^3	0.199 × 0.174 × 0.157
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.136 to 149.832
Index ranges	-8 ≤ h ≤ 11, -23 ≤ k ≤ 26, -11 ≤ l ≤ 10
Reflections collected	7617
Independent reflections	1770 [R_{int} = 0.0406, R_{sigma} = 0.0239]
Data/restraints/parameters	1770/1/152
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0766, wR_2 = 0.1784
Final R indexes [all data]	R_1 = 0.0842, wR_2 = 0.1821
Largest diff. peak/hole / e Å^{-3}	1.13/-0.90

Table S61 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 8-Mn(hfac)$_2$NCCH$_3$(OH$_2$). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mn1	5954.7(16)	7500	4398.1(16)	25.2(4)
F1	4339(5)	6166.9(19)	8114(4)	40.7(10)
F2	2659(4)	6009.5(18)	6478(4)	36.9(9)
F6	8709(4)	5282.0(17)	4198(4)	37.2(10)
F3	4315(4)	5322.8(17)	6857(5)	39.8(10)
F4	9766(4)	6105.8(17)	3425(5)	38.7(10)
F5	8169(5)	5646.2(19)	2044(4)	40.2(10)
O1	4639(5)	6784.7(19)	5342(5)	28.9(10)
O2	7284(5)	6750.7(18)	3603(5)	25.3(9)
O3	4567(7)	7500	2459(8)	29.6(14)
N1	7155(9)	7500	6624(9)	34.6(19)
C1	5057(7)	6252(3)	5615(6)	24.0(13)

Table S61 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 8-Mn(hfac)$_2$NCCH$_3$(OH$_2$). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C2	6269(7)	5937(3)	5055(7)	27.0(13)
C3	7270(7)	6205(3)	4070(7)	25.6(13)
C4	4097(7)	5923(3)	6760(7)	28.9(14)
C5	8493(7)	5802(3)	3461(7)	29.9(14)
C6	6883(12)	7500	7854(11)	35(2)
C7	6437(13)	7500	9434(11)	42(3)

Table S62 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 8-Mn(hfac)$_2$NCCH$_3$(OH$_2$). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	24.0(7)	25.3(7)	26.4(7)	0	0.3(6)	0
F1	40(2)	56(3)	26.1(18)	-0.5(18)	5.9(18)	-7.1(19)
F2	24.4(19)	44(2)	42(2)	7.8(18)	1.8(18)	-1.9(17)
F6	32(2)	33(2)	46(2)	6.1(17)	7.6(19)	9.0(16)
F3	37(2)	32(2)	50(2)	9.7(18)	13(2)	1.1(17)
F4	28(2)	38(2)	51(2)	-2.1(19)	9.9(19)	-0.8(17)
F5	41(2)	50(2)	29.8(19)	-8.0(17)	4.9(19)	7.9(19)
O1	26(2)	30(2)	30(2)	1.3(18)	8.2(19)	-0.5(19)
O2	18(2)	29(2)	28(2)	2.1(17)	0.2(18)	0.8(17)
O3	31(4)	28(3)	30(3)	0	-3(3)	0
N1	33(4)	45(5)	26(4)	0	-7(4)	0
C1	23(3)	30(3)	20(3)	0(2)	1(3)	-1(2)
C2	28(3)	25(3)	29(3)	2(2)	-4(3)	0(3)
C3	19(3)	31(3)	27(3)	-4(2)	-1(3)	-1(2)
C4	21(3)	37(3)	29(3)	0(3)	-5(3)	1(3)
C5	27(3)	34(3)	29(3)	-2(3)	2(3)	-2(3)
C6	37(6)	32(5)	35(5)	0	-6(5)	0
C7	46(6)	45(6)	35(5)	0	8(5)	0

Table S63 Bond Lengths for 8-Mn(hfac)$_2$NCCH$_3$(OH$_2$).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	O1	2.139(4)	O2	C3	1.259(7)
Mn1	O1^1	2.139(4)	O3	H3^1	0.84(2)
Mn1	O2	2.152(4)	O3	H3	0.84(2)
Mn1	O2^1	2.152(4)	N1	C6	1.135(12)
Mn1	O3	2.155(7)	C1	C2	1.393(9)
Mn1	N1	2.283(8)	C1	C4	1.528(9)
F1	C4	1.348(7)	C2	H2	0.9500
F2	C4	1.346(7)	C2	C3	1.399(9)

Table S63 Bond Lengths for 8-Mn(hfac)$_2$NCCH$_3$(OH$_2$).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F6	C5	1.325(7)	C3	C5	1.519(9)
F3	C4	1.323(7)	C6	C7	1.480(14)
F4	C5	1.335(7)	C7	H7A	0.9800
F5	C5	1.352(7)	C7	H7B	0.9800
O1	C1	1.244(7)	C7	H7C	0.9800

[1]+X,3/2-Y,+Z

Table S64 Bond Angles for 8-Mn(hfac)$_2$NCCH$_3$(OH$_2$).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Mn1	O1[1]	93.3(2)	O1	C1	C4	113.2(5)
O1	Mn1	O2	84.09(16)	C2	C1	C4	117.9(5)
O1[1]	Mn1	O2	175.90(17)	C1	C2	C3	122.7(6)
O1	Mn1	O2[1]	175.90(17)	O2	C3	C2	127.7(6)
O1[1]	Mn1	O2[1]	84.08(16)	O2	C3	C5	114.5(5)
O1	Mn1	O3	89.67(18)	C2	C3	C5	117.8(5)
O1[1]	Mn1	O3	89.67(18)	F1	C4	C1	109.5(5)
O1	Mn1	N1	85.3(2)	F2	C4	F1	105.9(5)
O1[1]	Mn1	N1	85.3(2)	F2	C4	C1	111.3(5)
O2	Mn1	O2[1]	98.4(2)	F3	C4	F1	107.7(5)
O2	Mn1	O3	93.44(17)	F3	C4	F2	107.2(5)
O2[1]	Mn1	O3	93.44(17)	F3	C4	C1	114.8(5)
O2[1]	Mn1	N1	91.31(18)	F6	C5	F4	107.8(5)
O2	Mn1	N1	91.31(18)	F6	C5	F5	107.0(5)
O3	Mn1	N1	172.7(3)	F6	C5	C3	114.8(5)
C1	O1	Mn1	125.8(4)	F4	C5	F5	106.9(5)
C3	O2	Mn1	126.6(4)	F4	C5	C3	111.1(5)
C6	N1	Mn1	138.8(8)	F5	C5	C3	108.9(5)
O1	C1	C2	128.9(6)	N1	C6	C7	176.7(12)

[1]+X,3/2-Y,+Z

Table S65 Hydrogen Bonds for 8-Mn(hfac)$_2$NCCH$_3$(OH$_2$).

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O3	H3	O2[1]	0.84(2)	2.07(5)	2.808(7)	147(7)

[1]-1/2+X,3/2-Y,1/2-Z

Table S66 Torsion Angles for 8-Mn(hfac)$_2$NCCH$_3$(OH$_2$).

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Mn1	O1	C1	C2	-18.8(9)	O2	C3	C5	F5	-75.8(7)
Mn1	O1	C1	C4	159.3(4)	C1	C2	C3	O2	3.4(10)
Mn1	O2	C3	C2	9.4(9)	C1	C2	C3	C5	-176.2(6)
Mn1	O2	C3	C5	-171.0(4)	C2	C1	C4	F1	106.4(6)
O1	C1	C2	C3	1.8(10)	C2	C1	C4	F2	-136.8(6)
O1	C1	C4	F1	-72.0(7)	C2	C1	C4	F3	-14.8(8)
O1	C1	C4	F2	44.8(7)	C2	C3	C5	F6	-16.0(8)
O1	C1	C4	F3	166.8(5)	C2	C3	C5	F4	-138.6(6)
O2	C3	C5	F6	164.3(5)	C2	C3	C5	F5	103.9(6)
O2	C3	C5	F4	41.7(7)	C4	C1	C2	C3	-176.2(6)

Table S67 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 8-Mn(hfac)$_2$NCCH$_3$(OH$_2$).

Atom	*x*	*y*	*z*	U(eq)
H3	4150(80)	7830(20)	2240(90)	44
H2	6422.96	5522.53	5355.61	32
H7A	7007.21	7190.12	9975.77	63
H7B	5388.67	7402.9	9509.3	63
H7C	6621.06	7906.97	9864.48	63

Table 68 Atomic Occupancy for 8-Mn(hfac)$_2$NCCH$_3$(OH$_2$).

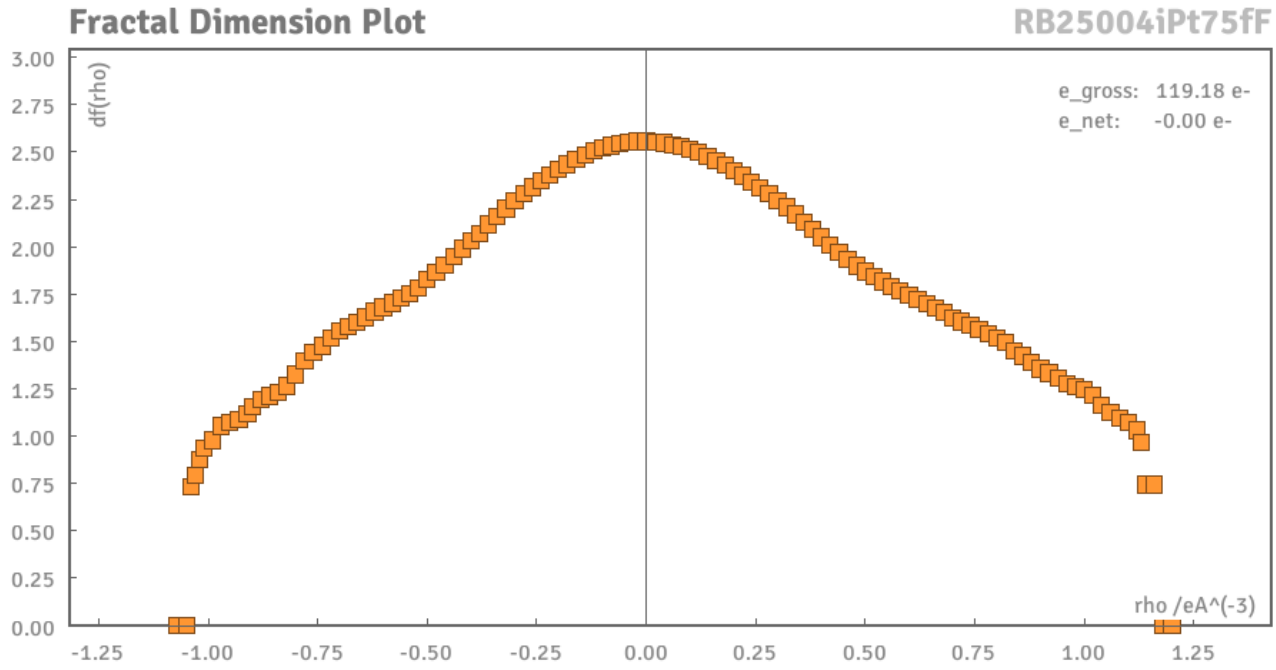
Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
H7A	0.5	H7B	0.5	H7C	0.5

Experimental

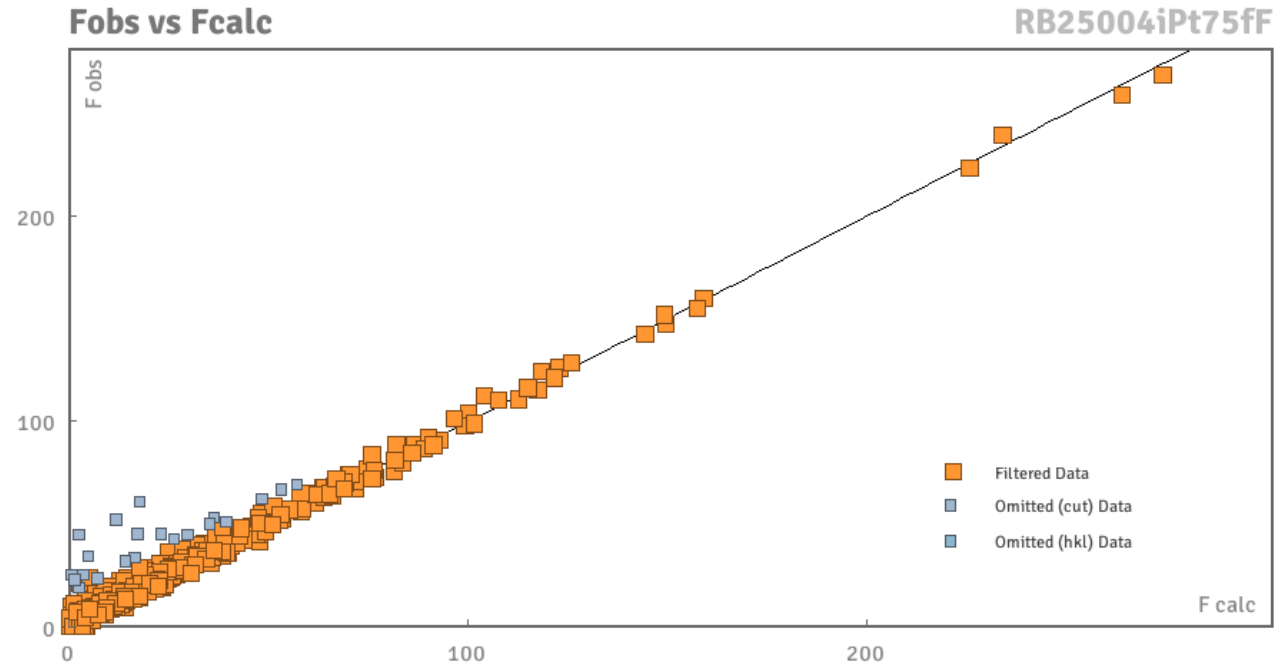
Single crystals of $C_{12}H_7NO_5F_{12}Mn$ **8-Mn(hfac)$_2$NCCH$_3$(OH$_2$)**were grown from a concentrated DCM solution of **8** during the failed coordination of Mn(hfac)$_2$(THF)$_2$ with a ligand recrystallized from acetonitrile. A suitable crystal was selected and mounted in Paratone™ oil on a 100 μm MiTeGen loop on a SuperNova, Dual, Cu at home/near, Pilatus 200K diffractometer. The crystal was kept at 100.0(2) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

The largest diff. peak 1.13 e/Å^3 is found near Mn (on both sides, via symmetry, and repeated a second time at half height and double the distance. This seems to be diagnostic of a 'Fourier truncation ripple'. The statistics of this excess ED can be seen from the somewhat distorted Fractal Dimensions Plot (shown on the following page).



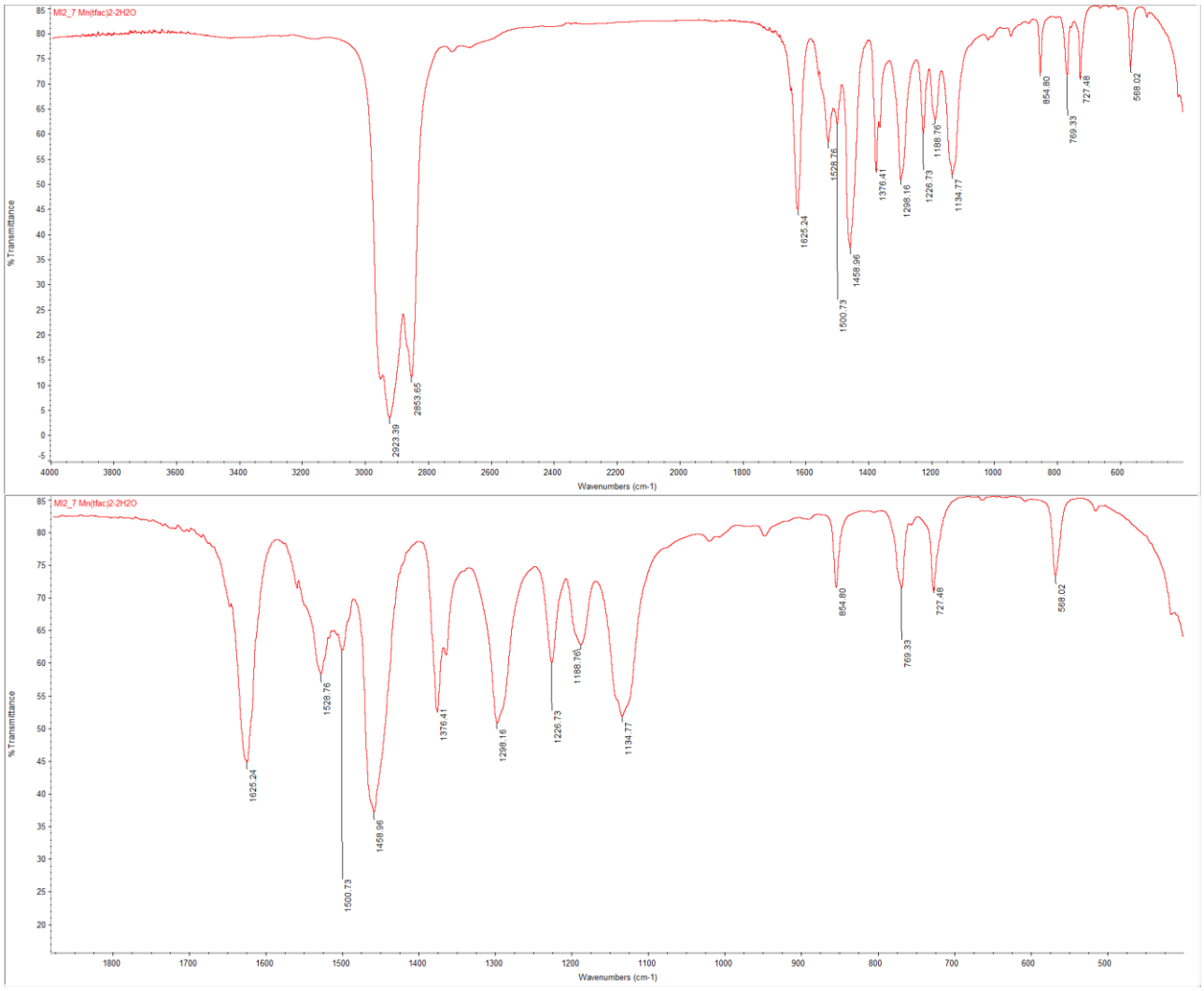
Beyond the residual peaks, this dataset also contains an unusually high number of data that have poor agreement between Fobs and Fcal (e.g. as plotted in Olex 2).



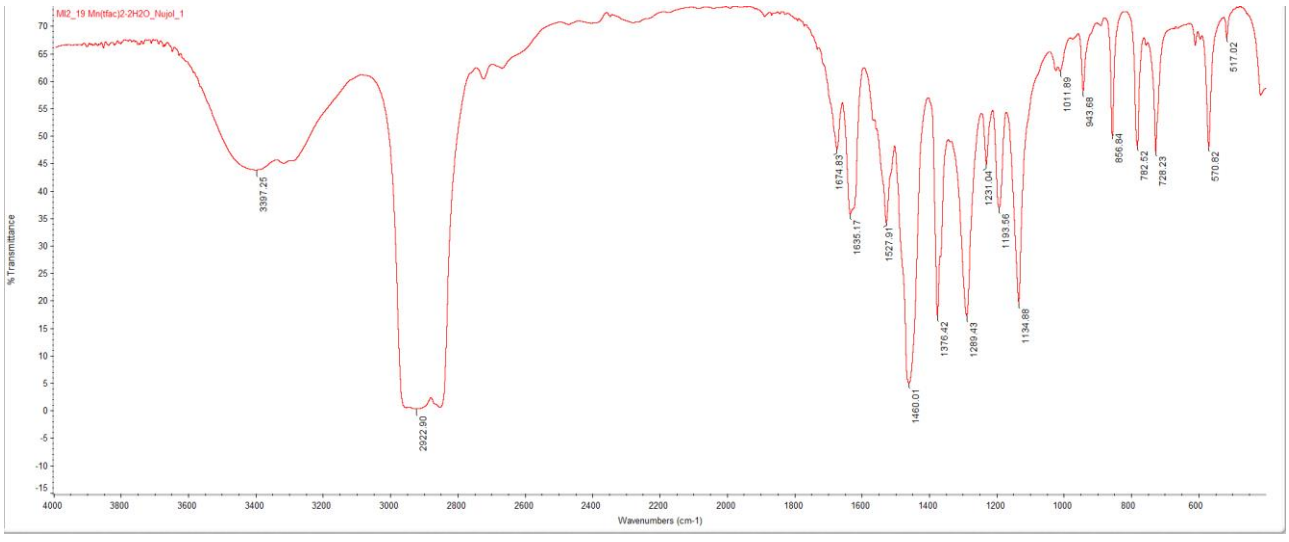
These data were omitted from the refinement. A careful review of the frames, further attempts at improving the absorption correction, etc. did not lead to an improved data quality. What is obvious from the diffraction peaks is that overall crystal quality for this sample was marginal, despite e.g. the R_{int} value of 4.06%, which would normally indicate higher data quality.

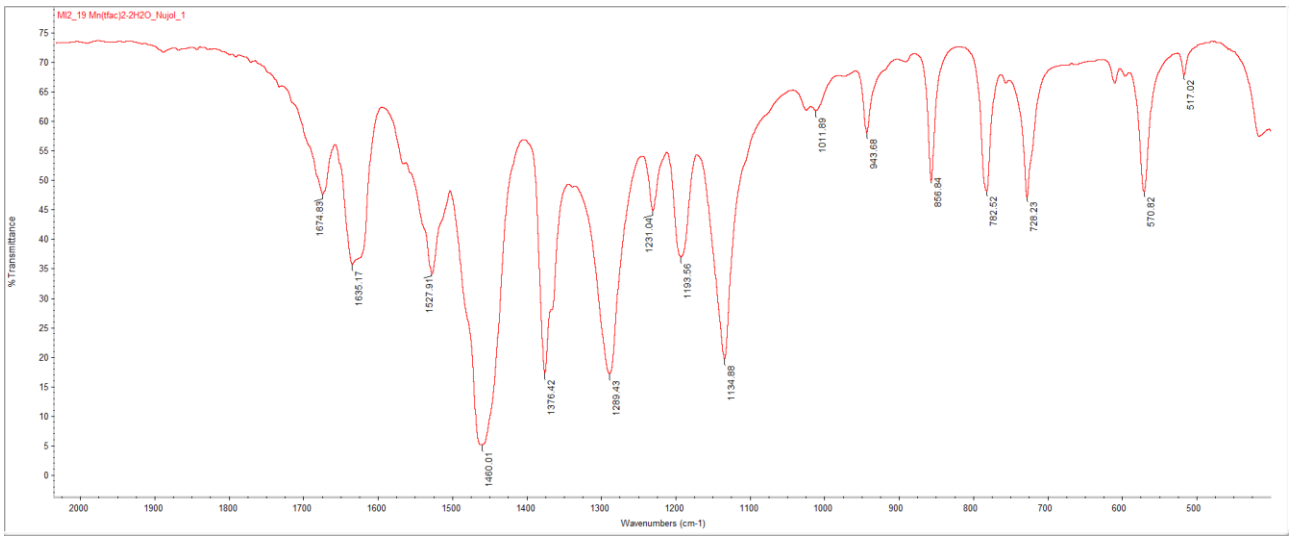
10. Archival FTIR spectra of the complexes

Potassium tris(1,1,1-trifluoroacetylacetonato)manganate(II) polymer $\{K[Mn(tfac)_3]\}_\infty$ **1**.

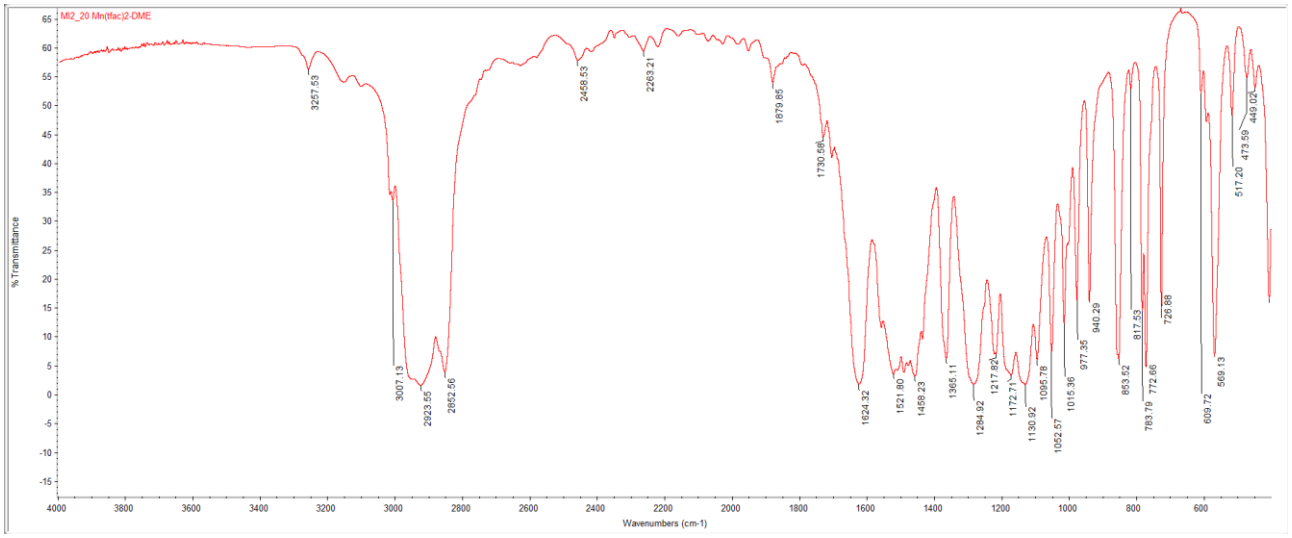


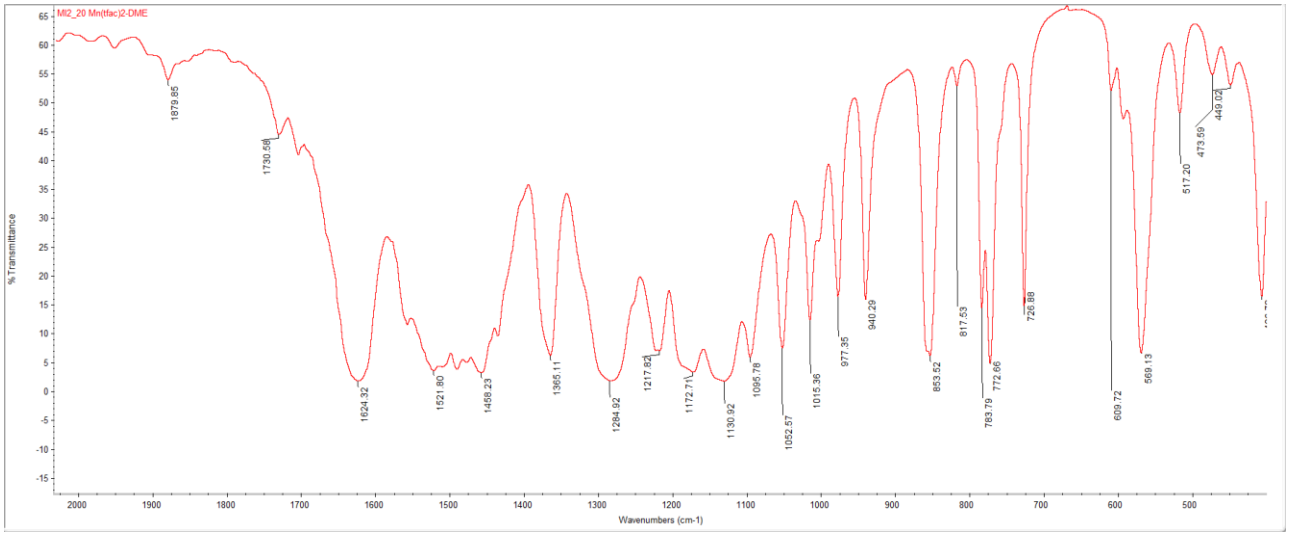
$Mn(tfac)_2(OH_2)_2 \cdot H_2O$ **2**



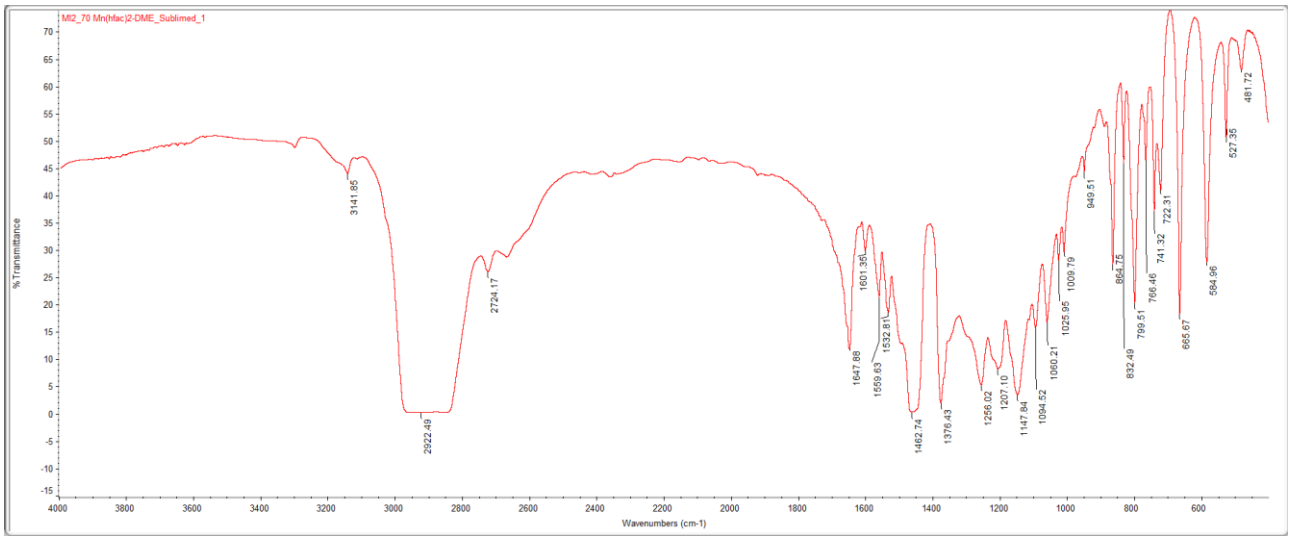


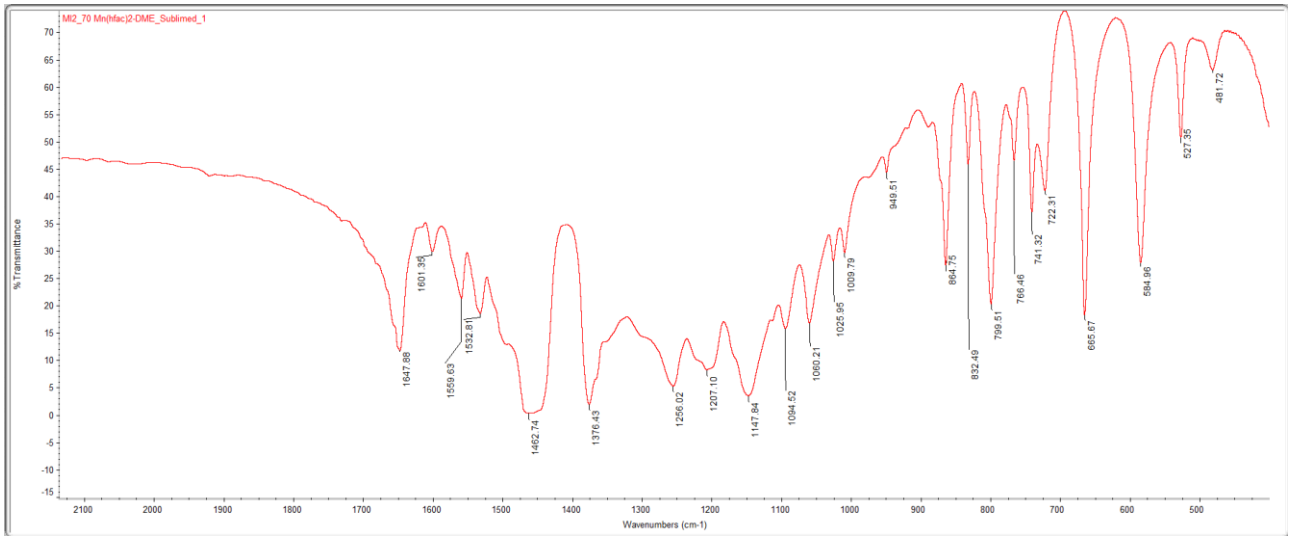
Dimethoxyethanebis(1,1,1-trifluoroacetylacetonato)manganese(II) $Mn(tfac)_2(DME)$ **4**



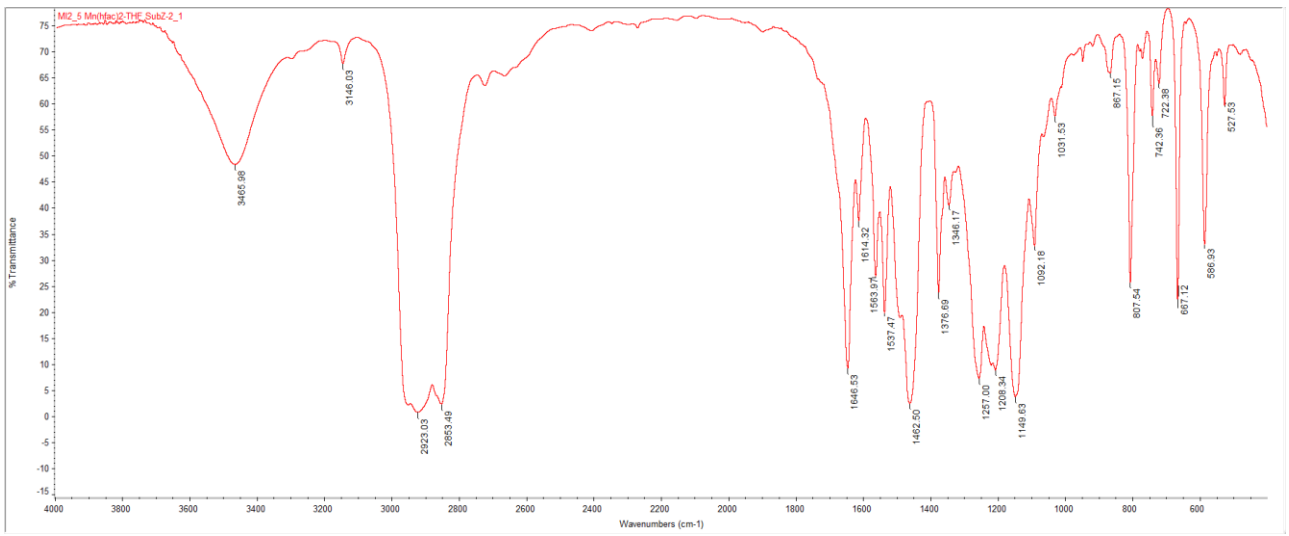


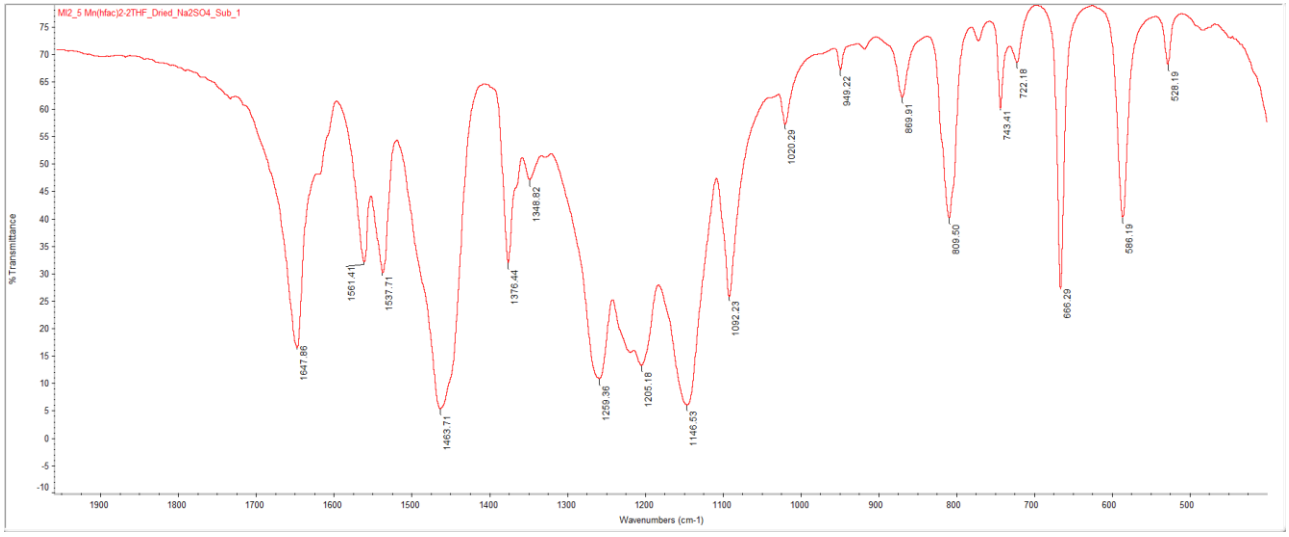
Dimethoxyethanebis(1,1,1,5,5,5-hexafluoroacetylacetonato)manganese(II) $Mn(hfac)_2(DME)$ **5**





Bis(tetrahydrofuran)bis(1,1,1,5,5,5-hexafluoroacetylacetonato)manganese(II) $Mn(hfac)_2(OH_2)(THF)$ **6**





Bis(tetrahydrofuran)bis(1,1,1,5,5,5-hexafluoroacetylacetonato)manganese(II) $Mn(hfac)_2(THF)_2$ **7**