Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Light- or oxidation-triggered CO release from $[Mn^{I}(CO)_3(\kappa^3\text{-}L)]$ complexes: reaction intermediates and a new synthetic route to $[Mn_2^{III/IV}(\mu\text{-}O)_2(L)_2]$ compounds

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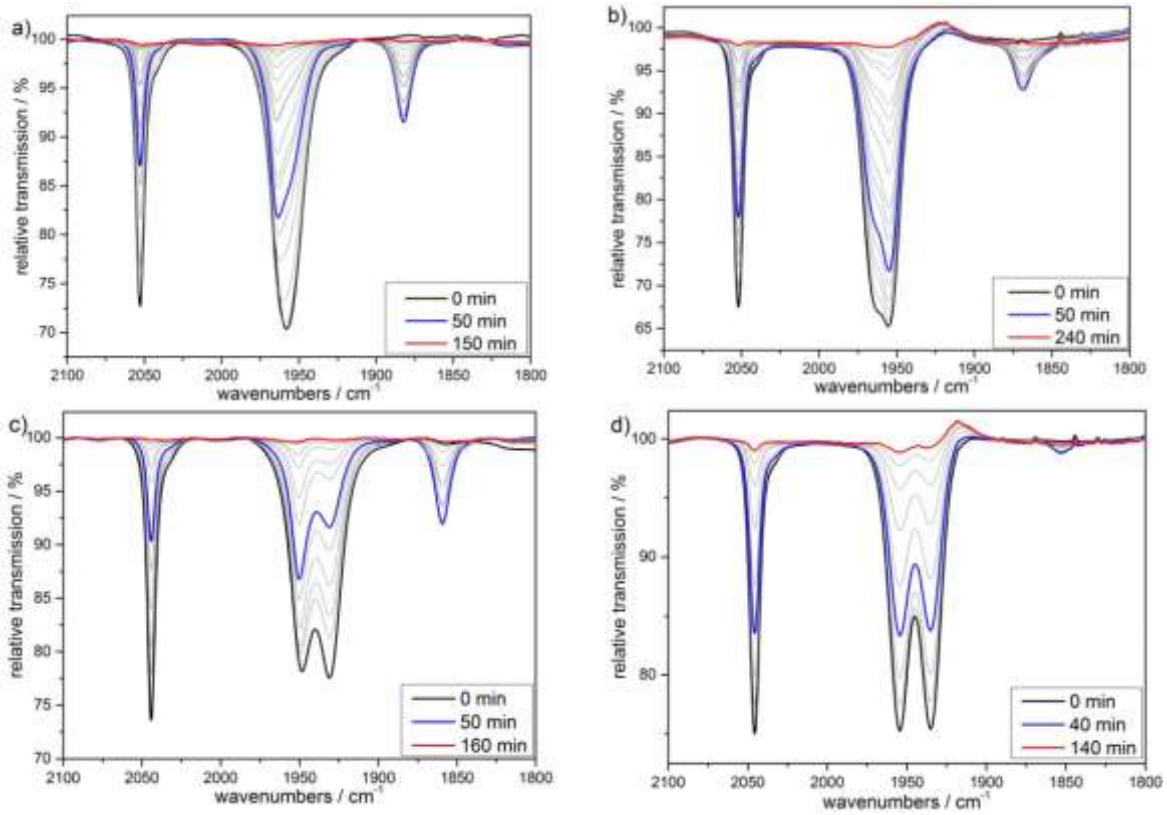


Figure S1. IR monitoring of the CO release of **1** and **2** initialized by UV irradiation. Conditions: **a)** 10 mM solution of $[Mn^{I}(CO)_3(tpm)]$ in MeCN, **b)** 10 mM solution of $[Mn^{I}(CO)_3(tpm)]$ in EtOH/H_2O (9:1), **c)** 10 mM solution of $[Mn^{I}(CO)_3(bpza)]$ in MeCN, **d)** 10 mM solution of $[Mn^{I}(CO)_3(bpza)]$ in EtOH/H_2O (9:1), λ_{irr} = 365 nm.

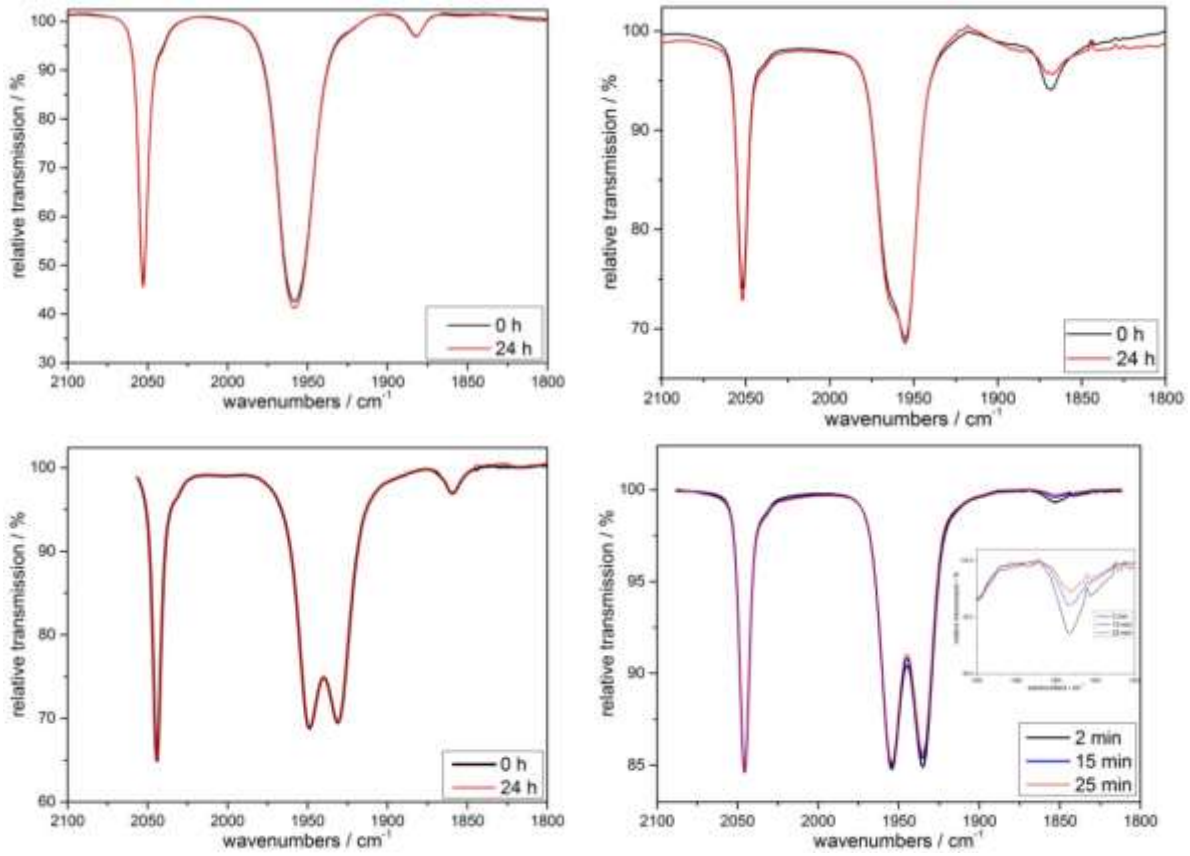


Figure S2. IR monitoring of the dark stability of the irradiation (λ_{irr} = 365 nm) intermediates with two COs of **1** (top) and **2** (bottom) in MeCN (left) and EtOH/H_2O (9:1) (right). 5 - 10 mM solutions of **1** and **2** were irradiated for 30 min and then left in the dark as the CO band at 1850 cm^{-1} was monitored over 24 h.

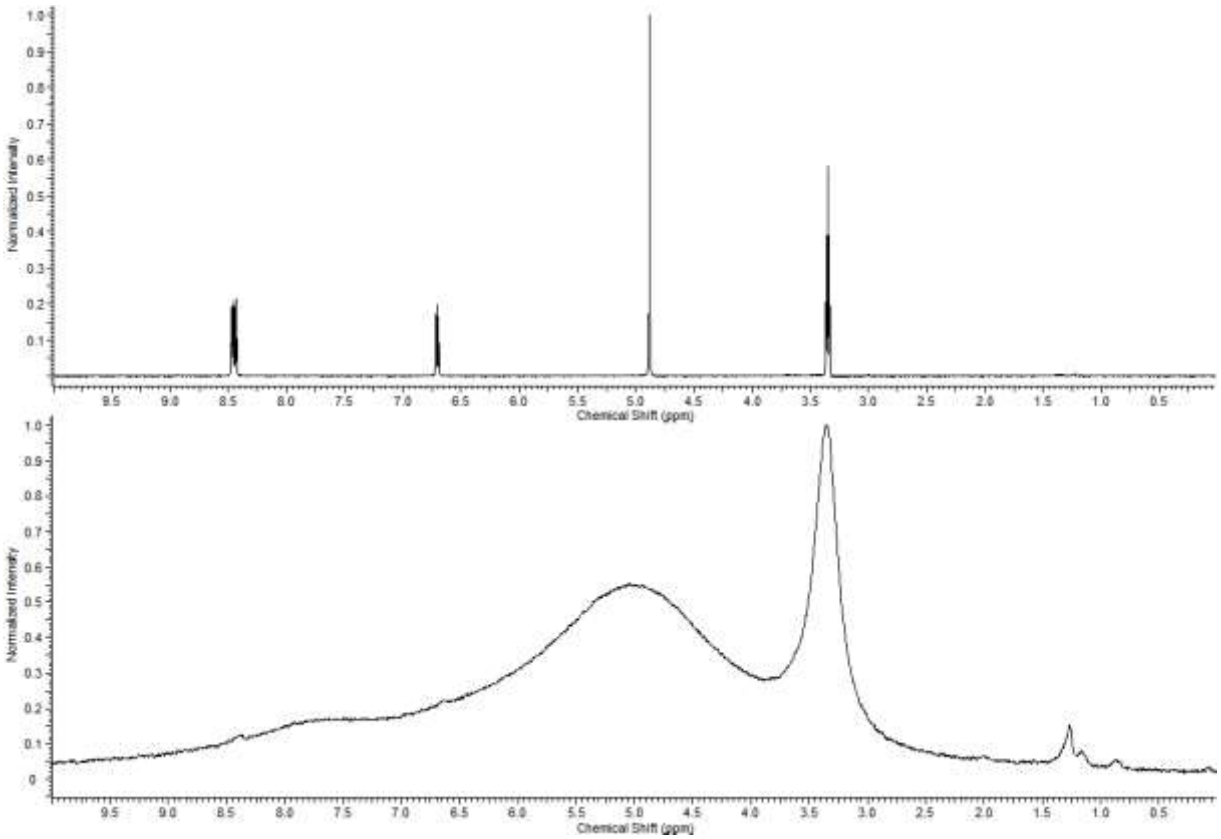


Figure S3. Comparison of the 1H-NMR spectra of [$Mn^{I}(CO)_3$(tpm)] in CD_3CN before and after irradiation (365 nm, 24 h, without oxygen), which shows that the irradiated solution contains a paramagnetic substance.

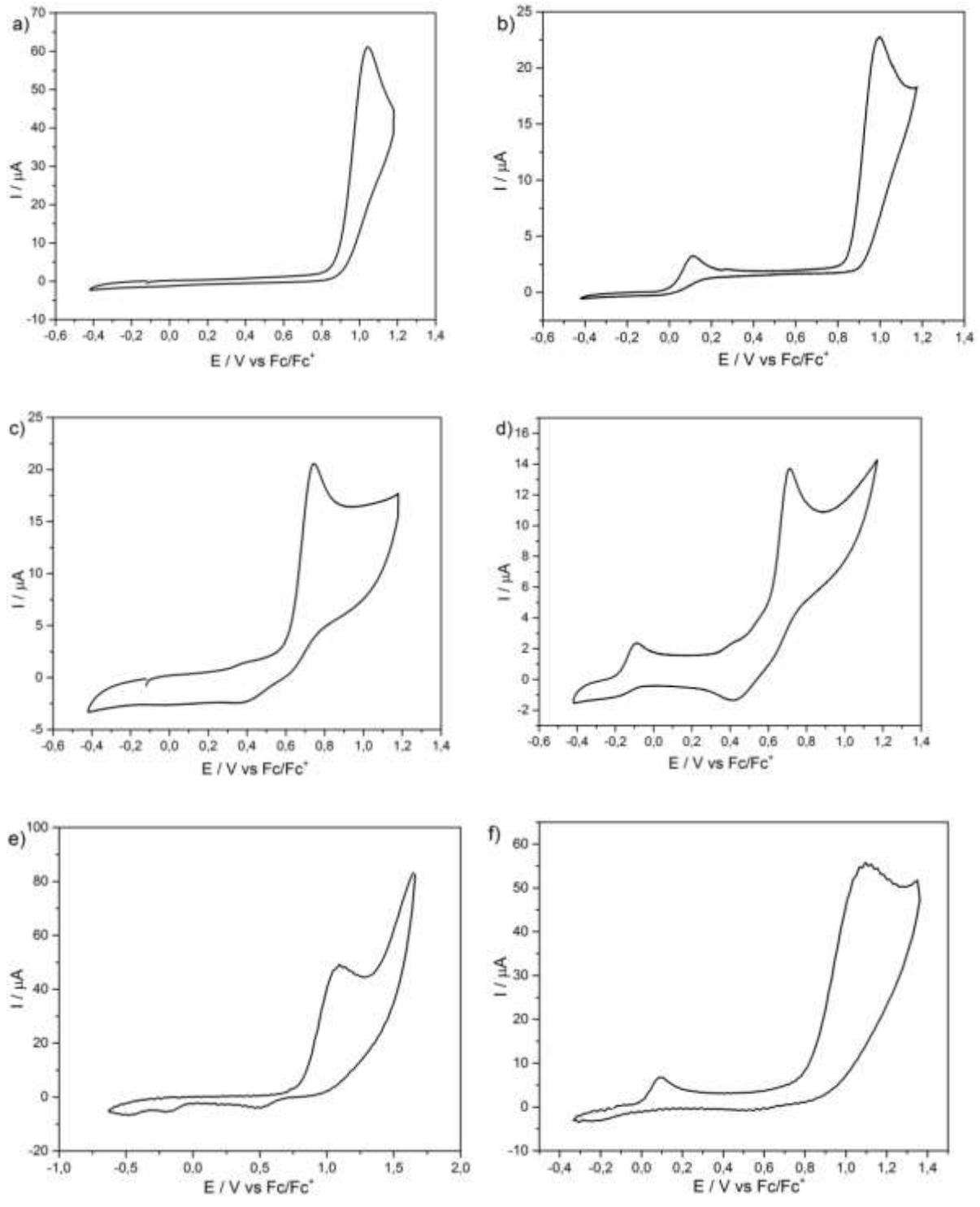


Figure S4. Cyclic voltammograms (scan rate: 100 mV/s) of a 5-10 mM solutions of **1** (**a** and **b**), **2** (**c** and **d**), **3** (**e** and **f**) in MeCN with $(Bu)_4N[PF_6]$ (0.1 M) as electrolyte. Potentials are calculated *vs.* Fc/Fc^+. The CVs on the right are measured after the solutions were irradiated (365 nm) for 30 min.

Figure S5. Modified Specac Omni-Cell™ with Platinum net electrode in optical window (CaF_2), a platinum net as counter electrode and a platinum wire as quasi reference electrode.

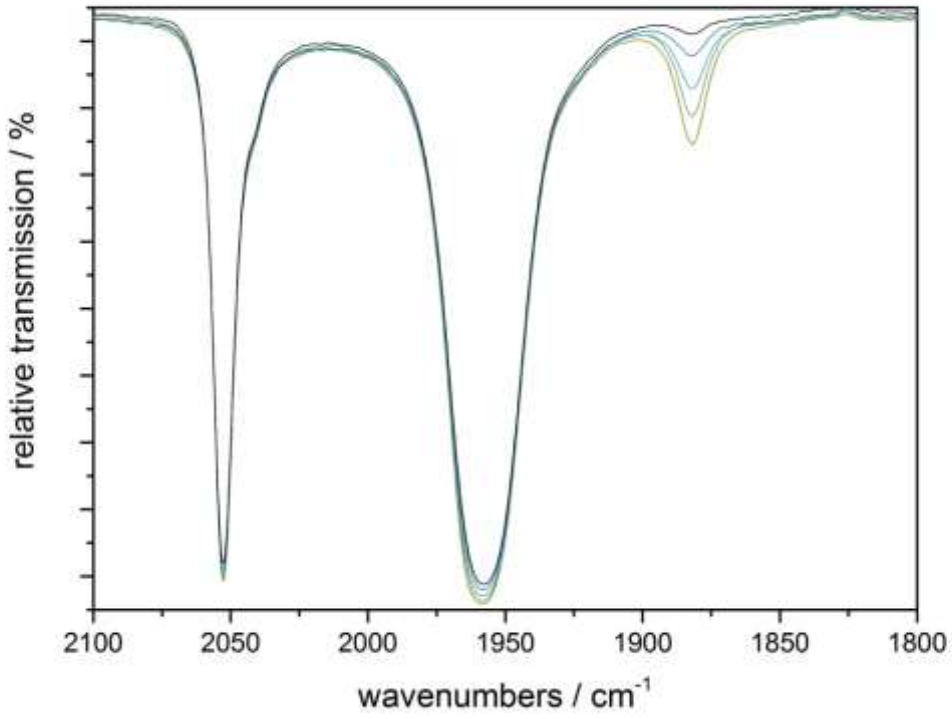


Figure S6. IR monitoring of the electrochemical oxidation of $[Mn(CO)_2(tpm)(solv)]$ between 0.8 V and 1.0 V (vs. q-Pt).

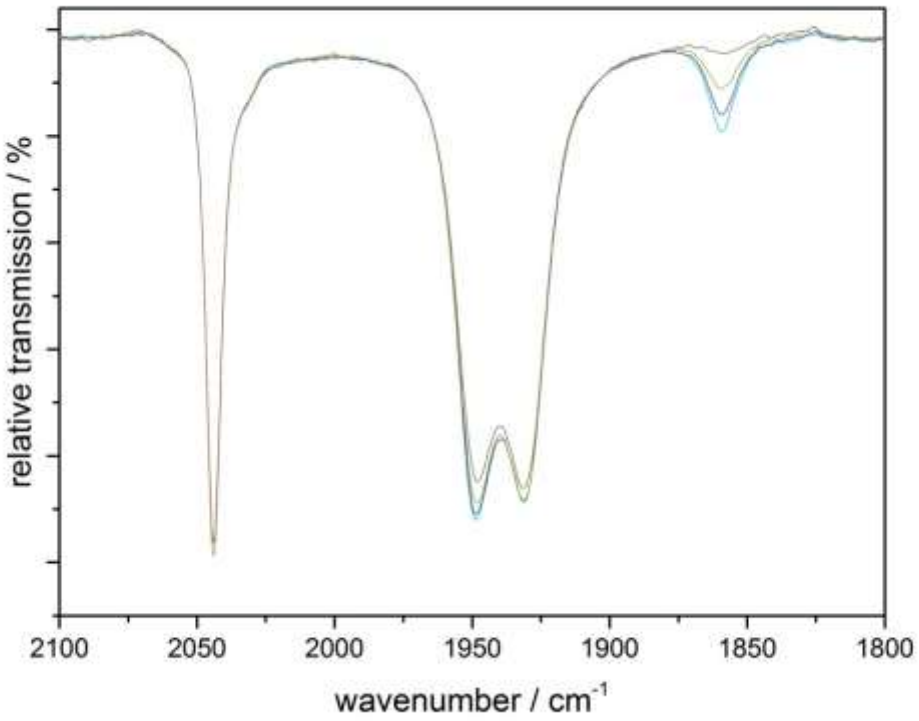


Figure S7. IR monitoring of the electrochemical oxidation of $[Mn(CO)_2(bpza)(solv)]$ between 0.4 V and 0.6 V (vs. q-Pt).

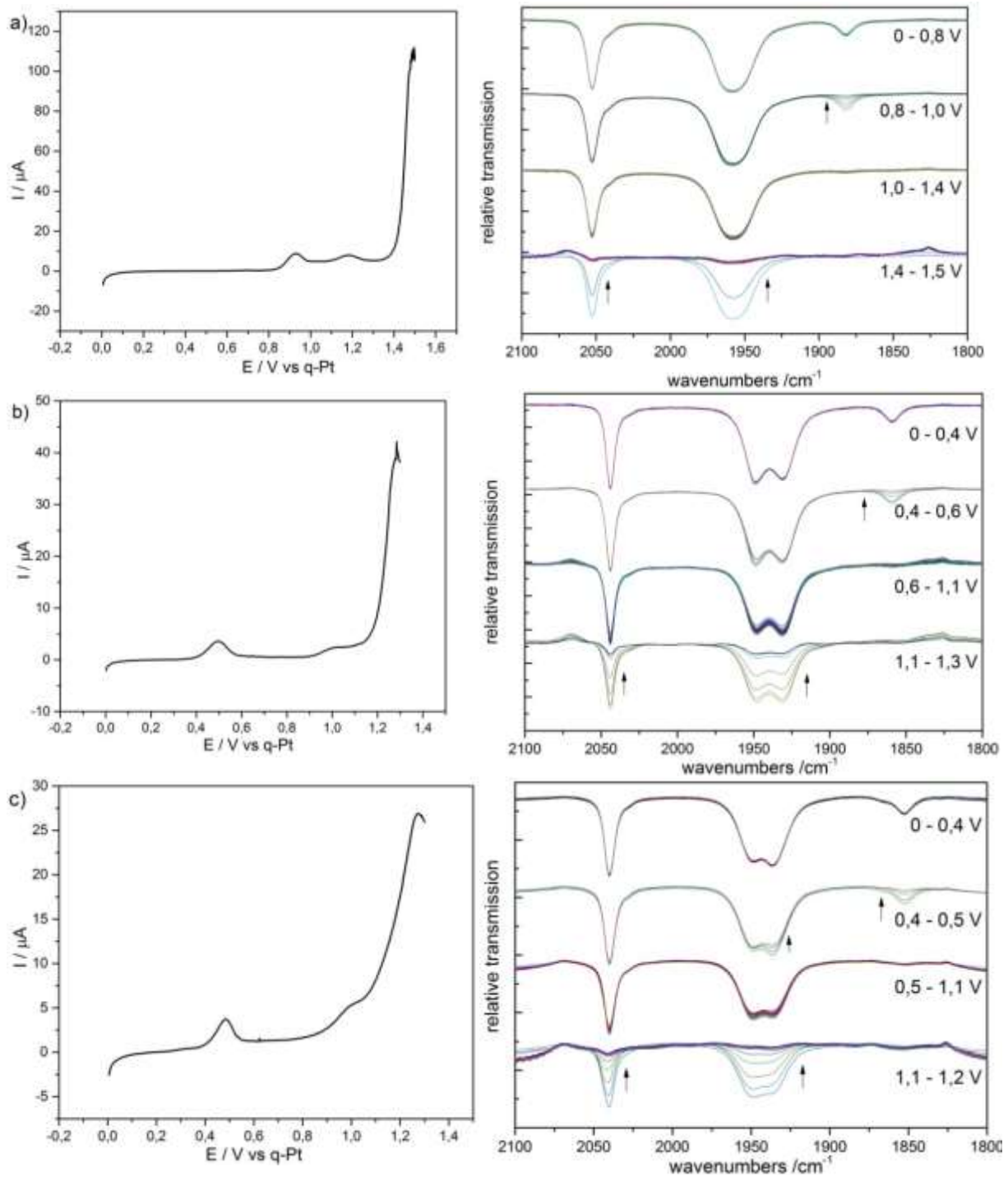


Figure S8. LSVs (scan rate: 1 mV/s) of pre-irradiated 10 mM solutions (365 nm, 30 min) of **a) 1**, **b) 2** and **c) 3** in MeCN with $(Bu)_4N[PF_6]$ (0.1 M) as electrolyte in a Modified Specac Omni-Cell™ (Figure S4). The corresponding IR-spectra were measured every 30 s and are shown on the right side.

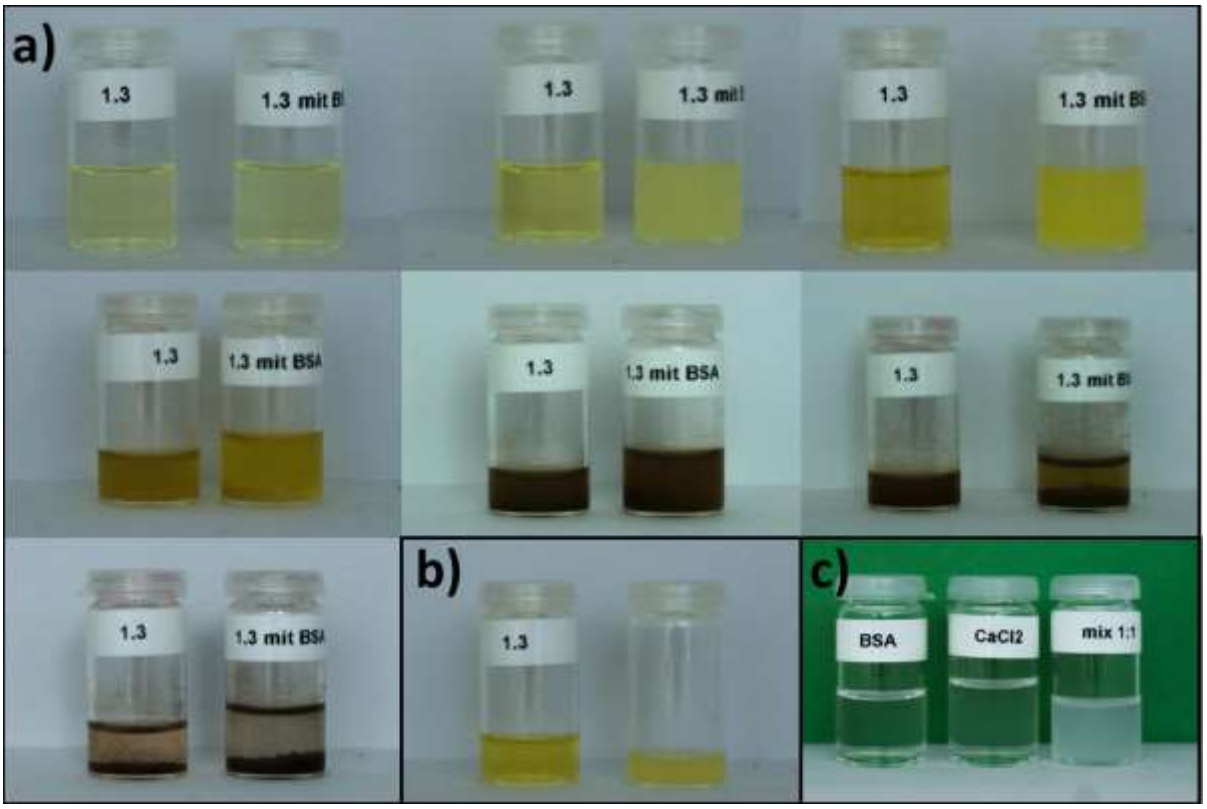
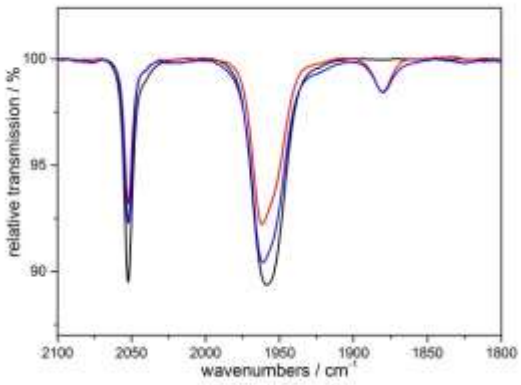
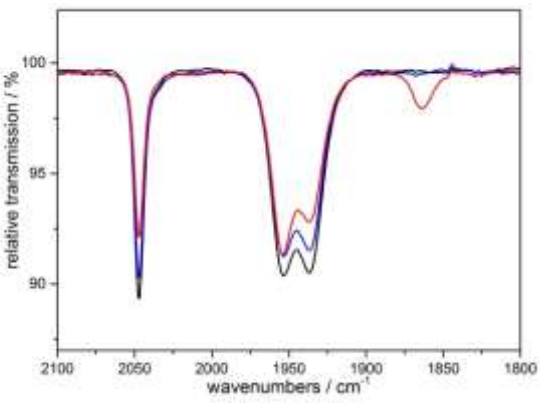


Figure S9. Visual Comparison of the influence of BSA on the UV-irradiation (λ_{irr} = 365 nm) of a 10 mM solution of **1** in H_2O/MeCN (4:3). a) Comparison of different irradiation times of 10 mM solution of **1** and the same solution containing BSA (ca. 10 mM amino acid monomer). First row: 0, 30, 60 min, second row: 2, 4, 6 h, third row: 12 h. b) left: 10 mM solution of 1 irradiated for 1 h and right: the same solution with BSA added after irradiation. c) left: 10 mM (amino acid monomer) solution of BSA, middle: 10 mM solution of $CaCl_2$ and on the right: a mixture 1:1 of these two solutions.

a)



b)



c)

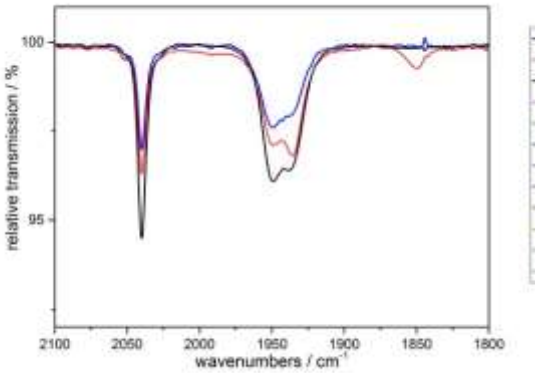


Figure S10. IR monitoring of the CO release of a) **1** b) **2** and c) **3** initialized by UV irradiation. Conditions: 1 mM solution CORM in H_2O/MeCN (4:3) 10 mM (amino acid monomer) BSA, λ_{irr} = 365 nm. 0 min (black) and 30 min (red) of irradiation and 30 min irradiation plus 12 h dark (blue).

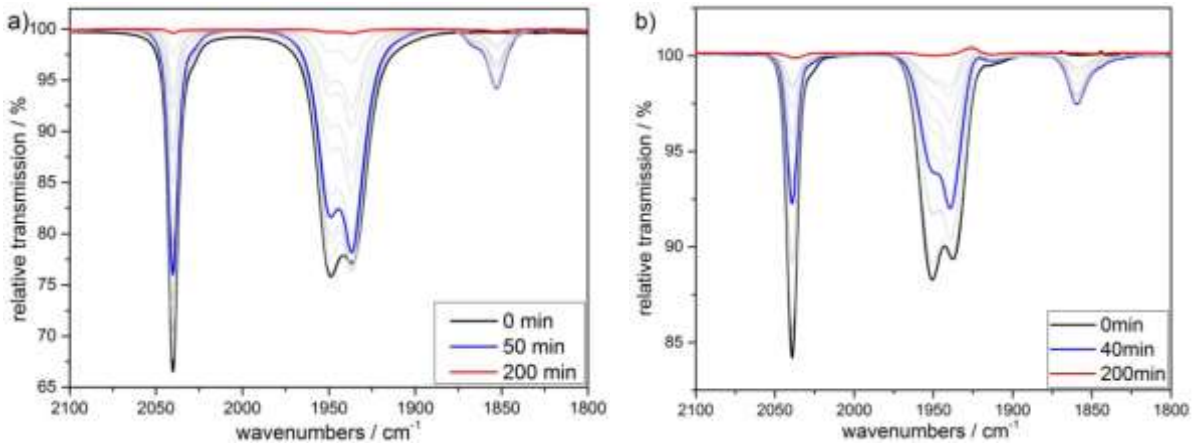


Figure S11. IR monitoring of the CO release of **3** initialized by UV irradiation. Conditions: **a)** 10 mM solution of [$Mn^{I}(CO)_3$(tpa)] in MeCN, **b)** 10 mM solution of 3 in EtOH/H_2O (9:1), λ_{irr} = 365 nm.

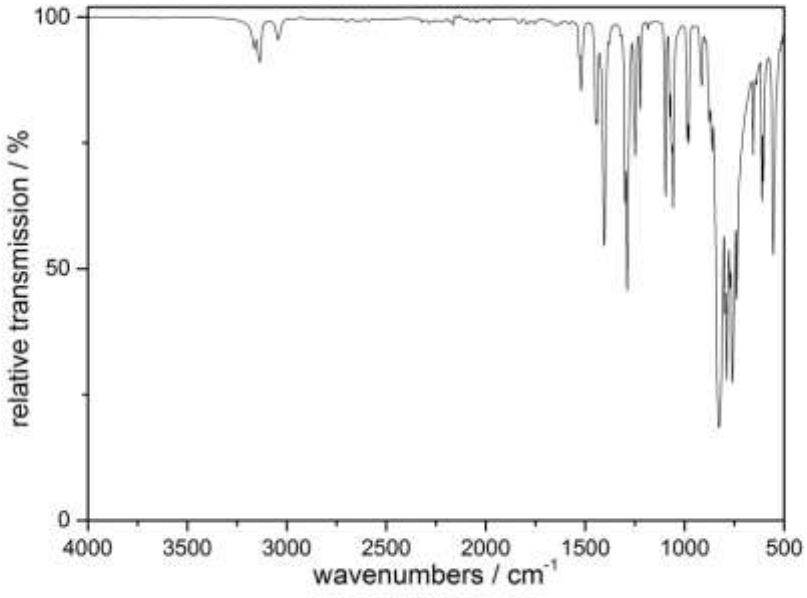


Figure S12. IR spectrum of $[Mn(tpm)_2][PF_6]_2$ derived by UV-irradiation of **1** in MeCN, λ_{irr} = 365 nm**.**

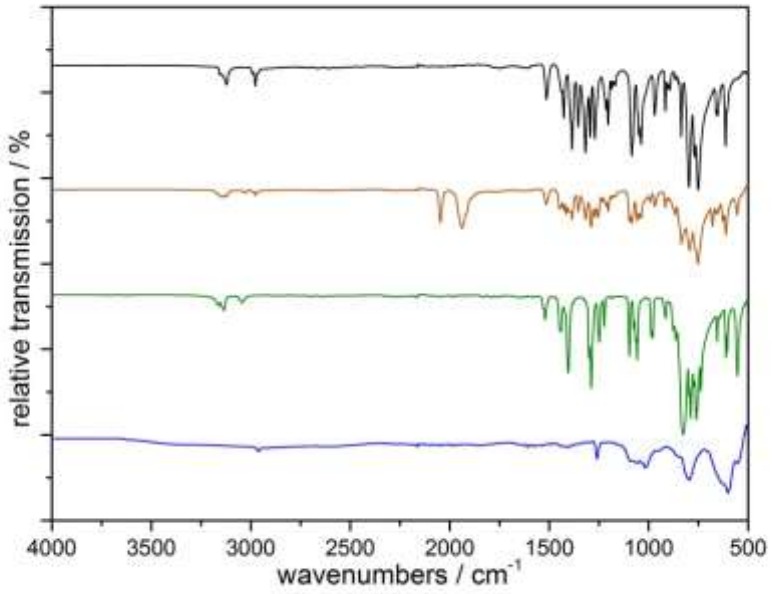


Figure S13. Comparison of the IR spectrum of $[Mn(tpm)_2][PF_6]_2$ (green) derived by UV-irradiation of **1** in MeCN, λ_{irr} = 365 nm, with the IR spectra of free tpm (black), **1** (brown) and precipitated MnO_x (blue).

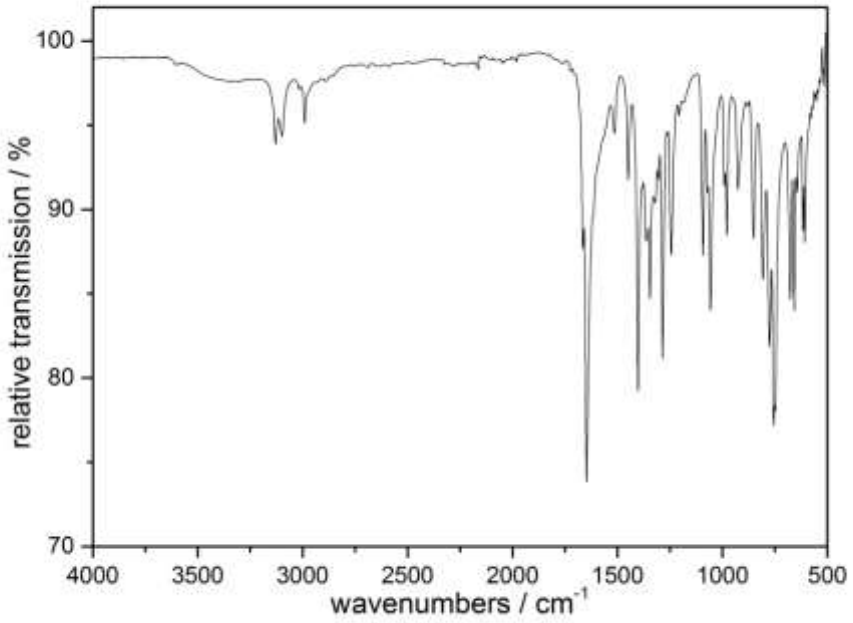


Figure S14. IR spectrum of $[Mn_2(bpza)_4]$ derived by UV-irradiation of **2** in MeOH/H_2O (9:1), λ_{irr} = 365 nm**.**

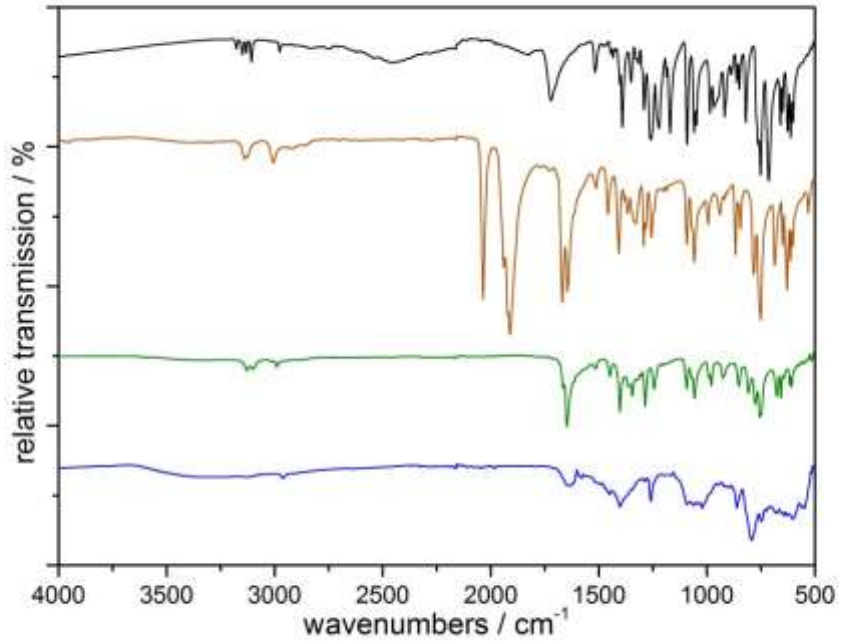


Figure S15. Comparison of the IR spectrum of $[Mn_2(bpza)_4]$ (green) derived by UV-irradiation of **2** in MeOH/H_2O (9:1), λ_{irr} = 365 nm, with the IR spectra of free bpza (black), **2** (brown) and precipitated MnO_x (blue).

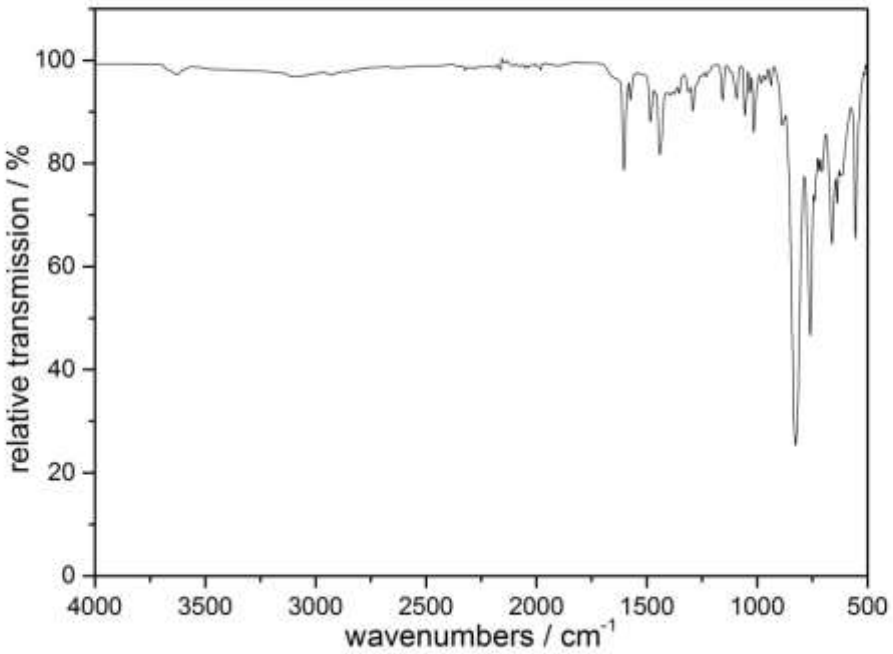


Figure S16. IR spectrum of $[Mn_2(\mu\text{-}O)_2\kappa^4\text{-}tpa)_2][PF_6]_3$ derived by UV-irradiation of **3** in MeCN, λ_{irr} = 365 nm**.**

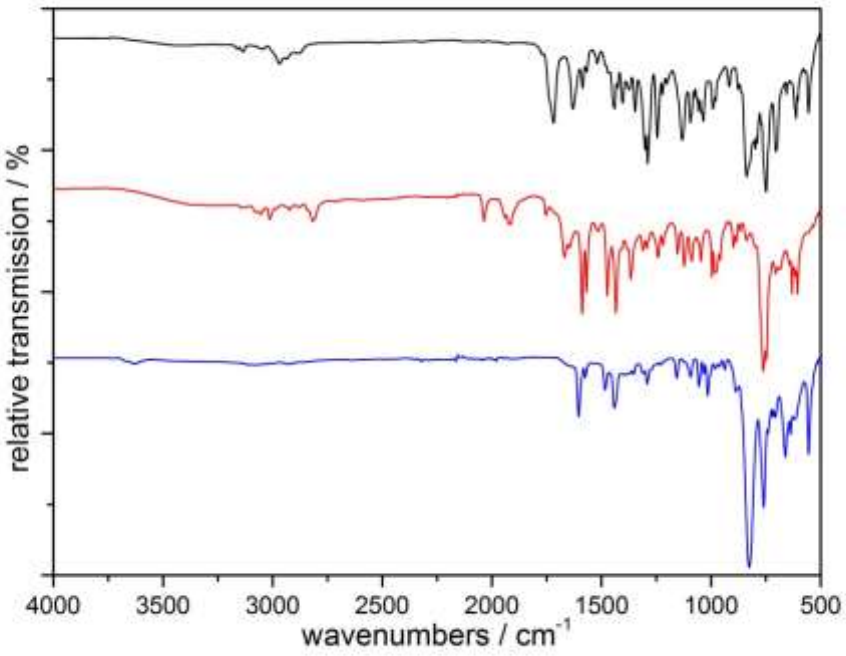


Figure S17. Comparison of the IR spectrum of $[Mn_2(\mu\text{-}O)_2\kappa^4\text{-}tpa)_2][PF_6]_3$ (blue) derived by UV-irradiation of **3** in MeOH/H_2O (9:1), λ_{irr} = 365 nm, with the IR spectra of free tpa (black) and **3** (red).

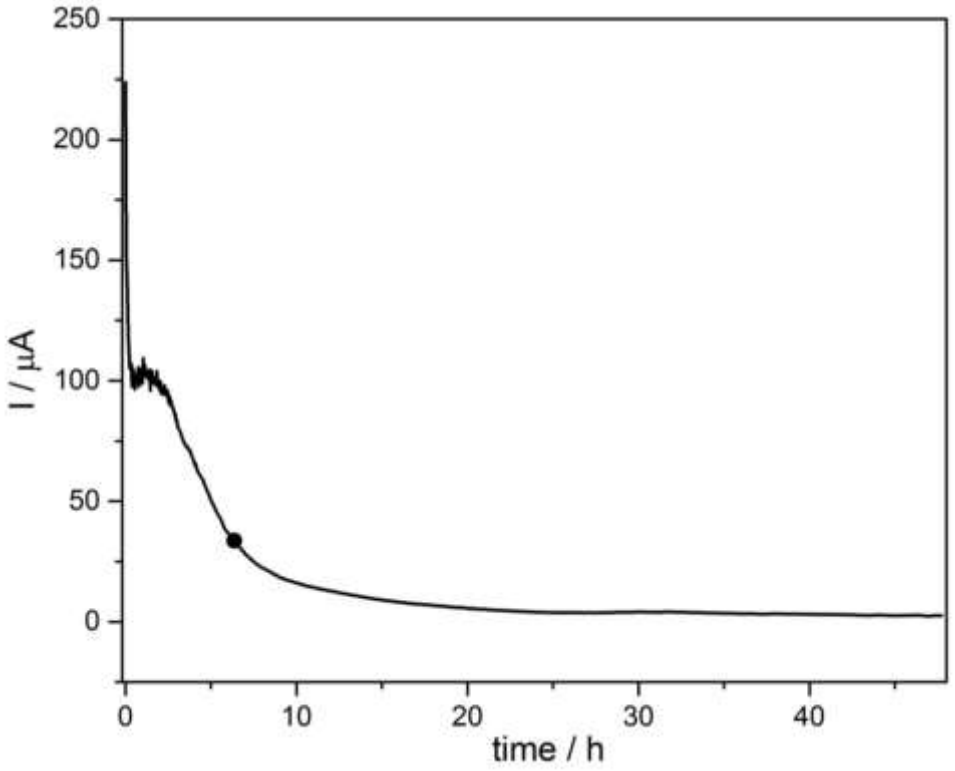


Figure S18. I *vs.* t-diagram of the electrochemical, chronoamperometric synthesis of $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)_2][PF_6]_3$.

Crystallographic tables

Tables S1. Tables of the molecular structure of $[Mn(tpm)_2][PF_6]_2$

Crystal data and structure refinement for $[Mn(tpm)_2][PF_6]_2$.

Identification code	p21n_a
Empirical formula	$C_{20}H_{20}N_{12}F_{12}P_2Mn$
Formula weight	773.36
Temperature/K	100.02
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.3422(4)
b/Å	16.6653(7)
c/Å	10.7977(5)
α/°	90
β/°	95.322(2)
γ/°	90
Volume/Å^3	1494.68(12)
Z	2
ρ_{calc}g/cm^3	1.718
μ/mm^{-1}	0.660
F(000)	774.0
Crystal size/mm^3	0.18 × 0.06 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.508 to 65.384
Index ranges	-12 ≤ h ≤ 12, -25 ≤ k ≤ 25, -16 ≤ l ≤ 16
Reflections collected	49069
Independent reflections	5491 [R_{int} = 0.0283, R_{sigma} = 0.0163]
Data/restraints/parameters	5491/0/214
Goodness-of-fit on F^2	1.620
Final R indexes [I>=2σ (I)]	R_1 = 0.0397, wR_2 = 0.1200
Final R indexes [all data]	R_1 = 0.0448, wR_2 = 0.1225
Largest diff. peak/hole / e Å^{-3}	1.12/-0.34

Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for $[Mn(tpm)_2][PF_6]_2$. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mn1	5000	5000	5000	14.82(9)
C1	3632.7(17)	5576.2(9)	7558.6(13)	13.1(2)
N1	6231.3(16)	5566.7(9)	6693.0(13)	18.2(3)
C2	6240(2)	6071.7(10)	8625.2(15)	19.2(3)

N2	3128.4(18)	5925.8(9)	5362.6(12)	18.6(3)
F3	3668.8(13)	872.8(7)	5305.2(10)	25.8(2)
C3	7778(2)	6140.3(13)	8283.7(18)	26.1(4)
N3	3762.7(17)	4323.1(8)	6406.5(13)	18.1(3)
C4	7714(2)	5816.8(12)	7077.9(18)	24.8(3)
N4	5343.1(15)	5725.0(8)	7657.4(12)	14.2(2)
C5	2238.4(19)	4293(1)	8018.8(15)	18.6(3)
N5	2815.3(15)	6046.1(8)	6562.5(11)	13.9(2)
C6	2101(2)	3556.6(10)	7443.6(18)	23.7(3)
N6	3260.6(16)	4734.2(8)	7387.2(12)	14.5(2)
C10	2139(2)	6423.8(11)	4695.0(16)	23.2(3)
C9	1185(2)	6860.2(11)	5459.5(16)	22.7(3)
C8	1645.2(18)	6603.9(10)	6650.8(15)	16.9(3)
C7	3075(2)	3603.3(10)	6451.6(17)	22.5(3)
P1	2725.6(5)	1448.3(2)	4282.4(4)	15.44(9)
F1	1952.9(13)	1913.0(6)	5408.4(9)	20.2(2)
F2	3496.1(15)	974.0(8)	3207.5(10)	30.1(3)
F4	4211.7(16)	2051.7(8)	4409.4(13)	35.3(3)
F5	1769.5(18)	2022.3(9)	3305.3(11)	39.1(3)
F6	1235.2(14)	839.2(7)	4216.1(12)	30.0(3)

Anisotropic Displacement Parameters ($Å^2×10^3$) for $[Mn(tpm)_2][PF_6]_2$. 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	15.53(15)	15.42(16)	14.18(15)	-3.32(11)	4.92(11)	0.51(11)
C1	13.2(6)	13.2(6)	12.8(6)	-0.8(5)	1.2(4)	-0.3(5)
N1	13.6(5)	23.5(7)	18.0(6)	-4.1(5)	4.3(4)	-1.8(5)
C2	18.1(7)	22.1(7)	16.5(6)	-2.6(5)	-2.5(5)	-1.8(6)
N2	23.0(6)	22.1(7)	11.0(5)	-0.9(5)	2.7(5)	6.8(5)
F3	24.6(5)	32.1(6)	21.0(5)	8.3(4)	3.2(4)	10.4(4)
C3	17.6(7)	35(1)	24.8(8)	-4.5(7)	-2.7(6)	-6.1(7)
N3	22.7(6)	13.2(6)	19.3(6)	-3.7(5)	6.7(5)	-0.8(5)
C4	14.7(7)	33.4(9)	26.5(8)	-4.8(7)	3.2(6)	-4.5(6)
N4	12.5(5)	16.7(6)	13.4(5)	-1.3(4)	1.0(4)	-0.7(4)
C5	17.6(7)	18.1(7)	20.9(7)	4.2(5)	5.4(5)	-0.9(5)
N5	15.1(5)	14.8(6)	11.8(5)	-1.4(4)	1.5(4)	3.1(4)
C6	23.9(8)	16.4(7)	31.7(9)	2.0(6)	7.7(7)	-3.6(6)
N6	15.7(5)	13.4(5)	14.8(5)	-0.8(4)	4.3(4)	-0.9(4)
C10	27.6(8)	25.5(8)	16.0(7)	0.9(6)	-0.3(6)	8.4(6)
C9	23.2(8)	22.4(8)	22.1(7)	1.1(6)	-0.5(6)	8.8(6)
C8	15.0(6)	15.8(7)	19.9(7)	-2.1(5)	2.4(5)	3.2(5)
C7	26.1(8)	14.4(7)	27.8(8)	-1.9(6)	5.7(6)	-3.1(6)
P1	17.12(18)	17.43(19)	11.94(16)	0.58(13)	2.29(13)	0.65(13)
F1	25.7(5)	17.8(5)	17.9(4)	-3.6(3)	6.1(4)	0.0(4)
F2	34.1(6)	37.8(7)	19.8(5)	-4.8(4)	10.4(4)	8.3(5)

F4	31.5(6)	32.8(7)	43.9(7)	-2.6(5)	16.2(5)	-14.3(5)
F5	49.9(8)	46.7(8)	20.9(5)	13.7(5)	4.8(5)	24.2(6)
F6	22.0(5)	31.1(6)	37.3(6)	-16.1(5)	4.2(4)	-7.9(4)

Bond Lengths for $[Mn(tpm)_2][PF_6]_2$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	N1[1]	2.2227(14)	F3	P1	1.6117(11)
Mn1	N1	2.2227(14)	C3	C4	1.406(3)
Mn1	N2[1]	2.2549(14)	N3	N6	1.3595(18)
Mn1	N2	2.2549(14)	N3	C7	1.333(2)
Mn1	N3	2.2215(14)	C5	C6	1.375(2)
Mn1	N3[1]	2.2215(14)	C5	N6	1.357(2)
C1	N4	1.4424(19)	N5	C8	1.3577(19)
C1	N5	1.4488(19)	C6	C7	1.405(3)
C1	N6	1.4453(19)	C10	C9	1.402(2)
N1	C4	1.335(2)	C9	C8	1.376(2)
N1	N4	1.3587(18)	P1	F1	1.6244(11)
C2	C3	1.372(2)	P1	F2	1.5885(12)
C2	N4	1.3567(19)	P1	F4	1.5923(13)
N2	N5	1.3601(17)	P1	F5	1.5838(12)
N2	C10	1.334(2)	P1	F6	1.6015(12)

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

Bond Angles for $[Mn(tpm)_2][PF_6]_2$.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N1	Mn1	N1[1]	180.0	N1	N4	C1	121.06(12)
N1	Mn1	N2	80.85(5)	C2	N4	C1	126.97(13)
N1	Mn1	N2[1]	99.15(5)	C2	N4	N1	111.84(13)
N1[1]	Mn1	N2	99.15(5)	N6	C5	C6	106.66(15)
N1[1]	Mn1	N2[1]	80.85(5)	N2	N5	C1	120.58(12)
N2[1]	Mn1	N2	180.0	C8	N5	C1	127.58(13)
N3	Mn1	N1[1]	97.93(5)	C8	N5	N2	111.76(13)
N3	Mn1	N1	82.07(5)	C5	C6	C7	105.35(15)
N3[1]	Mn1	N1[1]	82.07(5)	N3	N6	C1	120.73(12)
N3[1]	Mn1	N1	97.93(5)	C5	N6	C1	126.82(13)
N3[1]	Mn1	N2	98.30(5)	C5	N6	N3	111.83(13)
N3[1]	Mn1	N2[1]	81.70(5)	N2	C10	C9	111.17(15)
N3	Mn1	N2	81.70(5)	C8	C9	C10	105.37(14)
N3	Mn1	N2[1]	98.30(5)	N5	C8	C9	106.68(14)
N3[1]	Mn1	N3	180.0	N3	C7	C6	111.05(15)
N4	C1	N5	110.87(12)	F3	P1	F1	88.46(6)
N4	C1	N6	112.07(12)	F2	P1	F3	89.98(6)
N6	C1	N5	110.43(12)	F2	P1	F1	178.39(6)

C4	N1	Mn1	137.15(12)	F2	P1	F4	90.72(7)
C4	N1	N4	104.85(13)	F2	P1	F6	90.98(7)
N4	N1	Mn1	118.01(9)	F4	P1	F3	89.43(7)
N4	C2	C3	106.93(15)	F4	P1	F1	89.67(6)
N5	N2	Mn1	117.61(10)	F4	P1	F6	177.63(7)
C10	N2	Mn1	137.35(11)	F5	P1	F3	178.45(7)
C10	N2	N5	105.02(13)	F5	P1	F1	90.02(6)
C2	C3	C4	105.11(15)	F5	P1	F2	91.53(7)
N6	N3	Mn1	118.22(10)	F5	P1	F4	90.91(8)
C7	N3	Mn1	135.32(12)	F5	P1	F6	90.70(8)
C7	N3	N6	105.09(14)	F6	P1	F3	88.92(7)
N1	C4	C3	111.28(16)	F6	P1	F1	88.59(6)

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

Torsion Angles for $[Mn(tpm)_2][PF_6]_2$.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Mn1	N1	C4	C3	179.89(14)	N4	N1	C4	C3	-0.4(2)
Mn1	N1	N4	C1	-3.77(19)	N4	C2	C3	C4	0.0(2)
Mn1	N1	N4	C2	-179.81(11)	C5	C6	C7	N3	-0.5(2)
Mn1	N2	N5	C1	-1.65(18)	N5	C1	N4	N1	-60.41(18)
Mn1	N2	N5	C8	-178.66(11)	N5	C1	N4	C2	114.99(17)
Mn1	N2	C10	C9	178.47(14)	N5	C1	N6	N3	66.10(17)
Mn1	N3	N6	C1	-4.68(18)	N5	C1	N6	C5	-104.08(17)
Mn1	N3	N6	C5	166.86(11)	N5	N2	C10	C9	-0.3(2)
Mn1	N3	C7	C6	-164.36(13)	C6	C5	N6	C1	172.43(15)
C1	N5	C8	C9	-177.10(15)	C6	C5	N6	N3	1.52(19)
C2	C3	C4	N1	0.3(2)	N6	C1	N4	N1	63.48(18)
N2	N5	C8	C9	-0.35(19)	N6	C1	N4	C2	-121.12(16)
N2	C10	C9	C8	0.1(2)	N6	C1	N5	N2	-61.52(18)
C3	C2	N4	C1	-176.01(16)	N6	C1	N5	C8	114.98(16)
C3	C2	N4	N1	-0.3(2)	N6	N3	C7	C6	1.4(2)
C4	N1	N4	C1	176.45(15)	N6	C5	C6	C7	-0.6(2)
C4	N1	N4	C2	0.41(19)	C10	N2	N5	C1	177.44(14)
N4	C1	N5	N2	63.30(18)	C10	N2	N5	C8	0.43(19)
N4	C1	N5	C8	-120.20(16)	C10	C9	C8	N5	0.1(2)
N4	C1	N6	N3	-58.03(17)	C7	N3	N6	C1	-173.33(14)
N4	C1	N6	C5	131.79(15)	C7	N3	N6	C5	-1.79(18)

Experimental

Single crystals of $C_{20}H_{20}N_{12}F_{12}P_2Mn$ $[Mn(tpm)_2][PF_6]_2$ were obtained by crystallization from MeCN. A suitable crystal was selected and measured on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 100.2 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the XL [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. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of $[Mn(tpm)_2][PF_6]_2$

Crystal Data for $C_{20}H_{20}N_{12}F_{12}P_2Mn$ (M =773.36 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 8.3422(4) Å, b = 16.6653(7) Å, c = 10.7977(5) Å, β = 95.322(2)°, V = 1494.68(12) Å^3, Z = 2, T = 100.02 K, μ(MoKα) = 0.660 mm^{-1}, *Dcalc* = 1.718 g/cm^3, 49069 reflections measured (4.508° ≤ 2Θ ≤ 65.384°), 5491 unique (R_{int} = 0.0283, R_{sigma} = 0.0163) which were used in all calculations. The final R_1 was 0.0397 (I > 2σ(I)) and wR_2 was 0.1225 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.
Details:
N/A

This report has been created with Olex2, compiled on 2016.02.19 svn.r3266 for OlexSys.

Tables S2. Tables of the molecular structure of $[Mn_2(bpza)_4]$

Crystal data and structure refinement for $[Mn_2(bpza)_4]$.

Identification code	p-1_a
Empirical formula	$C_{32}H_{44}N_{16}O_{16}Mn_2$
Formula weight	1018.71
Temperature/K	100.03
Crystal system	triclinic
Space group	P-1
a/Å	8.3617(10)
b/Å	10.9758(10)
c/Å	12.1705(12)
α/°	103.770(4)
β/°	95.537(4)
γ/°	94.757(3)
Volume/Å^3	1073.30(19)
Z	1
ρ_{calc}g/cm^3	1.576
μ/mm^{-1}	0.677
F(000)	526.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.47 to 73.394
Index ranges	-13 ≤ h ≤ 11, -18 ≤ k ≤ 17, -18 ≤ l ≤ 19
Reflections collected	41322
Independent reflections	9236 [R_{int} = 0.0188, R_{sigma} = 0.0194]
Data/restraints/parameters	9236/12/322
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0299, wR_2 = 0.0766
Final R indexes [all data]	R_1 = 0.0342, wR_2 = 0.0793
Largest diff. peak/hole / e Å^{-3}	0.57/-0.29

Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for [Mn$_2$(bpza)$_4$]. U$_{eq}$ is defined as 1/3 of of the trace of the orthogonalised U$_{IJ}$ tensor.

Atom	*x*	*y*	*z*	U(eq)
Mn1	1102.4(2)	7133.4(2)	6726.1(2)	9.93(3)
C1	3238.4(10)	9426.1(7)	8683.1(7)	11.14(13)
N1	3327.1(9)	8483.6(7)	6657.7(6)	11.99(12)
O1	2494.9(8)	7181.8(6)	8359.4(5)	13.62(11)
O2	4184.2(9)	8190.4(6)	9911.7(6)	16.39(12)
C2	3306.4(10)	8147.6(7)	9020.5(7)	11.07(13)
N2	3923.6(9)	9372.7(6)	7625.0(6)	11.33(12)
O3	1741.0(8)	5303.6(6)	6013.1(6)	15.84(12)
N3	445.2(9)	8990.9(7)	7843.1(7)	14.86(13)
C3	1048.6(12)	10856.9(8)	9120.4(8)	16.43(15)
O4	3129.5(9)	5974.4(6)	4746.5(6)	17.92(13)
C4	-559.5(12)	10768.0(9)	8720.4(9)	19.15(17)
N4	1611.1(9)	9775.9(6)	8586.3(6)	12.15(12)
N6	2021.7(9)	2823.4(7)	5049.0(6)	11.22(12)
C6	5152.9(10)	10161.7(8)	7451.5(8)	13.65(14)
N5	401.1(9)	2512.9(7)	4768.4(7)	14.12(13)
C5	-876.5(11)	9590.6(9)	7929.0(9)	18.08(16)
N8	2728.2(8)	3537.5(7)	3411.9(6)	11.17(11)
C8	4225.7(10)	8724.4(8)	5868.4(7)	12.97(14)
N7	1281.2(9)	3601.7(7)	2824.7(6)	12.02(12)
C7	5388.2(11)	9764.1(8)	6323.9(8)	14.89(14)
C9	2902.2(10)	3785.4(7)	4643.1(7)	10.69(13)
C16	1607.9(11)	3619.7(8)	1779.1(7)	14.65(14)
C15	3267.5(12)	3602.6(9)	1691.7(8)	17.62(16)
C14	3947.2(11)	3562.1(8)	2756.6(8)	15.05(14)
C13	-11.2(12)	1775.6(11)	5446.3(9)	23.1(2)
C12	1321.3(13)	1630.9(12)	6174.7(10)	25.7(2)
C11	2598.2(11)	2325.3(9)	5904.4(8)	17.02(15)
C10	2521.2(10)	5149.4(7)	5170.6(7)	12.00(13)
O101	1025.4(10)	6359.0(7)	1046.6(7)	24.98(15)
O103	3345.4(11)	7022.8(8)	2901.4(7)	25.43(16)
O105	7902.8(10)	5092.4(7)	10910.4(7)	23.21(15)
O107	5548.5(12)	6695.8(10)	11256.4(8)	31.59(19)

Anisotropic Displacement Parameters (Å^2×10^3) for [Mn$_2$(bpza)$_4$]. 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	9.17(5)	9.62(5)	9.94(6)	1.13(4)	-0.07(4)	0.14(4)
C1	11.4(3)	11.1(3)	9.6(3)	1.0(2)	-0.1(2)	-0.1(2)
N1	13.7(3)	11.0(3)	9.7(3)	0.5(2)	0.6(2)	-1.2(2)
O1	16.0(3)	11.0(2)	12.2(3)	2.20(19)	-2.3(2)	-0.7(2)
O2	19.3(3)	16.6(3)	11.7(3)	3.4(2)	-4.3(2)	0.7(2)
C2	11.0(3)	12.2(3)	9.9(3)	2.4(2)	1.2(2)	1.4(2)
N2	11.5(3)	10.7(3)	10.5(3)	1.2(2)	0.3(2)	-1.1(2)
O3	18.4(3)	13.6(3)	14.5(3)	0.1(2)	4.3(2)	3.1(2)
N3	11.4(3)	12.1(3)	18.1(3)	-0.6(2)	-1.4(2)	1.0(2)
C3	20.0(4)	10.9(3)	17.2(4)	-0.1(3)	4.1(3)	3.0(3)
O4	22.0(3)	12.2(3)	18.1(3)	2.8(2)	2.1(2)	-2.7(2)
C4	18.3(4)	14.7(3)	24.8(5)	3.0(3)	5.7(3)	6.2(3)
N4	11.9(3)	10.0(3)	12.9(3)	0.1(2)	0.5(2)	0.9(2)
N6	10.2(3)	11.7(3)	11.3(3)	2.6(2)	0.1(2)	0.5(2)
C6	12.3(3)	12.7(3)	15.0(4)	3.8(3)	-0.4(3)	-2.5(3)
N5	10.7(3)	17.1(3)	14.4(3)	6.2(2)	-1.4(2)	-2.5(2)
C5	13.2(4)	15.7(3)	24.3(4)	2.7(3)	1.2(3)	3.9(3)
N8	9.3(3)	12.6(3)	10.7(3)	1.1(2)	1.4(2)	0.8(2)
C8	14.3(3)	13.1(3)	11.5(3)	3.3(3)	2.0(3)	-0.3(3)
N7	11.1(3)	13.1(3)	11.2(3)	2.2(2)	0.5(2)	0.6(2)
C7	14.1(3)	15.9(3)	14.7(4)	5.4(3)	1.2(3)	-2.2(3)
C9	9.5(3)	11.1(3)	10.2(3)	0.8(2)	0.7(2)	0.2(2)
C16	16.5(4)	15.4(3)	11.7(3)	2.8(3)	2.2(3)	0.9(3)
C15	17.3(4)	22.0(4)	13.9(4)	3.6(3)	5.9(3)	2.2(3)
C14	12.0(3)	17.5(3)	15.2(4)	1.7(3)	4.6(3)	2.5(3)
C13	17.0(4)	32.1(5)	23.4(5)	18.0(4)	-2.2(3)	-6.1(4)
C12	20.0(4)	36.9(5)	25.1(5)	21.5(4)	-2.9(4)	-3.0(4)
C11	15.1(4)	22.2(4)	14.8(4)	7.9(3)	-1.5(3)	2.1(3)
C10	11.1(3)	11.0(3)	11.8(3)	0.1(2)	-1.6(2)	0.4(2)
O101	27.5(4)	18.7(3)	27.8(4)	4.0(3)	4.5(3)	1.0(3)
O103	30.4(4)	23.9(3)	20.4(3)	6.1(3)	2.0(3)	-7.0(3)
O105	23.3(4)	21.2(3)	29.3(4)	11.7(3)	7.5(3)	5.3(3)
O107	33.0(4)	42.7(5)	28.0(4)	18.7(4)	8.8(3)	20.5(4)

Bond Lengths for $[Mn_2(bpza)_4]$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	N1	2.3011(8)	O4	C10	1.2417(11)
Mn1	O1	2.1915(7)	C4	C5	1.4033(13)
Mn1	O3	2.1235(7)	N6	N5	1.3593(10)
Mn1	N3	2.3058(8)	N6	C9	1.4458(11)
Mn1	$N5^1$	2.2395(8)	N6	C11	1.3539(11)
Mn1	$N7^1$	2.2529(8)	C6	C7	1.3762(13)
C1	C2	1.5568(11)	N5	$Mn1^1$	2.2395(8)
C1	N2	1.4499(11)	N5	C13	1.3345(12)

C1	N4	1.4458(11)	N8	N7	1.3605(10)
N1	N2	1.3587(10)	N8	C9	1.4484(11)
N1	C8	1.3359(11)	N8	C14	1.3558(11)
O1	C2	1.2652(10)	C8	C7	1.4019(12)
O2	C2	1.2385(10)	N7	Mn1[1]	2.2529(8)
N2	C6	1.3536(11)	N7	C16	1.3314(11)
O3	C10	1.2532(11)	C9	C10	1.5543(12)
N3	N4	1.3530(10)	C16	C15	1.4033(13)
N3	C5	1.3326(12)	C15	C14	1.3763(13)
C3	C4	1.3725(14)	C13	C12	1.3994(14)
C3	N4	1.3549(11)	C12	C11	1.3715(14)

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

Bond Angles for [$Mn_2(bpza)_4$].

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N1	Mn1	N3	79.67(3)	C3	C4	C5	104.91(8)
O1	Mn1	N1	79.94(3)	N3	N4	C1	119.55(7)
O1	Mn1	N3	79.20(3)	N3	N4	C3	111.80(7)
O1	Mn1	N5[1]	168.30(3)	C3	N4	C1	128.59(7)
O1	Mn1	N7[1]	95.75(3)	N5	N6	C9	122.08(7)
O3	Mn1	N1	104.70(3)	C11	N6	N5	111.62(7)
O3	Mn1	O1	90.76(3)	C11	N6	C9	124.99(7)
O3	Mn1	N3	168.28(3)	N2	C6	C7	106.80(7)
O3	Mn1	N5[1]	100.91(3)	N6	N5	Mn1[1]	126.37(6)
O3	Mn1	N7[1]	93.77(3)	C13	N5	Mn1[1]	128.04(6)
N5[1]	Mn1	N1	96.14(3)	C13	N5	N6	104.63(7)
N5[1]	Mn1	N3	89.27(3)	N3	C5	C4	111.30(8)
N5[1]	Mn1	N7[1]	84.37(3)	N7	N8	C9	120.33(7)
N7[1]	Mn1	N1	161.02(3)	C14	N8	N7	111.29(7)
N7[1]	Mn1	N3	81.37(3)	C14	N8	C9	126.09(7)
N2	C1	C2	110.41(7)	N1	C8	C7	111.39(8)
N4	C1	C2	112.11(7)	N8	N7	Mn1[1]	123.12(5)
N4	C1	N2	110.14(7)	C16	N7	Mn1[1]	125.47(6)
N2	N1	Mn1	117.86(5)	C16	N7	N8	105.22(7)
C8	N1	Mn1	137.29(6)	C6	C7	C8	105.10(7)
C8	N1	N2	104.68(7)	N6	C9	N8	113.03(6)
C2	O1	Mn1	125.45(5)	N6	C9	C10	114.15(7)
O1	C2	C1	117.54(7)	N8	C9	C10	110.10(7)
O2	C2	C1	115.47(7)	N7	C16	C15	111.35(8)
O2	C2	O1	126.99(8)	C14	C15	C16	104.84(8)
N1	N2	C1	121.15(7)	N8	C14	C15	107.25(8)
C6	N2	C1	126.81(7)	N5	C13	C12	111.64(9)
C6	N2	N1	112.03(7)	C11	C12	C13	104.84(8)
C10	O3	Mn1	118.67(6)	N6	C11	C12	107.23(8)

N4	N3	Mn1	119.31(6)	O3	C10	C9	117.05(7)
C5	N3	Mn1	135.59(6)	O4	C10	O3	127.58(8)
C5	N3	N4	104.99(7)	O4	C10	C9	115.18(8)
N4	C3	C4	106.99(8)				

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

Torsion Angles for [$Mn_2(bpza)_4$].

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Mn1	N1	N2	C1	3.36(10)	N6	N5	C13	C12	1.22(13)
Mn1	N1	N2	C6	-175.51(6)	N6	C9	C10	O3	12.04(10)
Mn1	N1	C8	C7	174.72(7)	N6	C9	C10	O4	-172.64(7)
Mn1	O1	C2	C1	3.59(11)	N5	N6	C9	N8	-57.20(10)
Mn1	O1	C2	O2	-175.17(7)	N5	N6	C9	C10	69.66(10)
Mn1	O3	C10	O4	7.84(12)	N5	N6	C11	C12	1.82(11)
Mn1	O3	C10	C9	-177.51(5)	N5	C13	C12	C11	-0.17(14)
Mn1	N3	N4	C1	-1.20(10)	C5	N3	N4	C1	-178.07(8)
Mn1	N3	N4	C3	176.04(6)	C5	N3	N4	C3	-0.83(10)
Mn1	N3	C5	C4	-175.57(7)	N8	N7	C16	C15	-1.64(10)
$Mn1^1$	N5	C13	C12	170.48(8)	N8	C9	C10	O3	140.40(8)
$Mn1^1$	N7	C16	C15	-154.40(6)	N8	C9	C10	O4	-44.28(9)
C1	N2	C6	C7	-179.55(8)	C8	N1	N2	C1	179.48(7)
N1	N2	C6	C7	-0.77(10)	C8	N1	N2	C6	0.61(9)
N1	C8	C7	C6	-0.23(10)	N7	N8	C9	N6	68.63(9)
C2	C1	N2	N1	57.40(10)	N7	N8	C9	C10	-60.34(9)
C2	C1	N2	C6	-123.91(9)	N7	N8	C14	C15	-1.98(10)
C2	C1	N4	N3	-58.40(10)	N7	C16	C15	C14	0.49(11)
C2	C1	N4	C3	124.88(9)	C9	N6	N5	$Mn1^1$	21.08(11)
N2	C1	C2	O1	-63.67(10)	C9	N6	N5	C13	-169.42(8)
N2	C1	C2	O2	115.24(8)	C9	N6	C11	C12	168.94(9)
N2	C1	N4	N3	64.96(9)	C9	N8	N7	$Mn1^1$	-40.36(9)
N2	C1	N4	C3	-	C9	N8	N7	C16	166.06(7)
N2	N1	C8	C7	-0.22(10)	C9	N8	C14	C15	-164.67(8)
N2	C6	C7	C8	0.58(10)	C16	C15	C14	N8	0.89(10)
C3	C4	C5	N3	-0.07(12)	C14	N8	N7	$Mn1^1$	155.81(6)
C4	C3	N4	C1	177.73(8)	C14	N8	N7	C16	2.24(9)
C4	C3	N4	N3	0.80(11)	C14	N8	C9	N6	-130.10(8)
N4	C1	C2	O1	59.54(10)	C14	N8	C9	C10	100.92(9)
N4	C1	C2	O2	-121.56(8)	C13	C12	C11	N6	-0.97(13)
N4	C1	N2	N1	-66.94(9)	C11	N6	N5	$Mn1^1$	-171.37(6)
N4	C1	N2	C6	111.75(9)	C11	N6	N5	C13	-1.87(11)
N4	N3	C5	C4	0.54(11)	C11	N6	C9	N8	136.96(9)
N4	C3	C4	C5	-0.43(11)	C11	N6	C9	C10	-96.18(10)

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

Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for

Atom	*x*	*y*	*z*	U(eq)
H1	3909	10096	9295	13
H3	1653	11546	9668	20
H4	-1297	11372	8933	23
H6	5740	10856	8002	16
H5	-1902	9263	7509	22
H8	4094	8251	5097	16
H7	6170	10118	5938	18
H9	4073	3760	4889	13
H16	818	3641	1170	18
H15	3804	3616	1041	21
H14	5063	3553	2989	18
H13	-1078	1396	5436	28
H12	1338	1156	6734	31
H11	3685	2436	6253	20
H10A	1449(18)	5814(14)	447(12)	37
H10B	17(13)	5971(15)	1115(14)	37
H10C	2445(16)	6817(16)	2343(11)	38
H10D	3200(20)	6525(14)	3416(11)	38
H10E	7633(19)	4396(11)	11202(14)	35
H10F	7040(16)	5592(13)	11011(15)	35
H10G	4940(20)	6935(18)	10667(11)	47
H10H	4861(19)	6642(18)	11816(11)	47

Experimental

Single crystals of $C_{32}H_{44}N_{16}O_{16}Mn_2$ [$Mn_2(bpza)_4$] were obtained by crystallization from EtOH/H2O. A suitable crystal was selected and measured on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 100.3 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the XL [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. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of [$Mn_2(bpza)_4$]

Crystal Data for $C_{32}H_{44}N_{16}O_{16}Mn_2$ (M =1018.71 g/mol): triclinic, space group P-1 (no. 2), a = 8.3617(10) Å, b = 10.9758(10) Å, c = 12.1705(12) Å, α = 103.770(4)°, β = 95.537(4)°, γ = 94.757(3)°, V = 1073.30(19) Å^3, Z = 1, T = 100.03 K, μ(MoKα) = 0.677 mm^{-1}, *Dcalc* = 1.576 g/cm^3, 41322 reflections measured (3.47° ≤ 2Θ ≤ 73.394°), 9236 unique (R_{int} = 0.0188, R_{sigma} = 0.0194) which were used in all calculations. The final R_1 was 0.0299 (I > 2σ(I)) and wR_2 was 0.0793 (all data).

Refinement model description

Number of restraints - 12, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All O(H,H) groups
2. Restrained distances
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 O101-H10A = O101-H10B = O103-H10C = O103-H10D = O105-H10E = O105-H10F
 0.9584 with sigma of 0.01
 O107-H10H = O107-H10G
 0.9584 with sigma of 0.01
 H10A-H10B = H10C-H10D = H10E-H10F = H10H-H10G
 1.5151 with sigma of 0.01
3.a Ternary CH refined with riding coordinates:
 C1(H1), C9(H9)
3.b Aromatic/amide H refined with riding coordinates:
 C3(H3), C4(H4), C6(H6), C5(H5), C8(H8), C7(H7), C16(H16), C15(H15), C14(H14),
 C13(H13), C12(H12), C11(H11)
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This report has been created with Olex2, compiled on 2016.02.19 svn.r3266 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Tables S3. Tables of the molecular structure of $[Mn(CO)_3(tpa)][PF_6]$.

Crystal data and structure refinement for $[Mn(CO)_3(tpa)][PF_6]$.

Identification code	p21n_a
Empirical formula	$C_{21}H_{18}N_4O_3F_{5.97}PMn$
Formula weight	573.52
Temperature/K	100.09
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.9782(7)
b/Å	13.3015(9)
c/Å	15.8036(11)
α/°	90
β/°	100.432(3)
γ/°	90
Volume/Å^3	2269.6(3)
Z	4
ρ_{calc}g/cm^3	1.678
μ/mm^{-1}	0.734
F(000)	1159.0
Crystal size/mm^3	0.16 × 0.16 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.03 to 66.816
Index ranges	-16 ≤ h ≤ 16, -18 ≤ k ≤ 18, -24 ≤ l ≤ 22
Reflections collected	37391
Independent reflections	7822 [R_{int} = 0.0227, R_{sigma} = 0.0239]
Data/restraints/parameters	7822/211/454
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0324, wR_2 = 0.0801
Final R indexes [all data]	R_1 = 0.0431, wR_2 = 0.0854
Largest diff. peak/hole / e Å^{-3}	0.49/-0.33

Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for [Mn(CO)$_3$(tpa)][PF$_6$]. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mn1	8084.4(2)	6606.3(2)	3920.0(2)	14.78(5)
N1	7120.6(9)	6381.6(8)	2654.9(6)	15.87(19)
O1	10066.0(9)	5095.2(8)	3945.8(7)	29.9(2)
C1	9298.0(11)	5683(1)	3911.5(8)	20.0(2)
N2	6654.4(9)	7599.5(8)	3868.9(6)	15.62(18)
O2	9626.2(9)	8207.0(8)	3354.0(7)	29.2(2)
C2	9039.8(11)	7589.4(10)	3578.3(8)	20.0(2)
N3	6929.3(9)	5474.2(8)	4164.9(7)	16.50(19)
O3	9334(1)	7071.9(9)	5689.2(7)	32.5(2)
C3	8805.0(11)	6878.1(10)	5015.4(8)	20.7(2)
C7	5430.5(13)	3819.6(11)	4317.9(10)	26.4(3)
C6	5352.9(12)	4311.4(10)	3536.8(9)	22.6(2)
C5	6119.6(10)	5130.9(9)	3481.5(8)	17.2(2)
C4	6038.2(11)	5690.5(10)	2653.0(8)	19.0(2)
N4	6945.5(10)	4955.7(9)	914.2(7)	24.0(2)
C8	6264.3(13)	4168.5(11)	5023.5(9)	25.4(3)
C9	6991.2(11)	4990.6(10)	4925.1(8)	20.9(2)
C10	6635.7(11)	7392.2(10)	2357.4(8)	18.4(2)
C11	6105.9(10)	7878.3(9)	3069.2(8)	17.1(2)
C12	5141.3(11)	8564.9(10)	2925.8(9)	20.9(2)
C13	4733.3(12)	8986.2(10)	3626.4(9)	24.4(3)
C14	5300.1(12)	8706.8(10)	4447.5(9)	22.6(2)
C15	6255.6(11)	8012.8(9)	4546.5(8)	18.1(2)
C16	7976.4(11)	5976.3(11)	2091.4(8)	20.5(2)
C17	7446.7(11)	5853.2(10)	1149.2(8)	20.4(2)
C18	7544.9(13)	6609.1(11)	561.3(9)	26.9(3)
C19	7132.6(13)	6432.1(13)	-309.8(9)	30.6(3)
C20	6642.8(13)	5502.0(12)	-558.7(9)	28.5(3)
C21	6554.2(13)	4798.2(12)	67.5(9)	28.0(3)
P91A	7220(13)	8406(10)	7295(11)	7.1(13)
F91A	7151(15)	7257(10)	6846(13)	42(3)
F93A	6290(14)	7976(15)	7937(11)	56(3)
F92A	7032(16)	9435(12)	7668(8)	37(3)
F94A	8483(19)	8215(15)	8101(12)	15(2)
F95A	8159(14)	8400(9)	6610(10)	21(2)
F96A	6128(15)	8602(12)	6515(10)	23(3)
P91B	7179(11)	8412(12)	7242(8)	41(4)
F91B	6970(30)	7279(14)	7025(14)	40(4)
F93B	6012(17)	8444(19)	7680(15)	70(5)
F92B	7540(30)	9554(15)	7540(20)	49(5)
F94B	7950(20)	8002(15)	8114(9)	45(4)
F95B	8410(16)	8444(16)	6877(15)	53(5)

F96B	6470(20)	8837(14)	6338(8)	45(4)
P91C	7149(4)	8354(3)	7345(3)	20.5(8)
F91C	6993(4)	7191(2)	7248(4)	51(1)
F93C	6386(3)	8391(4)	8092(2)	49.9(8)
F92C	7369(5)	9555(2)	7450(4)	42.7(9)
F94C	8378(6)	8184(5)	8016(3)	39.6(13)
F95C	7936(5)	8420(4)	6613(3)	72.8(15)
F96C	5900(4)	8537(4)	6664(3)	52.7(12)

Anisotropic Displacement Parameters ($Å^2×10^3$) $[Mn(CO)_3(tpa)][PF_6]$. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	12.00(8)	17.02(10)	13.97(9)	1.22(6)	-1.22(6)	0.40(6)
N1	13.3(4)	18.7(5)	14.9(4)	0.7(4)	0.9(3)	0.1(3)
O1	24.1(4)	35.8(6)	29.0(5)	2.8(4)	2.7(4)	12.1(4)
C1	17.1(5)	25.3(6)	16.6(5)	2.5(5)	0.0(4)	0.8(4)
N2	14.8(4)	15.0(5)	16.4(4)	1.7(4)	0.8(3)	-1.1(3)
O2	24.1(5)	31.6(6)	31.3(5)	3.8(4)	3.3(4)	-8.1(4)
C2	16.2(5)	23.5(6)	18.6(5)	0.1(5)	-1.5(4)	0.1(4)
N3	15.1(4)	16.8(5)	17.4(5)	-0.5(4)	2.5(3)	1.9(3)
O3	35.2(5)	34.1(6)	22.6(5)	-3.4(4)	-9.9(4)	-0.2(4)
C3	18.7(5)	20.9(6)	20.8(6)	1.5(5)	-1.4(4)	1.5(4)
C7	27.5(6)	20.3(7)	33.9(7)	1.1(5)	12.5(5)	-2.8(5)
C6	22.2(5)	21.6(6)	24.9(6)	-4.3(5)	6.7(5)	-2.6(5)
C5	16.3(5)	16.9(6)	18.5(5)	-2.4(4)	3.3(4)	0.9(4)
C4	17.0(5)	21.1(6)	17.7(5)	-0.3(4)	-0.4(4)	-3.5(4)
N4	25.4(5)	24.0(6)	21.3(5)	-0.9(4)	0.8(4)	6.0(4)
C8	28.0(6)	23.8(7)	26.2(6)	6.8(5)	10.0(5)	3.8(5)
C9	20.6(5)	23.7(6)	18.3(6)	3.6(5)	3.7(4)	4.9(4)
C10	17.3(5)	20.9(6)	15.7(5)	4.4(4)	0.0(4)	1.4(4)
C11	14.6(5)	17.5(6)	18.1(5)	2.9(4)	-0.3(4)	-1.3(4)
C12	17.7(5)	19.7(6)	23.6(6)	4.6(5)	-1.0(4)	1.6(4)
C13	20.3(5)	19.9(6)	32.5(7)	3.0(5)	3.9(5)	4.6(5)
C14	22.0(5)	19.6(6)	26.7(6)	-1.1(5)	5.6(5)	1.7(5)
C15	19.2(5)	16.3(6)	18.6(5)	0.5(4)	2.6(4)	-1.3(4)
C16	15.8(5)	28.2(7)	16.9(5)	-1.5(5)	1.7(4)	3.2(4)
C17	16.2(5)	28.1(7)	17.0(5)	-2.1(5)	2.8(4)	3.4(4)
C18	25.9(6)	33.4(8)	21.4(6)	0.9(5)	4.0(5)	-6.9(5)
C19	27.8(6)	45.3(9)	18.8(6)	5.2(6)	4.1(5)	-1.0(6)
C20	24.2(6)	42.2(8)	17.1(6)	-4.5(5)	-1.4(5)	9.4(6)
C21	28.9(6)	28.3(7)	24.5(7)	-7.1(5)	-1.7(5)	7.8(5)
P91A	7.7(19)	3(2)	11(3)	-1.3(19)	4.0(18)	-3.9(14)
F91A	44(5)	23(3)	56(7)	-10(4)	4(4)	-2(3)
F93A	67(6)	59(7)	55(6)	4(5)	41(5)	-12(5)
F92A	56(6)	29(4)	23(4)	-7(3)	1(3)	13(4)

F94A	18(4)	22(5)	5(3)	3(2)	0(3)	1(3)
F95A	17(3)	36(4)	14(4)	-3(3)	12(3)	-1(3)
F96A	22(5)	23(4)	19(4)	-7(3)	-6(3)	1(3)
P91B	50(5)	48(6)	24(5)	12(3)	9(3)	14(4)
F91B	56(9)	49(6)	20(7)	10(5)	20(6)	0(5)
F93B	61(7)	97(11)	58(9)	22(7)	30(6)	29(6)
F92B	59(10)	54(7)	33(8)	1(5)	6(7)	16(5)
F94B	60(8)	54(7)	22(5)	5(4)	9(5)	33(6)
F95B	43(6)	69(9)	49(8)	3(7)	15(5)	-2(5)
F96B	65(8)	44(7)	24(5)	7(4)	2(5)	11(6)
P91C	17.1(9)	22.6(12)	22.0(9)	3.2(5)	4.6(5)	0.0(5)
F91C	41.6(10)	20.1(9)	87(3)	-8.8(13)	1.1(16)	-6.9(7)
F93C	38.7(10)	67(2)	53.2(14)	0.8(13)	31.9(10)	4.5(11)
F92C	46.3(17)	18.7(9)	57(2)	3.8(9)	-8.1(13)	-2.0(9)
F94C	27.6(15)	48(2)	37(2)	-8.1(13)	-10.1(13)	15.1(13)
F95C	58(2)	136(3)	30.8(14)	-9.1(14)	24.9(15)	-22.5(16)
F96C	31.1(15)	62.3(16)	55(2)	-2.8(14)	-19.6(13)	6.8(11)

Bond Lengths for $[Mn(CO)_3(tpa)][PF_6]$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	N1	2.1071(10)	C13	C14	1.3845(19)
Mn1	C1	1.8137(13)	C14	C15	1.3847(18)
Mn1	N2	2.0422(10)	C16	C17	1.5062(17)
Mn1	C2	1.8185(13)	C17	C18	1.3865(19)
Mn1	N3	2.0501(11)	C18	C19	1.389(2)
Mn1	C3	1.8049(13)	C19	C20	1.378(2)
N1	C4	1.5020(15)	C20	C21	1.379(2)
N1	C10	1.4902(16)	P91A	F91A	1.681(16)
N1	C16	1.5065(16)	P91A	F93A	1.67(2)
O1	C1	1.1440(16)	P91A	F92A	1.519(16)
N2	C11	1.3498(15)	P91A	F94A	1.72(2)
N2	C15	1.3454(16)	P91A	F95A	1.63(2)
O2	C2	1.1392(16)	P91A	F96A	1.58(2)
N3	C5	1.3481(15)	P91B	F91B	1.553(9)
N3	C9	1.3536(16)	P91B	F93B	1.563(10)
O3	C3	1.1461(16)	P91B	F92B	1.620(9)
C7	C6	1.386(2)	P91B	F94B	1.576(10)
C7	C8	1.388(2)	P91B	F95B	1.563(10)
C6	C5	1.3896(18)	P91B	F96B	1.600(9)
C5	C4	1.4947(17)	P91C	F91C	1.560(4)
N4	C17	1.3386(18)	P91C	F93C	1.568(5)
N4	C21	1.3456(18)	P91C	F92C	1.620(4)
C8	C9	1.3791(19)	P91C	F94C	1.575(6)
C10	C11	1.5028(18)	P91C	F95C	1.566(6)
C11	C12	1.3856(17)	P91C	F96C	1.600(5)

C12	C13	1.386(2)

Bond Angles for [Mn(CO)$_3$(tpa)][PF$_6$].

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	Mn1	N1	98.07(5)	C18	C17	C16	121.38(12)
C1	Mn1	N2	176.52(5)	C17	C18	C19	119.35(14)
C1	Mn1	C2	91.19(6)	C20	C19	C18	118.40(14)
C1	Mn1	N3	89.11(5)	C19	C20	C21	118.65(13)
N2	Mn1	N1	78.69(4)	N4	C21	C20	123.83(14)
N2	Mn1	N3	89.16(4)	F91A	P91A	F94A	98.4(11)
C2	Mn1	N1	92.17(5)	F93A	P91A	F91A	87.7(10)
C2	Mn1	N2	90.21(5)	F93A	P91A	F94A	90.0(13)
C2	Mn1	N3	173.71(5)	F92A	P91A	F91A	169.8(13)
N3	Mn1	N1	81.58(4)	F92A	P91A	F93A	86.1(10)
C3	Mn1	N1	174.92(5)	F92A	P91A	F94A	89.7(10)
C3	Mn1	C1	87.00(6)	F92A	P91A	F95A	114.2(15)
C3	Mn1	N2	96.23(5)	F92A	P91A	F96A	91.0(10)
C3	Mn1	C2	87.97(6)	F95A	P91A	F91A	72.5(9)
C3	Mn1	N3	98.32(5)	F95A	P91A	F93A	159.6(12)
C4	N1	Mn1	110.48(7)	F95A	P91A	F94A	88.2(11)
C4	N1	C16	110.95(10)	F96A	P91A	F91A	81.4(9)
C10	N1	Mn1	105.12(7)	F96A	P91A	F93A	94.0(11)
C10	N1	C4	108.31(9)	F96A	P91A	F94A	176.0(17)
C10	N1	C16	111.21(10)	F96A	P91A	F95A	87.9(12)
C16	N1	Mn1	110.60(7)	F91B	P91B	F93B	91.5(13)
O1	C1	Mn1	176.87(11)	F91B	P91B	F92B	173.3(15)
C11	N2	Mn1	115.09(8)	F91B	P91B	F94B	83.7(12)
C15	N2	Mn1	126.26(8)	F91B	P91B	F95B	92.7(13)
C15	N2	C11	118.60(10)	F91B	P91B	F96B	96.8(12)
O2	C2	Mn1	179.04(11)	F93B	P91B	F92B	91.3(13)
C5	N3	Mn1	115.99(8)	F93B	P91B	F94B	88.4(10)
C5	N3	C9	118.03(11)	F93B	P91B	F96B	94.8(9)
C9	N3	Mn1	125.68(8)	F94B	P91B	F92B	90.2(13)
O3	C3	Mn1	175.23(12)	F94B	P91B	F96B	176.8(11)
C6	C7	C8	118.88(13)	F95B	P91B	F93B	174.5(14)
C7	C6	C5	119.07(12)	F95B	P91B	F92B	84.2(13)
N3	C5	C6	122.30(12)	F95B	P91B	F94B	88.4(10)
N3	C5	C4	117.34(11)	F95B	P91B	F96B	88.4(10)
C6	C5	C4	120.32(11)	F96B	P91B	F92B	89.1(12)
C5	C4	N1	112.41(9)	F91C	P91C	F93C	92.4(3)
C17	N4	C21	117.13(12)	F91C	P91C	F92C	177.7(3)
C9	C8	C7	119.04(13)	F91C	P91C	F94C	89.4(3)
N3	C9	C8	122.67(12)	F91C	P91C	F95C	92.8(3)
N1	C10	C11	108.45(10)	F91C	P91C	F96C	91.1(3)
N2	C11	C10	114.53(10)	F93C	P91C	F92C	88.9(3)

N2	C11	C12	122.16(12)	F93C	P91C	F94C	90.4(3)
C12	C11	C10	123.30(11)	F93C	P91C	F96C	89.6(3)
C11	C12	C13	118.94(12)	F94C	P91C	F92C	88.8(3)
C14	C13	C12	119.00(12)	F94C	P91C	F96C	179.5(4)
C13	C14	C15	119.18(13)	F95C	P91C	F93C	174.8(4)
N2	C15	C14	122.11(12)	F95C	P91C	F92C	85.9(4)
C17	C16	N1	116.92(9)	F95C	P91C	F94C	89.1(3)
N4	C17	C16	115.91(12)	F95C	P91C	F96C	90.9(3)
N4	C17	C18	122.60(12)	F96C	P91C	F92C	90.7(3)

Torsion Angles for [Mn(CO)$_3$(tpa)][PF$_6$].

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Mn1	N1	C4	C5	-15.61(12)	N4	C17	C18	C19	-1.3(2)
Mn1	N1	C10	C11	-44.08(10)	C8	C7	C6	C5	0.7(2)
Mn1	N1	C16	C17	-175.29(9)	C9	N3	C5	C6	0.46(17)
Mn1	N2	C11	C10	0.96(13)	C9	N3	C5	C4	178.37(11)
Mn1	N2	C11	C12	-178.47(9)	C10	N1	C4	C5	-
Mn1	N2	C15	C14	177.86(9)	C10	N1	C16	C17	-58.89(14)
Mn1	N3	C5	C6	174.51(9)	C10	C11	C12	C13	-
Mn1	N3	C5	C4	-7.58(14)	C11	N2	C15	C14	0.39(18)
Mn1	N3	C9	C8	-	C11	C12	C13	C14	-0.12(19)
N1	C10	C11	N2	29.92(13)	C12	C13	C14	C15	-0.2(2)
N1	C10	C11	C12	-	C13	C14	C15	N2	0.06(19)
N1	C16	C17	N4	-91.17(14)	C15	N2	C11	C10	178.71(10)
N1	C16	C17	C18	92.51(15)	C15	N2	C11	C12	-0.72(17)
N2	C11	C12	C13	0.59(19)	C16	N1	C4	C5	107.42(11)
N3	C5	C4	N1	15.67(15)	C16	N1	C10	C11	-163.80(9)
C7	C6	C5	N3	-0.81(19)	C16	C17	C18	C19	174.79(12)
C7	C6	C5	C4	-	C17	N4	C21	C20	0.0(2)
C7	C8	C9	N3	-0.2(2)	C17	C18	C19	C20	-0.3(2)
C6	C7	C8	C9	-0.2(2)	C18	C19	C20	C21	1.6(2)
C6	C5	C4	N1	-	C19	C20	C21	N4	-1.6(2)
C5	N3	C9	C8	0.04(18)	C21	N4	C17	C16	-
C4	N1	C10	C11	74.03(11)	C21	N4	C17	C18	1.40(19)
C4	N1	C16	C17	61.74(14)					

Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for [Mn(CO)$_3$(tpa)][PF$_6$].

Atom	*x*	*y*	*z*	U(eq)
H7	4922	3253	4370	32
H6	4783	4091	3046	27
H4A	5264	6089	2547	23
H4B	6000	5202	2176	23

H8	6333	3846	5566	30
H9	7559	5227	5411	25
H10A	5986	7324	1837	22
H10B	7312	7812	2210	22
H12	4766	8744	2356	25
H13	4074	9460	3545	29
H14	5037	8988	4937	27
H15	6642	7822	5111	22
H16A	8701	6430	2144	25
H16B	8284	5313	2321	25
H18	7891	7242	752	32
H19	7187	6940	-724	37
H20	6372	5349	-1150	34
H21	6196	4165	-109	34

Atomic Occupancy for [Mn(CO)$_3$(tpa)][PF$_6$].

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
P91A	0.160(11)	F91A	0.160(11)	F93A	0.160(11)
F92A	0.160(11)	F94A	0.160(11)	F95A	0.160(11)
F96A	0.160(11)	P91B	0.098(7)	F91B	0.098(7)
F93B	0.098(7)	F92B	0.098(7)	F94B	0.098(7)
F95B	0.098(7)	F96B	0.098(7)	P91C	0.737(12)
F91C	0.737(12)	F93C	0.737(12)	F92C	0.737(12)
F94C	0.737(12)	F95C	0.737(12)	F96C	0.737(12)

Experimental

Single crystals of $C_{21}H_{18}N_4O_3F_{5.97}PMn$ [Mn(CO)$_3$(tpa)][PF$_6$] were obtained by recrystallization in EtOH. A suitable crystal was selected and measured on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 100.9 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the XL [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. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of [Mn(CO)$_3$(tpa)][PF$_6$]

Crystal Data for $C_{21}H_{18}N_4O_3F_{5.9675}PMn$ (M =573.52 g/mol): monoclinic, space group P2$_1$/n (no. 14), a = 10.9782(7) Å, b = 13.3015(9) Å, c = 15.8036(11) Å, β = 100.432(3)°, V = 2269.6(3) Å^3, Z = 4, T = 100.09 K, μ(MoKα) = 0.734 mm^{-1}, *Dcalc* = 1.678 g/cm^3, 37391 reflections measured (4.03° ≤ 2Θ ≤ 66.816°), 7822 unique (R_{int} = 0.0227, R_{sigma} = 0.0239) which were used in all calculations. The final R_1 was 0.0324 (I > 2σ(I)) and wR_2 was 0.0854 (all data).

Refinement model description

Number of restraints - 211, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
2. Rigid body (RIGU) restrains
 P91A, F91A, F93A, F92A, F94A, F95A, F96A, P91B, F91B, F93B, F92B, F94B, F95B,
 F96B, P91C, F91C, F93C, F92C, F94C, F95C, F96C
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 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
3. Same fragment restrains
{P91A, F91A, F93A, F92A, F94A, F95A, F96A, P91B, F91B, F93B, F92B, F94B, F95B,
F96B} sigma for 1-2: 0.01, 1-3: 0.04
{P91A, F91A, F93A, F92A, F94A, F95A, F96A, P91C, F91C, F93C, F92C, F94C, F95C,
F96C} sigma for 1-2: 0.01, 1-3: 0.04
as
{P91A, F91A, F93A, F92A, F94A, F95A, F96A, P91B, F91B, F93B, F92B, F94B, F95B,
F96B}
4. Others
 1*[Sof(P91B)+Sof(F91B)+Sof(F93B)+Sof(F92B)+Sof(F94B)+Sof(F95B)+Sof(F96B)]+1*
 [Sof(P91A)+Sof(F91A)+Sof(F93A)+Sof(F92A)+Sof(F94A)+Sof(F95A)+Sof(F96A)]+1*
 [Sof(P91C)+Sof(F91C)+Sof(F93C)+Sof(F92C)+Sof(F94C)+Sof(F95C)+Sof(F96C)]=1 with
 esd of 0.01
 Sof(P91B)=Sof(F91B)=Sof(F93B)=Sof(F92B)=Sof(F94B)=Sof(F95B)=Sof(F96B)=FVAR(1)
 Sof(P91A)=Sof(F91A)=Sof(F93A)=Sof(F92A)=Sof(F94A)=Sof(F95A)=Sof(F96A)=FVAR(2)
 Sof(P91C)=Sof(F91C)=Sof(F93C)=Sof(F92C)=Sof(F94C)=Sof(F95C)=Sof(F96C)=FVAR(3)
5.a Secondary CH2 refined with riding coordinates:
 C4(H4A,H4B), C10(H10A,H10B), C16(H16A,H16B)
5.b Aromatic/amide H refined with riding coordinates:
 C7(H7), C6(H6), C8(H8), C9(H9), C12(H12), C13(H13), C14(H14), C15(H15),
 C18(H18), C19(H19), C20(H20), C21(H21)
```

This report has been created with Olex2, compiled on 2016.02.19 svn.r3266 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Tables S4. Tables of the molecular structure of UV irradiation derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$.

Crystal data and structure refinement for UV irradiation derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$.

Identification code	p-1_a
Empirical formula	$C_{38}H_{39}N_9O_2F_{18}P_3Mn_2$
Formula weight	1198.57
Temperature/K	99.97
Crystal system	triclinic
Space group	P-1
a/Å	12.6170(8)
b/Å	18.8980(12)
c/Å	19.9575(13)
α/°	85.848(2)
β/°	88.135(2)
γ/°	77.867(2)
Volume/Å^3	4639.3(5)
Z	4
ρ_{calc}g/cm^3	1.716
μ/mm^{-1}	0.767
F(000)	2412.0
Crystal size/mm^3	0.11 × 0.1 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.046 to 60.5
Index ranges	-17 ≤ h ≤ 17, -26 ≤ k ≤ 26, -28 ≤ l ≤ 27
Reflections collected	300185
Independent reflections	25833 [R_{int} = 0.0653, R_{sigma} = 0.0446]
Data/restraints/parameters	25833/443/1557
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0491, wR_2 = 0.0996

Final R indexes [all data]	R_1 = 0.0868, wR_2 = 0.1169
Largest diff. peak/hole / e Å^{-3}	0.69/-0.56

Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for UV irradiation derived [$Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C(1A)	5073.0(17)	3769.9(12)	5421.6(12)	18.8(5)
C(1B)	2806(2)	1095.7(13)	1396.6(13)	24.7(5)
C(2A)	4724.1(18)	3053.7(12)	5521.5(11)	18.1(4)
C(3A)	3646.3(18)	2990.1(13)	5571.6(12)	21.8(5)
C(4A)	3420(2)	2302.3(14)	5640.6(12)	25.7(5)
C(5A)	4258(2)	1699.2(14)	5656.6(12)	26.7(5)
C(6A)	5312(2)	1803.5(13)	5602.6(12)	23.7(5)
C(7A)	5957.0(19)	3746.4(13)	6517.4(11)	20.8(5)
C(7B)	2625(2)	2142.3(14)	2108.6(12)	24.7(5)
C(8A)	6392.3(18)	3026.4(13)	6897.3(12)	20.3(5)
C(8B)	1735.4(18)	2808.8(13)	2017.1(11)	20.2(5)
C(9A)	6184(2)	2919.2(14)	7581.8(12)	27.2(5)
C(9B)	1187(2)	3126.9(15)	2569.5(13)	28.4(6)
C(10A)	6660(2)	2275.2(15)	7918.5(12)	27.7(6)
C(10B)	401(2)	3753.4(17)	2469.7(14)	36.8(7)
C(11A)	7325(2)	1739.8(14)	7568.4(12)	25.3(5)
C(11B)	173(2)	4044.3(16)	1825.5(14)	33.2(6)
C(12A)	7489.2(18)	1867.6(13)	6885.3(12)	21.0(5)
C(12B)	741.1(19)	3705.1(14)	1291.2(13)	26.5(5)
C(13A)	6658.3(18)	4320.0(12)	5500.0(12)	19.4(5)
C(13B)	4262.7(19)	1775.0(14)	1408.3(13)	24.7(5)
C(14A)	7825.2(18)	4144.8(12)	5718.8(11)	18.4(5)
C(14B)	4498.3(19)	2520.3(14)	1259.7(12)	23.1(5)
C(15A)	8408(2)	4668.3(13)	5819.5(13)	25.5(5)
C(15B)	5457(2)	2706.7(16)	1429.7(14)	33.1(6)
C(16A)	9477(2)	4447.2(14)	6022.8(14)	29.4(6)
C(16B)	5606(2)	3400.0(17)	1240.0(14)	35.0(6)
C(17A)	9921.4(19)	3715.5(14)	6129.2(13)	26.0(5)
C(17B)	4798(2)	3890.7(15)	903.0(14)	31.2(6)
C(18A)	9292.4(19)	3223.6(13)	6017.0(12)	21.2(5)
C(18B)	3857(2)	3672.5(13)	757.0(12)	25.4(5)
C(19A)	10155.3(18)	1227.7(12)	4578.5(12)	18.5(5)
C(19B)	2206.6(19)	3922.6(12)	−1348.0(12)	22.1(5)
C(20A)	10373.3(18)	1979.5(12)	4500.4(11)	17.7(4)
C(20B)	3375.8(19)	3759.3(13)	−1134.3(12)	22.5(5)

C(21A)	11397.8(19)	2139.3(14)	4473.2(12)	22.9(5)
C(21B)	4080(2)	4223.0(14)	-1263.1(13)	28.4(6)
C(22A)	11490(2)	2859.0(14)	4422.3(12)	25.1(5)
C(22B)	5132(2)	4013.8(15)	-1018.9(14)	30.5(6)
C(23A)	10559(2)	3400.1(14)	4395.1(12)	26.0(5)
C(23B)	5456(2)	3344.3(15)	-674.2(13)	28.5(6)
C(24A)	9563.4(19)	3212.6(12)	4421.5(11)	19.8(5)
C(24B)	4719.6(19)	2903.8(14)	-563.8(12)	24.2(5)
C(25A)	9298.5(19)	1195.9(13)	3476.0(11)	19.9(5)
C(25B)	2272(2)	2920.3(13)	-2110.6(11)	21.8(5)
C(26A)	8880.7(18)	1922.4(12)	3108.8(11)	18.9(5)
C(26B)	3214.6(18)	2287.5(13)	-2029.9(11)	19.4(5)
C(27A)	9146(2)	2066.3(14)	2442.6(12)	25.8(5)
C(27B)	3851.5(19)	2031.5(14)	-2576.2(12)	24.6(5)
C(28A)	8623(2)	2709.6(14)	2114.0(13)	28.4(6)
C(28B)	4672(2)	1424.9(15)	-2475.8(13)	28.9(6)
C(29A)	7866(2)	3199.5(14)	2461.8(12)	25.0(5)
C(29B)	4848.0(19)	1090.1(14)	-1836.7(13)	26.5(5)
C(30A)	7663.8(18)	3033.4(13)	3132.3(12)	19.6(5)
C(30B)	4190.9(18)	1372.6(13)	-1310.1(12)	20.8(5)
C(31A)	8607.2(18)	620.7(12)	4502.4(12)	18.6(5)
C(31B)	675.7(18)	3281.3(13)	-1366.8(12)	22.4(5)
C(32A)	7427.9(18)	818.3(12)	4319.5(11)	18.6(5)
C(32B)	475.4(18)	2531.7(13)	-1194.3(12)	21.3(5)
C(33A)	6804.0(19)	318.7(13)	4223.2(13)	24.1(5)
C(33B)	-460(2)	2306.4(15)	-1340.9(13)	29.0(6)
C(34A)	5728(2)	567.9(14)	4046.8(14)	27.9(6)
C(34B)	-561(2)	1608.0(16)	-1129.3(14)	32.6(6)
C(35A)	5317.7(19)	1305.2(13)	3961.7(13)	24.3(5)
C(35B)	289(2)	1142.5(14)	-797.4(13)	28.0(5)
C(36A)	5977.0(19)	1780.6(13)	4067.4(12)	21.7(5)
C(36B)	1211(2)	1388.7(13)	-672.6(12)	22.3(5)
C(101)	-2037(2)	4320.2(18)	-2221.9(15)	37.3(7)
C(102)	-2402(4)	5019.4(18)	-1934.0(17)	58.4(10)
N(1A)	9136.8(15)	1217.1(10)	4224.5(9)	15.9(4)
N(1B)	1873.8(15)	3224.1(10)	-1452.3(9)	18.0(4)
N(2A)	9478.2(15)	2515.5(10)	4478.7(9)	16.2(4)
N(2B)	3696.3(15)	3118.3(11)	-781.5(10)	20.2(4)
N(3A)	8166.7(14)	2402.8(10)	3446.5(9)	16.2(4)
N(3B)	3390.6(15)	1962.1(10)	-1412(1)	18.4(4)
N(4A)	7008.4(15)	1539.6(10)	4256.3(9)	18.1(4)
N(4B)	1290.7(15)	2075.6(10)	-855.8(9)	18.7(4)
N(5A)	6112.8(15)	3727.2(10)	5771.0(9)	17.1(4)
N(5B)	3067.8(16)	1821.2(11)	1468.2(10)	20.9(4)
N(6A)	8266.4(15)	3432.3(10)	5806.8(10)	18.9(4)
N(6B)	1510.2(15)	3099.9(11)	1389(1)	20.7(4)
N(7A)	7035.4(14)	2503(1)	6560.9(9)	17.5(4)

N(7B1)	1172.8(17)	1784.9(12)	885.5(10)	26.4(5)
C(2B1)	1619(2)	1175.1(14)	1245.0(13)	27.1(5)
C(3B1)	1043(2)	644.4(16)	1437.2(16)	37.9(7)
C(4B1)	-27(3)	751.7(19)	1242.6(18)	47.2(9)
C(5B1)	-491(2)	1377(2)	880.0(16)	45.1(8)
C(6B1)	124(2)	1890.9(17)	710.3(14)	34.5(7)
N(8A)	5539.4(15)	2467.7(10)	5535.4(9)	18.6(4)
N(8B)	3717.6(16)	2995.5(11)	923.2(10)	21.0(4)
N(101)	-1766(2)	3774.6(18)	-2440.1(14)	51.1(7)
N(92)	7042(2)	1319.9(16)	2531.0(14)	46.6(7)
C(93)	6568(4)	181.1(19)	2094(2)	70.1(13)
C(94)	6859(2)	814.5(17)	2333.4(15)	38.0(7)
O(1A)	7178.4(12)	2985.9(8)	4634.7(8)	18.3(3)
O(1B)	3120.0(12)	1926.1(8)	15.0(8)	19.1(3)
O(2A)	8077.4(12)	1895.0(8)	5334.1(8)	18.3(3)
O(2B)	1781.7(12)	3104.3(8)	-65.3(8)	18.9(3)
P(1A)	6984(8)	770(4)	-92(4)	26.4(17)
F(1A)	5711(9)	1099(9)	-55(9)	41(3)
F(2A)	7202(11)	1558(4)	-321(8)	38(2)
F(3A)	6874(11)	623(9)	-867(5)	38(3)
F(4A)	6784(10)	-18(5)	136(10)	39(3)
F(5A)	7108(12)	924(10)	678(4)	34(3)
F(6A)	8258(9)	433(11)	-136(11)	45(3)
P(1B)	7045(16)	758(7)	-91(6)	27(4)
F(1B)	5784(17)	1115(17)	-15(17)	35(5)
F(2B)	7300(20)	1557(9)	-90(15)	36(4)
F(3B)	6970(20)	862(17)	-895(7)	40(4)
F(4B)	6800(20)	-34(9)	-113(14)	31(4)
F(5B)	7140(20)	662(17)	711(6)	35(4)
F(6B)	8320(16)	427(17)	-149(16)	39(5)
P(1C)	6896(10)	754(5)	-51(4)	26.3(16)
F(1C)	5614(10)	1015(10)	44(10)	35(3)
F(2C)	6941(13)	1511(6)	-463(7)	42(2)
F(3C)	6716(10)	407(9)	-739(6)	38(2)
F(4C)	6815(14)	8(6)	357(8)	41(2)
F(5C)	7042(17)	1118(9)	632(6)	36(3)
F(6C)	8184(10)	503(13)	-134(13)	44(3)
F(7)	-758.3(14)	3804.6(11)	43.3(10)	55.0(5)
F(8)	-2150.4(15)	3926.8(10)	-654.7(9)	47.2(5)
F(9)	-2261.5(18)	3417.8(11)	383.1(11)	61.0(6)
F(10)	-1881.9(17)	4402.0(12)	820.4(10)	63.9(6)
F(11)	-1775.3(17)	4919.9(11)	-223.5(12)	61.7(6)
F(12)	-3273.8(13)	4529.5(10)	112.7(10)	51.1(5)
P(3A)	3817(6)	3690(5)	3392(6)	17.0(17)
F(13A)	2513(8)	3888(11)	3352(11)	22(3)
F(14A)	3848(17)	4521(6)	3195(10)	27(3)
F(15A)	3754(12)	2865(5)	3622(8)	27(4)

F(16A)	3700(15)	3874(8)	4178(6)	21(2)
F(17A)	5106(7)	3477(8)	3447(10)	27(3)
F(18A)	3909(15)	3510(8)	2623(6)	27(3)
P(3B)	3806(9)	3669(7)	3282(8)	32(2)
F(13B)	2517(10)	3933(16)	3393(13)	30(4)
F(14B)	3920(20)	4491(8)	3120(14)	34(4)
F(15B)	3690(20)	2840(9)	3437(13)	35(4)
F(16B)	3938(17)	3741(12)	4082(8)	42(4)
F(17B)	5091(9)	3412(9)	3205(13)	45(3)
F(18B)	3646(16)	3584(11)	2508(8)	38(3)
P(3C)	3842(11)	3697(8)	3449(8)	24(3)
F(13C)	2571(13)	3898(16)	3275(17)	28(5)
F(14C)	3910(20)	4532(9)	3324(13)	22(3)
F(15C)	3760(20)	2861(9)	3588(17)	43(9)
F(16C)	3500(20)	3833(16)	4229(9)	30(4)
F(17C)	5092(11)	3510(13)	3648(13)	28(3)
F(18C)	4120(20)	3565(14)	2680(9)	36(5)
P(4)	7574.1(5)	5187.7(3)	3352.9(3)	21.35(13)
F(19)	7269.1(14)	4922.1(8)	2655.6(8)	35.8(4)
F(20)	6634.5(13)	4856.8(9)	3730.1(8)	37.6(4)
F(21)	8418.5(13)	4437.3(8)	3497.2(8)	35.8(4)
F(22)	6733.6(11)	5945.1(8)	3205.0(8)	29.7(3)
F(23)	8514.4(11)	5527.1(8)	2973.6(8)	30.0(3)
F(24)	7881.3(13)	5461.1(9)	4047.1(8)	34.9(4)
P(5)	7132.0(5)	-260.3(3)	6578.5(3)	23.81(14)
F(25)	7328.1(15)	104.2(10)	7244.1(8)	44.5(4)
F(26)	6156.1(14)	403.8(9)	6386.4(9)	43.1(4)
F(27)	6294.5(11)	-669.9(8)	6985.2(7)	28.6(3)
F(28)	7976.5(14)	140.6(9)	6173.2(9)	41.8(4)
F(29)	8099.1(11)	-938.2(8)	6768.2(9)	36.1(4)
F(30)	6931.3(13)	-628.6(9)	5910.6(8)	35.7(4)
F(31)	11347.3(13)	2122.8(8)	6668.7(9)	35.2(4)
F(32)	11446.8(14)	1317.3(9)	7575.3(8)	39.1(4)
F(33)	11145.9(16)	1245.6(10)	5994.2(9)	50.1(5)
F(34)	10005.1(13)	1508.5(10)	6886.7(12)	55.8(6)
F(35)	12565.4(11)	1058.8(8)	6680.5(8)	28.7(3)
F(36)	11232.8(13)	440.3(8)	6896.4(9)	39.9(4)
P(2)	-2006.7(5)	4170.3(4)	81.2(4)	28.48(15)
P(6)	11278.8(5)	1282.3(3)	6788.7(4)	25.15(14)
Mn(1A)	8067.3(3)	2160.8(2)	4453.5(2)	15.18(8)
Mn(1B)	2541.2(3)	2525.4(2)	-665.5(2)	16.25(8)
Mn(2A)	7158.5(3)	2740.0(2)	5545.3(2)	15.71(8)
Mn(2B)	2355.7(3)	2507.6(2)	650.3(2)	17.78(8)

Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for UV irradiation derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$. 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}
C(1A)	17(1)	19.2(11)	19.7(12)	-2.5(9)	-2.7(8)	-2.0(8)
C(1B)	29.4(13)	21.4(12)	21.8(12)	-0.6(10)	0.3(10)	-1.8(10)
C(2A)	19.5(11)	21.6(11)	12.8(10)	-2.6(9)	-1.3(8)	-2.8(9)
C(3A)	19.2(11)	28.3(13)	18.3(12)	-3.5(10)	-2.3(9)	-5.1(9)
C(4A)	26.2(12)	37.5(14)	17.1(12)	0.1(10)	-3.2(9)	-15.0(11)
C(5A)	36.7(14)	26.1(13)	20.4(13)	-1(1)	-1.7(10)	-13.5(11)
C(6A)	33.5(13)	19.2(11)	17.9(12)	-1.8(9)	-1.5(10)	-3.6(10)
C(7A)	24.2(11)	22.3(12)	16.3(11)	-5.6(9)	0.8(9)	-4.3(9)
C(7B)	31.5(13)	28.1(13)	13.5(11)	-1.7(9)	-2.2(9)	-3.8(10)
C(8A)	19.7(11)	23.9(12)	18.7(12)	-4.6(9)	-0.9(9)	-7.0(9)
C(8B)	18.1(11)	30.0(13)	14.9(11)	-5.3(9)	-0.2(8)	-9.0(9)
C(9A)	31.4(13)	32.0(14)	18.8(12)	-6.2(10)	4.2(10)	-6.9(11)
C(9B)	24.3(12)	44.9(16)	17.6(12)	-10.4(11)	2.0(9)	-8.5(11)
C(10A)	35.3(14)	36.1(15)	13.5(12)	-1.7(10)	1.5(10)	-11.9(11)
C(10B)	26.3(13)	55.2(19)	27.2(15)	-18.7(13)	3.3(11)	0.2(12)
C(11A)	27.9(12)	28.0(13)	21.0(12)	1.4(10)	-4.6(10)	-8.4(10)
C(11B)	22.9(12)	42.8(16)	30.5(15)	-14.6(12)	-3.0(11)	5.7(11)
C(12A)	19.9(11)	23.5(12)	20.2(12)	-2.3(9)	-2.4(9)	-5.4(9)
C(12B)	22.8(12)	33.7(14)	21.6(13)	-7.7(11)	-3.8(10)	-0.1(10)
C(13A)	20.3(11)	17.0(11)	21.3(12)	-1.7(9)	-0.9(9)	-5.0(9)
C(13B)	19.7(11)	28.7(13)	22.8(13)	1.5(10)	-4.2(9)	1.1(10)
C(14A)	20.8(11)	16.0(11)	18.5(11)	-2.8(9)	0.5(9)	-3.8(9)
C(14B)	21.0(11)	30.7(13)	16.8(12)	-3.4(10)	-1.4(9)	-2.3(10)
C(15A)	24.0(12)	16.5(11)	36.0(15)	-2.4(10)	-2.5(10)	-3.2(9)
C(15B)	23.8(13)	46.2(17)	29.5(15)	-2.9(12)	-5.2(11)	-6.7(12)
C(16A)	25.2(13)	26.4(13)	39.2(16)	-5.7(11)	-3.4(11)	-9.5(10)
C(16B)	30.9(14)	46.2(17)	33.5(16)	-9.4(13)	-1.4(11)	-18.0(13)
C(17A)	18.5(11)	29.9(13)	28.5(13)	-0.6(11)	-3.7(10)	-2.8(10)
C(17B)	38.5(15)	30.6(14)	28.1(14)	-9.9(11)	4.2(11)	-13.4(12)
C(18A)	22.0(11)	19.1(11)	20.3(12)	0.0(9)	0.5(9)	0.3(9)
C(18B)	30.8(13)	24.4(12)	20.4(12)	-6.6(10)	2.7(10)	-2.6(10)
C(19A)	17.5(10)	17.8(11)	20.0(12)	-3.5(9)	-4.0(8)	-1.6(8)
C(19B)	24.9(12)	17.9(11)	22.4(12)	-2.6(9)	-4.3(9)	-0.9(9)
C(20A)	18.1(10)	20.0(11)	14.2(11)	-2.7(9)	-2.0(8)	-1.4(8)
C(20B)	24.7(12)	22.0(12)	19.9(12)	-7.7(9)	-0.4(9)	-0.6(9)
C(21A)	18.7(11)	31.6(13)	18.2(12)	-2.9(10)	-2.9(9)	-4.1(9)
C(21B)	32.5(14)	24.2(13)	29.5(14)	-6.3(11)	-1.3(11)	-6.7(11)
C(22A)	25.1(12)	36.0(14)	17.5(12)	0.1(10)	-2.3(9)	-14.5(10)
C(22B)	30.3(13)	34.5(15)	30.9(15)	-14.1(12)	1.4(11)	-12.7(11)
C(23A)	38.4(14)	23.8(12)	17.9(12)	2.3(10)	-2.6(10)	-12.3(11)
C(23B)	23.2(12)	36.1(15)	27.3(14)	-15.0(11)	-2.2(10)	-3.8(11)
C(24A)	28.2(12)	16.2(11)	14.9(11)	-1.1(9)	-1.2(9)	-4.5(9)
C(24B)	22.7(12)	26.3(12)	22.1(12)	-10.4(10)	-3.8(9)	1.6(10)
C(25A)	23.1(11)	22.2(11)	14.9(11)	-5.8(9)	-0.3(9)	-3.9(9)

C(25B)	28.9(12)	22.8(12)	13.1(11)	-2.8(9)	-2.4(9)	-3.2(10)
C(26A)	20.1(11)	20.6(11)	17.7(11)	-3.5(9)	-1.6(9)	-7.4(9)
C(26B)	20.4(11)	23.0(12)	17.0(11)	-6.4(9)	-1.5(9)	-7.3(9)
C(27A)	29.8(13)	27.3(13)	19.6(12)	-6.8(10)	4.2(10)	-3(1)
C(27B)	24.2(12)	33.8(14)	17.8(12)	-8.6(10)	2.1(9)	-8.5(10)
C(28A)	38.9(15)	31.9(14)	15.1(12)	-1.1(10)	1.6(10)	-9.3(11)
C(28B)	25.5(12)	38.5(15)	24.1(13)	-15.3(11)	5.8(10)	-6.3(11)
C(29A)	31.9(13)	23.8(12)	19.8(12)	0.4(10)	-3.4(10)	-7.1(10)
C(29B)	20.2(11)	29.9(13)	29.3(14)	-10.9(11)	-1.4(10)	-1.8(10)
C(30A)	18.5(11)	20.6(11)	21.1(12)	-3.3(9)	-2.8(9)	-6.1(9)
C(30B)	20.2(11)	22.2(12)	20.4(12)	-5.1(9)	-3.1(9)	-3.3(9)
C(31A)	21.0(11)	13.6(10)	20.9(12)	-1.2(9)	-1.1(9)	-3.2(8)
C(31B)	19.2(11)	24.9(12)	21.1(12)	0(1)	-4.8(9)	-0.3(9)
C(32A)	20.9(11)	15.7(11)	18.9(11)	-2.8(9)	1.3(9)	-2.7(8)
C(32B)	19.3(11)	25.7(12)	18.2(12)	-2.3(9)	-3.1(9)	-2.4(9)
C(33A)	24.7(12)	17.0(11)	30.9(14)	-4.2(10)	-1(1)	-3.8(9)
C(33B)	23.3(12)	37.3(15)	27.2(14)	-3.2(11)	-6.6(10)	-6.6(11)
C(34A)	23.9(12)	26.1(13)	35.8(15)	-4.9(11)	-1.9(11)	-8.8(10)
C(34B)	31.2(14)	40.1(16)	31.2(15)	-7.0(12)	-3.8(11)	-16.0(12)
C(35A)	20.5(11)	26.3(13)	25.5(13)	-3(1)	-1.9(9)	-2.7(10)
C(35B)	35.9(14)	27.4(13)	23.8(13)	-5.3(10)	0.8(11)	-13.0(11)
C(36A)	22.4(11)	20.3(11)	20.6(12)	-3.9(9)	2.1(9)	0.2(9)
C(36B)	27.4(12)	20.9(12)	18.8(12)	-3.5(9)	1.3(9)	-4.8(9)
C(101)	37.9(16)	49.0(19)	27.4(15)	7.6(14)	-10.0(12)	-16.5(14)
C(102)	101(3)	40.9(19)	36.4(19)	9.1(15)	-18.4(19)	-24(2)
N(1A)	17.8(9)	15.4(9)	14.8(9)	-2.5(7)	-1.5(7)	-3.2(7)
N(1B)	20.9(9)	17.8(9)	14.3(9)	-1.4(7)	-2.6(7)	-1.3(7)
N(2A)	18.9(9)	17.5(9)	12.0(9)	-2.0(7)	-1.7(7)	-2.7(7)
N(2B)	20.4(9)	23.2(10)	16.1(10)	-6.9(8)	-2.5(7)	-0.1(8)
N(3A)	15.6(9)	19.3(9)	14.7(9)	-2.5(7)	-1.2(7)	-5.5(7)
N(3B)	19.1(9)	18.7(9)	17.9(10)	-4.9(8)	-0.3(7)	-3.8(7)
N(4A)	19.6(9)	17.4(9)	16.9(9)	-3.3(7)	1.1(7)	-2.6(7)
N(4B)	18.7(9)	22.1(10)	15.2(9)	-2.8(8)	-0.9(7)	-3.1(8)
N(5A)	17.9(9)	18.5(9)	15.2(9)	-2.0(7)	-0.8(7)	-3.9(7)
N(5B)	21.7(10)	22.6(10)	17.3(10)	-2.1(8)	-2.6(8)	-1.7(8)
N(6A)	20.2(9)	17.2(9)	18.6(10)	-3.5(8)	1.1(7)	-2.1(7)
N(6B)	19.1(9)	24.3(10)	18.8(10)	-5.7(8)	-1.9(8)	-2.9(8)
N(7A)	14.9(9)	21.7(10)	17.1(10)	-1.9(8)	-1.4(7)	-5.8(7)
N(7B1)	25.3(10)	32.8(12)	21.2(11)	-9.8(9)	-1.0(8)	-3.4(9)
C(2B1)	29.4(13)	28.2(13)	25.1(13)	-11.7(11)	2.8(10)	-6.2(10)
C(3B1)	43.0(16)	29.6(14)	45.1(18)	-18.3(13)	11.0(13)	-13.1(13)
C(4B1)	43.7(18)	50(2)	58(2)	-36.1(17)	16.6(16)	-24.7(16)
C(5B1)	31.9(15)	72(2)	39.5(18)	-36.8(17)	6.1(13)	-18.4(16)
C(6B1)	26.3(13)	53.4(18)	24.4(14)	-19.5(13)	-2(1)	-4.1(12)
N(8A)	21.3(9)	18.9(9)	14.9(9)	-1.2(7)	-1.2(7)	-2.1(7)
N(8B)	22.6(10)	24.7(10)	15.2(10)	-4.6(8)	-0.3(8)	-2.7(8)
N(101)	48.6(17)	64(2)	37.3(16)	0.0(14)	-3.8(13)	-5.3(15)

N(92)	50.4(16)	51.4(17)	41.8(16)	3.2(13)	-12.3(13)	-19.5(14)
C(93)	107(3)	41(2)	70(3)	16.8(18)	-51(2)	-32(2)
C(94)	39.6(16)	40.9(17)	36.4(16)	10.5(13)	-17.5(13)	-17.0(13)
O(1A)	20.0(8)	19.8(8)	15.5(8)	0.0(6)	-2.8(6)	-5.1(6)
O(1B)	20.9(8)	17.7(8)	16.2(8)	-2.7(6)	-0.4(6)	1.8(6)
O(2A)	21.0(8)	19.2(8)	15.0(8)	-0.1(6)	-2.5(6)	-5.2(6)
O(2B)	19.8(8)	20.3(8)	14.6(8)	-3.2(6)	-1.3(6)	1.5(6)
P(1A)	21(3)	26(3)	31(3)	2.3(18)	-10(2)	0.1(18)
F(1A)	25(4)	46(5)	50(6)	2(4)	-12(3)	1(3)
F(2A)	44(5)	35(3)	36(5)	1(3)	-10(4)	-14(2)
F(3A)	46(4)	34(6)	32(3)	-6(3)	-12(3)	-2(4)
F(4A)	41(3)	32(3)	46(7)	7(4)	-18(5)	-12(2)
F(5A)	40(4)	35(7)	29(3)	0(3)	-7(2)	-11(5)
F(6A)	23(4)	54(6)	56(7)	-10(5)	-6(3)	3(3)
P(1B)	44(7)	25(6)	12(5)	-11(4)	-5(4)	-6(4)
F(1B)	45(7)	27(9)	35(10)	-9(7)	-6(5)	-5(5)
F(2B)	50(8)	28(5)	30(9)	-5(5)	-13(7)	-9(5)
F(3B)	58(8)	42(10)	24(5)	-2(4)	-9(4)	-23(7)
F(4B)	41(7)	28(5)	26(9)	-9(5)	-7(6)	-6(4)
F(5B)	49(7)	37(10)	19(5)	-5(4)	-3(4)	-7(7)
F(6B)	45(7)	38(10)	33(10)	-11(7)	-2(5)	-6(6)
P(1C)	24(2)	28(3)	26(2)	-7.6(19)	-0.1(17)	-1.2(17)
F(1C)	23(3)	40(5)	40(5)	-6(4)	3(3)	2(3)
F(2C)	48(6)	40(3)	36(5)	3(3)	1(3)	-9(3)
F(3C)	42(4)	38(5)	32(4)	-13(3)	-5(3)	2(3)
F(4C)	48(4)	28(3)	46(6)	4(3)	-13(4)	-6(2)
F(5C)	45(4)	32(6)	30(3)	-7(3)	-7(3)	-6(4)
F(6C)	24(4)	49(6)	55(7)	-6(5)	-3(3)	1(3)
F(7)	28.6(9)	74.8(14)	55.6(12)	-21(1)	-10.2(8)	10.2(9)
F(8)	54.2(11)	56.9(12)	30.4(9)	-6.8(8)	-10.4(8)	-8.5(9)
F(9)	75.5(15)	41.8(11)	59.7(13)	11.5(10)	16.2(11)	-6.1(10)
F(10)	63.8(13)	79.6(15)	37.8(11)	-27.4(10)	-19.2(9)	19.4(11)
F(11)	58.6(13)	42.9(11)	87.9(17)	7.6(11)	-11.4(11)	-23.2(10)
F(12)	27.5(9)	53.9(12)	68.2(13)	-11.7(10)	-7.7(8)	3.3(8)
P(3A)	16(3)	14(3)	21(3)	-9(2)	4.8(19)	-1(2)
F(13A)	19(4)	21(5)	24(6)	-10(4)	1(3)	1(3)
F(14A)	43(6)	19(3)	21(7)	-6(3)	-1(5)	-11(3)
F(15A)	24(6)	18(4)	37(7)	-6(4)	6(5)	-1(4)
F(16A)	16(6)	27(4)	20(3)	-2(3)	-1(3)	0(4)
F(17A)	18(2)	28(4)	33(8)	-2(5)	2(3)	-2(2)
F(18A)	28(6)	30(4)	26(4)	-14(3)	3(3)	-7(4)
P(3B)	31(3)	30(3)	37(4)	3(3)	-9(3)	-10(2)
F(13B)	31(5)	24(8)	33(8)	4(6)	-6(4)	-6(4)
F(14B)	31(6)	33(5)	41(8)	-2(4)	-4(5)	-12(4)
F(15B)	32(5)	30(4)	43(8)	-3(4)	-5(5)	-6(3)
F(16B)	41(8)	53(7)	32(5)	-6(4)	-11(4)	-5(5)
F(17B)	29(3)	50(5)	57(9)	-10(5)	-4(4)	-10(3)

F(18B)	35(7)	47(6)	34(5)	-11(4)	-3(3)	-8(4)
P(3C)	20(4)	17(4)	34(5)	7(3)	-12(3)	-1(3)
F(13C)	21(6)	41(10)	23(8)	2(6)	-8(5)	-6(5)
F(14C)	28(5)	20(5)	18(7)	3(4)	-6(5)	-6(3)
F(15C)	44(15)	16(9)	68(19)	17(9)	-8(12)	-8(8)
F(16C)	24(8)	46(7)	24(5)	4(4)	-4(4)	-17(6)
F(17C)	18(3)	34(5)	30(8)	-1(6)	4(4)	-3(3)
F(18C)	56(12)	41(5)	20(5)	-16(4)	10(5)	-25(6)
P(4)	22.1(3)	17.9(3)	21.6(3)	0.8(2)	1.8(2)	0.3(2)
F(19)	49(1)	31.5(8)	29.0(9)	-4.7(7)	-5.2(7)	-11.4(7)
F(20)	36.8(9)	34.9(9)	41.8(10)	4.7(7)	11.4(7)	-13.0(7)
F(21)	40.8(9)	23.7(8)	34.2(9)	5.2(7)	3.9(7)	9.7(7)
F(22)	22.1(7)	22.3(7)	41.1(9)	2.0(6)	0.2(6)	2.1(6)
F(23)	21.0(7)	33.5(8)	33.6(9)	6.0(7)	2.2(6)	-4.9(6)
F(24)	38.7(9)	38.8(9)	25.0(8)	-7.4(7)	-4.2(7)	-0.7(7)
P(5)	25.5(3)	20.4(3)	23.3(3)	1.3(2)	3.0(2)	-1.1(2)
F(25)	65.4(12)	45.6(10)	30.6(9)	-6.5(8)	0.7(8)	-28.7(9)
F(26)	50(1)	27.5(8)	39.9(10)	5.3(7)	7.1(8)	15.3(7)
F(27)	21.0(7)	33.1(8)	30.5(8)	2.3(6)	2.6(6)	-5.0(6)
F(28)	52.5(11)	34.8(9)	40.6(10)	3.6(8)	14.6(8)	-19.2(8)
F(29)	19.3(7)	33.2(9)	51.6(11)	12.5(8)	0.1(7)	-1.0(6)
F(30)	40.3(9)	38.0(9)	26.9(8)	-9.0(7)	2.5(7)	-1.9(7)
F(31)	34.2(8)	21.0(8)	49.1(10)	-3.2(7)	-6.7(7)	-1.6(6)
F(32)	47.4(10)	41.8(10)	27.8(9)	-7.6(7)	6.1(7)	-7.7(8)
F(33)	67.1(13)	45.8(11)	37.7(10)	-7.0(8)	-30.1(9)	-6.5(9)
F(34)	19.6(8)	44.4(11)	102.5(17)	-5.5(11)	-3.6(9)	-4.1(7)
F(35)	23.9(7)	29.1(8)	31.6(8)	-5.9(6)	0.0(6)	-1.0(6)
F(36)	37.3(9)	23.6(8)	61.7(12)	-4.0(8)	-3.3(8)	-11.8(7)
P(2)	24.8(3)	31.4(4)	26.7(4)	-2.6(3)	-5.5(3)	0.9(3)
P(6)	21.2(3)	21.2(3)	33.3(4)	-5.7(3)	-5.9(3)	-2.6(2)
Mn(1A)	16.64(16)	16.44(16)	13.15(16)	-2.16(13)	-0.71(12)	-4.51(13)
Mn(1B)	17.04(16)	17.94(17)	12.70(16)	-2.71(13)	-1.45(12)	-0.45(13)
Mn(2A)	17.34(16)	17.69(17)	12.54(16)	-2.17(13)	-0.24(12)	-4.25(13)
Mn(2B)	18.57(16)	20.54(17)	12.67(17)	-2.97(13)	-1.41(13)	0.26(13)

Bond Lengths for UV irradiation derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C(1A)	C(2A)	1.507(3)	N(1B)	Mn(1B)	2.0582(18)
C(1A)	N(5A)	1.490(3)	N(2A)	Mn(1A)	2.0329(19)
C(1B)	N(5B)	1.494(3)	N(2B)	Mn(1B)	2.015(2)
C(1B)	C(2B1)	1.511(3)	N(3A)	Mn(1A)	2.0342(19)
C(2A)	C(3A)	1.390(3)	N(3B)	Mn(1B)	2.0367(19)
C(2A)	N(8A)	1.343(3)	N(4A)	Mn(1A)	2.019(2)
C(3A)	C(4A)	1.384(4)	N(4B)	Mn(1B)	2.001(2)
C(4A)	C(5A)	1.381(4)	N(5A)	Mn(2A)	2.1148(18)

C(5A)	C(6A)	1.385(4)	N(5B)	Mn(2B)	2.1103(19)
C(6A)	N(8A)	1.342(3)	N(6A)	Mn(2A)	2.203(2)
C(7A)	C(8A)	1.514(3)	N(6B)	Mn(2B)	2.0490(19)
C(7A)	N(5A)	1.498(3)	N(7A)	Mn(2A)	2.0519(19)
C(7B)	C(8B)	1.505(3)	N(7B1)	C(2B1)	1.339(3)
C(7B)	N(5B)	1.496(3)	N(7B1)	C(6B1)	1.350(3)
C(8A)	C(9A)	1.391(3)	N(7B1)	Mn(2B)	2.243(2)
C(8A)	N(7A)	1.346(3)	C(2B1)	C(3B1)	1.383(4)
C(8B)	C(9B)	1.388(3)	C(3B1)	C(4B1)	1.387(4)
C(8B)	N(6B)	1.346(3)	C(4B1)	C(5B1)	1.370(5)
C(9A)	C(10A)	1.376(4)	C(5B1)	C(6B1)	1.382(4)
C(9B)	C(10B)	1.382(4)	N(8A)	Mn(2A)	2.210(2)
C(10A)	C(11A)	1.387(4)	N(8B)	Mn(2B)	2.213(2)
C(10B)	C(11B)	1.376(4)	N(92)	C(94)	1.129(4)
C(11A)	C(12A)	1.384(3)	C(93)	C(94)	1.440(5)
C(11B)	C(12B)	1.385(3)	O(1A)	Mn(1A)	1.7720(16)
C(12A)	N(7A)	1.346(3)	O(1A)	Mn(2A)	1.8436(16)
C(12B)	N(6B)	1.342(3)	O(1B)	Mn(1B)	1.7761(15)
C(13A)	C(14A)	1.511(3)	O(1B)	Mn(2B)	1.8499(15)
C(13A)	N(5A)	1.494(3)	O(2A)	Mn(1A)	1.7923(16)
C(13B)	C(14B)	1.507(4)	O(2A)	Mn(2A)	1.8330(16)
C(13B)	N(5B)	1.493(3)	O(2B)	Mn(1B)	1.7956(15)
C(14A)	C(15A)	1.380(3)	O(2B)	Mn(2B)	1.8239(15)
C(14A)	N(6A)	1.346(3)	P(1A)	F(1A)	1.598(5)
C(14B)	C(15B)	1.388(4)	P(1A)	F(2A)	1.603(5)
C(14B)	N(8B)	1.346(3)	P(1A)	F(3A)	1.607(5)
C(15A)	C(16A)	1.391(3)	P(1A)	F(4A)	1.595(5)
C(15B)	C(16B)	1.386(4)	P(1A)	F(5A)	1.602(5)
C(16A)	C(17A)	1.382(3)	P(1A)	F(6A)	1.601(5)
C(16B)	C(17B)	1.382(4)	P(1B)	F(1B)	1.599(8)
C(17A)	C(18A)	1.377(4)	P(1B)	F(2B)	1.607(8)
C(17B)	C(18B)	1.382(4)	P(1B)	F(3B)	1.606(8)
C(18A)	N(6A)	1.343(3)	P(1B)	F(4B)	1.596(8)
C(18B)	N(8B)	1.344(3)	P(1B)	F(5B)	1.602(8)
C(19A)	C(20A)	1.499(3)	P(1B)	F(6B)	1.603(8)
C(19A)	N(1A)	1.491(3)	P(1C)	F(1C)	1.598(6)
C(19B)	C(20B)	1.511(3)	P(1C)	F(2C)	1.609(6)
C(19B)	N(1B)	1.497(3)	P(1C)	F(3C)	1.608(6)
C(20A)	C(21A)	1.386(3)	P(1C)	F(4C)	1.596(6)
C(20A)	N(2A)	1.349(3)	P(1C)	F(5C)	1.604(6)
C(20B)	C(21B)	1.380(4)	P(1C)	F(6C)	1.601(6)
C(20B)	N(2B)	1.347(3)	F(7)	P(2)	1.5833(17)
C(21A)	C(22A)	1.385(4)	F(8)	P(2)	1.5974(18)
C(21B)	C(22B)	1.396(4)	F(9)	P(2)	1.595(2)
C(22A)	C(23A)	1.385(4)	F(10)	P(2)	1.5909(19)
C(22B)	C(23B)	1.384(4)	F(11)	P(2)	1.581(2)
C(23A)	C(24A)	1.374(3)	F(12)	P(2)	1.6012(17)

C(23B)	C(24B)	1.375(4)	P(3A)	F(13A)	1.612(5)
C(24A)	N(2A)	1.341(3)	P(3A)	F(14A)	1.600(5)
C(24B)	N(2B)	1.346(3)	P(3A)	F(15A)	1.610(5)
C(25A)	C(26A)	1.508(3)	P(3A)	F(16A)	1.626(6)
C(25A)	N(1A)	1.503(3)	P(3A)	F(17A)	1.597(5)
C(25B)	C(26B)	1.502(3)	P(3A)	F(18A)	1.592(6)
C(25B)	N(1B)	1.501(3)	P(3B)	F(13B)	1.610(7)
C(26A)	C(27A)	1.382(3)	P(3B)	F(14B)	1.600(7)
C(26A)	N(3A)	1.340(3)	P(3B)	F(15B)	1.610(7)
C(26B)	C(27B)	1.387(3)	P(3B)	F(16B)	1.629(7)
C(26B)	N(3B)	1.341(3)	P(3B)	F(17B)	1.598(7)
C(27A)	C(28A)	1.385(3)	P(3B)	F(18B)	1.589(7)
C(27B)	C(28B)	1.381(4)	P(3C)	F(13C)	1.612(7)
C(28A)	C(29A)	1.389(4)	P(3C)	F(14C)	1.601(6)
C(28B)	C(29B)	1.385(4)	P(3C)	F(15C)	1.609(6)
C(29A)	C(30A)	1.380(3)	P(3C)	F(16C)	1.626(7)
C(29B)	C(30B)	1.384(3)	P(3C)	F(17C)	1.598(7)
C(30A)	N(3A)	1.347(3)	P(3C)	F(18C)	1.590(7)
C(30B)	N(3B)	1.345(3)	P(4)	F(19)	1.5979(17)
C(31A)	C(32A)	1.506(3)	P(4)	F(20)	1.5964(16)
C(31A)	N(1A)	1.492(3)	P(4)	F(21)	1.5982(15)
C(31B)	C(32B)	1.504(3)	P(4)	F(22)	1.6068(14)
C(31B)	N(1B)	1.498(3)	P(4)	F(23)	1.6071(16)
C(32A)	C(33A)	1.377(3)	P(4)	F(24)	1.5999(16)
C(32A)	N(4A)	1.353(3)	P(5)	F(25)	1.5893(18)
C(32B)	C(33B)	1.382(3)	P(5)	F(26)	1.5968(16)
C(32B)	N(4B)	1.359(3)	P(5)	F(27)	1.6037(16)
C(33A)	C(34A)	1.388(3)	P(5)	F(28)	1.5993(17)
C(33B)	C(34B)	1.387(4)	P(5)	F(29)	1.6049(15)
C(34A)	C(35A)	1.381(3)	P(5)	F(30)	1.5985(17)
C(34B)	C(35B)	1.388(4)	F(31)	P(6)	1.6091(16)
C(35A)	C(36A)	1.377(3)	F(32)	P(6)	1.5988(18)
C(35B)	C(36B)	1.376(4)	F(33)	P(6)	1.6078(18)
C(36A)	N(4A)	1.342(3)	F(34)	P(6)	1.5831(17)
C(36B)	N(4B)	1.346(3)	F(35)	P(6)	1.6008(15)
C(101)	C(102)	1.458(5)	F(36)	P(6)	1.6030(17)
C(101)	N(101)	1.130(4)	Mn(1A)	Mn(2A)	2.6298(5)
N(1A)	Mn(1A)	2.0680(18)	Mn(1B)	Mn(2B)	2.6272(5)

Bond Angles for UV irradiation derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N(5A)	C(1A)	C(2A)	109.94(17)	F(4C)	P(1C)	F(2C)	178.4(8)
N(5B)	C(1B)	C(2B1)	110.56(19)	F(4C)	P(1C)	F(3C)	89.7(5)
C(3A)	C(2A)	C(1A)	123.5(2)	F(4C)	P(1C)	F(5C)	91.1(7)
N(8A)	C(2A)	C(1A)	114.8(2)	F(4C)	P(1C)	F(6C)	91.6(9)

N(8A)	C(2A)	C(3A)	121.6(2)	F(5C)	P(1C)	F(2C)	89.2(7)
C(4A)	C(3A)	C(2A)	118.5(2)	F(5C)	P(1C)	F(3C)	178.3(9)
C(5A)	C(4A)	C(3A)	119.9(2)	F(6C)	P(1C)	F(2C)	90.0(9)
C(4A)	C(5A)	C(6A)	118.4(2)	F(6C)	P(1C)	F(3C)	91.0(9)
N(8A)	C(6A)	C(5A)	122.1(2)	F(6C)	P(1C)	F(5C)	90.5(9)
N(5A)	C(7A)	C(8A)	113.65(18)	F(13A)	P(3A)	F(16A)	88.5(8)
N(5B)	C(7B)	C(8B)	114.47(19)	F(14A)	P(3A)	F(13A)	89.6(8)
C(9A)	C(8A)	C(7A)	121.2(2)	F(14A)	P(3A)	F(15A)	177.3(8)
N(7A)	C(8A)	C(7A)	118.0(2)	F(14A)	P(3A)	F(16A)	88.8(7)
N(7A)	C(8A)	C(9A)	120.7(2)	F(15A)	P(3A)	F(13A)	89.1(7)
C(9B)	C(8B)	C(7B)	120.6(2)	F(15A)	P(3A)	F(16A)	88.7(6)
N(6B)	C(8B)	C(7B)	118.3(2)	F(17A)	P(3A)	F(13A)	178.5(9)
N(6B)	C(8B)	C(9B)	121.0(2)	F(17A)	P(3A)	F(14A)	91.7(8)
C(10A)	C(9A)	C(8A)	119.4(2)	F(17A)	P(3A)	F(15A)	89.5(7)
C(10B)	C(9B)	C(8B)	119.2(2)	F(17A)	P(3A)	F(16A)	90.8(7)
C(9A)	C(10A)	C(11A)	119.5(2)	F(18A)	P(3A)	F(13A)	90.6(8)
C(11B)	C(10B)	C(9B)	119.3(2)	F(18A)	P(3A)	F(14A)	91.3(7)
C(12A)	C(11A)	C(10A)	118.9(2)	F(18A)	P(3A)	F(15A)	91.1(7)
C(10B)	C(11B)	C(12B)	119.2(2)	F(18A)	P(3A)	F(16A)	179.0(8)
N(7A)	C(12A)	C(11A)	121.3(2)	F(18A)	P(3A)	F(17A)	90.1(6)
N(6B)	C(12B)	C(11B)	121.4(2)	F(13B)	P(3B)	F(16B)	87.9(10)
N(5A)	C(13A)	C(14A)	109.06(18)	F(14B)	P(3B)	F(13B)	90.5(11)
N(5B)	C(13B)	C(14B)	110.17(19)	F(14B)	P(3B)	F(15B)	179.4(11)
C(15A)	C(14A)	C(13A)	123.3(2)	F(14B)	P(3B)	F(16B)	90.8(9)
N(6A)	C(14A)	C(13A)	114.9(2)	F(15B)	P(3B)	F(13B)	89.7(11)
N(6A)	C(14A)	C(15A)	121.8(2)	F(15B)	P(3B)	F(16B)	89.7(9)
C(15B)	C(14B)	C(13B)	123.5(2)	F(17B)	P(3B)	F(13B)	177.6(10)
N(8B)	C(14B)	C(13B)	114.8(2)	F(17B)	P(3B)	F(14B)	89.4(10)
N(8B)	C(14B)	C(15B)	121.7(2)	F(17B)	P(3B)	F(15B)	90.4(9)
C(14A)	C(15A)	C(16A)	118.6(2)	F(17B)	P(3B)	F(16B)	89.7(7)
C(16B)	C(15B)	C(14B)	118.5(2)	F(18B)	P(3B)	F(13B)	90.8(10)
C(17A)	C(16A)	C(15A)	119.5(2)	F(18B)	P(3B)	F(14B)	90.6(10)
C(17B)	C(16B)	C(15B)	119.8(3)	F(18B)	P(3B)	F(15B)	88.8(9)
C(18A)	C(17A)	C(16A)	118.7(2)	F(18B)	P(3B)	F(16B)	178.1(10)
C(16B)	C(17B)	C(18B)	118.7(3)	F(18B)	P(3B)	F(17B)	91.6(7)
N(6A)	C(18A)	C(17A)	122.1(2)	F(13C)	P(3C)	F(16C)	88.2(10)
N(8B)	C(18B)	C(17B)	121.8(2)	F(14C)	P(3C)	F(13C)	90.4(10)
N(1A)	C(19A)	C(20A)	109.03(17)	F(14C)	P(3C)	F(15C)	178.9(12)
N(1B)	C(19B)	C(20B)	108.95(18)	F(14C)	P(3C)	F(16C)	89.4(10)
C(21A)	C(20A)	C(19A)	124.6(2)	F(15C)	P(3C)	F(13C)	89.3(11)
N(2A)	C(20A)	C(19A)	114.73(19)	F(15C)	P(3C)	F(16C)	89.5(10)
N(2A)	C(20A)	C(21A)	120.6(2)	F(17C)	P(3C)	F(13C)	177.9(12)
C(21B)	C(20B)	C(19B)	124.4(2)	F(17C)	P(3C)	F(14C)	89.1(10)
N(2B)	C(20B)	C(19B)	114.8(2)	F(17C)	P(3C)	F(15C)	91.2(10)
N(2B)	C(20B)	C(21B)	120.7(2)	F(17C)	P(3C)	F(16C)	89.7(9)
C(22A)	C(21A)	C(20A)	119.0(2)	F(18C)	P(3C)	F(13C)	89.5(10)
C(20B)	C(21B)	C(22B)	118.5(2)	F(18C)	P(3C)	F(14C)	91.0(10)

C(23A)	C(22A)	C(21A)	119.3(2)	F(18C)	P(3C)	F(15C)	90.0(10)
C(23B)	C(22B)	C(21B)	119.9(3)	F(18C)	P(3C)	F(16C)	177.7(11)
C(24A)	C(23A)	C(22A)	119.4(2)	F(18C)	P(3C)	F(17C)	92.5(9)
C(24B)	C(23B)	C(22B)	118.9(2)	F(19)	P(4)	F(21)	90.37(9)
N(2A)	C(24A)	C(23A)	121.1(2)	F(19)	P(4)	F(22)	89.67(9)
N(2B)	C(24B)	C(23B)	120.9(2)	F(19)	P(4)	F(23)	89.63(9)
N(1A)	C(25A)	C(26A)	112.56(18)	F(19)	P(4)	F(24)	179.41(10)
N(1B)	C(25B)	C(26B)	112.46(18)	F(20)	P(4)	F(19)	90.50(9)
C(27A)	C(26A)	C(25A)	122.0(2)	F(20)	P(4)	F(21)	90.49(9)
N(3A)	C(26A)	C(25A)	116.3(2)	F(20)	P(4)	F(22)	90.01(8)
N(3A)	C(26A)	C(27A)	121.4(2)	F(20)	P(4)	F(23)	179.55(9)
C(27B)	C(26B)	C(25B)	121.4(2)	F(20)	P(4)	F(24)	89.95(9)
N(3B)	C(26B)	C(25B)	117.3(2)	F(21)	P(4)	F(22)	179.50(10)
N(3B)	C(26B)	C(27B)	121.3(2)	F(21)	P(4)	F(23)	89.94(8)
C(26A)	C(27A)	C(28A)	118.7(2)	F(21)	P(4)	F(24)	90.01(9)
C(28B)	C(27B)	C(26B)	118.7(2)	F(22)	P(4)	F(23)	89.56(8)
C(27A)	C(28A)	C(29A)	119.6(2)	F(24)	P(4)	F(22)	89.95(8)
C(27B)	C(28B)	C(29B)	119.7(2)	F(24)	P(4)	F(23)	89.92(9)
C(30A)	C(29A)	C(28A)	118.7(2)	F(25)	P(5)	F(26)	90.38(10)
C(30B)	C(29B)	C(28B)	119.0(2)	F(25)	P(5)	F(27)	89.61(9)
N(3A)	C(30A)	C(29A)	121.3(2)	F(25)	P(5)	F(28)	90.52(10)
N(3B)	C(30B)	C(29B)	121.0(2)	F(25)	P(5)	F(29)	90.36(10)
N(1A)	C(31A)	C(32A)	108.06(17)	F(25)	P(5)	F(30)	179.77(11)
N(1B)	C(31B)	C(32B)	108.06(18)	F(26)	P(5)	F(27)	89.64(9)
C(33A)	C(32A)	C(31A)	124.0(2)	F(26)	P(5)	F(28)	90.93(10)
N(4A)	C(32A)	C(31A)	114.6(2)	F(26)	P(5)	F(29)	178.93(11)
N(4A)	C(32A)	C(33A)	121.4(2)	F(26)	P(5)	F(30)	89.61(9)
C(33B)	C(32B)	C(31B)	124.7(2)	F(27)	P(5)	F(29)	89.59(8)
N(4B)	C(32B)	C(31B)	114.5(2)	F(28)	P(5)	F(27)	179.41(10)
N(4B)	C(32B)	C(33B)	120.8(2)	F(28)	P(5)	F(29)	89.83(9)
C(32A)	C(33A)	C(34A)	118.7(2)	F(30)	P(5)	F(27)	90.16(9)
C(32B)	C(33B)	C(34B)	118.9(2)	F(30)	P(5)	F(28)	89.71(10)
C(35A)	C(34A)	C(33A)	119.5(2)	F(30)	P(5)	F(29)	89.64(9)
C(33B)	C(34B)	C(35B)	119.7(2)	F(7)	P(2)	F(8)	89.58(10)
C(36A)	C(35A)	C(34A)	119.4(2)	F(7)	P(2)	F(9)	89.63(12)
C(36B)	C(35B)	C(34B)	119.2(2)	F(7)	P(2)	F(10)	91.02(10)
N(4A)	C(36A)	C(35A)	121.1(2)	F(7)	P(2)	F(12)	179.05(12)
N(4B)	C(36B)	C(35B)	121.0(2)	F(8)	P(2)	F(12)	89.65(10)
N(101)	C(101)	C(102)	179.0(4)	F(9)	P(2)	F(8)	88.74(11)
C(19A)	N(1A)	C(25A)	112.72(17)	F(9)	P(2)	F(12)	89.79(11)
C(19A)	N(1A)	C(31A)	112.34(17)	F(10)	P(2)	F(8)	178.73(13)
C(19A)	N(1A)	Mn(1A)	105.41(13)	F(10)	P(2)	F(9)	90.14(13)
C(25A)	N(1A)	Mn(1A)	110.07(13)	F(10)	P(2)	F(12)	89.74(11)
C(31A)	N(1A)	C(25A)	111.06(17)	F(11)	P(2)	F(7)	91.27(12)
C(31A)	N(1A)	Mn(1A)	104.76(13)	F(11)	P(2)	F(8)	90.79(12)
C(19B)	N(1B)	C(25B)	113.06(19)	F(11)	P(2)	F(9)	178.98(12)
C(19B)	N(1B)	C(31B)	112.45(17)	F(11)	P(2)	F(10)	90.32(13)

C(19B)	N(1B)	Mn(1B)	104.82(13)	F(11)	P(2)	F(12)	89.29(11)				
C(25B)	N(1B)	Mn(1B)	110.32(13)	F(32)	P(6)	F(31)	89.97(9)				
C(31B)	N(1B)	C(25B)	110.90(18)	F(32)	P(6)	F(33)	178.38(11)				
C(31B)	N(1B)	Mn(1B)	104.77(14)	F(32)	P(6)	F(35)	89.70(9)				
C(20A)	N(2A)	Mn(1A)	114.03(15)	F(32)	P(6)	F(36)	90.74(10)				
C(24A)	N(2A)	C(20A)	120.6(2)	F(33)	P(6)	F(31)	89.69(10)				
C(24A)	N(2A)	Mn(1A)	125.16(15)	F(34)	P(6)	F(31)	90.17(9)				
C(20B)	N(2B)	Mn(1B)	113.87(16)	F(34)	P(6)	F(32)	90.91(11)				
C(24B)	N(2B)	C(20B)	121.0(2)	F(34)	P(6)	F(33)	90.67(11)				
C(24B)	N(2B)	Mn(1B)	125.11(17)	F(34)	P(6)	F(35)	179.28(12)				
C(26A)	N(3A)	C(30A)	120.1(2)	F(34)	P(6)	F(36)	90.91(10)				
C(26A)	N(3A)	Mn(1A)	115.26(15)	F(35)	P(6)	F(31)	89.45(8)				
C(30A)	N(3A)	Mn(1A)	124.20(16)	F(35)	P(6)	F(33)	88.72(10)				
C(26B)	N(3B)	C(30B)	120.3(2)	F(35)	P(6)	F(36)	89.48(9)				
C(26B)	N(3B)	Mn(1B)	114.42(15)	F(36)	P(6)	F(31)	178.71(10)				
C(30B)	N(3B)	Mn(1B)	124.47(16)	F(36)	P(6)	F(33)	89.57(10)				
C(32A)	N(4A)	Mn(1A)	114.01(15)	N(1A)	Mn(1A)	Mn(2A)	136.72(5)				
C(36A)	N(4A)	C(32A)	119.9(2)	N(2A)	Mn(1A)	N(1A)	81.06(7)				
C(36A)	N(4A)	Mn(1A)	126.12(16)	N(2A)	Mn(1A)	N(3A)	84.38(7)				
C(32B)	N(4B)	Mn(1B)	114.09(16)	N(2A)	Mn(1A)	Mn(2A)	97.70(5)				
C(36B)	N(4B)	C(32B)	120.3(2)	N(3A)	Mn(1A)	N(1A)	83.05(7)				
C(36B)	N(4B)	Mn(1B)	125.58(16)	N(3A)	Mn(1A)	Mn(2A)	140.15(5)				
C(1A)	N(5A)	C(7A)	112.20(18)	N(4A)	Mn(1A)	N(1A)	79.92(7)				
C(1A)	N(5A)	C(13A)	110.64(17)	N(4A)	Mn(1A)	N(2A)	160.11(7)				
C(1A)	N(5A)	Mn(2A)	107.54(13)	N(4A)	Mn(1A)	N(3A)	87.62(8)				
C(7A)	N(5A)	Mn(2A)	109.28(13)	N(4A)	Mn(1A)	Mn(2A)	100.10(5)				
C(13A)	N(5A)	C(7A)	110.53(18)	O(1A)	Mn(1A)	N(1A)	178.14(8)				
C(13A)	N(5A)	Mn(2A)	106.44(13)	O(1A)	Mn(1A)	N(2A)	97.43(7)				
C(1B)	N(5B)	C(7B)	112.49(19)	O(1A)	Mn(1A)	N(3A)	95.75(7)				
C(1B)	N(5B)	Mn(2B)	106.76(14)	O(1A)	Mn(1A)	N(4A)	101.48(7)				
C(7B)	N(5B)	Mn(2B)	108.91(14)	O(1A)	Mn(1A)	O(2A)	88.52(7)				
C(13B)	N(5B)	C(1B)	110.57(18)	O(1A)	Mn(1A)	Mn(2A)	44.41(5)				
C(13B)	N(5B)	C(7B)	110.83(19)	O(2A)	Mn(1A)	N(1A)	92.63(7)				
C(13B)	N(5B)	Mn(2B)	107.03(14)	O(2A)	Mn(1A)	N(2A)	93.56(7)				
C(14A)	N(6A)	Mn(2A)	112.85(15)	O(2A)	Mn(1A)	N(3A)	175.45(7)				
C(18A)	N(6A)	C(14A)	119.2(2)	O(2A)	Mn(1A)	N(4A)	93.05(8)				
C(18A)	N(6A)	Mn(2A)	127.92(16)	O(2A)	Mn(1A)	Mn(2A)	44.11(5)				
C(8B)	N(6B)	Mn(2B)	114.24(15)	N(1B)	Mn(1B)	Mn(2B)	135.17(5)				
C(12B)	N(6B)	C(8B)	119.8(2)	N(2B)	Mn(1B)	N(1B)	81.62(8)				
C(12B)	N(6B)	Mn(2B)	125.82(17)	N(2B)	Mn(1B)	N(3B)	83.58(8)				
C(8A)	N(7A)	C(12A)	120.2(2)	N(2B)	Mn(1B)	Mn(2B)	97.73(6)				
C(8A)	N(7A)	Mn(2A)	114.72(15)	N(3B)	Mn(1B)	N(1B)	83.40(8)				
C(12A)	N(7A)	Mn(2A)	124.99(16)	N(3B)	Mn(1B)	Mn(2B)	141.35(6)				
C(2B1)	N(7B1)	C(6B1)	119.1(3)	N(4B)	Mn(1B)	N(1B)	80.69(8)				
C(2B1)	N(7B1)	Mn(2B)	112.18(17)	N(4B)	Mn(1B)	N(2B)	161.24(8)				
C(6B1)	N(7B1)	Mn(2B)	128.7(2)	N(4B)	Mn(1B)	N(3B)	88.23(8)				
N(7B1)	C(2B1)	C(1B)	115.1(2)	N(4B)	Mn(1B)	Mn(2B)	99.18(6)				

N(7B1)	C(2B1)	C(3B1)	122.1(3)	O(1B)	Mn(1B)	N(1B)	179.71(8)
C(3B1)	C(2B1)	C(1B)	122.7(2)	O(1B)	Mn(1B)	N(2B)	98.13(8)
C(2B1)	C(3B1)	C(4B1)	118.3(3)	O(1B)	Mn(1B)	N(3B)	96.73(7)
C(5B1)	C(4B1)	C(3B1)	119.9(3)	O(1B)	Mn(1B)	N(4B)	99.57(8)
C(4B1)	C(5B1)	C(6B1)	119.1(3)	O(1B)	Mn(1B)	O(2B)	88.58(7)
N(7B1)	C(6B1)	C(5B1)	121.5(3)	O(1B)	Mn(1B)	Mn(2B)	44.69(5)
C(2A)	N(8A)	Mn(2A)	113.21(15)	O(2B)	Mn(1B)	N(1B)	91.28(7)
C(6A)	N(8A)	C(2A)	119.4(2)	O(2B)	Mn(1B)	N(2B)	93.10(8)
C(6A)	N(8A)	Mn(2A)	127.06(16)	O(2B)	Mn(1B)	N(3B)	174.08(8)
C(14B)	N(8B)	Mn(2B)	112.95(16)	O(2B)	Mn(1B)	N(4B)	93.48(8)
C(18B)	N(8B)	C(14B)	119.5(2)	O(2B)	Mn(1B)	Mn(2B)	43.89(5)
C(18B)	N(8B)	Mn(2B)	127.46(16)	N(5A)	Mn(2A)	N(6A)	75.99(7)
N(92)	C(94)	C(93)	177.0(4)	N(5A)	Mn(2A)	N(8A)	77.40(7)
Mn(1A)	O(1A)	Mn(2A)	93.31(7)	N(5A)	Mn(2A)	Mn(1A)	136.03(5)
Mn(1B)	O(1B)	Mn(2B)	92.84(7)	N(6A)	Mn(2A)	N(8A)	152.26(7)
Mn(1A)	O(2A)	Mn(2A)	93.00(7)	N(6A)	Mn(2A)	Mn(1A)	102.97(5)
Mn(1B)	O(2B)	Mn(2B)	93.08(7)	N(7A)	Mn(2A)	N(5A)	83.18(7)
F(1A)	P(1A)	F(2A)	90.1(7)	N(7A)	Mn(2A)	N(6A)	85.62(7)
F(1A)	P(1A)	F(3A)	89.5(7)	N(7A)	Mn(2A)	N(8A)	83.58(7)
F(1A)	P(1A)	F(5A)	91.0(7)	N(7A)	Mn(2A)	Mn(1A)	140.77(5)
F(1A)	P(1A)	F(6A)	179.3(10)	N(8A)	Mn(2A)	Mn(1A)	101.55(5)
F(2A)	P(1A)	F(3A)	89.4(5)	O(1A)	Mn(2A)	N(5A)	93.76(7)
F(4A)	P(1A)	F(1A)	90.6(7)	O(1A)	Mn(2A)	N(6A)	95.63(7)
F(4A)	P(1A)	F(2A)	179.3(7)	O(1A)	Mn(2A)	N(7A)	176.33(7)
F(4A)	P(1A)	F(3A)	90.6(5)	O(1A)	Mn(2A)	N(8A)	93.78(7)
F(4A)	P(1A)	F(5A)	90.1(5)	O(1A)	Mn(2A)	Mn(1A)	42.27(5)
F(4A)	P(1A)	F(6A)	89.0(8)	O(2A)	Mn(2A)	N(5A)	178.74(8)
F(5A)	P(1A)	F(2A)	89.9(6)	O(2A)	Mn(2A)	N(6A)	103.44(7)
F(5A)	P(1A)	F(3A)	179.1(7)	O(2A)	Mn(2A)	N(7A)	97.92(7)
F(6A)	P(1A)	F(2A)	90.3(8)	O(2A)	Mn(2A)	N(8A)	103.31(7)
F(6A)	P(1A)	F(3A)	89.8(8)	O(2A)	Mn(2A)	O(1A)	85.16(7)
F(6A)	P(1A)	F(5A)	89.6(8)	O(2A)	Mn(2A)	Mn(1A)	42.89(5)
F(1B)	P(1B)	F(2B)	88.5(12)	N(5B)	Mn(2B)	N(7B1)	76.87(8)
F(1B)	P(1B)	F(3B)	90.7(12)	N(5B)	Mn(2B)	N(8B)	76.29(8)
F(1B)	P(1B)	F(5B)	89.9(12)	N(5B)	Mn(2B)	Mn(1B)	136.04(6)
F(1B)	P(1B)	F(6B)	177.7(15)	N(6B)	Mn(2B)	N(5B)	83.65(8)
F(3B)	P(1B)	F(2B)	88.8(9)	N(6B)	Mn(2B)	N(7B1)	83.57(8)
F(4B)	P(1B)	F(1B)	91.8(12)	N(6B)	Mn(2B)	N(8B)	84.87(7)
F(4B)	P(1B)	F(2B)	178.5(10)	N(6B)	Mn(2B)	Mn(1B)	140.31(6)
F(4B)	P(1B)	F(3B)	89.7(9)	N(7B1)	Mn(2B)	Mn(1B)	102.88(5)
F(4B)	P(1B)	F(5B)	91.1(9)	N(8B)	Mn(2B)	N(7B1)	151.75(8)
F(4B)	P(1B)	F(6B)	90.3(12)	N(8B)	Mn(2B)	Mn(1B)	102.47(5)
F(5B)	P(1B)	F(2B)	90.4(9)	O(1B)	Mn(2B)	N(5B)	93.59(7)
F(5B)	P(1B)	F(3B)	179.0(12)	O(1B)	Mn(2B)	N(6B)	176.76(8)
F(5B)	P(1B)	F(6B)	88.9(12)	O(1B)	Mn(2B)	N(7B1)	94.16(7)
F(6B)	P(1B)	F(2B)	89.5(12)	O(1B)	Mn(2B)	N(8B)	96.15(7)
F(6B)	P(1B)	F(3B)	90.5(12)	O(1B)	Mn(2B)	Mn(1B)	42.47(5)

F(1C)	P(1C)	F(2C)	89.7(7)	O(2B)	Mn(2B)	N(5B)	178.24(8)
F(1C)	P(1C)	F(3C)	90.1(8)	O(2B)	Mn(2B)	N(6B)	97.30(7)
F(1C)	P(1C)	F(5C)	88.4(9)	O(2B)	Mn(2B)	N(7B1)	104.69(8)
F(1C)	P(1C)	F(6C)	178.9(11)	O(2B)	Mn(2B)	N(8B)	102.29(7)
F(3C)	P(1C)	F(2C)	90.0(6)	O(2B)	Mn(2B)	O(1B)	85.51(7)
F(4C)	P(1C)	F(1C)	88.7(8)	O(2B)	Mn(2B)	Mn(1B)	43.04(5)

Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for UV irradiation derived [Mn$_2$(μ-O)$_2$(κ^4- tpa)][PF$_6$]$_3$.

Atom	*x*	*y*	*z*	U(eq)
H(1AA)	5168	3892	4936	23
H(1AB)	4506	4157	5603	23
H(1BA)	2979	788	1818	30
H(1BB)	3254	854	1029	30
H(3A)	3077	3409	5559	26
H(4A)	2690	2245	5677	31
H(5A)	4114	1224	5703	32
H(6A)	5893	1392	5614	28
H(7AA)	5173	3898	6622	25
H(7AB)	6323	4116	6677	25
H(7BA)	3225	2268	2351	30
H(7BB)	2343	1770	2394	30
H(9A)	5718	3287	7815	33
H(9B)	1349	2916	3011	34
H(10A)	6534	2198	8387	33
H(10B)	23	3981	2842	44
H(11A)	7662	1293	7794	30
H(11B)	−369	4473	1748	40
H(12A)	7931	1499	6640	25
H(12B)	583	3905	846	32
H(13A)	6281	4788	5671	23
H(13B)	6629	4365	5003	23
H(13C)	4568	1461	1043	30
H(13D)	4611	1556	1833	30
H(15A)	8085	5169	5752	31
H(15B)	5999	2367	1670	40
H(16A)	9900	4797	6088	35
H(16B)	6262	3537	1341	42
H(17A)	10646	3555	6277	31
H(17B)	4887	4369	774	37
H(18A)	9594	2720	6091	25
H(18B)	3292	4010	533	31
H(19A)	10768	881	4385	22
H(19B)	10080	1081	5061	22
H(19C)	1738	4182	−997	27

H(19D)	2125	4237	-1770	27
H(21A)	12027	1761	4489	27
H(21B)	3855	4675	-1512	34
H(22A)	12184	2980	4406	30
H(22B)	5625	4330	-1089	37
H(23A)	10609	3896	4359	31
H(23B)	6176	3192	-516	34
H(24A)	8925	3583	4399	24
H(24B)	4936	2442	-331	29
H(25A)	8920	835	3313	24
H(25B)	10081	1036	3372	24
H(25C)	2493	3306	-2411	26
H(25D)	1672	2764	-2326	26
H(27A)	9677	1730	2214	31
H(27B)	3726	2269	-3011	30
H(28A)	8781	2815	1653	34
H(28B)	5115	1238	-2844	35
H(29A)	7495	3641	2242	30
H(29B)	5411	673	-1761	32
H(30A)	7160	3370	3377	24
H(30B)	4307	1147	-870	25
H(31A)	8678	560	4997	22
H(31B)	8958	158	4311	22
H(31C)	304	3489	-1788	27
H(31D)	390	3602	-1003	27
H(33A)	7104	-187	4276	29
H(33B)	-1024	2625	-1583	35
H(34A)	5278	234	3985	33
H(34B)	-1208	1449	-1211	39
H(35A)	4587	1483	3832	29
H(35B)	234	660	-658	34
H(36A)	5697	2288	4005	26
H(36B)	1800	1069	-454	27
H(10C)	-2081	5386	-2190	88
H(10D)	-2177	4982	-1465	88
H(10E)	-3194	5160	-1953	88
H(3B1)	1373	217	1696	45
H(4B1)	-438	392	1361	57
H(5B1)	-1225	1457	747	54
H(6B1)	-199	2328	465	41
H(93A)	6219	307	1658	105
H(93B)	6066	3	2417	105
H(93C)	7223	-198	2045	105

Atomic Occupancy for UV irradiation derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
P(1A)	0.47(3)	F(1A)	0.47(3)	F(2A)	0.47(3)
F(3A)	0.47(3)	F(4A)	0.47(3)	F(5A)	0.47(3)
F(6A)	0.47(3)	P(1B)	0.151(18)	F(1B)	0.151(18)
F(2B)	0.151(18)	F(3B)	0.151(18)	F(4B)	0.151(18)
F(5B)	0.151(18)	F(6B)	0.151(18)	P(1C)	0.38(2)
F(1C)	0.38(2)	F(2C)	0.38(2)	F(3C)	0.38(2)
F(4C)	0.38(2)	F(5C)	0.38(2)	F(6C)	0.38(2)
P(3A)	0.44(3)	F(13A)	0.44(3)	F(14A)	0.44(3)
F(15A)	0.44(3)	F(16A)	0.44(3)	F(17A)	0.44(3)
F(18A)	0.44(3)	P(3B)	0.28(2)	F(13B)	0.28(2)
F(14B)	0.28(2)	F(15B)	0.28(2)	F(16B)	0.28(2)
F(17B)	0.28(2)	F(18B)	0.28(2)	P(3C)	0.28(3)
F(13C)	0.28(3)	F(14C)	0.28(3)	F(15C)	0.28(3)
F(16C)	0.28(3)	F(17C)	0.28(3)	F(18C)	0.28(3)

Experimental

Single crystals of $C_{38}H_{39}N_9O_2F_{18}P_3Mn_2$ $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$were recrystallization in MeCN. A suitable crystal was selected and measured on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 99.97 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the XL [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. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of UV irradiation derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$

Crystal Data for $C_{38}H_{39}N_9O_2F_{18}P_3Mn_2$ (M =1198.57 g/mol): triclinic, space group P-1 (no. 2), a = 12.6170(8) Å, b = 18.8980(12) Å, c = 19.9575(13) Å, α = 85.848(2)°, β = 88.135(2)°, γ = 77.867(2)°, V = 4639.3(5) Å^3, Z = 4, T = 99.97 K, μ(MoKα) = 0.767 mm^{-1}, *Dcalc* = 1.716 g/cm^3, 300185 reflections measured (2.046° ≤ 2Θ ≤ 60.5°), 25833 unique (R_{int} = 0.0653, R_{sigma} = 0.0446) which were used in all calculations. The final R_1 was 0.0491 (I > 2σ(I)) and wR_2 was 0.1169 (all data).

Refinement model description

Number of restraints - 443, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2. Rigid body (RIGU) restrains
 P1A, F1A, F2A, F3A, F4A, F5A, F6A, P1B, F1B, F2B, F3B, F4B, F5B, F6B, P1C,
 F1C, F2C, F3C, F4C, F5C, F6C
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 P3A, F13A, F14A, F15A, F16A, F17A, F18A
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 P3B, F13B, F14B, F15B, F16B, F17B, F18B
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
3. Same fragment restrains
{P1A, F1A, F2A, F3A, F4A, F5A, F6A} sigma for 1-2: 0.01, 1-3: 0.04
as
{P1B, F1B, F2B, F3B, F4B, F5B, F6B}
{P1A, F1A, F2A, F3A, F4A, F5A, F6A} sigma for 1-2: 0.01, 1-3: 0.04
as
{P1C, F1C, F2C, F3C, F4C, F5C, F6C}
{P3A, F13A, F14A, F15A, F16A, F17A, F18A} sigma for 1-2: 0.01, 1-3: 0.04
as
```

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{P3B, F13B, F14B, F15B, F16B, F17B, F18B}
{P3A, F13A, F14A, F15A, F16A, F17A, F18A} sigma for 1-2: 0.01, 1-3: 0.04
as
{P3C, F13C, F14C, F15C, F16C, F17C, F18C}
4. Others
 1*[Sof(P1A)+Sof(F1A)+Sof(F2A)+Sof(F3A)+Sof(F4A)+Sof(F5A)+Sof(F6A)]+1*
 [Sof(P1B)+Sof(F1B)+Sof(F2B)+Sof(F3B)+Sof(F4B)+Sof(F5B)+Sof(F6B)]+1*[Sof(P1C)+
 Sof(F1C)+Sof(F2C)+Sof(F3C)+Sof(F4C)+Sof(F5C)+Sof(F6C)]=1 with esd of 0.01
 1*[Sof(P3A)+Sof(F13A)+Sof(F14A)+Sof(F15A)+Sof(F16A)+Sof(F17A)+Sof(F18A)]+1*
 [Sof(P3B)+Sof(F13B)+Sof(F14B)+Sof(F15B)+Sof(F16B)+Sof(F17B)+Sof(F18B)]+1*
 [Sof(P3C)+Sof(F13C)+Sof(F14C)+Sof(F15C)+Sof(F16C)+Sof(F17C)+Sof(F18C)]=1 with
 esd of 0.01
 Sof(P1A)=Sof(F1A)=Sof(F2A)=Sof(F3A)=Sof(F4A)=Sof(F5A)=Sof(F6A)=FVAR(1)
 Sof(P1B)=Sof(F1B)=Sof(F2B)=Sof(F3B)=Sof(F4B)=Sof(F5B)=Sof(F6B)=FVAR(2)
 Sof(P1C)=Sof(F1C)=Sof(F2C)=Sof(F3C)=Sof(F4C)=Sof(F5C)=Sof(F6C)=FVAR(3)
 Sof(P3A)=Sof(F13A)=Sof(F14A)=Sof(F15A)=Sof(F16A)=Sof(F17A)=Sof(F18A)=FVAR(4)
 Sof(P3B)=Sof(F13B)=Sof(F14B)=Sof(F15B)=Sof(F16B)=Sof(F17B)=Sof(F18B)=FVAR(5)
 Sof(P3C)=Sof(F13C)=Sof(F14C)=Sof(F15C)=Sof(F16C)=Sof(F17C)=Sof(F18C)=FVAR(6)
5.a Secondary CH2 refined with riding coordinates:
 C1A(H1AA,H1AB), C1B(H1BA,H1BB), C7A(H7AA,H7AB), C7B(H7BA,H7BB), C13A(H13A,
 H13B), C13B(H13C,H13D), C19A(H19A,H19B), C19B(H19C,H19D), C25A(H25A,H25B),
 C25B(H25C,H25D), C31A(H31A,H31B), C31B(H31C,H31D)
5.b Aromatic/amide H refined with riding coordinates:
 C3A(H3A), C4A(H4A), C5A(H5A), C6A(H6A), C9A(H9A), C9B(H9B), C10A(H10A),
 C10B(H10B), C11A(H11A), C11B(H11B), C12A(H12A), C12B(H12B), C15A(H15A),
 C15B(H15B), C16A(H16A), C16B(H16B), C17A(H17A), C17B(H17B), C18A(H18A),
 C18B(H18B), C21A(H21A), C21B(H21B), C22A(H22A), C22B(H22B), C23A(H23A),
 C23B(H23B), C24A(H24A), C24B(H24B), C27A(H27A), C27B(H27B), C28A(H28A),
 C28B(H28B), C29A(H29A), C29B(H29B), C30A(H30A), C30B(H30B), C33A(H33A),
 C33B(H33B), C34A(H34A), C34B(H34B), C35A(H35A), C35B(H35B), C36A(H36A),
 C36B(H36B), C3B1(H3B1), C4B1(H4B1), C5B1(H5B1), C6B1(H6B1)
5.c Idealised Me refined as rotating group:
 C102(H10C,H10D,H10E), C93(H93A,H93B,H93C)
```

This report has been created with Olex2, compiled on 2016.02.19 svn.r3266 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Tables S5. Tables of the molecular structure of electrochemically derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$.

Crystal data and structure refinement for electrochemically derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$.

Identification code	p-1_a
Empirical formula	$C_{38}H_{39}N_9O_2F_{18}P_3Mn_2$
Formula weight	1198.57
Temperature/K	99.99
Crystal system	triclinic
Space group	P-1
a/Å	10.2106(15)
b/Å	12.3868(19)
c/Å	19.944(3)
α/°	85.445(7)
β/°	86.987(7)
γ/°	66.838(7)
Volume/Å^3	2311.2(6)
Z	2
ρ_{calc}g/cm^3	1.722
μ/mm^{-1}	0.770

F(000)	1206.0
Crystal size/mm^3	0.15 × 0.13 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.048 to 61.474
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -28 ≤ l ≤ 28
Reflections collected	82416
Independent reflections	14279 [R_{int} = 0.0395, R_{sigma} = 0.0336]
Data/restraints/parameters	14279/782/935
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0414, wR_2 = 0.1007
Final R indexes [all data]	R_1 = 0.0614, wR_2 = 0.1121
Largest diff. peak/hole / e Å^{-3}	0.65/-0.46

Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for electrochemically derived [Mn_2(μ-O)$_2$(κ^4- tpa)][PF_6]$_3$. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mn(1)	5079.4(3)	4897.6(3)	658.1(2)	25.64(7)
N(1)	3689.3(16)	4905.7(14)	1463.6(7)	26.1(3)
O(1)	6260.6(13)	4910.2(13)	-41.2(6)	27.7(3)
N(3)	6503.9(17)	4615.6(15)	1400.9(7)	28.1(3)
Mn(2)	742.8(3)	9837.0(2)	5545.9(2)	23.35(7)
C(1)	3278(9)	3912(7)	1340(7)	27.9(17)
N(2)	5573(5)	3218(4)	781(3)	27.4(10)
C(2)	4609(7)	2890(6)	1127(4)	28.1(12)
C(3)	4804(6)	1737(5)	1263(3)	37.1(11)
C(4)	6059(5)	872(5)	1028(3)	37.5(11)
C(5)	7069(4)	1217(5)	679(2)	35.8(9)
C(6)	6802(4)	2382(4)	565(2)	30.8(9)
C(1B)	3241(15)	3890(10)	1441(10)	34(3)
N(2B)	5569(10)	2888(6)	913(4)	36.2(17)
C(2B)	4517(13)	2773(9)	1298(5)	39(2)
C(3B)	4565(11)	1666(7)	1511(4)	50.9(19)
C(4B)	5728(10)	688(6)	1318(4)	55.0(18)
C(5B)	6804(11)	818(6)	938(4)	49.5(18)
C(6B)	6724(8)	1927(6)	747(3)	43.1(16)
O(2)	-992.7(15)	9898.2(12)	5351.1(6)	28.2(3)
N(4)	4261.5(17)	6672.4(15)	888.5(8)	28.2(3)
C(18)	4846(2)	7453.8(19)	710.2(10)	33.9(4)
N(5)	2767.1(16)	9744.4(14)	5770.7(7)	24.2(3)
C(15)	2267(2)	8171(2)	1378.1(11)	40.1(5)
N(6)	1949.8(15)	8007.4(14)	5530.4(7)	23.2(3)
C(7)	4424(2)	4796.8(19)	2113.1(9)	30.6(4)

N(7)	614.3(17)	9483.0(13)	6556.6(7)	25.2(3)
C(8)	5989(2)	4517.8(16)	2024.9(8)	26.3(4)
N(8)	305.4(17)	11580.4(15)	5773.7(8)	28.0(3)
C(9)	6868(2)	4213.4(19)	2574.1(10)	37.2(5)
C(10)	8283(2)	4008(2)	2474.7(11)	46.8(6)
C(11)	8809(2)	4113(2)	1830.9(11)	40.6(5)
C(12)	7886(2)	4426.1(19)	1298.3(10)	32.6(4)
C(13)	2453(2)	6057.0(18)	1387.4(9)	30.5(4)
C(14)	2998(2)	7013.2(18)	1224.0(9)	30.2(4)
C(16)	2856(3)	8980(2)	1172.7(13)	46.8(6)
C(17)	4162(3)	8616(2)	839.5(12)	42.1(5)
C(019)	1358(2)	12981.2(18)	5796.5(11)	33.4(4)
C(19)	3807.9(19)	8740.5(17)	5417.3(9)	26.1(4)
C(29)	-467(2)	9008.6(18)	7560.4(9)	32.9(4)
C(28)	754(3)	8810(2)	7907.2(10)	40.9(5)
C(27)	1901(2)	8948(2)	7573.4(10)	40.6(5)
C(26)	1794(2)	9306.9(17)	6893.4(9)	28.5(4)
C(25)	2948(2)	9594.9(19)	6520.0(8)	30.0(4)
C(24)	1430(2)	7166(2)	5595.3(9)	33.1(4)
C(23)	2315(3)	5997(2)	5635.1(10)	43.6(6)
C(22)	3773(3)	5681.7(19)	5610.6(10)	41.4(5)
C(21)	4308(2)	6553.4(18)	5547.0(9)	33.1(4)
C(20)	3366.1(18)	7713.3(16)	5508.5(8)	23.8(3)
C(35)	-946(2)	12382(2)	5971(1)	33.3(4)
C(34)	-1112(2)	13509(2)	6079.0(11)	38.2(5)
C(33)	53(2)	13819(2)	5983.9(12)	39.7(5)
C(32)	1457(2)	11865.3(18)	5699.2(9)	27.4(4)
C(31)	2817(2)	10882.4(17)	5497.5(9)	27.6(4)
C(30)	-498(2)	9335.2(16)	6879.3(9)	26.9(4)
P(1)	-2440(5)	6987(6)	6606.8(16)	34.3(7)
F(1)	-4049(7)	7214(8)	6782(5)	59(2)
F(2)	-1983(6)	5722(6)	7004(3)	35.9(11)
F(3)	-2576(7)	6438(8)	5932(3)	45.2(12)
F(4)	-800(6)	6655(11)	6389(3)	57.3(19)
F(5)	-2879(11)	8215(7)	6194(4)	58.0(16)
F(6)	-2227(12)	7504(9)	7274(4)	67.4(19)
P(1B)	-2610(6)	7209(7)	6592(3)	39.0(11)
F(1B)	-4173(8)	7263(9)	6777(5)	30.3(18)
F(2B)	-1985(14)	5919(10)	6989(7)	60(3)
F(3B)	-2531(14)	6653(13)	5906(5)	71(3)
F(4B)	-1020(6)	7153(9)	6519(3)	40.9(14)
F(5B)	-3254(9)	8509(8)	6286(5)	39.6(15)
F(6B)	-2669(10)	7740(11)	7314(4)	47.4(17)
P(7)	4956(5)	7471(4)	3220.1(17)	33.0(6)
F(7)	4822(6)	7661(7)	4015(2)	60.4(15)
F(8)	4198(8)	6555(6)	3339(2)	42.7(11)
F(9)	6465(9)	6412(10)	3362(7)	36.0(18)

F(10)	5119(4)	7235(5)	2438.9(19)	44.0(9)
F(11)	3461(4)	8508(4)	3112(2)	60.3(11)
F(12)	5756(14)	8354(10)	3094(6)	49(2)
P(7B)	4909(6)	7485(5)	3373(2)	31.3(8)
F(7B)	5202(8)	7472(8)	4155(3)	44.1(13)
F(8B)	4151(10)	6581(7)	3560(3)	39.8(14)
F(13)	6418(12)	6401(13)	3291(10)	32(2)
F(14)	4662(7)	7469(7)	2597(3)	57.0(16)
F(15)	3433(6)	8553(5)	3460(3)	62.0(16)
F(16)	5687(17)	8380(13)	3220(8)	41(2)
P(13)	11202(3)	2200(4)	89.5(17)	35.6(6)
F(17)	11749(3)	3167(2)	-244(3)	68.5(10)
F(18)	11294(4)	2592(5)	818(2)	81.2(14)
F(19)	12802(7)	1281(7)	153(3)	52.5(10)
F(1A)	10603(4)	1277(4)	402(2)	81.3(11)
F(1C)	11066(3)	1819(3)	-648.0(11)	56.0(8)
F(1D)	9610(6)	3138(5)	19(3)	79.3(15)
P(2)	11134(15)	2359(19)	35(9)	27(2)
F(1E)	11776(16)	3278(13)	101(10)	56(3)
F(1F)	11030(20)	2291(17)	848(8)	49(4)
F(1G)	12720(30)	1320(30)	-8(14)	45(4)
F(1H)	10758(18)	1170(13)	130(12)	57(4)
F(1I)	11460(20)	2209(18)	-696(6)	63(4)
F(1J)	9550(20)	3215(17)	11(7)	27(3)
N(101)	554(14)	11974(12)	7527(8)	56(2)
C(101)	1300(20)	12281(15)	7784(8)	43(2)
C(102)	2293(14)	12673(11)	8076(3)	68(3)
N(102)	686(18)	11632(12)	7491(10)	53(3)
C(103)	1010(20)	12346(13)	7654(9)	43(3)
C(104)	1349(12)	13296(8)	7875(5)	61(3)

Anisotropic Displacement Parameters ($Å^2×10^3$) for electrochemically derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$. 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}
Mn(1)	21.86(13)	38.66(17)	16.07(12)	-6.51(10)	-0.31(9)	-10.61(12)
N(1)	25.3(7)	33.1(9)	21.4(7)	-5.8(6)	1.7(5)	-12.7(7)
O(1)	21.0(6)	43.0(8)	19.2(6)	-2.8(5)	-2.8(4)	-12.0(6)
N(3)	28.0(8)	34.7(9)	20.9(7)	-5.1(6)	-3.6(6)	-10.4(7)
Mn(2)	33.96(15)	22.44(14)	15.07(11)	-1.40(9)	-1.63(9)	-12.40(11)
C(1)	22(2)	40(3)	27(4)	-11(2)	9(2)	-17(2)
N(2)	18.7(14)	38(3)	27(2)	-13.2(19)	3.2(14)	-10.5(17)
C(2)	25.7(19)	37(2)	25(3)	-11.5(19)	-2.9(18)	-14.9(17)
C(3)	33(2)	45(2)	39(3)	-13(2)	-4.1(18)	-19.0(17)
C(4)	32(2)	38(2)	45(3)	-15.6(19)	-6(2)	-13.3(19)

C(5)	29.7(17)	41(3)	35(2)	-18.1(19)	-5.0(15)	-8.1(18)
C(6)	19.9(14)	43(3)	27(2)	-13.2(17)	-3.8(13)	-7.2(16)
C(1B)	43(5)	32(4)	30(5)	1(3)	-15(3)	-16(3)
N(2B)	49(3)	26(3)	27(3)	-7(2)	-14(2)	-6(2)
C(2B)	50(4)	35(3)	33(5)	-6(3)	-17(3)	-14(2)
C(3B)	72(5)	34(3)	53(5)	-1(3)	-30(3)	-25(3)
C(4B)	79(5)	30(3)	59(4)	-4(3)	-32(3)	-20(3)
C(5B)	74(5)	31(3)	39(3)	-8(2)	-28(3)	-10(3)
C(6B)	62(4)	27(3)	25(3)	-10(2)	-14(2)	1(3)
O(2)	43.4(8)	25.9(7)	17.3(5)	-1.5(5)	4.9(5)	-16.3(6)
N(4)	24.6(7)	29.8(9)	28.4(8)	-5.2(6)	1.9(6)	-8.4(7)
C(18)	31(1)	37.3(11)	35.5(10)	-0.7(8)	-4.9(8)	-15.4(9)
N(5)	30.4(8)	28.4(8)	18.1(6)	-3.2(6)	-0.8(5)	-15.9(7)
C(15)	36.3(11)	35.1(12)	41.4(11)	-12.6(9)	4.7(9)	-4.7(9)
N(6)	23.3(7)	29.2(8)	17.9(6)	-3.1(5)	0.1(5)	-11.0(6)
C(7)	38.1(10)	38.7(11)	19.6(8)	-5.1(7)	2.4(7)	-19.8(9)
N(7)	34.6(8)	21.8(7)	17.5(6)	-2.1(5)	-1.1(6)	-9.2(6)
C(8)	34.8(10)	21.8(9)	19.3(7)	-5.0(6)	-3.1(6)	-6.9(7)
N(8)	30.2(8)	35.7(9)	24.9(7)	5.3(6)	-8.3(6)	-20.6(7)
C(9)	42.0(11)	35.9(11)	21.1(8)	-2.4(8)	-6.3(8)	-0.9(9)
C(10)	35.7(11)	57.7(15)	29.9(10)	-7.5(10)	-12.2(8)	2.3(11)
C(11)	26.3(10)	49.6(14)	34.3(10)	-11.1(9)	-6.5(8)	-0.3(9)
C(12)	29.0(9)	40.7(12)	25.3(9)	-9.2(8)	-1.9(7)	-9.0(9)
C(13)	24.1(9)	36.7(11)	28.0(9)	-7.4(8)	7.0(7)	-8.9(8)
C(14)	26.5(9)	32.4(10)	28.6(9)	-7.3(7)	2.7(7)	-7.5(8)
C(16)	56.4(15)	30.4(12)	49.1(13)	-11.3(10)	-5.0(11)	-10.0(11)
C(17)	50.5(13)	36.9(12)	44.7(12)	-1.1(9)	-9.1(10)	-22.7(11)
C(019)	32.2(10)	33.4(11)	42.2(11)	-2.1(8)	-1.0(8)	-21.1(9)
C(19)	23.2(8)	33.2(10)	23.6(8)	-4.6(7)	0.4(6)	-12.4(8)
C(29)	41.5(11)	35.7(11)	23.4(8)	-2.9(7)	2.9(7)	-17.3(9)
C(28)	52.4(13)	55.5(14)	18.7(8)	5.0(8)	-4.0(8)	-26.4(12)
C(27)	46.7(12)	58.4(15)	22.1(9)	3.2(9)	-9.4(8)	-26.3(11)
C(26)	36(1)	31.2(10)	19.3(8)	-3.1(7)	-3.5(7)	-13.8(8)
C(25)	36.6(10)	38.3(11)	18.3(8)	-3.5(7)	-4.6(7)	-17.4(9)
C(24)	41.2(11)	48.2(13)	21.6(8)	-4.9(8)	3.6(7)	-30(1)
C(23)	76.3(17)	43.1(13)	26.2(10)	-6.5(9)	11.8(10)	-40.2(13)
C(22)	61.7(15)	25.1(10)	28.7(10)	-1.8(8)	12.2(9)	-9.2(10)
C(21)	30.3(10)	32.3(11)	26.1(9)	-1.8(7)	3.8(7)	-1.3(8)
C(20)	23.6(8)	28.9(9)	17.4(7)	-2.8(6)	0.3(6)	-8.7(7)
C(35)	27.0(9)	46.7(12)	30.4(9)	9.8(8)	-7.9(7)	-20.4(9)
C(34)	29.7(10)	42.4(13)	39.9(11)	6.6(9)	-3.4(8)	-12.7(9)
C(33)	40.7(12)	32.4(11)	49.0(12)	-1.3(9)	-2.1(9)	-17.7(10)
C(32)	30.6(9)	33.9(10)	25.2(8)	1.7(7)	-4.8(7)	-20.7(8)
C(31)	33.8(9)	31.7(10)	24.5(8)	-1.5(7)	-1.3(7)	-20.5(8)
C(30)	31.8(9)	24.2(9)	22.3(8)	-3.5(7)	-0.9(7)	-7.8(7)
P(1)	26.6(11)	46.8(17)	31.3(9)	17.3(8)	-7.8(6)	-19.2(11)
F(1)	37(3)	61(4)	74(4)	26(3)	-8(2)	-19(2)

F(2)	21.8(17)	41(2)	35.6(19)	13.1(15)	0.6(12)	-5.4(14)
F(3)	30.4(19)	69(3)	33.2(18)	10.8(15)	-2.2(13)	-18.2(19)
F(4)	33.2(17)	93(5)	55(2)	16(3)	-4.6(14)	-38(2)
F(5)	64(4)	52(3)	60(3)	27(2)	-13(2)	-29(3)
F(6)	87(5)	70(4)	63(3)	17.3(19)	-28(3)	-51(4)
P(1B)	18.8(11)	37.1(19)	60(2)	4.5(13)	-3.6(10)	-11.5(12)
F(1B)	16(2)	28(3)	43(4)	-3(3)	5(2)	-5(2)
F(2B)	57(4)	51(4)	61(4)	11(3)	3(3)	-13(3)
F(3B)	75(5)	73(5)	49(4)	-12(4)	-15(3)	-9(4)
F(4B)	31.4(19)	50(4)	43(2)	-5(2)	0.3(15)	-18(2)
F(5B)	27(3)	32(3)	55(3)	12(2)	-4(2)	-9(2)
F(6B)	44(3)	58(4)	45(2)	0(2)	-3(2)	-27(3)
P(7)	26.3(7)	34.2(9)	40.2(13)	-12.4(9)	1.9(8)	-12.2(6)
F(7)	61(3)	82(4)	46(2)	-35(2)	17.9(18)	-32(3)
F(8)	34.6(15)	48.9(19)	51(3)	-14(2)	7(2)	-22.9(13)
F(9)	30(2)	42(3)	37(3)	-2(2)	-5.8(17)	-16(2)
F(10)	43(2)	50.2(19)	36.0(16)	-5.3(13)	-9.3(13)	-13.0(17)
F(11)	32.9(15)	39.9(17)	96(3)	-14(2)	-2.2(19)	0.3(12)
F(12)	49(3)	37(3)	68(5)	-11(3)	2(3)	-25(2)
P(7B)	24.1(11)	26.1(12)	46(2)	-0.1(13)	-4.0(13)	-12.5(9)
F(7B)	38(3)	52(3)	46(3)	-13(2)	14.1(19)	-22(2)
F(8B)	29(2)	34(2)	60(4)	4(3)	0(3)	-17.6(18)
F(13)	29(3)	31(4)	35(4)	-10(3)	3(2)	-10(3)
F(14)	59(4)	71(4)	53(3)	13(2)	-25(2)	-39(3)
F(15)	27.8(18)	29(2)	123(5)	7(3)	4(3)	-6.7(15)
F(16)	40(3)	36(4)	55(4)	5(3)	-4(3)	-25(3)
P(13)	28.1(7)	43.8(12)	30.1(7)	-6.4(7)	5.9(6)	-9.1(6)
F(17)	58.5(13)	51.1(13)	99(3)	-3.5(15)	8.2(15)	-26.2(11)
F(18)	44.3(14)	144(4)	55.3(15)	-53.8(19)	3.8(11)	-28.9(17)
F(19)	35.1(12)	57.9(15)	53(3)	-5.4(19)	-2.3(15)	-5.2(10)
F(1A)	77(2)	124(3)	62.3(19)	28.0(17)	-9.0(15)	-66(2)
F(1C)	62.0(15)	69.5(17)	37(1)	-14.8(9)	0.5(9)	-24.3(12)
F(1D)	33.0(16)	103(3)	79(3)	-28(2)	-4.4(15)	2.4(17)
P(2)	18(3)	38(4)	31(3)	-7(3)	-7(2)	-14(3)
F(1E)	60(6)	56(6)	64(7)	-3(5)	-13(5)	-34(5)
F(1F)	42(7)	64(7)	26(4)	2(4)	-2(4)	-4(5)
F(1G)	32(5)	49(6)	44(9)	-12(6)	3(5)	-6(4)
F(1H)	42(5)	36(5)	94(9)	-11(5)	-4(6)	-15(4)
F(1I)	70(7)	76(8)	36(4)	-9(4)	-2(4)	-19(6)
F(1J)	21(5)	37(6)	20(5)	-10(4)	3(4)	-8(4)
N(101)	63(4)	51(8)	46(4)	-5(6)	3(3)	-16(5)
C(101)	56(5)	40(4)	28(5)	-4(3)	10(3)	-13(3)
C(102)	111(7)	92(6)	35(3)	-6(3)	13(3)	-76(6)
N(102)	74(5)	33(5)	51(4)	-7(4)	3(4)	-21(5)
C(103)	65(9)	33(4)	31(7)	-10(4)	17(5)	-21(6)
C(104)	81(6)	62(5)	59(4)	-26(4)	35(4)	-48(5)

Bond Lengths for electrochemically derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn(1)	Mn(1)[1]	2.6246(6)	C(16)	C(17)	1.381(4)
Mn(1)	N(1)	2.0849(15)	C(019)	C(33)	1.383(3)
Mn(1)	O(1)	1.7985(13)	C(019)	C(32)	1.374(3)
Mn(1)	O(1)[1]	1.8212(12)	C(19)	C(20)	1.504(3)
Mn(1)	N(3)	2.0437(15)	C(29)	C(28)	1.385(3)
Mn(1)	N(2)	1.936(5)	C(29)	C(30)	1.384(3)
Mn(1)	N(2B)	2.357(7)	C(28)	C(27)	1.379(3)
Mn(1)	N(4)	2.1017(17)	C(27)	C(26)	1.389(3)
N(1)	C(1)	1.489(8)	C(26)	C(25)	1.506(3)
N(1)	C(1B)	1.503(11)	C(24)	C(23)	1.371(3)
N(1)	C(7)	1.501(2)	C(23)	C(22)	1.382(4)
N(1)	C(13)	1.490(3)	C(22)	C(21)	1.384(3)
O(1)	Mn(1)[1]	1.8213(12)	C(21)	C(20)	1.378(3)
N(3)	C(8)	1.340(2)	C(35)	C(34)	1.371(3)
N(3)	C(12)	1.344(3)	C(34)	C(33)	1.386(3)
Mn(2)	Mn(2)[2]	2.6327(6)	C(32)	C(31)	1.504(3)
Mn(2)	O(2)[2]	1.8160(12)	P(1)	F(1)	1.578(5)
Mn(2)	O(2)	1.8053(15)	P(1)	F(2)	1.602(4)
Mn(2)	N(5)	2.0950(15)	P(1)	F(3)	1.591(4)
Mn(2)	N(6)	2.1132(16)	P(1)	F(4)	1.604(4)
Mn(2)	N(7)	2.0370(15)	P(1)	F(5)	1.580(4)
Mn(2)	N(8)	2.1084(17)	P(1)	F(6)	1.583(4)
C(1)	C(2)	1.517(7)	P(1B)	F(1B)	1.595(6)
N(2)	C(2)	1.346(6)	P(1B)	F(2B)	1.624(6)
N(2)	C(6)	1.351(5)	P(1B)	F(3B)	1.566(6)
C(2)	C(3)	1.369(7)	P(1B)	F(4B)	1.597(6)
C(3)	C(4)	1.395(6)	P(1B)	F(5B)	1.565(6)
C(4)	C(5)	1.398(7)	P(1B)	F(6B)	1.617(6)
C(5)	C(6)	1.361(7)	P(7)	F(7)	1.612(4)
C(1B)	C(2B)	1.516(11)	P(7)	F(8)	1.604(4)
N(2B)	C(2B)	1.334(10)	P(7)	F(9)	1.603(5)
N(2B)	C(6B)	1.354(9)	P(7)	F(10)	1.596(4)
C(2B)	C(3B)	1.386(10)	P(7)	F(11)	1.573(4)
C(3B)	C(4B)	1.386(10)	P(7)	F(12)	1.601(5)
C(4B)	C(5B)	1.356(11)	P(7B)	F(7B)	1.600(6)
C(5B)	C(6B)	1.368(10)	P(7B)	F(8B)	1.604(5)
O(2)	Mn(2)[2]	1.8159(12)	P(7B)	F(13)	1.608(6)
N(4)	C(18)	1.341(3)	P(7B)	F(14)	1.585(5)
N(4)	C(14)	1.348(2)	P(7B)	F(15)	1.578(5)
C(18)	C(17)	1.369(3)	P(7B)	F(16)	1.603(6)
N(5)	C(19)	1.481(2)	P(13)	F(17)	1.596(5)
N(5)	C(25)	1.503(2)	P(13)	F(18)	1.588(4)
N(5)	C(31)	1.490(2)	P(13)	F(19)	1.586(6)

C(15)	C(14)	1.383(3)	P(13)	F(1A)	1.570(5)
C(15)	C(16)	1.384(4)	P(13)	F(1C)	1.609(4)
N(6)	C(24)	1.339(2)	P(13)	F(1D)	1.589(7)
N(6)	C(20)	1.344(2)	P(2)	F(1E)	1.54(2)
C(7)	C(8)	1.501(3)	P(2)	F(1F)	1.62(2)
N(7)	C(26)	1.343(2)	P(2)	F(1G)	1.63(3)
N(7)	C(30)	1.344(2)	P(2)	F(1H)	1.66(2)
C(8)	C(9)	1.385(3)	P(2)	F(1I)	1.49(2)
N(8)	C(35)	1.336(3)	P(2)	F(1J)	1.55(3)
N(8)	C(32)	1.353(2)	N(101)	C(101)	1.131(8)
C(9)	C(10)	1.371(3)	C(101)	C(102)	1.452(8)
C(10)	C(11)	1.382(3)	N(102)	C(103)	1.134(8)
C(11)	C(12)	1.385(3)	C(103)	C(104)	1.454(9)
C(13)	C(14)	1.502(3)			

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

Bond Angles for electrochemically derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N(1)	Mn(1)	Mn(1)[1]	135.66(4)	C(18)	C(17)	C(16)	119.0(2)
N(1)	Mn(1)	N(2B)	76.3(2)	C(32)	C(019)	C(33)	118.84(19)
N(1)	Mn(1)	N(4)	78.27(6)	N(5)	C(19)	C(20)	109.49(14)
O(1)	Mn(1)	Mn(1)[1]	43.87(4)	C(30)	C(29)	C(28)	118.6(2)
O(1)[1]	Mn(1)	Mn(1)[1]	43.18(4)	C(27)	C(28)	C(29)	119.85(18)
O(1)	Mn(1)	N(1)	179.20(7)	C(28)	C(27)	C(26)	118.90(19)
O(1)[1]	Mn(1)	N(1)	92.48(6)	N(7)	C(26)	C(27)	121.07(19)
O(1)	Mn(1)	O(1)[1]	87.05(6)	N(7)	C(26)	C(25)	117.56(16)
O(1)	Mn(1)	N(3)	96.97(6)	C(27)	C(26)	C(25)	121.23(17)
O(1)[1]	Mn(1)	N(3)	175.43(6)	N(5)	C(25)	C(26)	112.93(14)
O(1)	Mn(1)	N(2)	98.94(15)	N(6)	C(24)	C(23)	121.4(2)
O(1)[1]	Mn(1)	N(2)	92.62(19)	C(24)	C(23)	C(22)	119.3(2)
O(1)[1]	Mn(1)	N(2B)	94.4(3)	C(23)	C(22)	C(21)	119.3(2)
O(1)	Mn(1)	N(2B)	104.4(2)	C(20)	C(21)	C(22)	118.8(2)
O(1)[1]	Mn(1)	N(4)	95.18(6)	N(6)	C(20)	C(19)	114.61(16)
O(1)	Mn(1)	N(4)	101.11(7)	N(6)	C(20)	C(21)	121.30(18)
N(3)	Mn(1)	Mn(1)[1]	140.80(5)	C(21)	C(20)	C(19)	124.06(17)
N(3)	Mn(1)	N(1)	83.51(6)	N(8)	C(35)	C(34)	121.66(18)
N(3)	Mn(1)	N(2B)	82.5(3)	C(35)	C(34)	C(33)	119.0(2)
N(3)	Mn(1)	N(4)	86.18(6)	C(019)	C(33)	C(34)	119.4(2)
N(2)	Mn(1)	Mn(1)[1]	97.94(18)	N(8)	C(32)	C(019)	121.34(19)
N(2)	Mn(1)	N(1)	81.74(15)	N(8)	C(32)	C(31)	115.02(17)
N(2)	Mn(1)	N(3)	84.65(19)	C(019)	C(32)	C(31)	123.64(17)
N(2)	Mn(1)	N(4)	158.81(17)	N(5)	C(31)	C(32)	108.57(15)
N(2B)	Mn(1)	Mn(1)[1]	102.9(2)	N(7)	C(30)	C(29)	121.47(18)
N(4)	Mn(1)	Mn(1)[1]	101.23(5)	F(1)	P(1)	F(2)	88.9(4)

N(4)	Mn(1)	N(2B)	153.2(2)	F(1)	P(1)	F(3)	88.7(4)
C(1)	N(1)	Mn(1)	103.0(4)	F(1)	P(1)	F(4)	174.6(5)
C(1)	N(1)	C(7)	115.8(6)	F(1)	P(1)	F(5)	91.5(4)
C(1)	N(1)	C(13)	111.3(4)	F(1)	P(1)	F(6)	93.8(5)
C(1B)	N(1)	Mn(1)	110.0(6)	F(2)	P(1)	F(4)	88.7(3)
C(7)	N(1)	Mn(1)	109.49(11)	F(3)	P(1)	F(2)	90.4(4)
C(7)	N(1)	C(1B)	109.1(8)	F(3)	P(1)	F(4)	86.5(3)
C(13)	N(1)	Mn(1)	105.83(11)	F(5)	P(1)	F(2)	178.2(4)
C(13)	N(1)	C(1B)	111.6(6)	F(5)	P(1)	F(3)	87.9(4)
C(13)	N(1)	C(7)	110.73(14)	F(5)	P(1)	F(4)	90.7(3)
Mn(1)	O(1)	Mn(1)[1]	92.95(6)	F(5)	P(1)	F(6)	92.8(4)
C(8)	N(3)	Mn(1)	114.36(13)	F(6)	P(1)	F(2)	88.8(4)
C(8)	N(3)	C(12)	120.34(16)	F(6)	P(1)	F(3)	177.4(4)
C(12)	N(3)	Mn(1)	125.01(12)	F(6)	P(1)	F(4)	91.0(3)
O(2)	Mn(2)	Mn(2)[2]	43.52(4)	F(1B)	P(1B)	F(2B)	88.0(6)
O(2)[2]	Mn(2)	Mn(2)[2]	43.20(5)	F(1B)	P(1B)	F(4B)	171.9(6)
O(2)	Mn(2)	O(2)[2]	86.72(6)	F(1B)	P(1B)	F(6B)	86.5(5)
O(2)	Mn(2)	N(5)	179.32(6)	F(3B)	P(1B)	F(1B)	93.6(6)
O(2)[2]	Mn(2)	N(5)	93.28(6)	F(3B)	P(1B)	F(2B)	91.5(7)
O(2)[2]	Mn(2)	N(6)	93.54(6)	F(3B)	P(1B)	F(4B)	93.8(6)
O(2)	Mn(2)	N(6)	100.27(6)	F(3B)	P(1B)	F(6B)	178.1(8)
O(2)[2]	Mn(2)	N(7)	175.97(7)	F(4B)	P(1B)	F(2B)	88.4(6)
O(2)	Mn(2)	N(7)	96.90(6)	F(4B)	P(1B)	F(6B)	86.1(5)
O(2)	Mn(2)	N(8)	102.70(6)	F(5B)	P(1B)	F(1B)	90.3(6)
O(2)[2]	Mn(2)	N(8)	94.59(6)	F(5B)	P(1B)	F(2B)	173.8(8)
N(5)	Mn(2)	Mn(2)[2]	136.48(4)	F(5B)	P(1B)	F(3B)	94.5(7)
N(5)	Mn(2)	N(6)	79.06(6)	F(5B)	P(1B)	F(4B)	92.4(4)
N(5)	Mn(2)	N(8)	77.97(6)	F(5B)	P(1B)	F(6B)	87.4(6)
N(6)	Mn(2)	Mn(2)[2]	99.49(4)	F(6B)	P(1B)	F(2B)	86.6(7)
N(7)	Mn(2)	Mn(2)[2]	140.39(5)	F(8)	P(7)	F(7)	90.0(4)
N(7)	Mn(2)	N(5)	83.08(6)	F(9)	P(7)	F(7)	87.6(5)
N(7)	Mn(2)	N(6)	84.09(6)	F(9)	P(7)	F(8)	89.3(6)
N(7)	Mn(2)	N(8)	86.36(6)	F(10)	P(7)	F(7)	178.0(4)
N(8)	Mn(2)	Mn(2)[2]	101.88(4)	F(10)	P(7)	F(8)	88.9(3)
N(8)	Mn(2)	N(6)	156.01(6)	F(10)	P(7)	F(9)	90.8(5)
N(1)	C(1)	C(2)	108.1(5)	F(10)	P(7)	F(12)	90.3(5)
C(2)	N(2)	Mn(1)	115.7(4)	F(11)	P(7)	F(7)	90.2(3)
C(2)	N(2)	C(6)	119.1(5)	F(11)	P(7)	F(8)	90.0(4)
C(6)	N(2)	Mn(1)	125.2(4)	F(11)	P(7)	F(9)	177.7(6)
N(2)	C(2)	C(1)	113.9(6)	F(11)	P(7)	F(10)	91.4(3)
N(2)	C(2)	C(3)	122.8(5)	F(11)	P(7)	F(12)	91.5(5)
C(3)	C(2)	C(1)	123.2(5)	F(12)	P(7)	F(7)	90.7(5)
C(2)	C(3)	C(4)	118.1(5)	F(12)	P(7)	F(8)	178.3(6)
C(3)	C(4)	C(5)	118.8(5)	F(12)	P(7)	F(9)	89.2(6)
C(6)	C(5)	C(4)	119.7(4)	F(7B)	P(7B)	F(8B)	89.0(4)
N(2)	C(6)	C(5)	121.3(4)	F(7B)	P(7B)	F(13)	89.6(7)
N(1)	C(1B)	C(2B)	110.5(9)	F(7B)	P(7B)	F(16)	88.5(7)

C(2B)	N(2B)	Mn(1)	109.8(6)	F(8B)	P(7B)	F(13)	90.2(8)
C(2B)	N(2B)	C(6B)	120.5(7)	F(14)	P(7B)	F(7B)	178.4(5)
C(6B)	N(2B)	Mn(1)	129.6(6)	F(14)	P(7B)	F(8B)	91.1(4)
N(2B)	C(2B)	C(1B)	117.2(9)	F(14)	P(7B)	F(13)	88.8(7)
N(2B)	C(2B)	C(3B)	120.4(8)	F(14)	P(7B)	F(16)	91.4(7)
C(3B)	C(2B)	C(1B)	122.3(9)	F(15)	P(7B)	F(7B)	89.9(4)
C(4B)	C(3B)	C(2B)	118.6(9)	F(15)	P(7B)	F(8B)	90.1(5)
C(5B)	C(4B)	C(3B)	120.4(7)	F(15)	P(7B)	F(13)	179.4(8)
C(4B)	C(5B)	C(6B)	119.1(7)	F(15)	P(7B)	F(14)	91.7(4)
N(2B)	C(6B)	C(5B)	120.9(8)	F(15)	P(7B)	F(16)	90.3(7)
Mn(2)	O(2)	Mn(2)[2]	93.27(6)	F(16)	P(7B)	F(8B)	177.5(7)
C(18)	N(4)	Mn(1)	126.28(13)	F(16)	P(7B)	F(13)	89.4(8)
C(18)	N(4)	C(14)	120.13(18)	F(17)	P(13)	F(1C)	89.7(2)
C(14)	N(4)	Mn(1)	113.52(13)	F(18)	P(13)	F(17)	90.7(2)
N(4)	C(18)	C(17)	121.4(2)	F(18)	P(13)	F(1C)	178.6(3)
C(19)	N(5)	Mn(2)	106.38(10)	F(18)	P(13)	F(1D)	91.3(3)
C(19)	N(5)	C(25)	112.58(15)	F(19)	P(13)	F(17)	90.0(4)
C(19)	N(5)	C(31)	111.47(14)	F(19)	P(13)	F(18)	88.8(3)
C(25)	N(5)	Mn(2)	109.70(11)	F(19)	P(13)	F(1C)	92.6(3)
C(31)	N(5)	Mn(2)	105.64(11)	F(19)	P(13)	F(1D)	178.9(5)
C(31)	N(5)	C(25)	110.74(14)	F(1A)	P(13)	F(17)	177.6(3)
C(14)	C(15)	C(16)	118.4(2)	F(1A)	P(13)	F(18)	90.4(3)
C(24)	N(6)	Mn(2)	125.96(14)	F(1A)	P(13)	F(19)	92.2(4)
C(24)	N(6)	C(20)	119.98(17)	F(1A)	P(13)	F(1C)	89.2(2)
C(20)	N(6)	Mn(2)	113.81(12)	F(1A)	P(13)	F(1D)	88.8(3)
C(8)	C(7)	N(1)	113.52(14)	F(1D)	P(13)	F(17)	89.0(3)
C(26)	N(7)	Mn(2)	115.08(13)	F(1D)	P(13)	F(1C)	87.3(3)
C(26)	N(7)	C(30)	120.08(15)	F(1E)	P(2)	F(1F)	85.7(10)
C(30)	N(7)	Mn(2)	124.64(12)	F(1E)	P(2)	F(1G)	90.7(17)
N(3)	C(8)	C(7)	118.01(15)	F(1E)	P(2)	F(1H)	164.1(15)
N(3)	C(8)	C(9)	120.88(19)	F(1E)	P(2)	F(1J)	97.7(14)
C(9)	C(8)	C(7)	121.05(17)	F(1F)	P(2)	F(1G)	94.9(15)
C(35)	N(8)	Mn(2)	127.06(13)	F(1F)	P(2)	F(1H)	83.2(13)
C(35)	N(8)	C(32)	119.71(18)	F(1G)	P(2)	F(1H)	78.9(18)
C(32)	N(8)	Mn(2)	113.24(13)	F(1I)	P(2)	F(1E)	96.6(13)
C(10)	C(9)	C(8)	119.28(19)	F(1I)	P(2)	F(1F)	169.2(17)
C(9)	C(10)	C(11)	119.66(19)	F(1I)	P(2)	F(1G)	74.6(14)
C(10)	C(11)	C(12)	118.9(2)	F(1I)	P(2)	F(1H)	92.3(11)
N(3)	C(12)	C(11)	120.90(19)	F(1I)	P(2)	F(1J)	100.3(13)
N(1)	C(13)	C(14)	108.94(15)	F(1J)	P(2)	F(1F)	89.8(12)
N(4)	C(14)	C(15)	121.1(2)	F(1J)	P(2)	F(1G)	170.6(17)
N(4)	C(14)	C(13)	114.85(17)	F(1J)	P(2)	F(1H)	93.7(11)
C(15)	C(14)	C(13)	124.04(18)	N(101)	C(101)	C(102)	176.6(17)
C(17)	C(16)	C(15)	119.9(2)	N(102)	C(103)	C(104)	176.9(18)

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

Torsion Angles for electrochemically derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Mn(1)	N(1)	C(1)	C(2)	42.9(9)	N(4)	Mn(1)	O(1)	Mn(1)^1	-94.71(7)
Mn(1)	N(1)	C(1B)	C(2B)	45.0(14)	N(4)	C(18)	C(17)	C(16)	1.3(3)
Mn(1)	N(1)	C(7)	C(8)	-9.3(2)	C(18)	N(4)	C(14)	C(15)	1.4(3)
Mn(1)	N(1)	C(13)	C(14)	-44.99(16)	C(18)	N(4)	C(14)	C(13)	179.39(17)
Mn(1)	N(3)	C(8)	C(7)	-8.8(2)	N(5)	C(19)	C(20)	N(6)	34.49(19)
Mn(1)	N(3)	C(8)	C(9)	173.74(15)	N(5)	C(19)	C(20)	C(21)	-
Mn(1)	N(3)	C(12)	C(11)	-	C(15)	C(16)	C(17)	C(18)	0.8(3)
Mn(1)	N(2)	C(2)	C(1)	1.9(9)	N(6)	Mn(2)	O(2)	Mn(2)^2	-93.01(6)
Mn(1)	N(2)	C(2)	C(3)	-179.4(6)	N(6)	C(24)	C(23)	C(22)	0.3(3)
Mn(1)	N(2)	C(6)	C(5)	179.3(4)	C(7)	N(1)	C(1)	C(2)	-76.6(8)
Mn(1)	N(2B)	C(2B)	C(1B)	4.3(14)	C(7)	N(1)	C(1B)	C(2B)	-75.2(12)
Mn(1)	N(2B)	C(2B)	C(3B)	179.6(9)	C(7)	N(1)	C(13)	C(14)	73.56(18)
Mn(1)	N(2B)	C(6B)	C(5B)	-179.2(6)	C(7)	C(8)	C(9)	C(10)	-177.6(2)
Mn(1)	N(4)	C(18)	C(17)	174.51(15)	N(7)	Mn(2)	O(2)	Mn(2)^2	-178.22(6)
Mn(1)	N(4)	C(14)	C(15)	-	N(7)	C(26)	C(25)	N(5)	-15.0(3)
Mn(1)	N(4)	C(14)	C(13)	2.1(2)	C(8)	N(3)	C(12)	C(11)	0.8(3)
N(1)	C(1)	C(2)	N(2)	-32.0(11)	C(8)	C(9)	C(10)	C(11)	0.3(4)
N(1)	C(1)	C(2)	C(3)	149.3(7)	N(8)	Mn(2)	O(2)	Mn(2)^2	93.97(6)
N(1)	C(1B)	C(2B)	N(2B)	-31.7(18)	N(8)	C(35)	C(34)	C(33)	-0.3(3)
N(1)	C(1B)	C(2B)	C(3B)	153.1(11)	N(8)	C(32)	C(31)	N(5)	-29.7(2)
N(1)	C(7)	C(8)	N(3)	12.3(3)	C(9)	C(10)	C(11)	C(12)	0.1(4)
N(1)	C(7)	C(8)	C(9)	-	C(10)	C(11)	C(12)	N(3)	-0.6(4)
N(1)	C(13)	C(14)	N(4)	29.1(2)	C(12)	N(3)	C(8)	C(7)	177.07(18)
N(1)	C(13)	C(14)	C(15)	-	C(12)	N(3)	C(8)	C(9)	-0.4(3)
O(1)^1	Mn(1)	O(1)	Mn(1)^1	-0.001(0)	C(13)	N(1)	C(1)	C(2)	155.9(6)
N(3)	Mn(1)	O(1)	Mn(1)^1	177.84(6)	C(13)	N(1)	C(1B)	C(2B)	162.1(9)
N(3)	C(8)	C(9)	C(10)	-0.2(3)	C(13)	N(1)	C(7)	C(8)	-
Mn(2)	N(5)	C(19)	C(20)	-43.90(15)	C(14)	N(4)	C(18)	C(17)	-2.5(3)
Mn(2)	N(5)	C(25)	C(26)	11.66(19)	C(14)	C(15)	C(16)	C(17)	-1.8(3)
Mn(2)	N(5)	C(31)	C(32)	46.03(15)	C(16)	C(15)	C(14)	N(4)	0.7(3)
Mn(2)	N(6)	C(24)	C(23)	-	C(16)	C(15)	C(14)	C(13)	-177.1(2)
Mn(2)	N(6)	C(20)	C(19)	-6.86(17)	C(019)	C(32)	C(31)	N(5)	151.02(18)
Mn(2)	N(6)	C(20)	C(21)	175.04(13)	C(19)	N(5)	C(25)	C(26)	-
Mn(2)	N(7)	C(26)	C(27)	-	C(19)	N(5)	C(31)	C(32)	161.16(14)
Mn(2)	N(7)	C(26)	C(25)	10.4(2)	C(29)	C(28)	C(27)	C(26)	1.2(4)
Mn(2)	N(7)	C(30)	C(29)	175.05(14)	C(28)	C(29)	C(30)	N(7)	-1.3(3)
Mn(2)	N(8)	C(35)	C(34)	-	C(28)	C(27)	C(26)	N(7)	-2.1(3)
Mn(2)	N(8)	C(32)	C(019)	177.06(15)	C(28)	C(27)	C(26)	C(25)	173.5(2)
Mn(2)	N(8)	C(32)	C(31)	-2.25(19)	C(27)	C(26)	C(25)	N(5)	169.31(19)
C(1)	N(1)	C(7)	C(8)	106.5(4)	C(26)	N(7)	C(30)	C(29)	0.4(3)
C(1)	N(1)	C(13)	C(14)	-156.2(5)	C(25)	N(5)	C(19)	C(20)	76.29(17)
C(1)	C(2)	C(3)	C(4)	178.5(8)	C(25)	N(5)	C(31)	C(32)	-72.67(18)
N(2)	Mn(1)	O(1)	Mn(1)^1	92.19(19)	C(24)	N(6)	C(20)	C(19)	178.55(15)

N(2)	C(2)	C(3)	C(4)	-0.1(10)	C(24)	N(6)	C(20)	C(21)	0.5(2)
C(2)	N(2)	C(6)	C(5)	1.3(8)	C(24)	C(23)	C(22)	C(21)	0.1(3)
C(2)	C(3)	C(4)	C(5)	1.3(8)	C(23)	C(22)	C(21)	C(20)	-0.1(3)
C(3)	C(4)	C(5)	C(6)	-1.2(7)	C(22)	C(21)	C(20)	N(6)	-0.1(3)
C(4)	C(5)	C(6)	N(2)	-0.1(6)	C(22)	C(21)	C(20)	C(19)	-
C(6)	N(2)	C(2)	C(1)	-180.0(7)	C(20)	N(6)	C(24)	C(23)	-0.5(3)
C(6)	N(2)	C(2)	C(3)	-1.2(10)	C(35)	N(8)	C(32)	C(019)	-2.6(3)
C(1B)	N(1)	C(7)	C(8)	111.1(5)	C(35)	N(8)	C(32)	C(31)	178.07(16)
C(1B)	N(1)	C(13)	C(14)	-164.6(8)	C(35)	C(34)	C(33)	C(019)	-1.3(3)
C(1B)	C(2B)	C(3B)	C(4B)	175.5(12)	C(33)	C(019)	C(32)	N(8)	1.0(3)
N(2B)	Mn(1)	O(1)	Mn(1)[1]	93.8(3)	C(33)	C(019)	C(32)	C(31)	-
N(2B)	C(2B)	C(3B)	C(4B)	0.4(15)	C(32)	N(8)	C(35)	C(34)	2.3(3)
C(2B)	N(2B)	C(6B)	C(5B)	3.6(13)	C(32)	C(019)	C(33)	C(34)	1.0(3)
C(2B)	C(3B)	C(4B)	C(5B)	1.0(12)	C(31)	N(5)	C(19)	C(20)	-
C(3B)	C(4B)	C(5B)	C(6B)	-0.1(10)	C(31)	N(5)	C(25)	C(26)	127.87(17)
C(4B)	C(5B)	C(6B)	N(2B)	-2.2(10)	C(30)	N(7)	C(26)	C(27)	1.3(3)
C(6B)	N(2B)	C(2B)	C(1B)	-178.0(12)	C(30)	N(7)	C(26)	C(25)	-
C(6B)	N(2B)	C(2B)	C(3B)	-2.7(16)	C(30)	C(29)	C(28)	C(27)	0.5(3)
O(2)[2]	Mn(2)	O(2)	Mn(2)[2]	-0.002(1)					

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

Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for electrochemically derived [Mn_2(μ-O)$_2$(κ^4- tpa)][PF_6]$_3$.

Atom	*x*	*y*	*z*	U(eq)
H(1A)	2565	4154	981	33
H(1B)	2853	3677	1754	33
H(3)	4104	1531	1509	44
H(4)	6224	62	1104	45
H(5)	7939	641	523	43
H(6)	7493	2611	329	37
H(1BA)	2531	4065	1086	41
H(1BB)	2789	3776	1878	41
H(3B)	3816	1579	1783	61
H(4B)	5772	-79	1452	66
H(5B)	7603	148	807	59
H(6B)	7490	2024	495	52
H(18)	5755	7196	490	41
H(15)	1381	8406	1619	48
H(7A)	3968	5545	2338	37
H(7B)	4289	4170	2412	37
H(9)	6495	4148	3015	45
H(10)	8899	3794	2847	56
H(11)	9787	3972	1755	49
H(12)	8235	4508	854	39

H(13A)	1875	6208	1810	37
H(13B)	1842	6042	1022	37
H(16)	2361	9785	1261	56
H(17)	4581	9163	702	50
H(019)	2171	13174	5736	40
H(19A)	4768	8516	5601	31
H(19B)	3850	8970	4932	31
H(29)	-1268	8922	7785	40
H(28)	802	8580	8374	49
H(27)	2751	8801	7805	49
H(25A)	2950	10330	6681	36
H(25B)	3883	8957	6623	36
H(24)	428	7383	5614	40
H(23)	1930	5409	5679	52
H(22)	4401	4876	5637	50
H(21)	5307	6356	5530	40
H(35)	-1742	12166	6038	40
H(34)	-2011	14068	6217	46
H(33)	-45	14599	6047	48
H(31A)	2922	10892	5001	33
H(31B)	3644	10983	5679	33
H(30)	-1323	9457	6635	32
H(10A)	2382	13321	7788	102
H(10B)	3226	12019	8112	102
H(10C)	1943	12945	8524	102
H(10D)	2379	13086	7832	92
H(10E)	1043	13424	8347	92
H(10F)	851	14018	7597	92

Atomic Occupancy for electrochemically derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
C(1)	0.581(3)	H(1A)	0.581(3)	H(1B)	0.581(3)
N(2)	0.581(3)	C(2)	0.581(3)	C(3)	0.581(3)
H(3)	0.581(3)	C(4)	0.581(3)	H(4)	0.581(3)
C(5)	0.581(3)	H(5)	0.581(3)	C(6)	0.581(3)
H(6)	0.581(3)	C(1B)	0.419(3)	H(1BA)	0.419(3)
H(1BB)	0.419(3)	N(2B)	0.419(3)	C(2B)	0.419(3)
C(3B)	0.419(3)	H(3B)	0.419(3)	C(4B)	0.419(3)
H(4B)	0.419(3)	C(5B)	0.419(3)	H(5B)	0.419(3)
C(6B)	0.419(3)	H(6B)	0.419(3)	P(1)	0.60(2)
F(1)	0.60(2)	F(2)	0.60(2)	F(3)	0.60(2)
F(4)	0.60(2)	F(5)	0.60(2)	F(6)	0.60(2)
P(1B)	0.40(2)	F(1B)	0.40(2)	F(2B)	0.40(2)
F(3B)	0.40(2)	F(4B)	0.40(2)	F(5B)	0.40(2)
F(6B)	0.40(2)	P(7)	0.581(3)	F(7)	0.581(3)

F(8)	0.581(3)	F(9)	0.581(3)	F(10)	0.581(3)
F(11)	0.581(3)	F(12)	0.581(3)	P(7B)	0.419(3)
F(7B)	0.419(3)	F(8B)	0.419(3)	F(13)	0.419(3)
F(14)	0.419(3)	F(15)	0.419(3)	F(16)	0.419(3)
P(13)	0.840(10)	F(17)	0.840(10)	F(18)	0.840(10)
F(19)	0.840(10)	F(1A)	0.840(10)	F(1C)	0.840(10)
F(1D)	0.840(10)	P(2)	0.160(10)	F(1E)	0.160(10)
F(1F)	0.160(10)	F(1G)	0.160(10)	F(1H)	0.160(10)
F(1I)	0.160(10)	F(1J)	0.160(10)	N(101)	0.519(14)
C(101)	0.519(14)	C(102)	0.519(14)	H(10A)	0.519(14)
H(10B)	0.519(14)	H(10C)	0.519(14)	N(102)	0.481(14)
C(103)	0.481(14)	C(104)	0.481(14)	H(10D)	0.481(14)
H(10E)	0.481(14)	H(10F)	0.481(14)		

Experimental

Single crystals of $C_{38}H_{39}N_9O_2F_{18}P_3Mn_2$ $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}\ tpa)][PF_6]_3$were obtained by recrystallization in $EtOH/H_2O$. A suitable crystal was selected and measured on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 99.99 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the XL [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. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of electrochemically derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}\ tpa)][PF_6]_3$

Crystal Data for $C_{38}H_{39}N_9O_2F_{18}P_3Mn_2$ (M =1198.57 g/mol): triclinic, space group P-1 (no. 2), a = 10.2106(15) Å, b = 12.3868(19) Å, c = 19.944(3) Å, α = 85.445(7)°, β = 86.987(7)°, γ = 66.838(7)°, V = 2311.2(6) $Å^3$, Z = 2, T = 99.99 K, μ(MoKα) = 0.770 mm^{-1}, *Dcalc* = 1.722 g/cm^3, 82416 reflections measured (2.048° ≤ 2Θ ≤ 61.474°), 14279 unique (R_{int} = 0.0395, R_{sigma} = 0.0336) which were used in all calculations. The final R_1 was 0.0414 (I > 2σ(I)) and wR_2 was 0.1121 (all data).

Refinement model description

Number of restraints - 782, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2. Restrained distances
 N1-C1 ≈ N1-C1B
 with sigma of 0.02
3. Uiso/Uaniso restraints and constraints
N1 ≈ C1B ≈ N2B ≈ C2B ≈ C3B ≈ C4B ≈ C5B ≈ C6B ≈
C1 ≈ N2 ≈ C2 ≈ C3 ≈ C4 ≈ C5 ≈ C6: within 2A with sigma
of 0.03 and sigma for terminal atoms of 0.06
4. Rigid body (RIGU) restrains
 N1, C1B, N2B, C2B, C3B, C4B, C5B, C6B, C1, N2, C2, C3, C4, C5, C6
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 P1, F1, F2, F3, F4, F5, F6, P1B, F1B, F2B, F3B, F4B, F5B, F6B, P7, F7, F8, F9,
  F10, F11, F12, P7B, F7B, F8B, F13, F14, F15, F16, P13, F17, F18, F19, F1A,
 F1C, F1D, P2, F1E, F1F, F1G, F1H, F1I, F1J
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 N101, C101, C102, N102, C103, C104
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
5. Same fragment restrains
{C1, N2, C2, C3, C4, C5, C6} sigma for 1-2: 0.02, 1-3: 0.04
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as
{C1B, N2B, C2B, C3B, C4B, C5B, C6B}
{P1, F1, F2, F3, F4, F5, F6} sigma for 1-2: 0.01, 1-3: 0.04
as
{P1B, F1B, F2B, F3B, F4B, F5B, F6B}
{P7, F7, F8, F9, F10, F11, F12} sigma for 1-2: 0.01, 1-3: 0.04
as
{P7B, F7B, F8B, F13, F14, F15, F16}
{N101, C101, C102} sigma for 1-2: 0.01, 1-3: 0.04
as
{N102, C103, C104}
6. Others
 1*[Sof(C1)+Sof(H1A)+Sof(H1B)+Sof(N2)+Sof(C2)+Sof(C3)+Sof(H3)+Sof(C4)+Sof(H4)+
 Sof(C5)+Sof(H5)+Sof(C6)+Sof(H6)+Sof(C1B)+Sof(H1BA)+Sof(H1BB)+Sof(N2B)+Sof(C2B)+
 Sof(C3B)+Sof(H3B)+Sof(C4B)+Sof(H4B)+Sof(C5B)+Sof(H5B)+Sof(C6B)+Sof(H6B)+
 Sof(P7)+Sof(F7)+Sof(F8)+Sof(F9)+Sof(F10)+Sof(F11)+Sof(F12)]+1*[Sof(P7B)+
 Sof(F7B)+Sof(F8B)+Sof(F13)+Sof(F14)+Sof(F15)+Sof(F16)]=1 with esd of 0.0001
 Sof(C1B)=Sof(H1BA)=Sof(H1BB)=Sof(N2B)=Sof(C2B)=Sof(C3B)=Sof(H3B)=Sof(C4B)=
 Sof(H4B)=Sof(C5B)=Sof(H5B)=Sof(C6B)=Sof(H6B)=1-FVAR(1)
 Sof(C1)=Sof(H1A)=Sof(H1B)=Sof(N2)=Sof(C2)=Sof(C3)=Sof(H3)=Sof(C4)=Sof(H4)=
 Sof(C5)=Sof(H5)=Sof(C6)=Sof(H6)=Sof(P7)=Sof(F7)=Sof(F8)=Sof(F9)=Sof(F10)=
 Sof(F11)=Sof(F12)=FVAR(1)
 Sof(P7B)=Sof(F7B)=Sof(F8B)=Sof(F13)=Sof(F14)=Sof(F15)=Sof(F16)=FVAR(2)
 Sof(N102)=Sof(C103)=Sof(C104)=Sof(H10D)=Sof(H10E)=Sof(H10F)=1-FVAR(3)
 Sof(N101)=Sof(C101)=Sof(C102)=Sof(H10A)=Sof(H10B)=Sof(H10C)=FVAR(3)
 Sof(P1B)=Sof(F1B)=Sof(F2B)=Sof(F3B)=Sof(F4B)=Sof(F5B)=Sof(F6B)=1-FVAR(4)
 Sof(P1)=Sof(F1)=Sof(F2)=Sof(F3)=Sof(F4)=Sof(F5)=Sof(F6)=FVAR(4)
 Sof(P2)=Sof(F1E)=Sof(F1F)=Sof(F1G)=Sof(F1H)=Sof(F1I)=Sof(F1J)=1-FVAR(5)
 Sof(P13)=Sof(F17)=Sof(F18)=Sof(F19)=Sof(F1A)=Sof(F1C)=Sof(F1D)=FVAR(5)
7.a Secondary CH2 refined with riding coordinates:
 C1(H1A,H1B), C1B(H1BA,H1BB), C7(H7A,H7B), C13(H13A,H13B), C19(H19A,H19B),
 C25(H25A,H25B), C31(H31A,H31B)
7.b Aromatic/amide H refined with riding coordinates:
 C3(H3), C4(H4), C5(H5), C6(H6), C3B(H3B), C4B(H4B), C5B(H5B), C6B(H6B),
 C18(H18), C15(H15), C9(H9), C10(H10), C11(H11), C12(H12), C16(H16), C17(H17),
 C019(H019), C29(H29), C28(H28), C27(H27), C24(H24), C23(H23), C22(H22),
 C21(H21), C35(H35), C34(H34), C33(H33), C30(H30)
7.c Idealised Me refined as rotating group:
 C102(H10A,H10B,H10C), C104(H10D,H10E,H10F)
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This report has been created with Olex2, compiled on 2016.02.19 svn.r3266 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Table S6. Comparison of the Mn-Ligand bond lengths of the two obtained structures of $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)]$ and literature data.

Literature (Towle et al.) $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][S_2O_6]_{1.5}$		UV irradiation derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$		Electrochemically derived $[Mn_2(\mu\text{-}O)_2(\kappa^4\text{-}tpa)][PF_6]_3$	
	Mn1		Mn2A		Mn1
Mn2	2.643	Mn1A	2.630	Mn1’	2.625
O1	1.835	O1A	1.844	O1	1.799
O2	1.839	O2A	1.833	O1’	1.821
N1	2.114	N5A	2.115	N1	2.085
N2	2.207	N6A	2.203	N2	1.936
N3	2.044	N7A	2.052	N3	2.044
N4	2.259	N8A	2.210	N4	2.102
	Mn2		Mn1A		Mn1’
Mn1	2.643	Mn2A	2.630	Mn1	2.625
O1	1.782	O1A	1.772	O1’	1.799
O2	1.771	O2A	1.792	O1	1.821
N5	2.081	N1A	2.068	N1’	2.085
N6	2.014	N2A	2.033	N2’	1.936
N7	2.027	N3A	2.034	N3’	2.044
N8	2.011	N4A	2.019	N4’	2.102