Seven-coordinated iron(II) spin-crossover molecule: some learning from iron substitution in the $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ solid solutions

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Electronic Supplementary Information

Table SI.1: Elemental microanalyses of the solid solution materials $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ [found, % (calcd, %)].

Figure SI.1 Dilution factor obtained as a function of the dilution factor expected for $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$. The full line corresponds to the ideal situation where *x(found) = x(calculated).*

Figure SI.2 Room temperature powder *X*-ray diffraction patterns of $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ series.

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Table SI.4: Crystal data of $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ with x = 0.638±0.009 at 250 K and 100 K.

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Figure SI.5 Molecular structure (a) and packing (b) of $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ with x = 0.638±0.009 at 100 K. The hydrogen atoms have been omitted for clarity.

Table SI.5:. Root-Mean-Square Deviations (RMSD) extracted from pairwise molecular overlays of the complexes studied in the paper, $[A(L_{222}N_3O_2)(CN)_2]$ with A = Mn, Fe or Fe_xMn_{1-x}. The average and the maximum values are reported as calculated by *Mercury*[40] for room-temperature (RT) and low temperatures (LT), when known. Let's recall that the lower the RMSD values are, the more similar are the molecular shapes. Gray boxes indicate the superimposition drawn in Figure 3.

Table SI.6: Selected geometric parameters (Å, °) for the $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ with x = 0.963±0.005 at 250 K.

Table SI.7: Selected geometric parameters (Å, °) for the $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ with x = 0.638±0.009 at 250 K.

Table SI.8: Selected geometric parameters (Å, °) for the $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ with x = 0.638±0.009 at 100 K.

Table SI.1 : Elemental microanalyses of the solid solution materials $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ [found, % (calcd, %)]

x	C	H	N	Fe	Mn
1	50.78(50.89)	5.88(5.78)	17.61(17.45)	14.22(13.92)	-
0.966	50.59(50.89)	5.94(5.78)	17.51(17.46)	13.82 (13.45)	0.49 (0.47)
0.964	49.58(50.89)	5.75(5.78)	16.96(17.46)	14.64(13.42)	0.55(0.49)
0.953	50.29(50.89)	5.76(5.78)	17.21(17.46)	13.98(13.27)	0.69(0.64)
0.949	50.04(50.89)	5.79(5.78)	17.19(17.46)	14.18 (13.21)	0.76 (0.70)
0.930	50.76(50.90)	5.95(5.78)	17.48(17.46)	12.39 (12.95)	0.94 (0.96)
0.912	50.68(50.90)	5.79(5.78)	17.45(17.46)	12.70 (12.70)	1.22 (1.21)
0.892	50.90(50.90)	5.66(5.78)	17.56(17.46)	12.86 (12.42)	1.56 (1.48)
0.867	50.46(50.9)	5.83(5.78)	17.31(17.46)	12.77(12.17)	1.83(1.73)
0.853	51.04(50.90)	5.83(5.78)	17.38(17.46)	12.03 (12.02)	1.91(1.88)
0.832	50.90(50.90)	5.84(5.78)	17.52(17.46)	11.71(11.58)	2.32(2.30)
0.812	50.84(50.90)	5.78(5.78)	17.54(17.46)	11.22(11.31)	2.55(2.58)
0.659	49.31(50.93)	5.64(5.78)	16.84(17.47)	9.24(9.18)	4.77(4.67)
0.550	49.68(50.94)	5.77(5.78)	16.89(17.47)	7.99(7.66)	6.53(6.17)
0.312	50.04(50.97)	5.34(5.78)	16.02(17.48)	4.41(4.35)	9.73(9.43)

Figure SI.1 Dilution factor obtained as a function of the dilution factor expected for $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$. The full line corresponds to the ideal situation where *x(found) = x(calculated).*

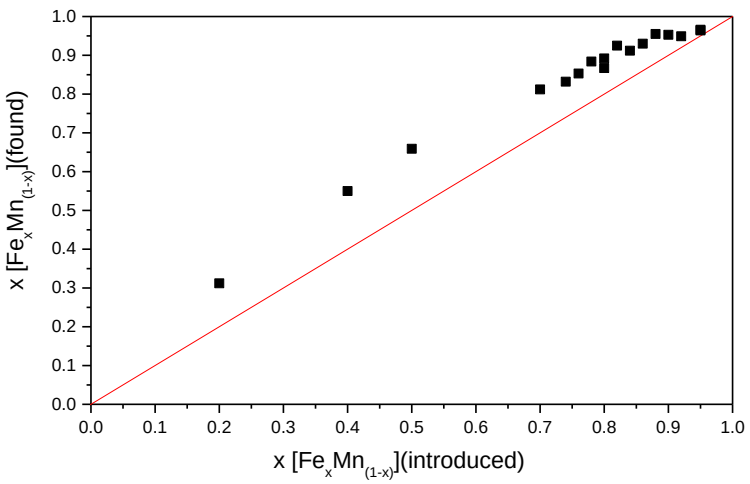

Figure SI.2 Room temperature powder *X*-ray diffraction patterns of $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ series.

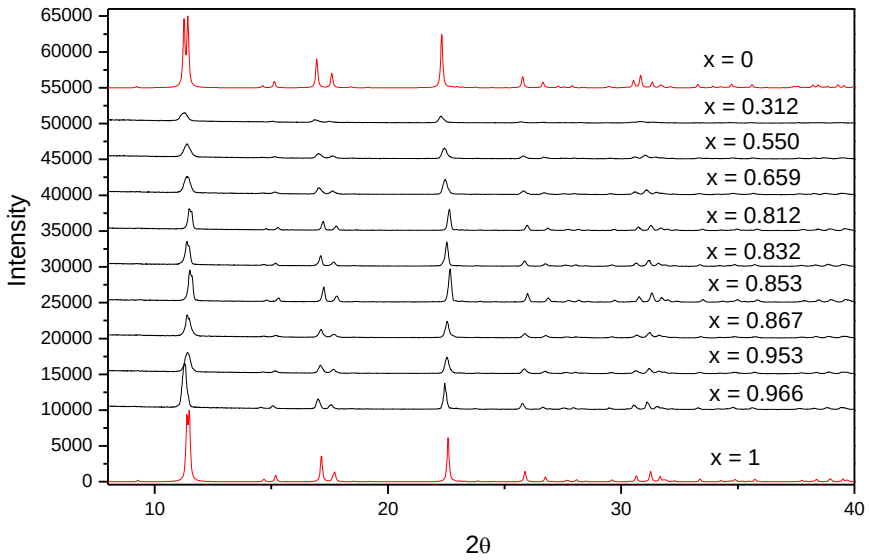

Table SI.2: Crystal data of $[Mn(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ at 270 K and 120 K.

Compound	$[Mn(L_{222}N_3O_2)(CN)_2]\cdot H_2O$	
Formula	$C_{17}H_{23}MnN_5O_3$	$C_{17}H_{23}MnN_5O_3$
λ (Å)	0.71073	0.71073
M_r (g.mol^{-1})	400.34	400.34
Colour	brown	brown
Crystal size (mm^3)	0.45 × 0.25 × 0.25	0.45 × 0.25 × 0.25
Crystal morphology	cubic	cubic
Temperature (K)	270(2)	120(2)
Crystal system	Monoclinic	Monoclinic
Space group	C 2/c	C 2/c
a (Å)	17.5613(3)	17.093(3)
b (Å)	12.0994(2)	11.990(2)
c (Å)	10.17850(10)	10.330(2)
β (°)	116.5790(10)	113.011(2)
V (Å^3)	1934.18(5)	1893.1(8)
Z	4	4
Density (g.cm^{-3})	1.375	1.405
μ (mm^{-1})	0.708	0.724
No. of total reflections	2815	8979
R_{obs}	0.0309	0.0319
$wR2_{obs}$	0.0839	0.0805
S	1.042	1.082

Table SI.3: Crystal data of $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ with x = 0.963±0.005 at room temperature.

Compound	$[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$, x = 0.963±0.005
Formula	$C_{17}H_{23}Mn_{0.04}Fe_{0.96}N_5O_3$
λ (Å)	0.71073
M_r (g.mol^{-1})	401.22
Colour	dark blue
Crystal size (mm^3)	0.08 × 0.08 × 0.08
Crystal morphology	cubic
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	C 2/c
a (Å)	17.3438(8)
b (Å)	12.0771(7)
c (Å)	10.1378(7)
β (°)	116.269(3)
V (Å^3)	1904.19(19)
Z	4
Density (g.cm^{-3})	1.400
μ (mm^{-1})	0.818
No. of total reflections	2586
R_{obs}	0.0773
$wR2_{obs}$	0.1536
S	0.989

Figure SI.3: Molecular structure (a) and packing (b) of $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ with x = 0.963±0.005 at room temperature. The hydrogen atoms have been omitted for clarity.

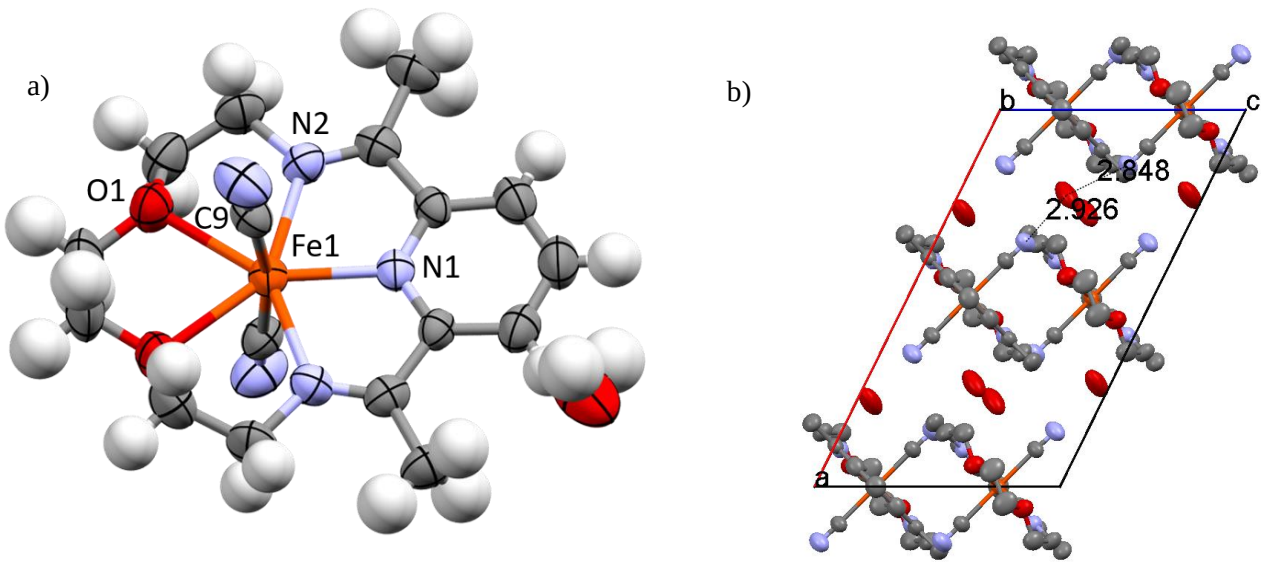

Table SI.4: Crystal data of $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ with x = 0.638±0.009 at 250 K and 100 K.

Compound	$[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$, x = 0.638±0.009	
Formula	$C_{17}H_{23}Mn_{0.36}Fe_{0.64}FeN_5O_3$	$C_{17}H_{23}Mn_{0.36}Fe_{0.64}N_5O_3$
λ (Å)	0.71073	0.71073
M_r (g.mol^{-1})	400.93	400.93
Colour	dark blue	dark blue
Crystal size (mm^3)	0.17 × 0.13 × 0.13	0.17 × 0.13 × 0.13
Crystal morphology	prism	prism
Temperature (K)	250(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	C 2/c	C 2/c
a (Å)	17.3332(4)	17.0528(5)
b (Å)	12.0778(4)	12.0023(4)
c (Å)	10.1168(2)	10.0974(3)
β (°)	116.210(2)	115.880(2)
V (Å^3)	1900.16(9)	1859.40(10)
Z	4	4
Density (g.cm^{-3})	1.403	1.433
μ (mm^{-1})	0.820	0.838
No. of total reflections	2164	2116
R_{obs}	0.0589	0.0631
$wR2_{obs}$	0.1105	0.1208
S	1.061	1.08

Figure SI.4: Molecular structure (a) and packing (b) of $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ with x = 0.638±0.009 at 250 K. The hydrogen atoms have been omitted for clarity.

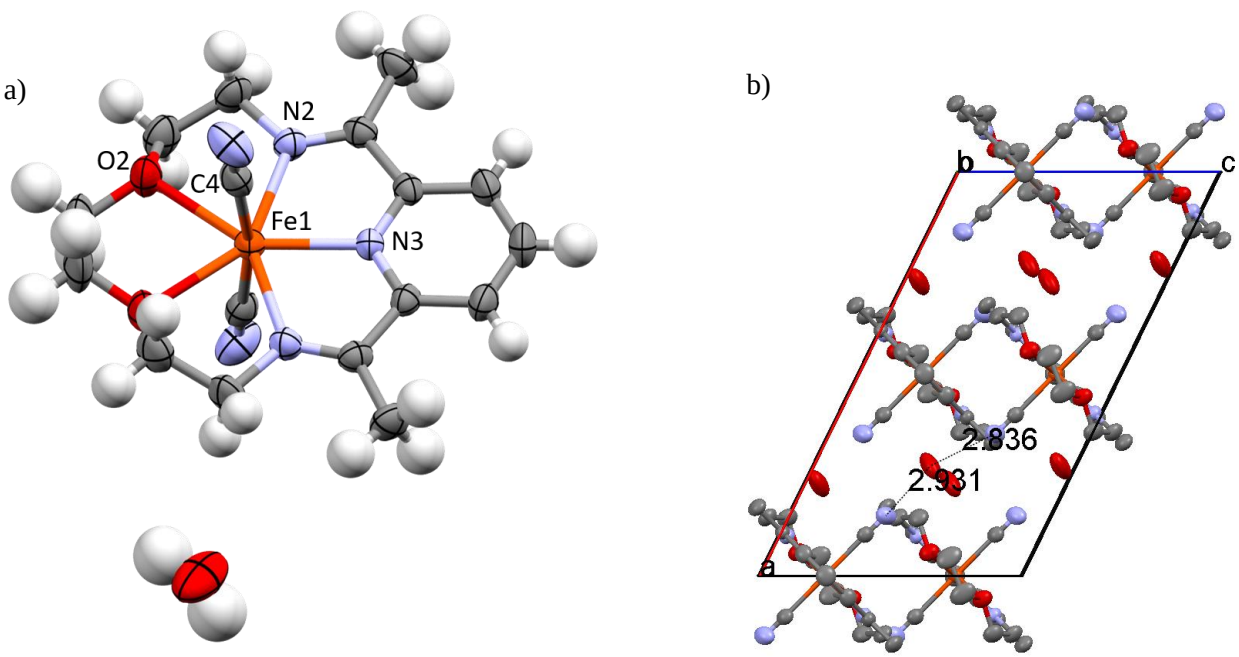

Figure SI.5: Molecular structure (a) and packing (b) of $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ with x = 0.638±0.009 at 100 K. The hydrogen atoms have been omitted for clarity.

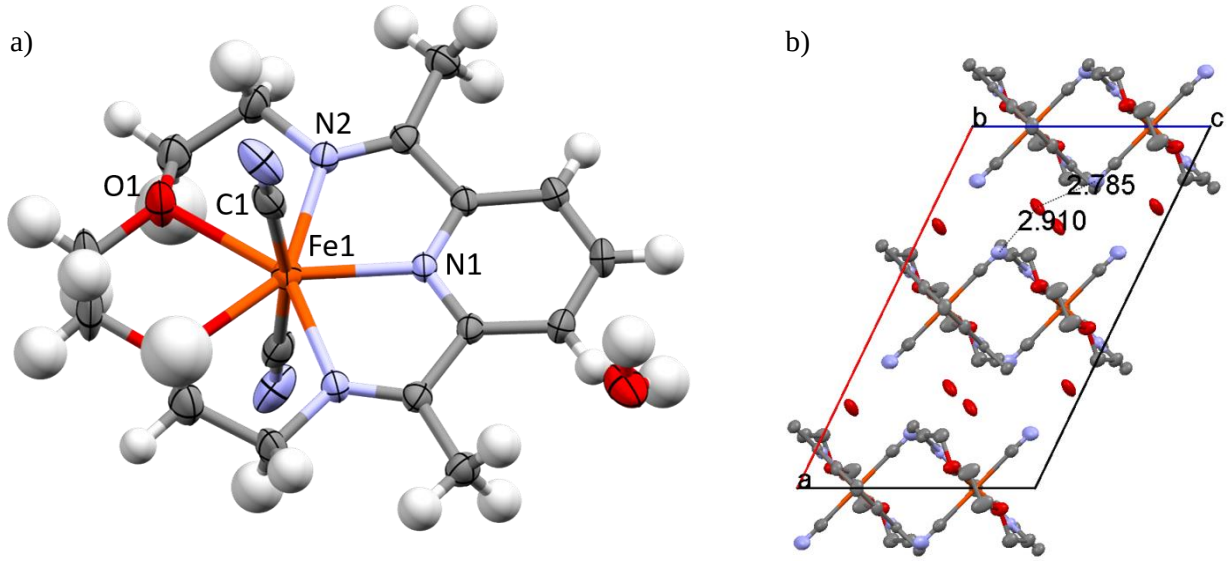

Table SI.5: Root-Mean-Square Deviations (RMSD) extracted from pairwise molecular overlays of the complexes studied in the paper, $[A(L_{222}N_3O_2)(CN)_2]$ with A = Mn, Fe or Fe_xMn_{1-x}. The average and the maximum values are reported as calculated by *Mercury* [40] for room-temperature (RT) and low temperatures (LT), when known. Let's recall that the lower the RMSD values are, the more similar are the molecular shapes. Gray boxes indicate the superimposition drawn in Figure 3.

RMSD (Å): average (max.)	**Mn, RT**			
Fe, RT	0.058 (0.131)	**Fe, RT**		
$Fe_{0.64}Mn_{0.36}$, RT	0.043 (0.118)	0.021 (0.060)	**$Fe_{0.64}Mn_{0.36}$, RT**	
Mn, LT	0.085 (0.267)	0.102 (0.298)	0.103 (0.307)	**Mn, LT**
$Fe_{0.96}Mn_{0.04}$, RT	0.060 (0.136)	0.012 (0.018)	0.022 (0.056)	0.101 (0.301)
$Fe_{0.64}Mn_{0.36}$, LT	0.045 (0.120)	0.019 (0.048)	0.009 (0.056)	0.095 (0.299)

Table SI.6: Selected geometric parameters (Å, °) for the $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ with x = 0.963±0.005 at room temperature.

Fe1 — N1	2.122(5)	Fe1 — N2	2.211(3)
Fe1 — O1	2.337(3)	Fe1 — C9	2.174(6)
N1 — Fe1 — N2	72.7(2)	C9 — Fe1 — N1	95.0(2)
N1 — Fe1 — O1	144.5(2)	C9 — Fe1 — N2	92.9(2)
N2 — Fe1 — O1	71.9(1)	C9 — Fe1 — O1	84.2(2)
N2 — Fe1 — $N2^i$	145.3(1)	C9 — Fe1 — $O1^i$	87.7(2)
N2 — Fe1 — $O1^i$	142.7(1)	C9 — Fe1 — $N2^i$	90.0(2)
O1 — Fe1 — $O1^i$	71.1(1)	C9 — Fe1 — $C9^i$	170.0(2)

Table SI.7: Selected geometric parameters (Å, °) for the $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ with x = 0.638±0.009 at 250 K.

Fe1 — N3	2.143(2)	Fe1 — N2	2.225(2)
Fe1 — O2	2.323(2)	Fe1 — C4	2.224(4)
N3 — Fe1 — N2	72.17(9)	C4 — Fe1 — N3	95.0(1)
N3 — Fe1 — O2	144.05(8)	C4 — Fe1 — N2	92.86(9)
N2 — Fe1 — O2	71.99(7)	C4 — Fe1 — O2	84.07(9)
N2 — Fe1 — $N2^i$	144.35(8)	C4 — Fe1 — $O2^i$	87.82(9)
N2 — Fe1 — $O2^i$	143.60(8)	C4 — Fe1 — $N2^i$	90.21(9)
O2 — Fe1 — $O2^i$	71.89(7)	C4 — Fe1 — $C4^i$	170.0(1)

Table SI.8: Selected geometric parameters (Å, °) for the $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ with x = 0.638±0.009 at 100 K.

Fe1 — N1	2.118(4)	Fe1 — N2	2.214(2)
Fe1 — O1	2.329(2)	Fe1 — C1	2.208(4)
N1 — Fe1 — N2	72.6(1)	C1 — Fe1 — N1	95.4(1)
N1 — Fe1 — O1	144.3(1)	C1 — Fe1 — N2	92.9(1)
N2 — Fe1 — O1	71.88(9)	C1 — Fe1 — O1	83.8(1)
N2 — Fe1 — $N2^i$	145.13(9)	C1 — Fe1 — $O1^i$	87.5(1)
N2 — Fe1 — $O1^i$	142.93(9)	C1 — Fe1 — $N2^i$	90.3(1)
O1 — Fe1 — $O1^i$	71.33(9)	C1 — Fe1 — $C1^i$	169.3(1)

Table SI.6: Kinetics performed at 148 K and 190 K after fast cooling at 10 K for the complex $[Fe_xMn_{1-x}(L_{222}N_3O_2)(CN)_2]\cdot H_2O$ with x = 0.949