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Syntheses, structures, and magnetic properties of three new Mn^{II}-$[Mo^{III}(CN)_7]^{4-}$ molecular magnets†

Xiao-Qin Wei,[a] Qian Pi,[a] Fu-Xing Shen,[a] Dong Shao,[a] Hai-Yan Wei,*[b] and Xin-Yi Wang*[a]

[a] State Key Laboratory of Coordination Chemistry, Collaborative Innovation Center of Advanced Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210023, China. Email: wangxy66@nju.edu.cn

[b] Jiangsu Key Laboratory of Biofunctional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing, 210023, China. Email: weihaiyan@njnu.edu.cn

Supporting Information

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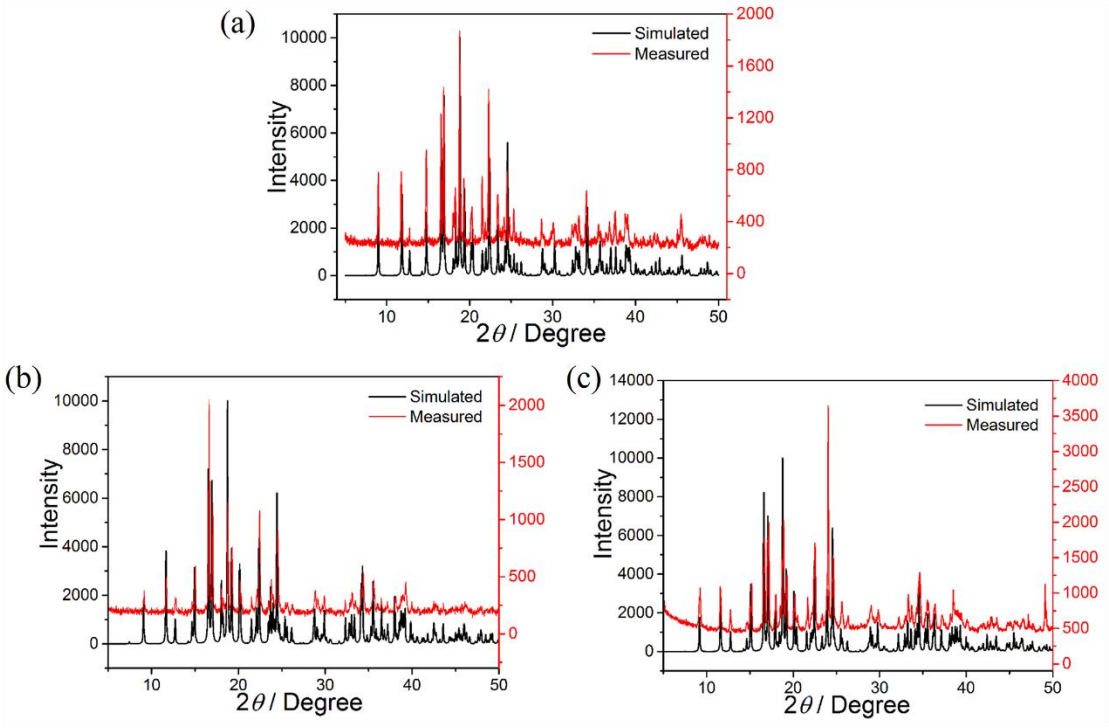
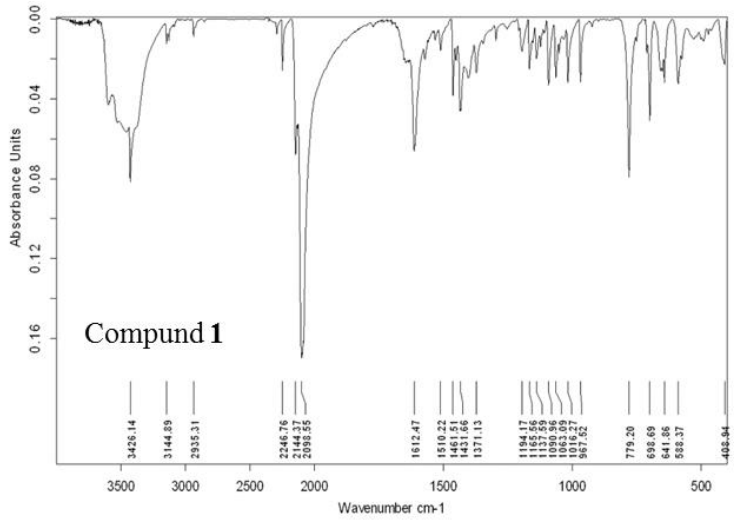


Figure S1. The PXRD of both simulated and measured patterns for **1**-**3** (a-c).



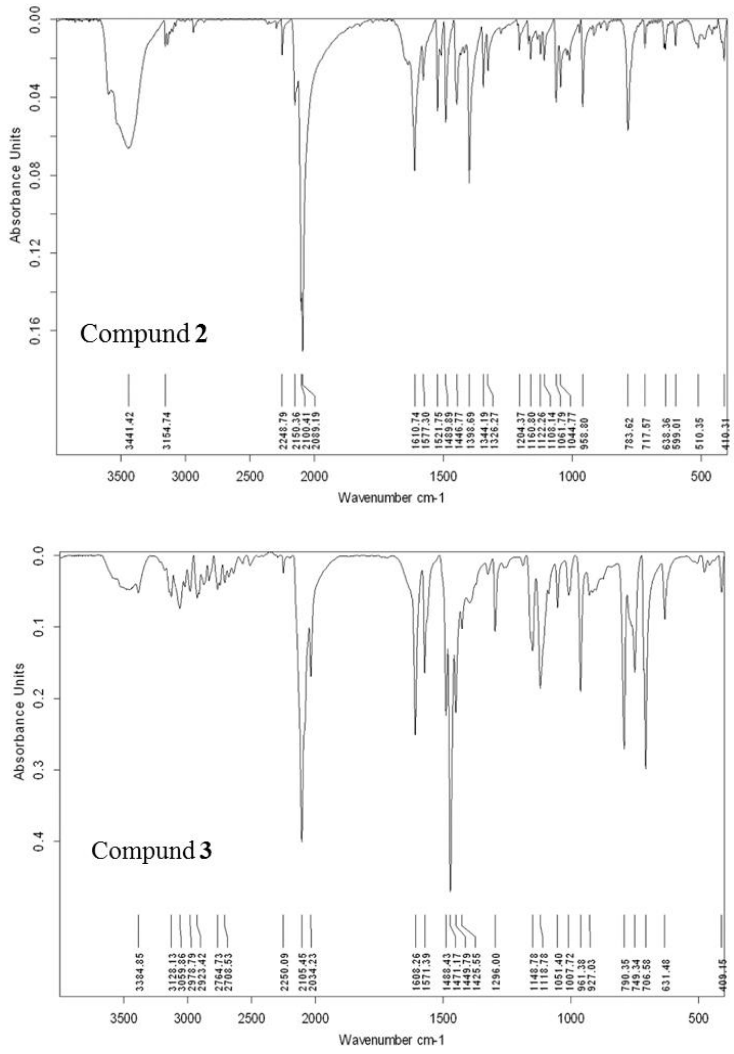


Figure S2. The IR spectrum for compounds **1**-**3**.

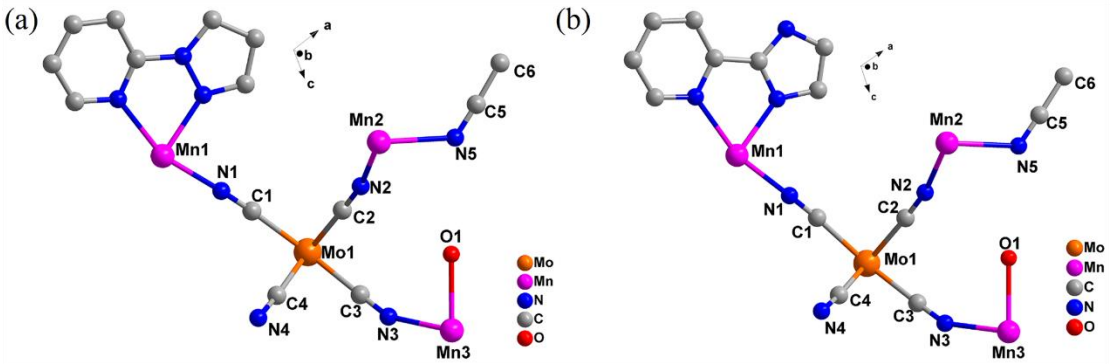


Figure S3. The asymmetric units for **2** and **3**. All the H atoms have been omitted for clarity.

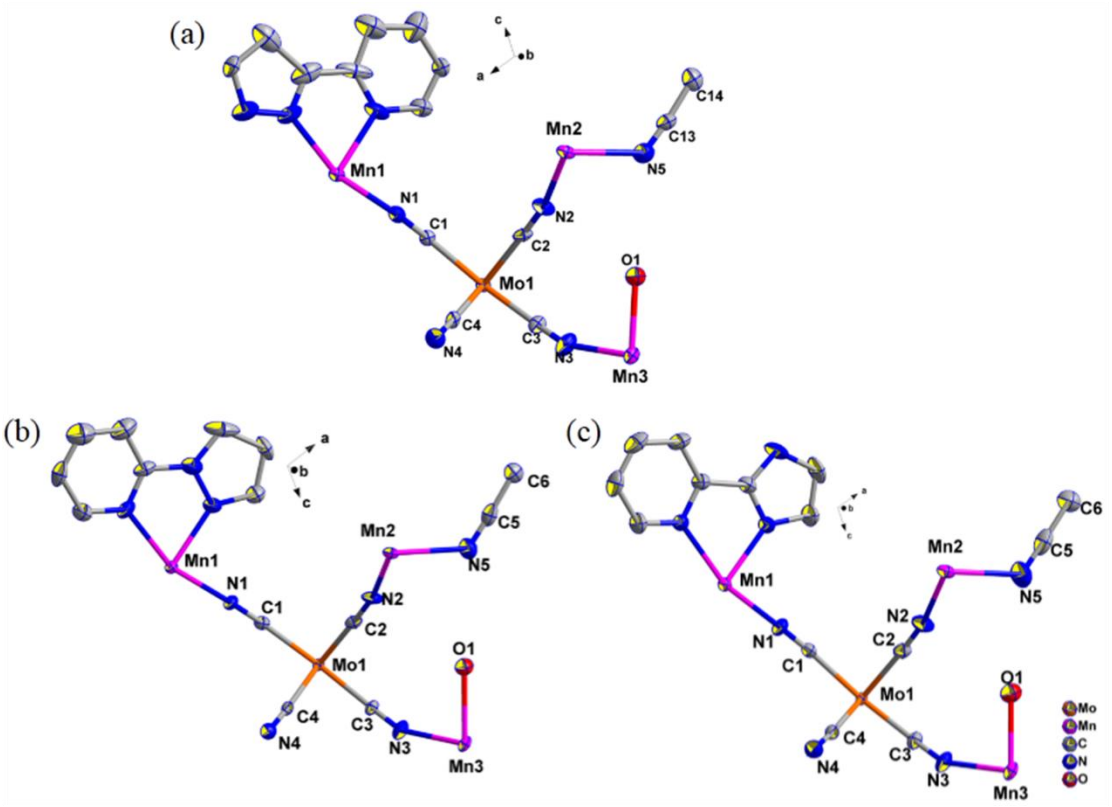


Figure S4. The ORTEP view of the asymmetric units for compounds 1-3 with thermal ellipsoids at 50% probability.

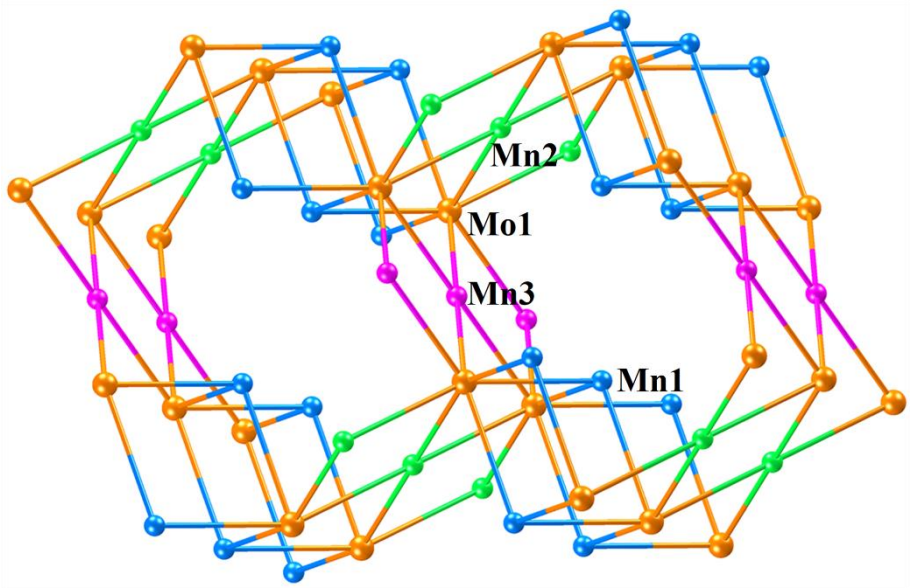


Figure S5. Schematic view of the 3,4,4,7,-connected topology for **1-3**.

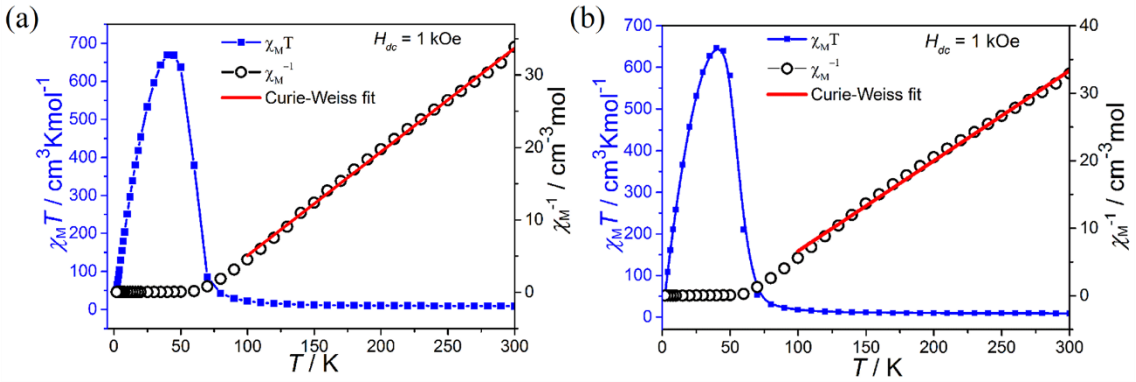


Figure S6. Temperature dependent $\chi_M T(T)$ and $\chi_M^{-1}(T)$ curves for **2** and **3** measured under a dc field of 1000 Oe.

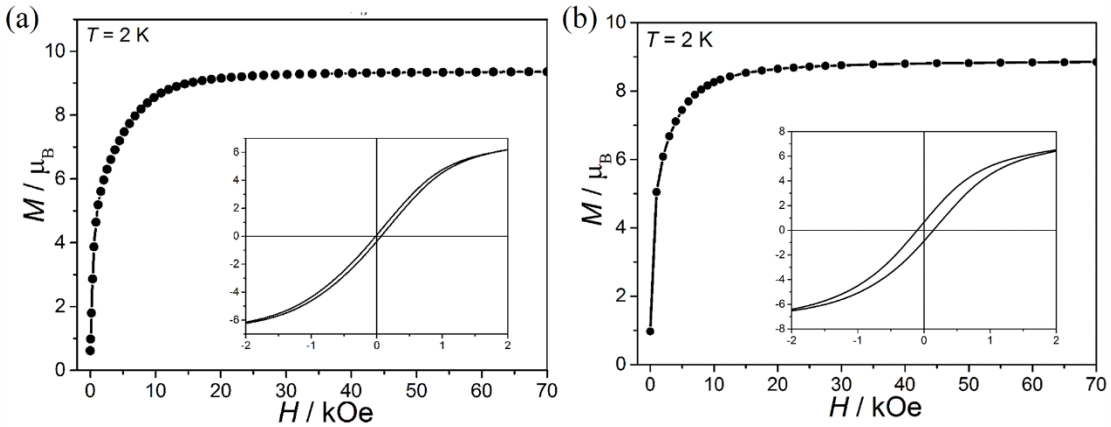


Figure S7. Field dependent magnetization curves and the hysteresis loops of **2** and **3** measured at 2 K.

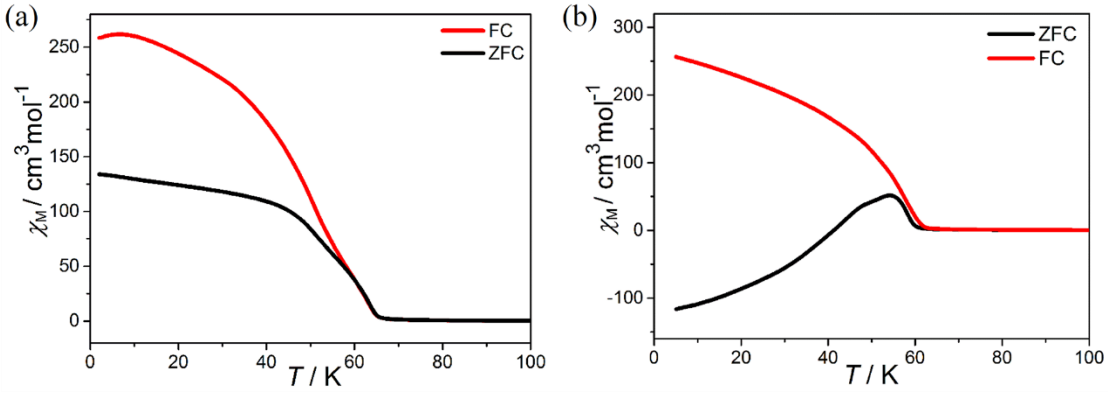


Figure S8. Zero-Field-Cooled and Field-Cooled (ZFC/FC) magnetization curves for **2** and **3** under a dc field of 10 Oe.

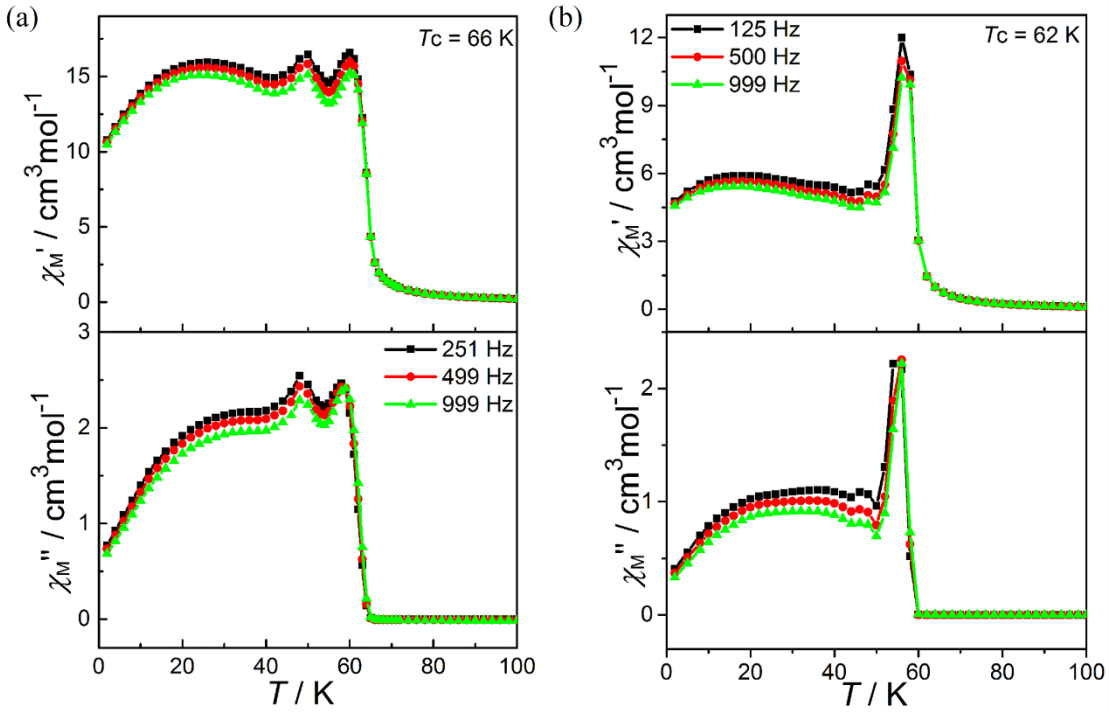


Figure S9. Temperature dependent ac susceptibilities for **2** and **3** collected under H_{ac} = 2 Oe and H_{dc} = 0 Oe.

Table S1. Selected bond lengths [Å] and angles [°] for complexes **1-3**.

Complex **1**			
Bonds lengths [A °]			
Mo(1)-C(3)	2.114(5)	Mn(2)-N(2)#4	2.195(4)
Mo(1)-C(3)#1	2.114(5)	Mn(2)-N(2)#5	2.195(4)
Mo(1)-C(2)	2.148(5)	Mn(2)-N(2)#6	2.195(4)
Mo(1)-C(2)#1	2.148(5)	Mn(2)-N(2)	2.195(4)
Mo(1)-C(4)#1	2.149(5)	Mn(2)-N(5)#4	2.355(8)
Mo(1)-C(4)	2.149(5)	Mn(2)-N(5)	2.355(8)
Mo(1)-C(1)	2.175(7)	N(3)-Mn(3)	2.177(4)
N(1)-Mn(1)	2.157(7)	Mn(3)-N(3)#5	2.177(4)
Mn(1)-N(4)#2	2.080(4)	Mn(3)-N(3)#7	2.177(4)
Mn(1)-N(4)#3	2.080(4)	Mn(3)-N(3)#8	2.177(4)
Mn(1)-N(6)	2.196(6)	Mn(3)-O(1)#8	2.289(7)
Mn(1)-N(7)	2.242(7)	O(1)-Mn(3)	2.289(7)
Bonds Angles [°]			
C(3)-Mo(1)-C(3)#1	75.0(3)	N(4)#3-Mn(1)-N(6)	127.42(13)
C(3)-Mo(1)-C(2)	76.50(19)	N(1)-Mn(1)-N(6)	88.9(3)
C(3)#1-Mo(1)-C(2)	124.4(2)	N(4)#2-Mn(1)-N(7)	92.46(19)
C(3)-Mo(1)-C(2)#1	124.4(2)	N(4)#3-Mn(1)-N(7)	92.46(19)
C(3)#1-Mo(1)-C(2)#1	76.50(19)	N(1)-Mn(1)-N(7)	161.7(3)

C(2)-Mo(1)-C(2)#1	81.9(3)	N(6)-Mn(1)-N(7)	72.7(3)
C(3)-Mo(1)-C(4)#1	119.27(19)	N(2)#4-Mn(2)-N(2)#5	93.7(2)
C(3)#1-Mo(1)-C(4)#1	74.40(19)	N(2)#4-Mn(2)-N(2)#6	86.3(2)
C(2)-Mo(1)-C(4)#1	159.76(19)	N(2)#5-Mn(2)-N(2)#6	180.0(2)
C(2)#1-Mo(1)-C(4)#1	97.00(18)	N(2)#4-Mn(2)-N(2)	179.999(1)
C(3)-Mo(1)-C(4)	74.40(19)	N(2)#5-Mn(2)-N(2)	86.3(2)
C(3)#1-Mo(1)-C(4)	119.27(19)	N(2)#6-Mn(2)-N(2)	93.7(2)
C(2)-Mo(1)-C(4)	97.00(18)	N(2)#4-Mn(2)-N(5)#4	94.54(18)
C(2)#1-Mo(1)-C(4)	159.76(19)	N(2)#5-Mn(2)-N(5)#4	85.46(18)
C(4)#1-Mo(1)-C(4)	77.0(2)	N(2)#6-Mn(2)-N(5)#4	94.54(18)
C(3)-Mo(1)-C(1)	142.28(13)	N(2)-Mn(2)-N(5)#4	85.46(18)
C(3)#1-Mo(1)-C(1)	142.28(13)	N(2)#4-Mn(2)-N(5)	85.46(18)
C(2)-Mo(1)-C(1)	81.34(19)	N(2)#5-Mn(2)-N(5)	94.54(18)
C(2)#1-Mo(1)-C(1)	81.34(19)	N(2)#6-Mn(2)-N(5)	85.46(19)
C(4)#1-Mo(1)-C(1)	78.52(19)	N(2)-Mn(2)-N(5)	94.54(18)
C(4)-Mo(1)-C(1)	78.52(19)	N(5)#4-Mn(2)-N(5)	179.999(1)
N(1)-C(1)-Mo(1)	177.6(6)	N(3)-Mn(3)-N(3)#5	91.6(2)
N(4)-C(4)-Mo(1)	177.0(4)	N(3)-Mn(3)-N(3)#7	88.4(2)
N(2)-C(2)-Mo(1)	177.3(4)	N(3)#5-Mn(3)-N(3)#7	180.0(3)
N(3)-C(3)-Mo(1)	175.0(4)	N(3)-Mn(3)-N(3)#8	180
N(4)#2-Mn(1)-N(4)#3	102.7(2)	N(3)#5-Mn(3)-N(3)#8	88.4(2)
N(4)#2-Mn(1)-N(1)	98.92(16)	N(3)#7-Mn(3)-N(3)#8	91.6(2)
N(4)#3-Mn(1)-N(1)	98.92(16)	N(3)-Mn(3)-O(1)#8	96.08(18)
N(4)#2-Mn(1)-N(6)	127.42(13)	N(3)#5-Mn(3)-O(1)#8	96.08(18)
C(1)-N(1)-Mn(1)	176.1(6)	N(3)#7-Mn(3)-O(1)#8	83.92(18)
C(2)-N(2)-Mn(2)	164.5(5)	N(3)#8-Mn(3)-O(1)#8	83.92(18)
C(13)-N(5)-Mn(2)	126.3(7)	N(3)-Mn(3)-O(1)	83.92(18)
C(8)-N(6)-Mn(1)	116.3(7)	N(3)#5-Mn(3)-O(1)	83.92(18)
C(12)-N(6)-Mn(1)	127.3(6)	N(3)#7-Mn(3)-O(1)	96.08(18)
C(7)-N(7)-Mn(1)	117.0(7)	N(3)#8-Mn(3)-O(1)	96.08(18)
N(8)-N(7)-Mn(1)	134.2(6)	O(1)#8-Mn(3)-O(1)	180.000(1)
C(4)-N(4)-Mn(1)#2	163.3(4)		

#1 x,-y,z #2 -x+1/2,-y+1/2,-z+1 #3 -x+1/2,y-1/2,-z+1 #4 -x,-y+1,-z+1 #5 x,-y+1,z #6 -x,y,-z+1 #7 -x,y,-z #8 -x,-y+1,-z

Complex **2**

Bonds lengths [A ¶]

Mo(1)-C(3)#1	2.127(3)	Mn(2)-N(2)	2.195(3)
Mo(1)-C(3)	2.127(3)	Mn(2)-N(2)#4	2.195(3)
Mo(1)-C(4)#1	2.148(3)	Mn(2)-N(2)#5	2.195(3)
Mo(1)-C(4)	2.148(3)	Mn(2)-N(2)#6	2.195(3)
Mo(1)-C(2)#1	2.161(3)	Mn(2)-N(5)	2.357(5)
Mo(1)-C(2)	2.161(3)	Mn(2)-N(5)#6	2.357(5)
Mo(1)-C(1)	2.181(4)	Mn(3)-N(3)	2.199(3)
Mn(1)-N(4)#2	2.094(3)	Mn(3)-N(3)#7	2.199(3)

Mn(1)-N(4)#3	2.094(3)	Mn(3)-N(3)#4	2.199(3)
Mn(1)-N(1)	2.148(4)	Mn(3)-N(3)#8	2.199(3)
Mn(1)-N(6)	2.179(4)	Mn(3)-O(1)#7	2.300(4)
Mn(1)-N(7)	2.259(4)	Mn(3)-O(1)	2.300(4)
Bonds Angles [º]			
C(3)#1-Mo(1)-C(3)	75.23(16)	N(4)#3-Mn(1)-N(1)	100.56(10)
C(3)#1-Mo(1)-C(4)#1	74.80(11)	N(4)#2-Mn(1)-N(6)	128.22(8)
C(3)-Mo(1)-C(4)#1	120.21(11)	N(4)#3-Mn(1)-N(6)	128.22(8)
C(3)#1-Mo(1)-C(4)	120.20(11)	N(1)-Mn(1)-N(6)	87.25(15)
C(3)-Mo(1)-C(4)	74.80(11)	N(4)#2-Mn(1)-N(7)	92.09(10)
C(4)#1-Mo(1)-C(4)	77.64(16)	N(4)#3-Mn(1)-N(7)	92.09(10)
C(3)#1-Mo(1)-C(2)#1	77.19(11)	N(1)-Mn(1)-N(7)	160.01(15)
C(3)-Mo(1)-C(2)#1	125.47(12)	N(6)-Mn(1)-N(7)	72.76(16)
C(4)#1-Mo(1)-C(2)#1	95.93(12)	N(2)-Mn(2)-N(2)#4	86.66(14)
C(4)-Mo(1)-C(2)#1	157.97(11)	N(2)-Mn(2)-N(2)#5	93.34(14)
C(3)#1-Mo(1)-C(2)	125.47(12)	N(2)#4-Mn(2)-N(2)#5	180.00(14)
C(3)-Mo(1)-C(2)	77.18(11)	N(2)-Mn(2)-N(2)#6	179.998(1)
C(4)#1-Mo(1)-C(2)	157.97(11)	N(2)#4-Mn(2)-N(2)#6	93.34(14)
C(4)-Mo(1)-C(2)	95.93(12)	N(2)#5-Mn(2)-N(2)#6	86.66(14)
C(2)#1-Mo(1)-C(2)	82.14(16)	N(2)-Mn(2)-N(5)	93.83(12)
C(3)#1-Mo(1)-C(1)	142.18(8)	N(2)#4-Mn(2)-N(5)	93.83(12)
C(3)-Mo(1)-C(1)	142.18(8)	N(2)#5-Mn(2)-N(5)	86.17(12)
C(4)#1-Mo(1)-C(1)	78.00(12)	N(2)#6-Mn(2)-N(5)	86.17(12)
C(4)-Mo(1)-C(1)	78.00(12)	N(2)-Mn(2)-N(5)#6	86.17(12)
C(2)#1-Mo(1)-C(1)	80.06(12)	N(2)#4-Mn(2)-N(5)#6	86.17(12)
C(2)-Mo(1)-C(1)	80.06(12)	N(2)#5-Mn(2)-N(5)#6	93.83(12)
N(4)#2-Mn(1)-N(4)#3	100.79(15)	N(2)#6-Mn(2)-N(5)#6	93.83(12)
N(4)#2-Mn(1)-N(1)	100.56(10)	N(5)-Mn(2)-N(5)#6	180
N(3)-C(3)-Mo(1)	176.3(3)	N(3)-Mn(3)-N(3)#7	180
N(2)-C(2)-Mo(1)	177.1(3)	N(3)-Mn(3)-N(3)#4	92.02(14)
N(4)-C(4)-Mo(1)	176.6(3)	N(3)#7-Mn(3)-N(3)#4	87.98(14)
N(1)-C(1)-Mo(1)	177.1(4)	N(3)-Mn(3)-N(3)#8	87.98(14)
C(10)-N(7)-Mn(1)	116.7(3)	N(3)#7-Mn(3)-N(3)#8	92.02(14)
C(14)-N(7)-Mn(1)	127.3(4)	N(3)#4-Mn(3)-N(3)#8	180.00(13)
C(7)-N(6)-Mn(1)	136.3(4)	N(3)-Mn(3)-O(1)#7	95.78(10)
N(8)-N(6)-Mn(1)	117.5(3)	N(3)#7-Mn(3)-O(1)#7	84.22(10)
C(1)-N(1)-Mn(1)	177.7(4)	N(3)#4-Mn(3)-O(1)#7	95.78(10)
C(4)-N(4)-Mn(1)#3	165.0(3)	N(3)#8-Mn(3)-O(1)#7	84.22(10)
C(2)-N(2)-Mn(2)	164.7(3)	N(3)-Mn(3)-O(1)	84.22(10)
C(3)-N(3)-Mn(3)	156.2(3)	N(3)#7-Mn(3)-O(1)	95.78(10)
C(5)-N(5)-Mn(2)	124.5(4)	N(3)#4-Mn(3)-O(1)	84.22(10)
N(3)#8-Mn(3)-O(1)	95.78(10)	O(1)#7-Mn(3)-O(1)	179.999(1)

#1 x,-y,z #2 -x+1/2,y-1/2,-z #3 -x+1/2,-y+1/2,-z #4 x,-y+1,z #5 -x+1,y,-z #6 -x+1,-y+1,-z #7 -x+1,-y+1,-z+1 #8 -x+1,y,-z+1

Complex **3**			
Bonds lengths [Aº]			
Mo(1)-C(3)	2.127(2)	Mn(2)-N(2)	2.196(2)
Mo(1)-C(3)#1	2.127(2)	Mn(2)-N(2)#4	2.196(2)
Mo(1)-C(4)#1	2.147(2)	Mn(2)-N(2)#5	2.196(2)
Mo(1)-C(4)	2.147(2)	Mn(2)-N(2)#6	2.196(2)
Mo(1)-C(2)#1	2.164(2)	Mn(2)-N(5)#6	2.353(4)
Mo(1)-C(2)	2.164(2)	Mn(2)-N(5)	2.353(4)
Mo(1)-C(1)	2.180(3)	Mn(3)-N(3)	2.216(2)
Mn(1)-N(4)#2	2.099(2)	Mn(3)-N(3)#7	2.216(2)
Mn(1)-N(4)#3	2.099(2)	Mn(3)-N(3)#4	2.2163(19)
Mn(1)-N(1)	2.149(3)	Mn(3)-N(3)#8	2.2163(19)
Mn(1)-N(7)	2.168(3)	Mn(3)-O(1)#7	2.283(3)
Mn(1)-N(6)	2.288(3)	Mn(3)-O(1)	2.283(3)
N(4)-Mn(1)#3	2.099(2)		
Bonds Angles [º]			
C(3)-Mo(1)-C(3)#1	74.59(12)	N(2)#5-Mn(2)-N(11)	91.6(5)
C(3)-Mo(1)-C(4)#1	120.77(9)	N(2)-Mn(2)-N(11)	86.3(5)
C(3)#1-Mo(1)-C(4)#1	75.46(8)	N(11)#5-Mn(2)-N(11)	176.8(12)
C(3)-Mo(1)-C(4)	75.46(8)	N(4)#6-Mn(3)-N(4)#3	87.0(7)
C(3)#1-Mo(1)-C(4)	120.77(9)	N(4)#6-Mn(3)-N(3)	178.5(6)
C(4)#1-Mo(1)-C(4)	78.00(12)	N(4)#3-Mn(3)-N(3)	92.21(10)
C(3)-Mo(1)-C(2)#1	124.88(8)	N(4)#6-Mn(3)-N(3)#7	92.20(10)
C(3)#1-Mo(1)-C(2)#1	77.38(8)	N(4)#3-Mn(3)-N(3)#7	178.5(6)
C(4)#1-Mo(1)-C(2)#1	95.96(9)	N(7)#3-Mn(2)-N(7)#4	92.0(5)
C(4)-Mo(1)-C(2)#1	157.62(8)	N(7)#3-Mn(2)-N(2)#5	178.2(6)
C(3)-Mo(1)-C(2)	77.38(8)	N(7)#4-Mn(2)-N(2)#5	86.24(12)
C(3)#1-Mo(1)-C(2)	124.88(8)	N(7)#3-Mn(2)-N(2)	86.24(12)
C(4)#1-Mo(1)-C(2)	157.63(8)	N(7)#4-Mn(2)-N(2)	178.2(6)
C(4)-Mo(1)-C(2)	95.96(9)	N(2)#5-Mn(2)-N(2)	95.6(6)
C(2)#1-Mo(1)-C(2)	81.41(12)	N(7)#3-Mn(2)-N(11)#5	93.7(5)
C(3)-Mo(1)-C(1)	142.55(6)	N(7)#4-Mn(2)-N(11)#5	88.5(5)
C(3)#1-Mo(1)-C(1)	142.55(6)	N(2)#5-Mn(2)-N(11)#5	86.3(5)
C(4)#1-Mo(1)-C(1)	77.77(8)	N(2)-Mn(2)-N(11)#5	91.6(5)
C(4)-Mo(1)-C(1)	77.77(8)	N(2)-Mn(2)-N(2)#4	86.30(11)
C(2)#1-Mo(1)-C(1)	79.90(8)	N(2)-Mn(2)-N(2)#5	93.70(11)
C(2)-Mo(1)-C(1)	79.90(8)	N(2)#4-Mn(2)-N(2)#5	180.00(11)
N(4)#2-Mn(1)-N(4)#3	99.26(12)	N(2)-Mn(2)-N(2)#6	180.00(9)
N(4)#2-Mn(1)-N(1)	100.48(8)	N(2)#4-Mn(2)-N(2)#6	93.70(11)
N(4)#3-Mn(1)-N(1)	100.48(8)	N(2)#5-Mn(2)-N(2)#6	86.30(11)
N(4)#2-Mn(1)-N(7)	128.62(6)	N(2)-Mn(2)-N(5)#6	87.41(10)
N(4)#3-Mn(1)-N(7)	128.62(6)	N(2)#4-Mn(2)-N(5)#6	87.41(10)
N(1)-Mn(1)-N(7)	89.16(11)	N(2)#5-Mn(2)-N(5)#6	92.59(10)
N(4)#2-Mn(1)-N(6)	90.25(7)	N(2)#6-Mn(2)-N(5)#6	92.59(10)

N(4)#3-Mn(1)-N(6)	90.25(7)	N(2)-Mn(2)-N(5)	92.59(10)
N(1)-Mn(1)-N(6)	163.31(11)	N(2)#4-Mn(2)-N(5)	92.59(10)
N(7)-Mn(1)-N(6)	74.14(10)	N(2)#5-Mn(2)-N(5)	87.41(10)
N(1)-C(1)-Mo(1)	176.4(3)	N(2)#6-Mn(2)-N(5)	87.41(10)
N(2)-C(2)-Mo(1)	176.9(2)	N(5)#6-Mn(2)-N(5)	180
N(3)-C(3)-Mo(1)	177.2(2)	N(3)-Mn(3)-N(3)#7	179.998(1)
N(4)-C(4)-Mo(1)	175.6(2)	N(3)-Mn(3)-N(3)#4	92.12(11)
C(1)-N(1)-Mn(1)	178.8(3)	N(3)#7-Mn(3)-N(3)#4	87.88(11)
C(12)-N(7)-Mn(1)	115.6(2)	N(3)-Mn(3)-N(3)#8	87.88(11)
C(14)-N(7)-Mn(1)	138.1(3)	N(3)#7-Mn(3)-N(3)#8	92.12(11)
C(7)-N(6)-Mn(1)	127.1(3)	N(3)#4-Mn(3)-N(3)#8	180.00(10)
C(11)-N(6)-Mn(1)	115.2(2)	N(3)-Mn(3)-O(1)#7	95.57(8)
C(11)-N(6)-Mn(1)	115.2(2)	C(2)-N(2)-Mn(2)	164.8(2)
C(4)-N(4)-Mn(1)#3	164.9(2)	C(5)-N(5)-Mn(2)	123.1(3)
C(3)-N(3)-Mn(3)	153.8(2)		

#1 x,-y,z #2 -x+1/2,y-1/2,-z #3 -x+1/2,-y+1/2,-z #4 x,-y+1,z #5 -x+1,y,-z
#6 -x+1,-y+1,-z #7 -x+1,-y+1,-z+1 #8 -x+1,y,-z+1

Table S2. Continuous Shape Measures calculation for complexes **1**-**3**.

Symmetry	Shape	Deviation value		
Mo1		**1**	**2**	**3**
D_{7h}	Heptagon	35.091	34.514	34.583
C_{6v}	Hexagonal pyramid	20.065	20.316	20.36
D_{5h}	Pentagonal bipyramid	6.751	6.728	6.692
C_{3v}	Capped octahedron	1.742	1.685	1.674
***C*$_{2v}$**	**Capped trigonal prism**	**0.536**	**0.416**	**0.404**
D_{5h}	Johnson pentagonal bipyramid (J13)	10.598	10.483	10.444
C_{3v}	Elongated triangular pyramid (J7)	21.605	21.486	21.426
Mn1		**1**	**2**	**3**
D_{5h}	Pentagon	29.259	28.660	28.697
C_{4v}	Vacant octahedron	6.016	6.050	5.908
***D*$_{3h}$**	**Trigonal bipyramid**	**2.115**	**2.473**	**2.351**
C_{4v}	Square pyramid	4.336	4.358	4.407
D_{3h}	Johnson trigonal bipyramid	4.419	4.776	4.417
Mn2		**1**	**2**	**3**
D_{6h}	Hexagon	31.408	31.793	32.012
C_{5v}	Pentagonal pyramid	29.354	29.505	29.463
***O*$_h$**	**Octahedron**	**0.378**	**0.311**	**0.243**
D_{3h}	Trigonal prism	15.575	15.722	15.91
C_{5v}	Johnson pentagonal pyramid (J2)	32.624	32.741	32.654
Mn3		**1**	**2**	**3**
D_{6h}	Hexagon	28.019	27.977	28.23

C_{5v}	Pentagonal pyramid	27.823	27.804	27.983
O_h	**Octahedron**	**0.462**	**0.448**	**0.369**
D_{3h}	Trigonal prism	15.870	15.93	15.973
C_{5v}	Johnson pentagonal pyramid (J2)	30.884	30.865	31.119