Electronic Supporting Information

An influence of fluorinated alkyl substituents on structure and magnetic properties of Mn(II) complexes with pyrazolyl–substituted nitronyl nitroxides

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Table of Contents:

Section S1. Additional data of X-ray diffraction analysis

Here it is worth mentioning the compound whose structure deserves a discussion as well. In one of the experiments, co–crystals of $[Mn(hfac)_2(NN–Pz–CH_2CHF_2)]_n$ with $[Mn(hfac)_2(NN–Pz–CH_2CHF_2)H_2O]$ were isolated and successfully characterised by the single–crystal X–ray analysis. Figure S1 shows that the structure of the complex is formed by packing of chains with geometry similar to that in $[Mn(hfac)_2(NN–Pz–CH_2CHF_2)]_n$ and molecular complexes $[Mn(hfac)_2(NN–Pz–CH_2CHF_2)H_2O]$ containing a coordinated water molecule. It is noteworthy here that in $[Mn(hfac)_2(NN–Pz–CH_2CHF_2)H_2O]$, the paramagnetic ligand is coordinated by the oxygen atom of the nitroxide group, consistently with the oxophilic nature of the manganese ion.

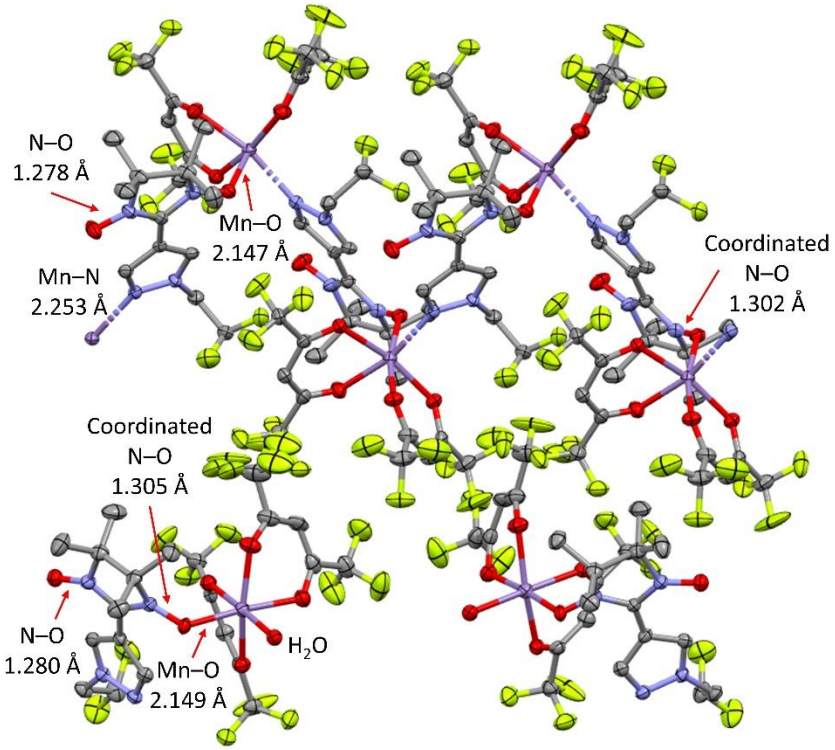

Figure S1. ORTEP drawings of a fragment of structure in co–crystal $[Mn(hfac)_2(NN–Pz–CH_2CHF_2)]_n \cdot n[Mn(hfac)_2(NN–Pz–CH_2CHF_2)H_2O]$.

Single–crystal X–ray analyses of $[Mn(hfac)_2(NN–Pz–CH_2CHF_2)]_n \cdot n[Mn(hfac)_2(NN–Pz–CH_2CHF_2)H_2O]$) were carried out at the Center for Molecular Composition Studies of INEOS RAS on a Bruker D8 Quest diffractometer with the APEX3 software.[1] The data were then integrated with SAINT. SADABS was used for scaling, empirical absorption corrections and the generation of data files for structure solution and refinement.

The structures were solved by a dual–space algorithm and refined in anisotropic approximation for non–hydrogen atoms against $F^2(hkl)$. Hydrogen atoms of methyl, methylene

and aromatic moieties were calculated according to that idealised geometry and refined with constraints applied to corresponding bond lengths and equivalent displacement parameters. All structures were solved with the ShelXT[2] software and refined in ShelXL.[3] Molecular graphics were drawn using OLEX2.[4]

CCDC 2239234 contains the supplementary crystallographic data for $[Mn(hfac)_2(NN–Pz–CH_2CHF_2)]_n \cdot n[Mn(hfac)_2(NN–Pz–CH_2CHF_2)H_2O]$. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.

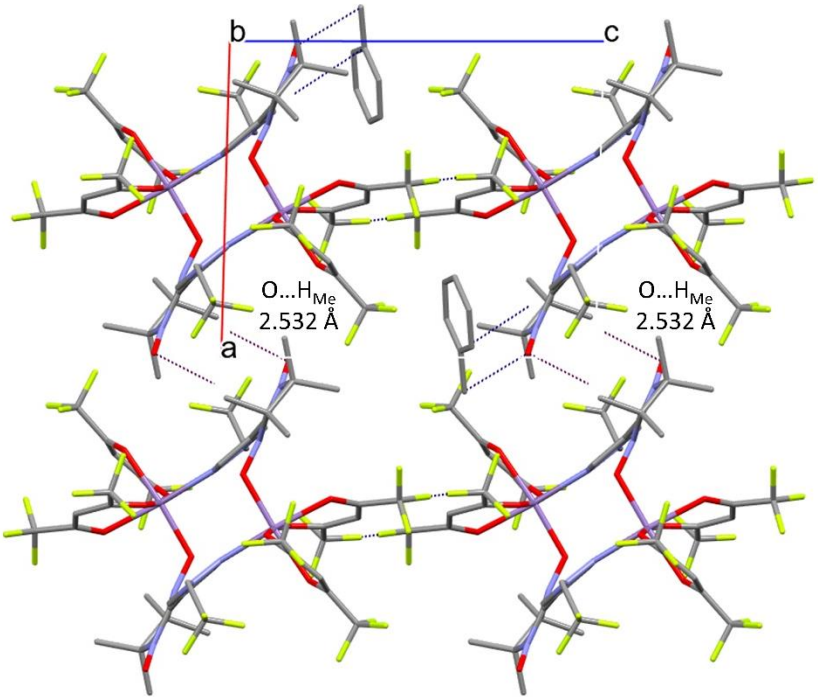

Figure S2. The packing diagram for $[Mn(hfac)_2(NN–Pz–CH_2CF_3)]_2 \cdot 2C_7H_8$ (hydrogen atoms are not shown).

Table S1. Selected geometric parameters and experimental J_1 values in the $[Mn(hfac)_2(NN–Pz–CH_2CF_3)]_2$ dimer and cousin dimeric complexes of $Mn(hfac)_2$ with nitronyl nitroxides.

Dimeric complex	d(Mn–O), Å	∠Mn–O–N, °	J_1 value,[a] cm^{-1}	Ref.
$[Mn(hfac)_2(NITpPy)]_2$	2.129(4)	123	–73	5
$[Mn(hfac)_2(NIT–thien–3–Py)]_2$	2.156(3)	131	–74	6
$[Mn(hfac)_2(QNXL–2NIT)]_2$	2.134(4)	125	–77	7
$[Mn(hfac)_2(NIT–Ph–m–OCH_2trz)]_2$	2.068–2.083[b]	123–127	–77	8
$[Mn(hfac)_2(NN–Pz–CH_2CF_3)]_2$	2.110(1)	124	–87	This work
$[Mn(hfac)_2(4–NITPhPyrim)]_2$	2.148(5)	133	–88	9
$[Mn(hfac)_2(NIT–3–Py)]_2$	2.115(4), 2.149(4)[b]	123, 121	–97	10
$[Mn(hfac)_2(NITPhIm)]_2$	2.124(3)	125	–100	11
$[Mn(hfac)_2(NIT–5–Pyrim)]_2$	2.130(2)	125	–103	10
$[Mn(hfac)_2(p–PONIT)]_2$	2.142(3)	127	–109	12
$[Mn(hfac)_2(NIT–3PyPh)]_2$	2.151(4)	123	–208	13
$[Mn(hfac)_2(4–QNNN)]_2$	2.132(1)	129	n.d.	14

[a] The spin Hamiltonian is defined as $H = –2J_1S_{Mn}\cdot S_R$. [b] Two independent molecules.

Table S2. Selected bond distances in $[Mn(hfac)_2(NN–Pz–CHF_2)]_n$ (Å).

Bond	Distance	Bond	Distance	Bond	Distance
Mn(1)–O(2)#1	2.1428(11)	F(1)–C(4)	1.332(2)	F(8)–C(16)	1.326(3)
Mn(1)–O(2)	2.1427(11)	F(2)–C(4)	1.324(2)	C(17A)–F(9A)	1.318(4)
Mn(1)–O(3)#1	2.1420(12)	C(12A)–F(3A)	1.348(4)	C(17A)–F(10A)	1.322(4)
Mn(1)–O(3)	2.1420(12)	C(12A)–F(4A)	1.313(4)	C(17A)–F(11A)	1.333(4)
Mn(1)–O(4)	2.1363(12)	C(12A)–F(5A)	1.330(3)	C(17A)–C(18)	1.535(4)
Mn(1)–O(4)#1	2.1362(12)	C(12A)–C(13)	1.548(3)	C(17B)–F(9B)	1.319(2)
Mn(2)–O(5)#2	2.1321(11)	C(12B)–F(3B)	1.348(4)	C(17B)–F(10B)	1.323(3)
Mn(2)–O(5)	2.1322(11)	C(12B)–F(4B)	1.313(4)	C(17B)–F(11B)	1.334(3)
Mn(2)–O(6)	2.1378(11)	C(12B)–F(5B)	1.330(3)	C(17B)–C(18)	1.536(2)
Mn(2)–O(6)#2	2.1378(11)	C(12B)–C(13)	1.547(3)	F(12)–C(21)	1.336(2)
Mn(2)–N(2)	2.2966(13)	F(6)–C(16)	1.335(3)	F(13)–C(21)	1.334(2)
Mn(2)–N(2)#2	2.2966(13)	F(7)–C(16)	1.332(2)	F(14)–C(21)	1.326(2)
O(1)–N(3)	1.2730(18)	N(1)–C(3)	1.345(2)	C(1)–C(2)	1.418(2)
O(2)–N(4)	1.3027(17)	N(1)–C(4)	1.439(2)	C(2)–C(3)	1.380(2)
O(3)–C(13)	1.247(2)	N(2)–C(1)	1.325(2)	C(2)–C(5)	1.439(2)
O(4)–C(15)	1.255(2)	N(3)–C(5)	1.356(2)	C(6)–C(7)	1.519(2)
O(5)–C(18)	1.259(2)	N(3)–C(6)	1.504(2)	C(6)–C(8)	1.530(2)
O(6)–C(20)	1.250(2)	N(4)–C(5)	1.336(2)	C(6)–C(9)	1.554(2)
N(1)–N(2)	1.3694(18)	N(4)–C(9)	1.5027(19)	C(9)–C(10)	1.532(2)
C(9)–C(11)	1.522(2)	C(14)–C(15)	1.387(3)	C(18)–C(19)	1.388(2)
C(13)–C(14)	1.397(3)	C(15)–C(16)	1.537(3)	C(19)–C(20)	1.397(2)
C(20)–C(21)	1.539(2)				

Table S3. Selected bond distances in $[Mn(hfac)_2(NN–Pz–CH_2CH_2F)]_n$ (Å).

Bond	Distance	Bond	Distance	Bond	Distance
Mn(1)–O(1)	2.145(2)	O(6)–C(21)	1.254(4)	C(20)–C(21)	1.386(5)
Mn(1)–O(3)	2.130(2)	N(1)–C(1)	1.324(4)	C(21)–C(22)	1.524(5)
Mn(1)–O(4)	2.176(2)	N(1)–C(2)	1.501(3)	C(4)–C(6)	1.408(4)
Mn(1)–O(5)	2.144(2)	N(2)–C(1)	1.354(4)	C(11)–C(12)	1.498(5)
Mn(1)–O(6)	2.173(2)	N(2)–C(3)	1.506(4)	C(13)–C(14)	1.532(5)
Mn(1)–N(3)#1	2.236(2)	N(3)–N(4)	1.365(3)	C(14)–C(15)	1.390(5)
F(1)–C(12)	1.400(4)	N(3)–C(6)	1.331(4)	C(15)–C(16)	1.384(5)
F(2)–C(13)	1.335(5)	N(4)–C(5)	1.345(4)	C(16)–C(17)	1.539(4)
F(3)–C(13)	1.327(5)	N(4)–C(11)	1.457(4)	C(18)–C(19)	1.530(4)
F(4)–C(13)	1.327(4)	C(1)–C(4)	1.439(4)	C(19)–C(20)	1.380(5)
F(5)–C(17)	1.333(4)	C(2)–C(3)	1.558(4)	F(11)–C(22)	1.327(5)
F(6)–C(17)	1.327(4)	C(2)–C(7)	1.515(4)	F(12)–C(22)	1.355(6)
F(7)–C(17)	1.313(4)	C(2)–C(8)	1.535(5)	F(13)–C(22)	1.339(6)
F(8)–C(18)	1.320(4)	C(3)–C(9)	1.524(5)	O(1)–N(1)	1.305(3)
F(9)–C(18)	1.333(5)	C(3)–C(10)	1.522(4)	O(2)–N(2)	1.278(3)
F(10)–C(18)	1.316(5)	C(4)–C(5)	1.391(4)	O(3)–C(14)	1.256(4)
O(4)–C(16)	1.256(3)	O(5)–C(19)	1.259(3)		

Table S4. Selected bond distances in $[Mn(hfac)_2(NN–Pz–CH_2CHF_2)]_n$ (Å).

Bond	Distance	Bond	Distance	Bond	Distance
Mn(1)—O(1)	2.1467 (18)	O(1)—N(1)	1.310 (3)	C(2)—C(3)	1.551 (4)
Mn(1)—O(3)	2.1606 (19)	O(2)—N(2)	1.277 (3)	C(2)—C(7)	1.532 (4)
Mn(1)—O(4)	2.1392 (19)	O(3)—C(13)	1.249 (3)	C(2)—C(8)	1.513 (4)
Mn(1)—O(5)	2.126 (2)	O(4)—C(15)	1.262 (3)	C(3)—C(9)	1.521 (4)
Mn(1)—O(6)	2.1780 (19)	O(5)—C(20)	1.251 (3)	C(3)—C(10)	1.528 (4)
Mn(1)—N(4)^{i}	2.248 (2)	O(6)—C(18)	1.258 (3)	C(4)—C(5)	1.388 (4)
F(1)—C(12)	1.363 (3)	N(1)—C(1)	1.329 (3)	C(4)—C(6)	1.396 (4)
F(2)—C(12)	1.370 (3)	N(1)—C(2)	1.495 (3)	C(11)—C(12)	1.499 (4)
F(3)—C(16)	1.328 (4)	N(2)—C(1)	1.355 (3)	C(13)—C(14)	1.398 (4)
F(4)—C(16)	1.348 (4)	N(2)—C(3)	1.509 (4)	C(13)—C(16)	1.538 (4)
F(5)—C(16)	1.327 (3)	N(3)—N(4)	1.359 (3)	C(14)—C(15)	1.378 (4)
F(6)—C(17)	1.310 (3)	N(3)—C(5)	1.334 (3)	C(15)—C(17)	1.528 (4)
F(7)—C(17)	1.335 (4)	N(3)—C(11)	1.459 (3)	C(18)—C(19)	1.381 (4)
F(8)—C(17)	1.328 (4)	N(4)—Mn(1)^{ii}	2.248 (2)	C(18)—C(22)	1.531 (4)
F(9)—C(21)	1.328 (4)	N(4)—C(6)	1.326 (3)	C(19)—C(20)	1.394 (4)
F(10)—C(21)	1.334 (4)	C(1)—C(4)	1.438 (4)	C(20)—C(21)	1.534 (4)
F(11)—C(21)	1.313 (4)				
F(12)—C(22)	1.332 (3)				
F(13)—C(22)	1.336 (3)				
F(14)—C(22)	1.327 (3)				

Symmetry codes: (i) $-x+1, y+1/2, -z+3/2$; (ii) $-x+1, y-1/2, -z+3/2$.

Table S5. Selected bond distances in $[Mn(hfac)_2(NN–Pz–CH_2CHF_2)]_n \cdot nC_7H_8$ (Å).

Bond	Distance	Bond	Distance	Bond	Distance
Mn(1)–O(1)	2.138(3)	C(24)–F(12A)	1.326(3)	C(11B)–C(12B)	1.503(8)
Mn(1)–O(3)	2.138(3)	C(24)–F(13A)	1.325(3)	F(1B)–C(12B)	1.382(8)
Mn(1)–O(4)	2.169(2)	C(24)–F(11B)	1.326(4)	C(12B)–F(14B)	1.281(9)
Mn(1)–O(5)	2.126(2)	C(24)–F(12B)	1.326(4)	C(16)–C(17)	1.380(5)
Mn(1)–O(6)	2.157(3)	C(24)–F(13B)	1.326(4)	C(17)–C(18)	1.391(5)
Mn(1)–N(4)#1	2.244(3)	C(24)–F(11C)	1.326(4)	C(21)–C(22)	1.392(6)
F(2A)–C(15A)	1.337(3)	C(24)–F(12C)	1.326(4)	C(22)–C(23)	1.390(6)
F(3A)–C(15A)	1.337(3)	C(24)–F(13C)	1.326(4)	C(25A)–C(26A)	1.378(3)
F(4A)–C(15A)	1.337(3)	C(24)–C(23)	1.539(7)	C(25A)–C(30A)	1.377(3)
C(15A)–C(16)	1.544(12)	O(1)–N(1)	1.309(4)	C(25A)–C(31A)	1.483(10)
F(2B)–C(15B)	1.337(4)	O(2)–N(2)	1.274(4)	C(26A)–C(27A)	1.379(3)
F(3B)–C(15B)	1.337(4)	O(3)–C(16)	1.260(5)	C(27A)–C(28A)	1.377(3)
F(4B)–C(15B)	1.337(4)	O(4)–C(18)	1.252(5)	C(28A)–C(29A)	1.377(3)
C(15B)–C(16)	1.55(2)	O(5)–C(21)	1.248(5)	C(29A)–C(30A)	1.378(3)
F(5A)–C(19A)	1.313(3)	O(6)–C(23)	1.242(5)	C(25B)–C(26B)	1.378(4)
F(6A)–C(19A)	1.314(3)	N(1)–C(1)	1.331(4)	C(25B)–C(30B)	1.379(4)
F(7A)–C(19A)	1.318(3)	N(1)–C(2)	1.493(4)	C(25B)–C(31B)	1.484(10)
C(19A)–C(18)	1.538(5)	N(2)–C(1)	1.355(5)	C(26B)–C(27B)	1.378(4)
F(5B)–C(19B)	1.314(4)	N(2)–C(3)	1.497(5)	C(27B)–C(28B)	1.378(4)
F(6B)–C(19B)	1.315(4)	N(3)–N(4)	1.366(4)	C(28B)–C(29B)	1.378(4)
F(7B)–C(19B)	1.315(4)	N(3)–C(10)	1.341(4)	C(29B)–C(30B)	1.378(4)
C(19B)–C(18)	1.538(6)	N(3)–C(11A)	1.455(5)		
C(20A)–F(8A)	1.343(3)	N(3)–C(11B)	1.455(5)		
C(20A)–F(9A)	1.343(3)	N(4)–C(9)	1.325(4)		
C(20A)–F(10A)	1.343(3)	C(1)–C(8)	1.431(5)		
C(20A)–C(21)	1.529(6)	C(2)–C(3)	1.552(6)		
C(20B)–F(8B)	1.340(4)	C(2)–C(4)	1.521(5)		
C(20B)–F(9B)	1.340(4)	C(2)–C(5)	1.522(6)		
C(20B)–F(10B)	1.340(4)	C(3)–C(6)	1.531(7)		
C(20B)–C(21)	1.526(6)	C(3)–C(7)	1.516(7)		
C(20C)–F(8C)	1.343(4)	C(8)–C(9)	1.414(5)		
C(20C)–F(9C)	1.343(4)	C(8)–C(10)	1.394(5)		
C(20C)–F(10C)	1.343(4)	C(11A)–C(12A)	1.503(8)		
C(20C)–C(21)	1.529(6)	F(1A)–C(12A)	1.382(8)		
C(24)–F(11A)	1.326(3)	C(12A)–F(14A)	1.283(8)		

Table S6. Selected bond distances in $[Mn(hfac)_2(NN–Pz–CH_2CF_3)]_2 \cdot 2C_7H_8$ (Å).

Bond	Distance	Bond	Distance	Bond	Distance
Mn(1)–O(2)	2.1101(14)	O(5)–C(19)	1.248(3)	C(4)–C(3)	1.4328(16)
Mn(1)–O(3)	2.1534(14)	O(6)–C(21)	1.260(3)	C(24)–C(23)	1.4331(16)
Mn(1)–O(4)	2.1776(15)	N(1)–C(1)	1.345(3)	C(1)–C(5)	1.4866(16)
Mn(1)–O(5)	2.1769(15)	N(1)–C(2)	1.507(3)	C(2)–C(3)	1.3707(17)
Mn(1)–O(6)	2.1327(14)	N(2)–C(1)	1.336(3)	C(3)–C(12)	1.5150(15)
Mn(1)–N(4)#1	2.2779(18)	N(2)–C(3)	1.502(2)	C(23)–C(32)	1.5108(15)
F(1)–C(12)	1.336(3)	N(3)–N(4)	1.372(2)	C(21)–C(25)	1.4861(15)
F(2)–C(12)	1.337(2)	N(3)–C(9)	1.343(3)	C(15)–C(14)	1.5147(16)
F(3)–C(12)	1.332(3)	N(3)–C(11)	1.451(2)	C(15)–C(16)	1.3892(18)
F(4)–C(13)	1.319(3)	N(4)–C(10)	1.331(3)	C(15)–C(20)	1.3918(17)
F(5)–C(13)	1.328(3)	C(1)–C(8)	1.443(3)	C(32)–C(33)	1.4957(16)
F(6)–C(13)	1.328(3)	C(2)–C(3)	1.563(3)	C(5)–C(10)	1.3924(18)
F(7A)–C(17A)	1.334(5)	C(2)–C(4)	1.522(3)	C(23B)–C(29B)	1.507(7)
F(8A)–C(17A)	1.311(5)	C(2)–C(5)	1.522(4)	C(24B)–C(25B)	1.384(3)
F(9A)–C(17A)	1.332(5)	C(3)–C(6)	1.532(3)	C(25B)–C(26B)	1.385(3)
C(17A)–C(16)	1.541(4)	C(3)–C(7)	1.519(3)	C(26B)–C(27B)	1.386(3)
F(7B)–C(17B)	1.341(6)	C(8)–C(9)	1.390(3)	C(27B)–C(28B)	1.386(3)
F(8B)–C(17B)	1.319(6)	C(8)–C(10)	1.399(3)	C(25A)–C(26A)	1.383(3)
F(9B)–C(17B)	1.339(5)	C(11)–C(12)	1.510(3)	C(26A)–C(27A)	1.383(3)
C(17B)–C(16)	1.549(4)	C(13)–C(14)	1.537(3)	C(27A)–C(28A)	1.384(3)
F(7C)–C(17C)	1.334(6)	C(14)–C(15)	1.388(3)	C(23B)–C(24B)	1.384(3)
F(8C)–C(17C)	1.312(6)	C(15)–C(16)	1.399(3)	C(23B)–C(28B)	1.386(3)
F(9C)–C(17C)	1.332(5)	C(19)–C(20)	1.401(3)	F(13)–C(22)	1.333(3)
C(17C)–C(16)	1.542(4)	C(20)–C(21)	1.388(3)	F(14)–C(22)	1.328(3)
F(10A)–C(18A)	1.324(4)	C(21)–C(22)	1.537(3)	F(15)–C(22)	1.326(3)
F(11A)–C(18A)	1.336(4)	C(23A)–C(24A)	1.388(3)	O(1)–N(1)	1.272(3)
F(12A)–C(18A)	1.335(4)	C(23A)–C(28A)	1.385(3)	O(2)–N(2)	1.304(2)
C(18A)–C(19)	1.543(3)	C(23A)–C(29A)	1.510(6)	O(3)–C(14)	1.247(3)
F(10B)–C(18B)	1.330(5)	C(24A)–C(25A)	1.384(3)	O(4)–C(16)	1.245(3)
F(11B)–C(18B)	1.340(5)	F(12B)–C(18B)	1.339(4)	C(18B)–C(19)	1.550(4)

Section S2. Powder X-ray Diffraction Data

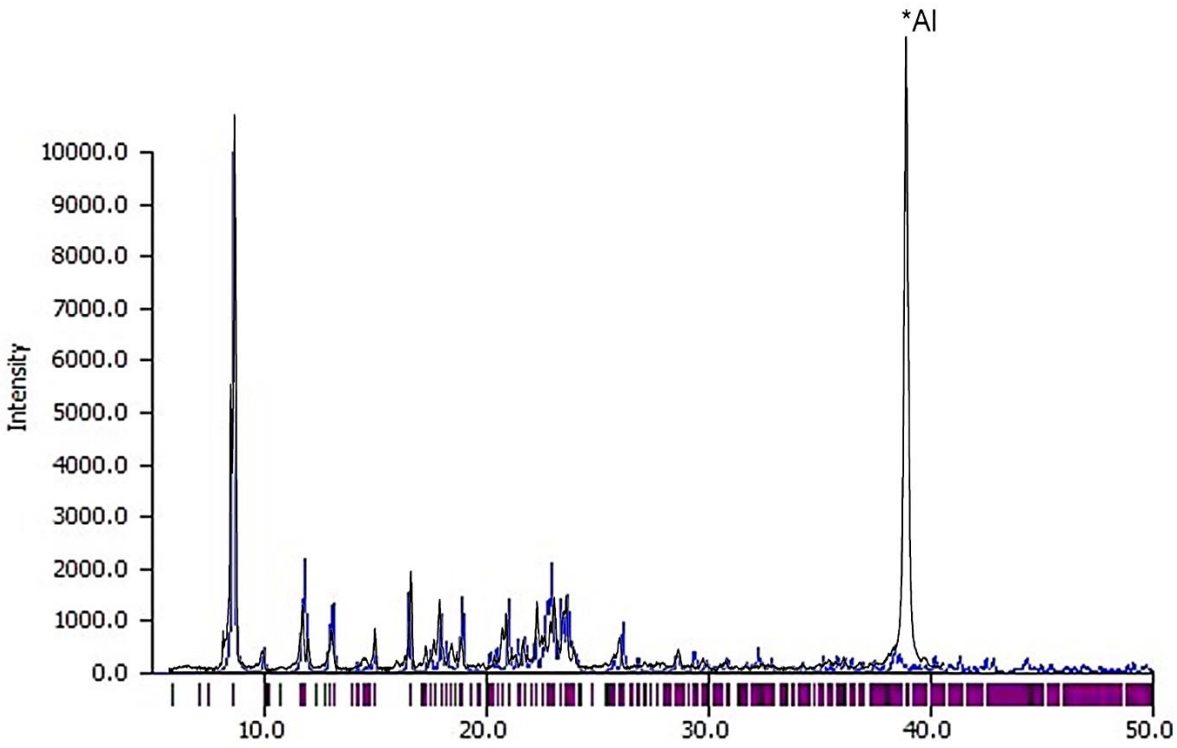

Figure S3. Experimental (black) and calculated (blue) powder X-ray diffraction pattern of $[Mn(hfac)_2(NN\text{-}Pz\text{-}CHF_2)]_n$.

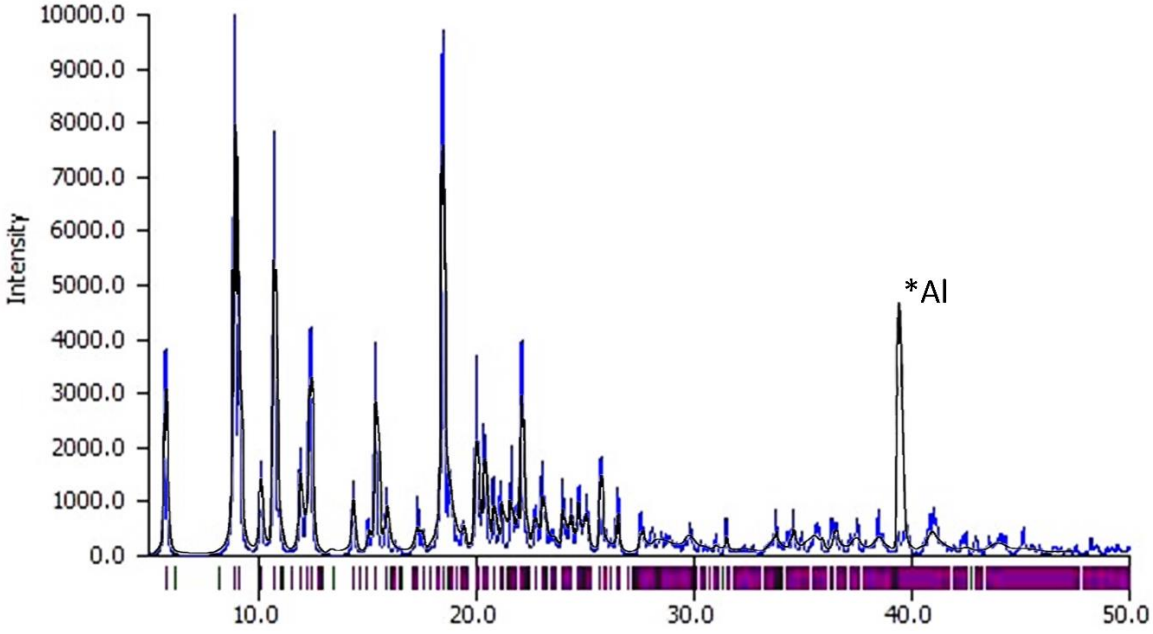

Figure S4. Experimental (black) and calculated (blue) powder X-ray diffraction pattern of $[Mn(hfac)_2(NN\text{-}Pz\text{-}CH_2CH_2F)]_n$.

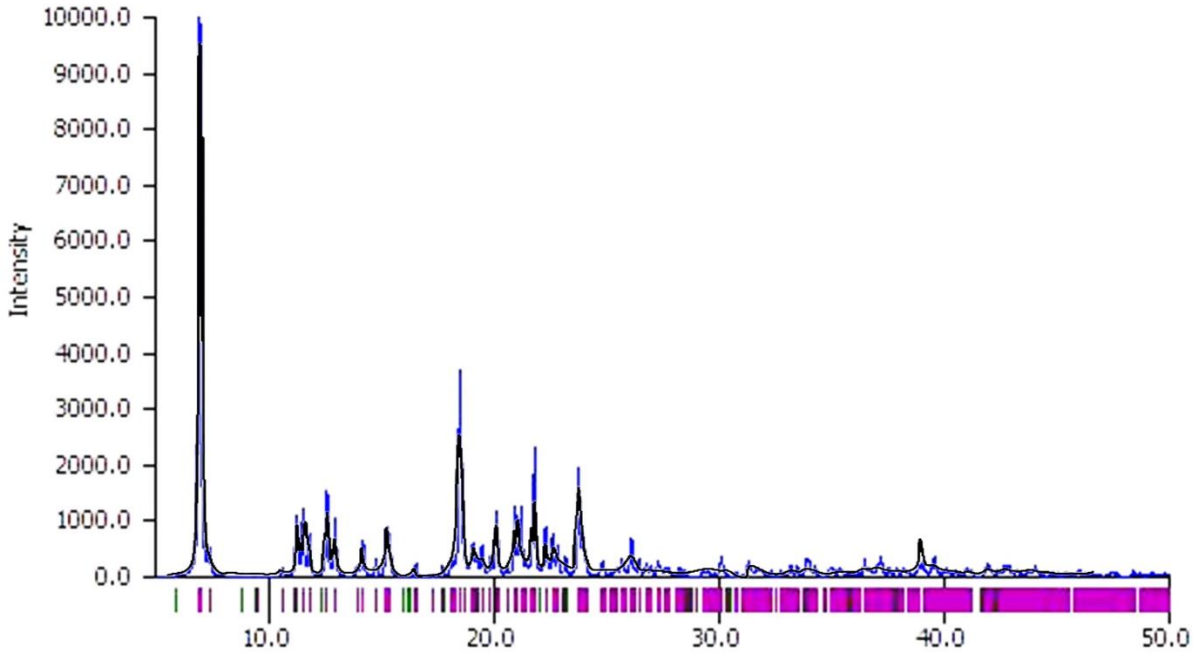

Figure S5. Experimental (black) and calculated (blue) powder X-ray diffraction pattern of $[Mn(hfac)_2(NN\text{-}Pz\text{-}CH_2CHF_2)]_n \cdot nC_7H_8$.

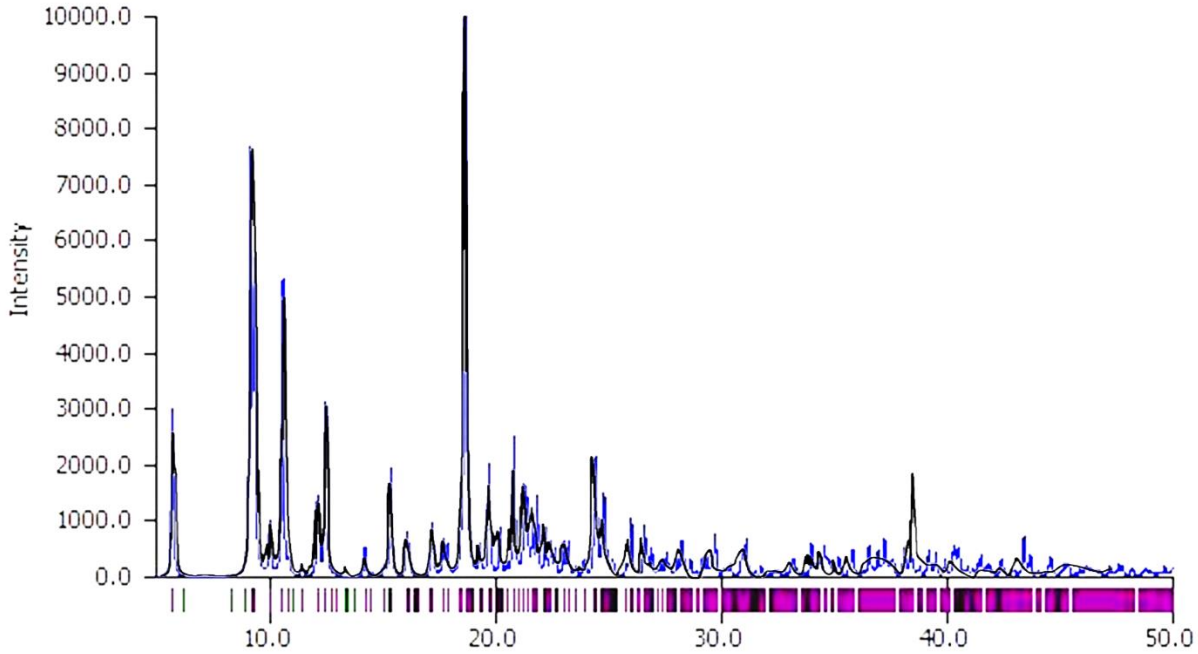

Figure S6. Experimental (black) and calculated (blue) powder X-ray diffraction pattern of $[Mn(hfac)_2(NN\text{-}Pz\text{-}CH_2CHF_2)]_n$.

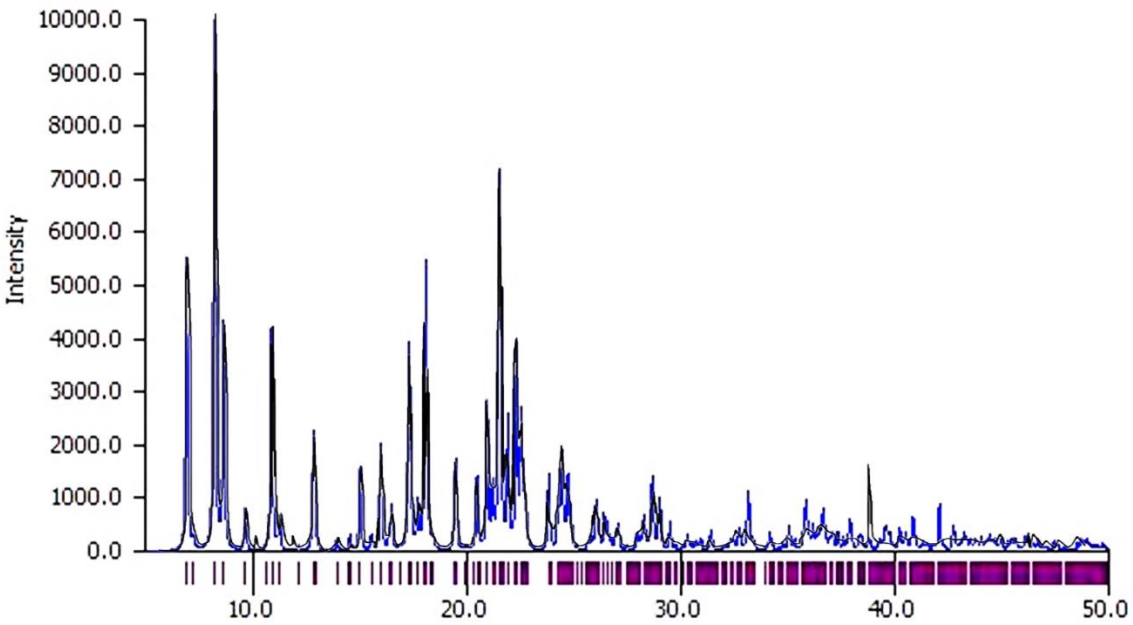

Figure S7. Experimental (black) and calculated (blue) powder X-ray diffraction pattern of $[Mn(hfac)_2(NN\text{-}Pz\text{-}CH_2CF_3)]_2 \cdot 2C_7H_8$.

Table S7. XRD data on the manganese–nitroxide complexes.

Compound	$[Mn(hfac)_2(NN\text{-}Pz\text{-}CHF_2)]_n$	$[Mn(hfac)_2(NN\text{-}Pz\text{-}CH_2CH_2F)]_n$	$[Mn(hfac)_2(NN\text{-}Pz\text{-}CH_2CHF_2)]_n \cdot nC_7H_8$	$[Mn(hfac)_2(NN\text{-}Pz\text{-}CH_2CHF_2)]_n$	$[Mn(hfac)_2(NN\text{-}Pz\text{-}CH_2CF_3)]_2 \cdot 2C_7H_8$
Empirical formula	$C_{21}H_{17}F_{14}MnN_4O_6$	$C_{22}H_{20}F_{13}MnN_4O_6$	$C_{29}H_{27}F_{14}MnN_4O_6$	$C_{22}H_{19}F_{14}MnN_4O_6$	$C_{58}H_{52}F_{30}Mn_2N_8O_{12}$
Formula weight	742.33	738.36	848.48	756.35	1732.95
Temperature, K	100.0(1)	100.0(1)	99.9(3)	100.0(1)	99.9(3)
Wavelength, Å	1.54184	1.54184	1.54184	0.71073	1.54184
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	I2/a	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions					
a, Å	26.0180(2)	16.0023(4)	14.9623(2)	16.0909(8)	11.01880(10)
b, Å	9.42480(10)	9.7163(2)	9.98830(10)	9.9125(4)	12.9099(2)
c, Å	24.7301(2)	20.6248(5)	23.8702(4)	20.0481(9)	13.1514(2)
α, °	90	90	90	90	75.0990(10)
β, °	107.3830(10)	106.565(3)	90.182(2)	106.374(3)	88.1200(10)
γ, °	90	90	90	90	76.9370(10)
Volume, $Å^3$	5787.22(9)	3073.72(13)	3567.33(8)	3068.0(2)	1760.47(4)
Z	8	4	4	4	1
Density (calcd.), $g \cdot cm^{-3}$	1.704	1.596	1.580	1.637	1.635
Abs. coefficient, mm^{-1}	4.975	4.630	4.117	0.558	4.227
F(000)	2960	1480	1712	1512	872
Crystal size, mm	0.70×0.11×0.07	0.05×0.03×0.02	0.35×0.07×0.06	0.23×0.31×0.39	0.32×0.30×0.20
Θ range, °	3.560 – 77.806	2.881 – 78.229	3.491 – 77.822	2.118 – 27.878	3.479 – 77.303
Index ranges	$-32 \le h \le 31$, $-11 \le k \le 11$, $-30 \le l \le 31$	$-20 \le h \le 19$, $-12 \le k \le 11$, $-25 \le l \le 26$	$-18 \le h \le 18$, $-10 \le k \le 12$, $-30 \le l \le 29$	$-17 \le h \le 21$, $-13 \le k \le 12$, $-26 \le l \le 22$	$-13 \le h \le 13$, $-16 \le k \le 16$, $-16 \le l \le 16$
Reflections					
collected	40209	40300	25876	30917	85727
independent [R_{int}]	6100 [0.0338]	6516 [0.0766]	7243 [0.0507]	7313 [0.0908]	7377 [0.0968]
observed with $I > 2\sigma(I)$	5800	5201	6213	4577	7099
Completeness to θ_{full} / θ_{max}	1.000 / 0.989	0.999 / 0.989	0.977 / 0.951	0.999 / 0.999	0.999 / 0.987
Data / restraints / parameters	6100 / 14 / 452	6516 / 0 / 420	7243 / 298 / 602	7313/ 0 / 429	7377 / 129 / 564
Goodness-of-fit on F^2	1.053	1.054	1.076	1.020	1.077
R1 / wR2 for $I > 2\sigma(I)$	0.0333 / 0.0827	0.0586 / 0.1601	0.0736 / 0.2032	0.0498 / 0.1009	0.0463 / 0.1268
R1 / wR2 (all data)	0.0352 / 0.0838	0.0714 / 0.1705	0.0824 / 0.2096	0.0975 / 0.1143	0.0473 / 0.1275
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, $e \cdot Å^{-3}$	0.491/ –0.526	0.626 / –0.588	1.049 / -0.559	0.474/ –0.520	0.643 / -0.650

Table S8. Crystallographic data on $Mn(hfac)_2(NN–Pz–CH_2CHF_2)]_n \cdot n[Mn(hfac)_2(NN–Pz–CH_2CHF_2)H_2O]$).

Empirical formula	$C_{22}H_{19}F_{14}MnN_4O_6 \cdot C_{22}H_{21}F_{14}MnN_4O_7$
Formula weight	1530.72
Temperature, K	100
Scan mode	ω and ϕ scans
Anode [Wavelength, Å]	MoKα [0.71073] sealed tube
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	30.298(3)
b, Å	9.7710(8)
c, Å	21.7394(18)
α, °	90
β, °	110.106(3)
γ, °	90
Volume, Å³	6043.5(9)
Z	4
Density(calcd.), g·cm⁻³	1.682
μ, mm⁻¹	0.569
T_{min}/T_{max}	0.6226/0.7453
F(000)	3064
Crystal size, mm	0.25×0.01×0.01
$2\theta_{min} – 2\theta_{max}$, °	2.901–20.366
Index ranges	$–37 \le h \le 37$, $–12 \le k \le 12$, $–26 \le l \le 22$
Reflections collected	38331
Independent reflections	11939
Reflections (I>2σ(I))	6316
Parameters	875
R_{int}	0.101
wR_2 (all reflections)	0.1786
R_1(I>σ(I))	0.0634
GOF	1.018
ρ_{min}/ρ_{max}, e·Å⁻³	–0.578/1.032
Restraints	48

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