Syntheses, structures and magnetic properties of four manganese(Ⅱ) and cobalt(Ⅱ) complexes

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Table S1 Crystallographic data of the complexes 1-4

Complex	(1)	(2)	(3)	(4)
Empirical formula	$C_{23}H_{20}MnN_2O_7$	$C_{20}H_{20}MnN_2O_8$	$C_{34}H_{27}CoN_4O_5$	$C_{41}H_{36}Co_2N_2O_{12}$
Formula weight	491.35	471.32	630.52	866.58
Temperature/K	298.15(2)	298.2(5)	298.15	273.15
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	P-1	P-1	P-1	$P2_1/n$
a/Å	7.7565(6)	7.3524(4)	9.8337(12)	16.394(3)
b/Å	9.5643(8)	10.8982(5)	10.0529(7)	13.578(3)
c/Å	15.1895(14)	24.6400(14)	15.735(3)	18.261(3)
α/°	96.781(7)	90.393(4)	98.507(10)	90.00
β/°	94.868(7)	90.391(4)	106.136(13)	115.509(3)
γ/°	110.509(7)	98.794(4)	97.295(8)	90.00
Volume/Å3	1038.33(15)	1951.05(18)	1454.4(3)	3668.5(12)
Z	2	4	2	4
ρcalcg/cm3	1.572	1.605	1.440	1.569
μ/mm-1	0.686	0.730	0.641	0.975
F(000)	506.0	972.0	652.0	1784.0
Crystal size/mm3	0.18 × 0.10 × 0.08	0.18 × 0.12 × 0.08	0.15 × 0.12 × 0.08	0.15 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71000)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.86 to 50	5.82 to 50	6.558 to 52.744	4.08 to 50
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 10, -18 ≤ l ≤ 18	-6 ≤ h ≤ 8, -12 ≤ k ≤ 10, -29 ≤ l ≤ 29	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -18 ≤ l ≤ 19	-19 ≤ h ≤ 19, -16 ≤ k ≤ 14, -21 ≤ l ≤ 13
Reflections collected	8071	15111	10765	18220
Independent reflections	3631 [Rint = 0.0630, Rsigma = 0.1019]	6868 [Rint = 0.0347, Rsigma = 0.0522]	5414 [R_{int} = 0.0896, R_{sigma} = 0.1721]	6436 [R_{int} = 0.1275, R_{sigma} = 0.1886]
Data/restraints/parameters	3631/3/310	6868/28/571	5414/0/397	6436/30/520
Goodness-of-fit on F2	1.021	1.208	1.019	0.834
Final R indexes [I>=2σ (I)]	R1 = 0.0536, wR2 = 0.0792	R1 = 0.0666, wR2 = 0.1517	R_1 = 0.0954, wR_2 = 0.1718	R_1 = 0.0655, wR_2 = 0.1303
Final R indexes [all data]	R1 = 0.0888, wR2 = 0.0958	R1 = 0.1142, wR2 = 0.1650	R_1 = 0.1735, wR_2 = 0.2229	R_1 = 0.1456, wR_2 = 0.1564
Largest diff. peak/hole / e Å-3	0.46/-0.35	0.73/-0.38	1.06/-0.33	1.06/-1.61
CCDC number	1044384	1045089	1045109	998418

[a] $R1=\Sigma||F_O|-|F_C||/\Sigma|F_O|$. [b] $wR2=|\Sigma w(|F_O|^2-|F_C|^2)|/\Sigma|w(F_O^2)^2|^{1/2}$.

Table S2 Selected bond lengths/Å and bond angles/° for complex (1) and (2)

Complex(1)					
Mn1-O4	2.152(2)	Mn1-$O2^E$	2.119(3)	Mn1-N2	2.226(3)
Mn1-$O1^D$	2.158(3)	Mn1-O2W	2.327(3)	Mn1-O1W	2.246(2)
O4-Mn1-$O1^D$	93.72(9)	O4-Mn1-O2W	93.10(11)	O4-Mn1-N2	92.85(10)
O4-Mn1-O1W	174.62(14)	$O2^E$-Mn1-O4	87.16(9)	$O2^E$-Mn1-$O1^D$	107.91(11)
$O2^E$-Mn1-O2W	82.39(13)	$O2^E$-Mn1-N2	161.80(11)	$O2^E$-Mn1-O1W	87.46(13)
$O1^D$-Mn1-O2W	167.91(11)	$O1^D$-Mn1-N2	90.25(11)	$O1^D$-Mn1-O1W	87.80(11)
N2-Mn1-O2W	79.44(13)	N2-Mn1-O1W	92.30(13)	O1W-Mn1-O2W	86.32(13)
Complex (2)					

Mn2-O5W	2.059(4)	Mn2-O7W	2.126(5)	Mn2-O8	2.109(4)
Mn2-O6W	2.060(4)	Mn2-O8W	2.077(4)	Mn2-N4	2.132(5)
Mn1-O2W	2.086(4)	Mn1-O4W	2.091(4)	Mn1-O6	2.120(4)
Mn1-O1W	2.126(5)	Mn1-O3W	2.104(4)	Mn1-N1	2.124(5)
O5W-Mn2-O7W	88.8(2)	O5W-Mn2-O8	174.9(2)	O5W-Mn2-O6W	92.12(18)
O5W-Mn2-O8W	86.55(18)	O5W-Mn2-N4	89.0(2)	O7W-Mn2-N4	177.8(2)
O8-Mn2-O7W	88.16(19)	O8-Mn2-N4	94.03(19)	O6W-Mn2-O7W	85.94(19)
O6W-Mn2-O8	91.78(16)	O6W-Mn2-O8W	174.36(18)	O6W-Mn2-N4	94.5(2)
O8W-Mn2-O7W	88.56(19)	O8W-Mn2-O8	89.24(16)	O8W-Mn2-N4	90.9(2)
O2W-Mn1-O4W	173.43(18)	O2W-Mn1-O6	92.25(15)	O2W-Mn1-O1W	86.48(16)
O2W-Mn1-O3W	90.43(16)	O2W-Mn1-N1	93.17(19)	O4W-Mn1-O6	89.79(16)
O4W-Mn1-O1W	87.34(17)	O4W-Mn1-O3W	87.40(17)	O4W-Mn1-N1	92.95(19)
O6-Mn1-O1W	88.25(17)	O6-Mn1-N1	93.26(18)	O3W-Mn1-O6	176.97(17)
O3W-Mn1-O1W	90.51(18)	O3W-Mn1-N1	87.99(19)	N1-Mn1-O1W	178.46(19)

Symmetry codes: [D] +X, -1+Y, +Z; [E] 1-X, 1-Y, 1-Z.

Table S3 Selected bond lengths/Å and bond angles/º for complex (3) and (4)

Complex (3)					
Co1-O2	2.046(4)	Co1-O3	2.142(5)	Co1-N4	2.059(6)
Co1-N1[A]	2.123(5)	Co1-O1W	2.193(5)	Co1-O4	2.233(4)
O2-Co1-O3	96.48(17)	O2-Co1-N4	109.4(2)	O2-Co1-N1[A]	86.96(18)
O2-Co1-O1W	90.16(17)	O2-Co1-O4	155.99(19)	O3-Co1-O1W	94.5(2)
O3-Co1-O4	59.93(17)	N4-Co1-O3	153.47(19)	N4-Co1-N1[A]	88.9(2)
N4-Co1-O1W	91.1(2)	N4-Co1-O4	94.5(2)	N1[A]-Co1-O3	86.9(2)
N1[A]-Co1-O1W	176.95(19)	N1[A]-Co1-O4	95.52(19)	O1W-Co1-O4	87.53(17)
Complex (4)					
Co1-N2	2.143(5)	Co1-O3W	2.168(5)	Co1-O4W	2.128(5)
Co1-O4[D]	2.001(5)	Co1-O2W	2.068(5)	Co1-O8	2.027(5)
Co2-O6	1.965(4)	Co2-O3[F]	1.950(5)	Co2-O1[E]	1.943(4)
Co2-N1	2.081(5)	N2-Co1-O3W	175.7(2)	O4W-Co1-N2	94.8(2)
O4W-Co1-O3W	83.40(19)	O4[D]-Co1-N2	86.2(2)	O4D-Co1-O3W	89.9(2)
O4D-Co1-O4W	87.5(3)	O4[D]-Co1-O2W	88.5(3)	O4D-Co1-O8	170.1(2)
O2W-Co1-N2	93.5(2)	O2W-Co1-O3W	88.0(2)	O2W-Co1-O4W	170.6(2)
O8-Co1-N2	103.7(2)	O8-Co1-O3W	80.3(2)	O8-Co1-O4W	92.4(3)
O8-Co1-O2W	90.0(3)	O6-Co2-N1	94.4(2)	O3[F]-Co2-O6	120.14(19)
O3[F]-Co2-N1	91.3(2)	O1[E]-Co2-O6	126.5(2)	O1[E]-Co2-O3[F]	112.7(2)
O1[E]-Co2-N1	92.3(2)				

Symmetry codes: [A] -1+X, -1+Y, -1+Z; [D] 3/2-X, 1/2+Y, 1/2-Z; [E] 1/2+X, -1/2-Y, 1/2+Z; [F] 1/2-X, 1/2+Y, 1/2-Z.

Table S4 **Hydrogen Bonding Geometry (Å, º) for Compound 2**

D – H ⋯ A	D – H / Å	H ⋯A / Å	D ⋯ A / Å	D – H ⋯A / °
O2W–H2W[A]···O2[A]	0.89	1.87	2.690(6)	152
O2W–H2W[B]···O7	0.89	1.88	2.673(5)	148
O5W–H5W[A]···O4[B]	0.88	2.06	2.699(7)	129
O5W–H5W[B]···O4[C]	0.88	2.10	2.726(6)	128
O7W–H7W[A]···O8[D]	0.89	2.07	2.950(7)	171
O4W–H4W[A]···O1W[E]	0.88	2.21	2.927(7)	139
O4W–H4W[B]···O2[F]	0.88	1.86	2.683(5)	156
O1W–H1W[A]···O6[E]	0.89	2.39	2.951(6)	121
O1W–H1W[B]···O7[G]	0.89	2.11	2.833(6)	138
O6W–H6W[A]···O3[A]	0.90	1.87	2.660(6)	146
O6W–H6W[B]···O5	0.89	1.88	2.712(7)	153
O8W–H8W[A]···O8[D]	0.89	2.12	2.994(6)	166
O8W–H8W[A]···O7W[D]	0.89	2.45	2.913(7)	112
O8W–H8W[B]···O5[C]	0.89	1.91	2.691(6)	145
O3W–H3W[A]···O1[G]	0.88	2.04	2.674(6)	128
O3W – H3W[B] • • • O1[F]	0.88	1.93	2.733(6)	152
O7W – H7W[B] • • • O3[B]	0.94(5)	1.90(6)	2.820(6)	167(5)

Symmetry codes: [A] x, y−1, z; [B] −x−1, −y, −z+1; [C] x+1, y, z; D: −x, −y−1, −z+1; [E] −x+1, −y+1, −z; [F] x−1, y−1, z; [G] −x+2, −y+1, −z.

Table S5 π-π and C-H···π interactions for Compound 3

C-H···π				
C-H···π	**C-H/Å**	**H···π/Å**	**C···π/Å**	**C-H···π/°**
C17-H17B···R3[F]	0.97	2.81	3.54	133
C20-H20···R5[G]	0.93	2.84	3.49	128

[F] -X, 1-Y, -Z; [G] -1-X,-Y,-1-Z R3:C5 C6 C7 C8 C9 C10; R4:C11 C12 C13 C14 C15 C16; R5:C23 C24 C25 C26 C27 C28			
π-π			
R···R	**Centroid-centroid distance/Å**	**Offset angle/°**	**Dihedral angle/°**
R4···R4[F]	3.64	23.07	0

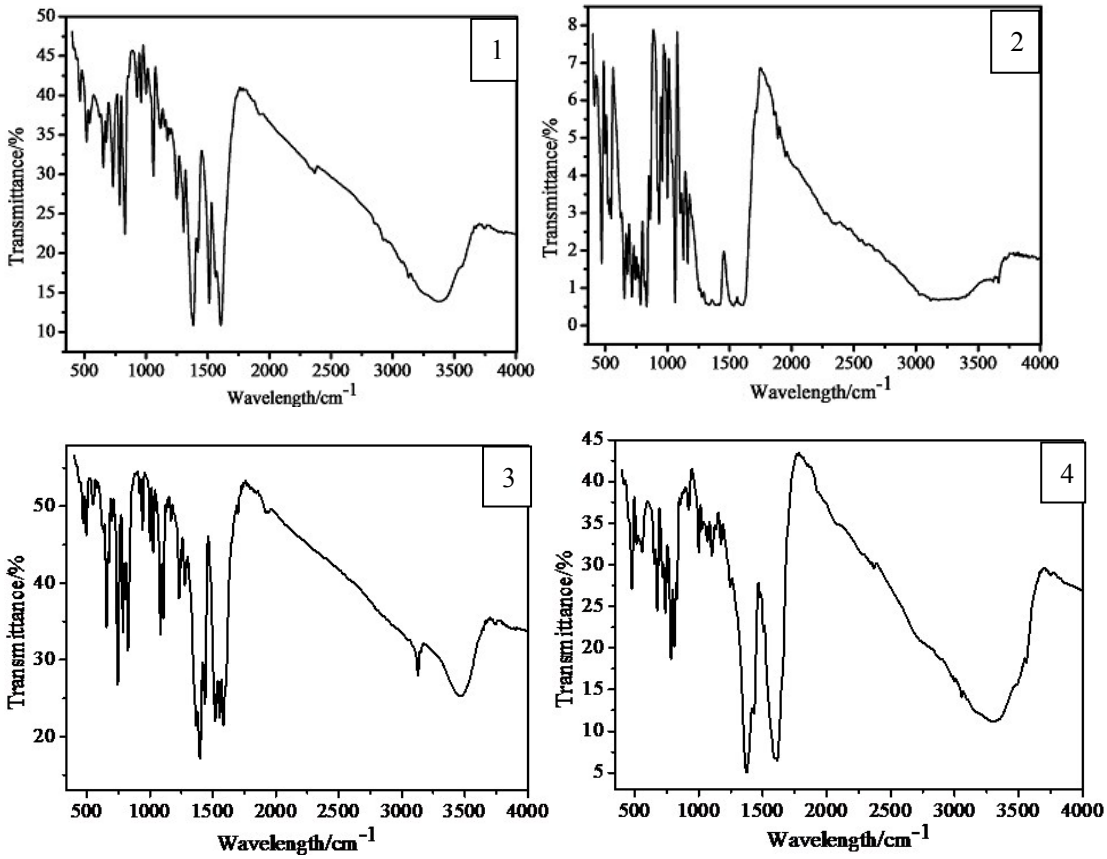


Figure S1. The IR spectra of the series complexes.

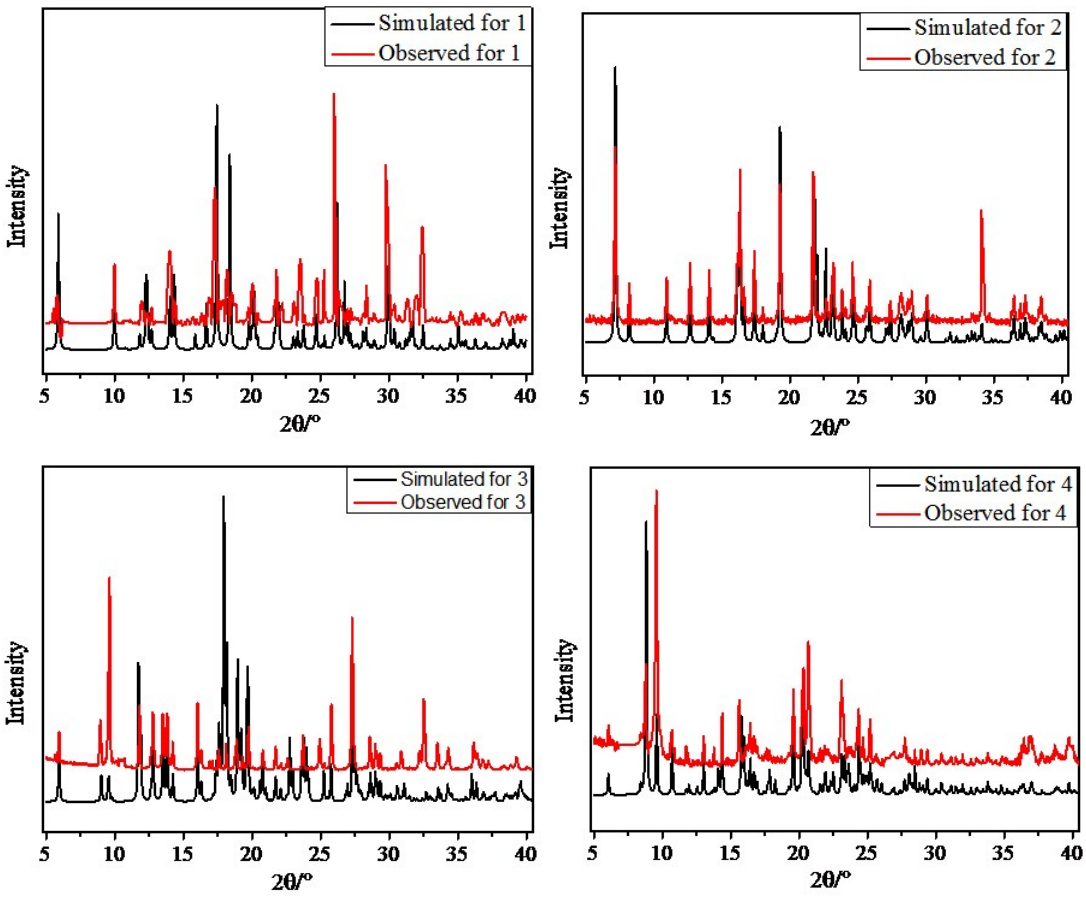


Figure S2. PXRD patterns of the series complexes. Black: Simulated from the X-ray single-crystal data; Red: observed for the as-synthesized solids.

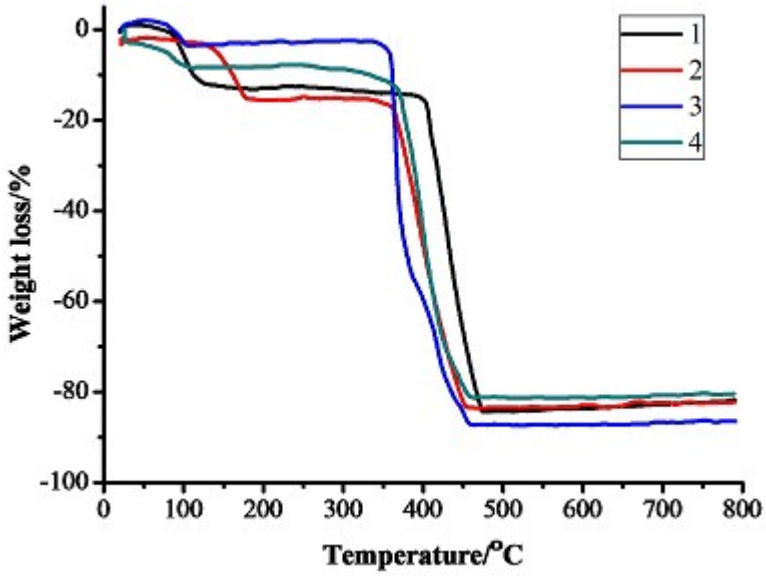
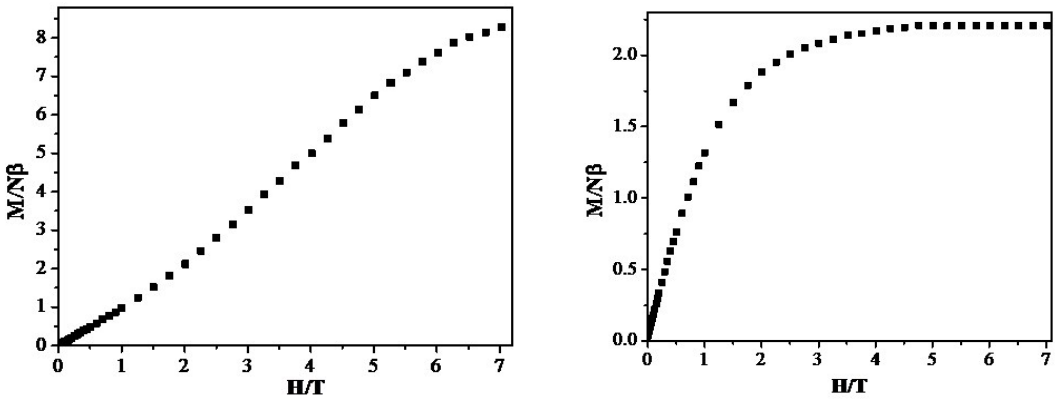


Figure S3 The TG curves of compounds **1-4**.



(a) (b)

Figure S4 Field-dependent magnetization for **1**(a) and **3**(b) at 1.90 K and 2.0 K.

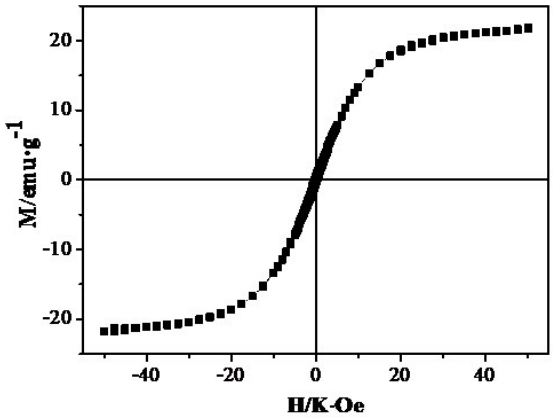


Figure S5 M-H loops taken for **3** at 2.0 K .

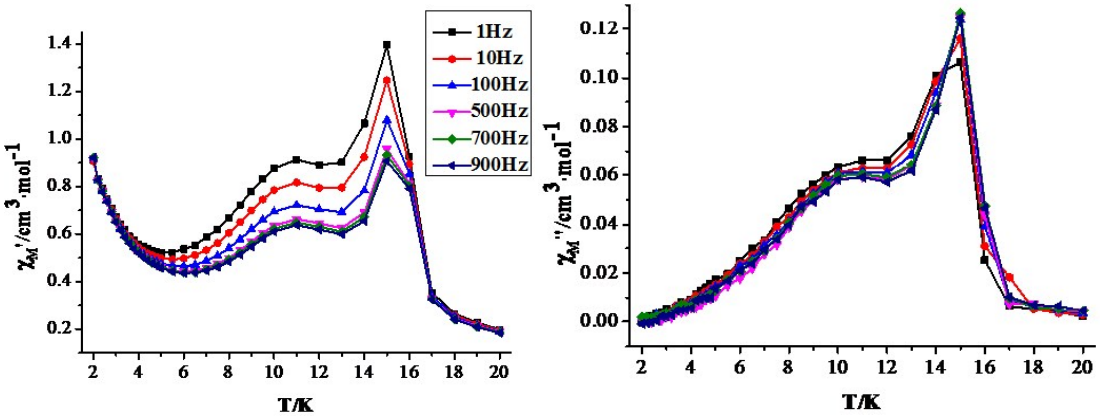


Figure S6 Temperature dependence of AC susceptibilities of **3** in H_{ac}=3 Oe and H_{dc}=0 Oe.