Supporting Information

Syntheses, structures, and magnetic properties of a series of trinuclear complexes with different spin configurations

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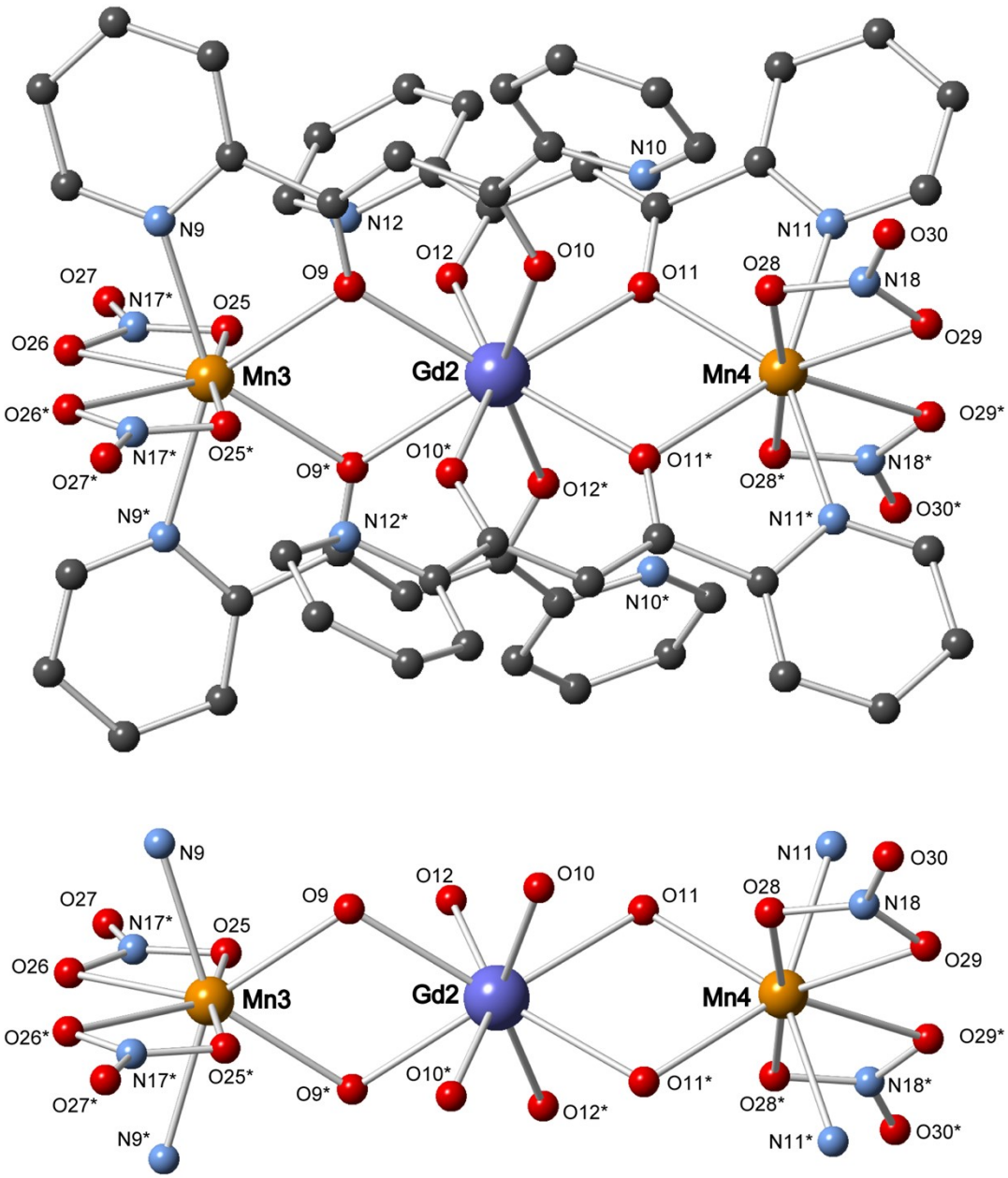

Figure S1. Molecular structures of Mn3–Gd2–Mn4 trinuclear moiety **2** (top) and its core (bottom).

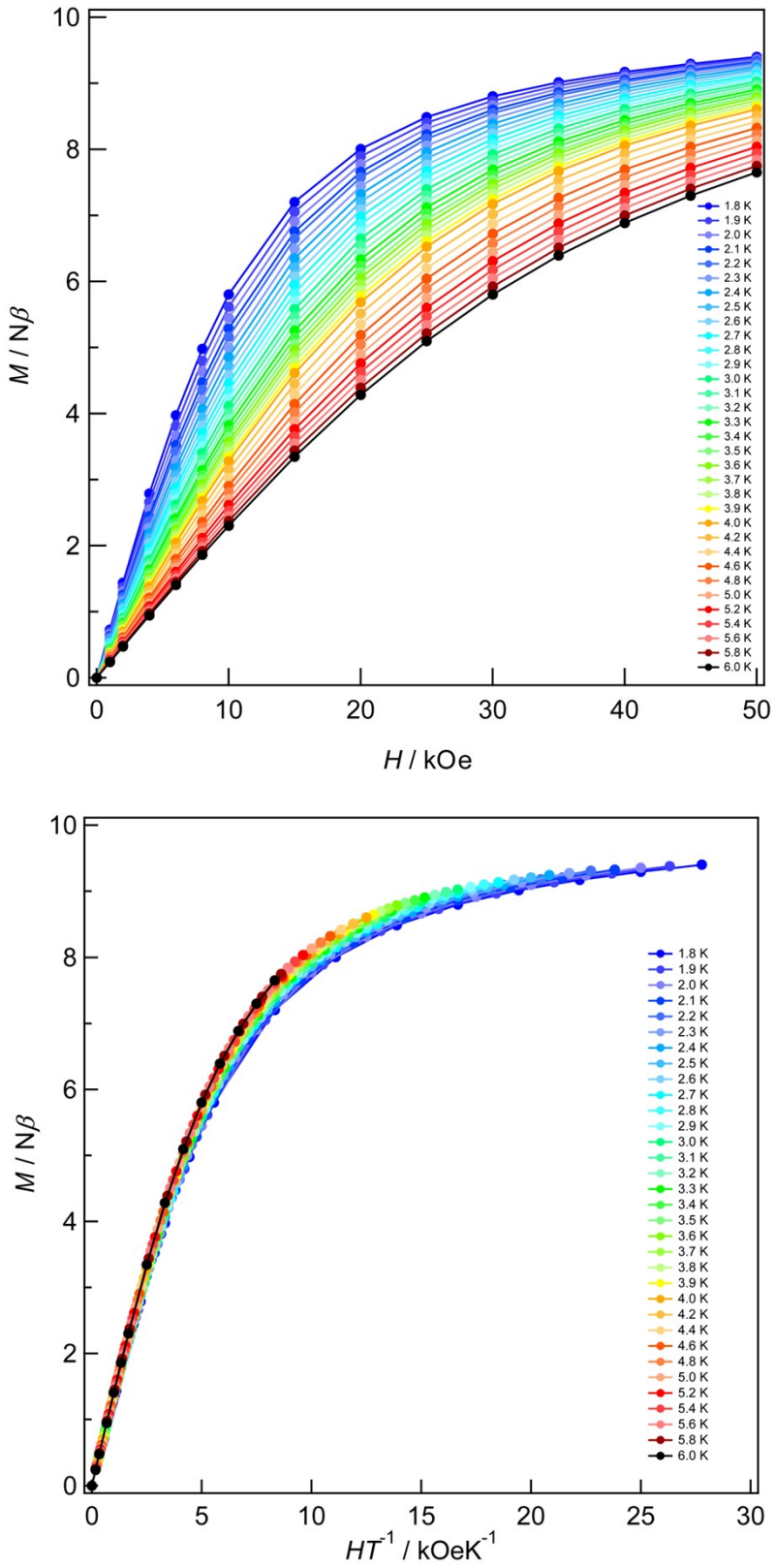

Figure S2. Field dependences of magnetization for **1'** (top) and the reduced magnetization curves (bottom).

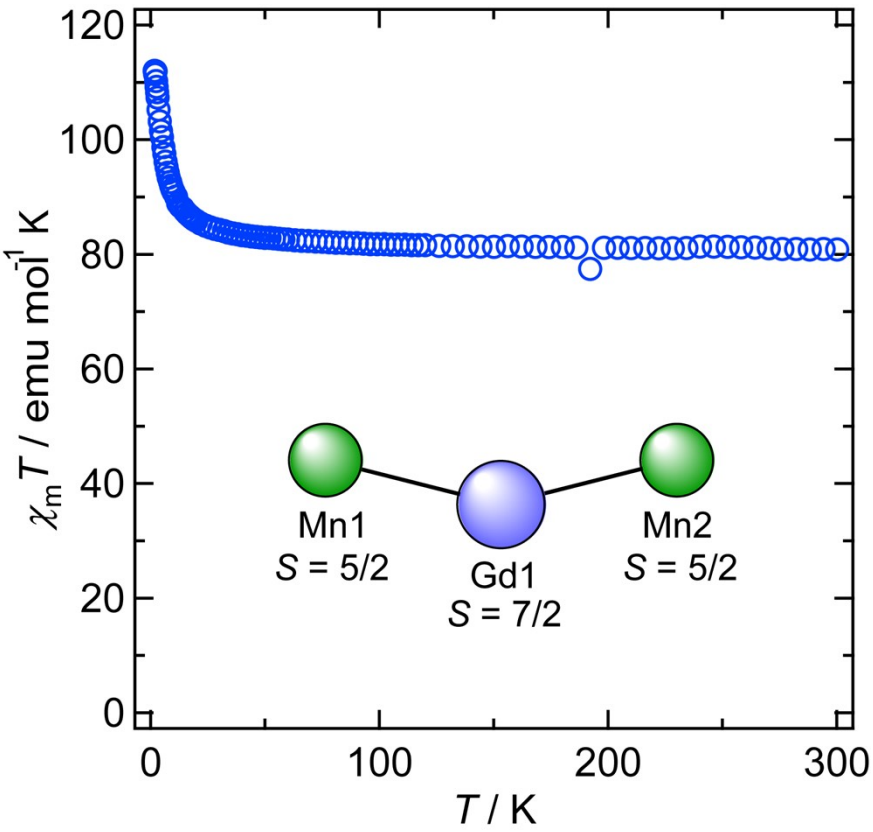

Figure S3. The $\chi_m T$ versus T plots of complex **2'**.

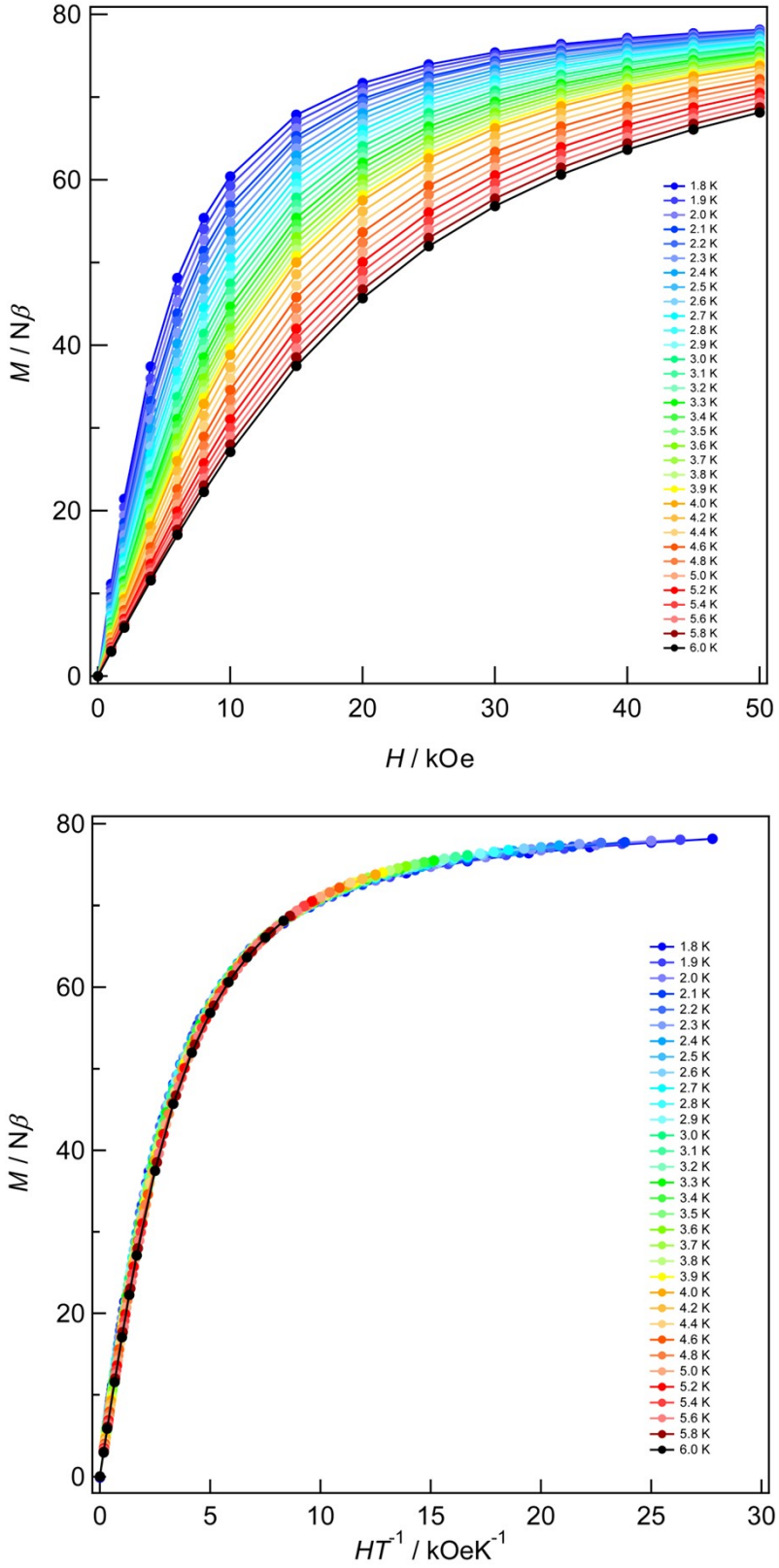

Figure S4. Field dependences of magnetization for **2'** (top) and the reduced magnetization curves (bottom).

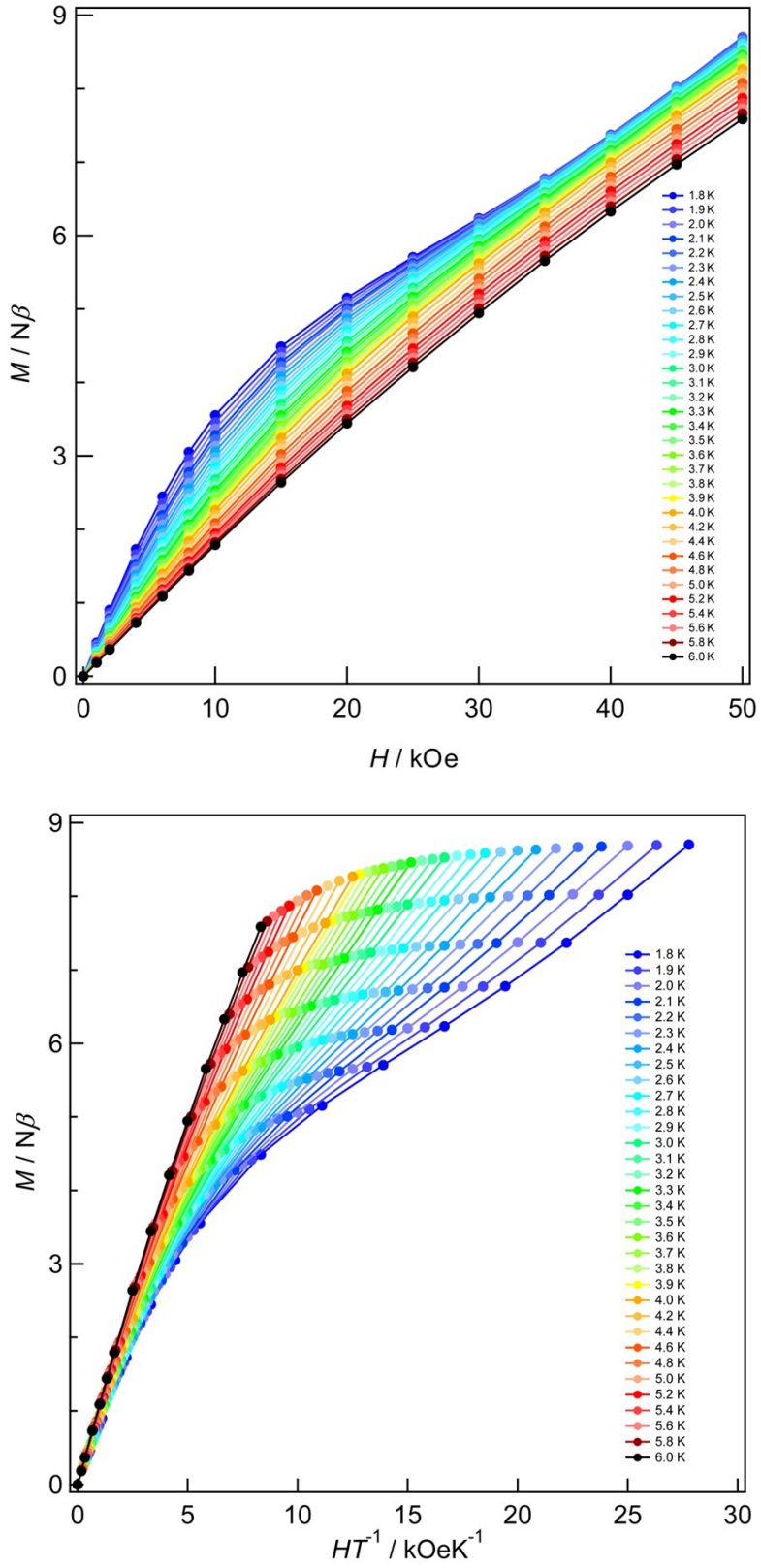

Figure S5. Field dependences of magnetization for **3'** (top) and the reduced magnetization curves (bottom).

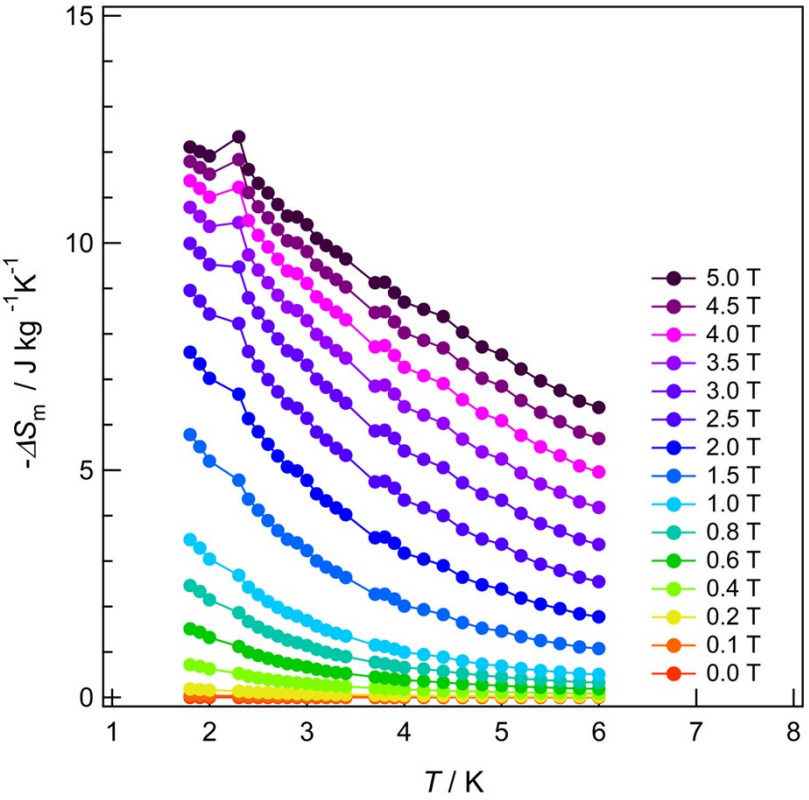

Figure S6. Calculated $-\Delta S_m$ over a range of fields for **1'**. The maximum value is 12.3 J kg^{-1} K^{-1}, calculated for 0 – 5 T at 2.3 K.

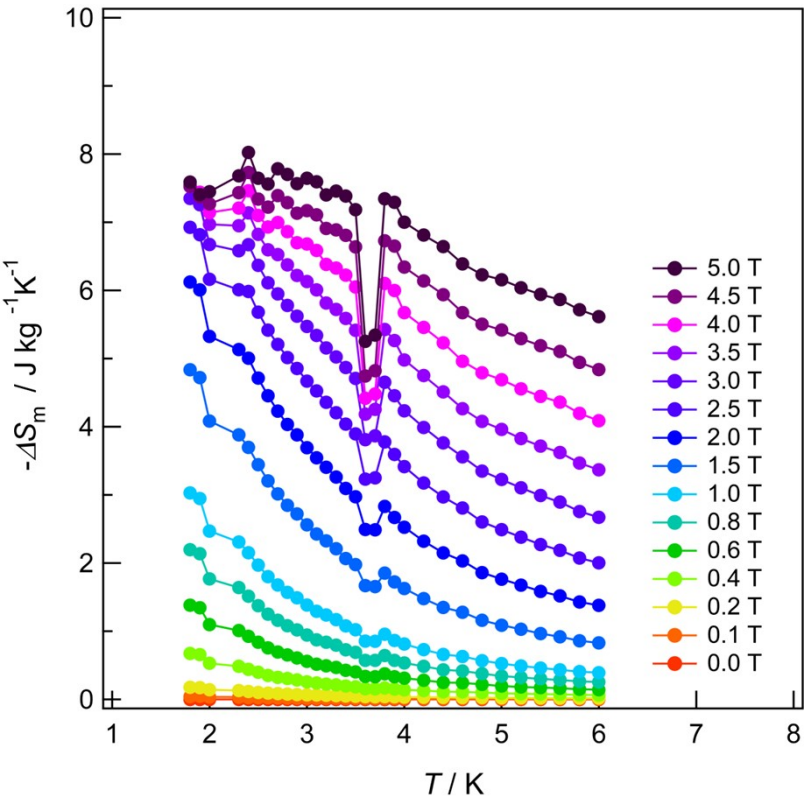

Figure S7. Calculated $-\Delta S_m$ over a range of fields for **3'**. The maximum value is 8.0 J kg^{-1} K^{-1}, calculated for 0 – 5 T at 2.4 K.

Table S1 Representative 3d-4f complexes exhibiting large $-\Delta S_m$ values.

	$-\Delta S_m$ **(J kg^{-1} K^{-1})**	ΔH (T)	T_{max} (K)	Ref.
MnGd	23.5	7	2.7	1
Mn_2Gd	24.8	5	2.4	This study
Co_3Dy	12.6	7	5	2
Cr_2Gd_3	28.7	9	2.2	3
Co_4Gd_2	20.0	7	3	4
Mn_4Gd_4	19.0	7	4	5
Mn_4Gd_6	33.7	7	3	6
Ni_6Gd_6	26.5	7	3	7
Co_6Gd_8	28.6	7	3	4
Mn_9Gd_9	28.0	7	3	6
$Mn_{12}Gd_6$	15.8	7	6	8
$Ni_{12}Gd_{36}$	36.3	7	3	9
$Co_{12}Gd_{30}$	44.7	7	1	10
$Co_{10}Gd_{42}$	41.3	7	2	11
$Ni_{10}Gd_{42}$	38.2	7	2	11
Co_7Gd_{42}	40.5	7	2	12
Ni_7Gd_{42}	38.4	7	2	12
$Ni_{56}Gd_{52}$	40.5	7	3	13
$Ni_{36}Gd_{102}$	41.3	7	2	14
$Ni_{64}Gd_{78}$	40.6	7	3	15
$Ni_{64}Gd_{96}$	42.8	7	3	16

Table S2. Crystal parameters of **1**, **2** and **3**.

	Comp. 1	Comp. 2	Comp. 3
Formula	$C_{74}H_{64}Mn_2N_{19}O_{32}Y_2$	$C_{98}H_{79.50}Gd_{3.50}Mn_3N_{30}O_{63.50}$	$C_{45.50}H_{37.50}Mn_3N_{13}O_{21}$
M / g mol^{-1}	2019.14	3408.61	1267.20
Temp. / K	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$	*P*ccn	*P***Error!**
a / Å	10.9358(17)	61.336(16)	13.930(5)
b / Å	16.744(3)	14.346(4)	14.155(5)
c / Å	47.214(8)	29.106(8)	16.875(6)
α / º	–	–	66.220(5)
β / º	94.178(2)	–	86.670(6)
γ / º	–	–	89.503(6)
V / Å^3	8622(2)	25612(12)	3039(2)
Z	4	8	2
d / g cm^{-3}	1.555	1.768	1.385
μ / mm^{-1}	1.714	2.185	0.694
F(000)	4096	13476	1289
Reflections			
collected / unique	49084 / 19532	144189 / 29346	17186 / 13308
R_{int}	0.1544	0.0762	0.0627
GOF	1.090	1.147	1.074
$R1$ ($I > 2\sigma(I)$)	0.1247	0.0810	0.1212
R_w2 ($I > 2\sigma(I)$]	0.2982	0.1858	0.3321
$\Delta\rho_{max}$ / e Å^{-3}	2.088	3.296	1.742
$\Delta\rho_{min}$ / e Å^{-3}	–1.778	–2.579	–1.568
CCDC No.	2107790	2107791	2107792

Table S3 Selected bond lengths and angles for all complexes.

Complex 1

Mn1···N3	2.250(10) Å	Mn2···O7	2.232(6) Å	Y1···O4	2.254(7) Å
Mn1···O12	2.260(8) Å	Mn2···O15	2.272(7) Å	Y1···O2	2.308(7) Å
Mn1···O9	2.265(8) Å	Mn2···O5	2.305(8) Å	Y1···O6	2.322(7) Å
Mn1···O3	2.273(7) Å	Mn2···N5	2.306(8) Å	Y1···O7	2.341(7) Å
Mn1···N1	2.280(10) Å	Mn2···N2	2.344(8) Å	Y1···O3	2.356(7) Å
Mn1···O1	2.317(7) Å	Mn2···N7	2.346(9) Å	Y1···O8	2.358(7) Å
Mn1···O10	2.474(9) Å	Mn2···O2	2.384(7) Å	Y1···O1	2.370(6) Å
Mn1···O13	2.488(8) Å	Mn2···O16	2.395(8) Å	Y1···O5	2.413(6) Å

Mn1···O1···Y1	107.6(3) deg.	Mn2···O5···Y1	98.7(2) deg.
Mn1···O3···Y1	109.6(3) deg.	Mn2···O7···Y1	103.0(2) deg.

Complex 2

Mn1···N1	2.239(9) Å	Mn3···O25	2.230(12) Å	Gd1···O6	2.355(7) Å
Mn1···N3	2.249(9) Å	Mn3···N9	2.271(13) Å	Gd1···O2	2.375(6) Å
Mn1···O13	2.270(7) Å	Mn3···O9	2.310(8) Å	Gd1···O8	2.377(6) Å
Mn1···O16	2.271(8) Å	Mn3···O26	2.486(12) Å	Gd1···O4	2.377(6) Å
Mn1···O3	2.276(7) Å			Gd1···O7	2.383(6) Å
Mn1···O1	2.331(6) Å			Gd1···O1	2.402(6) Å
Mn1···O17	2.432(8) Å			Gd1···O5	2.410(6) Å
Mn1···O14	2.575 Å			Gd1···O3	2.415(6) Å
Mn2···O22	2.216(7) Å	Mn4···O28	2.243(11) Å	Gd2···O10	2.353(9) Å
Mn2···N5	2.284(8) Å	Mn4···N11	2.273(9) Å	Gd2···O9	2.363(8) Å
Mn2···O19	2.285(7) Å	Mn4···O11	2.303(7) Å	Gd2···O12	2.375(7) Å
Mn2···O5	2.285(6) Å	Mn4···O29	2.510(9) Å	Gd2···O11	2.386(7) Å
Mn2···O7	2.302(6) Å				
Mn2···N7	2.302(8) Å				
Mn2···O20	2.421(7) Å				
Mn2···O23	2.581 Å				

Mn1···O1···Gd1	107.5(3) deg.	Mn2···O5···Gd1	110.1(3) deg.
Mn1···O3···Gd1	108.9(3) deg.	Mn2···O7···Gd1	110.5(3) deg.
Mn3···O9···Gd2	110.1(4) deg.	Mn4···O11···Gd2	108.9(3) deg.

Complex 3

Mn1···O3	2.249(6) Å	Mn2···O4	2.104(6) Å	Mn3···O13	2.245(6) Å
Mn1···O7	2.257(7) Å	Mn2···O6	2.142(5) Å	Mn3···N2	2.258(6) Å
Mn1···O10	2.274(6) Å	Mn2···O1	2.154(5) Å	Mn3···O5	2.267(5) Å
Mn1···N1	2.280(7) Å	Mn2···O2	2.161(5) Å	Mn3···O16	2.271(6) Å
Mn1···N3	2.290(8) Å	Mn2···O5	2.189(5) Å	Mn3···N5	2.272(7) Å
Mn1···O1	2.316(5) Å	Mn2···O3	2.192(5) Å	Mn3···O2	2.279(5) Å
Mn1···O11	2.398(7) Å			Mn3···O17	2.388(7) Å
Mn1···O8	2.435(6) Å			Mn3···O14	2.63 Å

Mn1···O1···Mn2	108.3(2) deg.	Mn2···O2···Mn3	107.9(2) deg.
Mn1···O3···Mn2	109.4(2) deg.	Mn2···O5···Mn3	107.4(2) deg.

Table S4 Bond valence sum calculations for all complexes.

	Mn1	Mn2	Mn3	Mn4
Complex 1				
Mn(II)	**2.052**	**2.062**		
Mn(III)	1.892	1.902		
Mn(IV)	1.857	1.866		
Complex 2				
Mn(II)	**2.055**	**2.015**	**2.066**	**2.032**
Mn(III)	1.895	1.858	1.906	1.874
Mn(IV)	1.859	1.824	1.870	1.839
Complex 3				
Mn(II)	**2.090**	**2.233**	**2.082**	
Mn(III)	1.927	2.059	1.920	
Mn(IV)	1.891	2.02	1.884	

Explanation of alerts in CIFCHECK:

Datablock: Comp1
Alert Level B

The following B-level alerts arise from the diffraction data being slightly weak.
PLAT220_ALERT_2_B NonSolvent Resd 1 C Ueq(max)/Ueq(min) Range 6.8 Ratio

The following B-level alerts arise from the atom O25 belong to coordinating nitrate ion, which is weakly bonding to Mn ion.
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of O25 Check

The following B-level alerts arise from the disorder of solvent molecule (p-Xylene).
PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C74 Check

The following B-level alerts arise from the diffraction data being slightly weak.
PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.02191 Ang.

Datablock: Comp2
Alert Level B

The following B-level alerts arise from the diffraction data being slightly weak.
PLAT230_ALERT_2_B Hirshfeld Test Diff for O44 --N23 . 10.8 s.u.
PLAT230_ALERT_2_B Hirshfeld Test Diff for O45 --N23 . 11.2 s.u.
PLAT234_ALERT_4_B Large Hirshfeld Difference O58 --N28 . 0.28 Ang.

The following B-level alerts arise from the atoms O55, O56, N23 belong to coordinating nitrate ion, which is weakly bonding to Mn ion.
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of O55 Check
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of O56 Check
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of N23 Check

The following B-level alerts arise from the disordered solvent molecules.
PLAT260_ALERT_2_B Large Average Ueq of Residue Including O65 0.353 Check
PLAT306_ALERT_2_B Isolated Oxygen Atom (H-atoms Missing ?) ..... O65 Check
PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C96 Check
PLAT430_ALERT_2_B Short Inter D...A Contact O62 ..O67 . 2.78 Ang. x,y,z = 1_555 Check

The following B-level alerts arise from the diffraction data being slightly weak.
PLAT601_ALERT_2_B Unit Cell Contains Solvent Accessible VOIDS of . 120 Ang3**
PLAT780_ALERT_1_B Coordinates do not Form a Properly Connected Set Please Do !
PLAT919_ALERT_3_B Reflection # Likely Affected by the Beamstop ... 1 Check
PLAT971_ALERT_2_B Check Calcd Resid. Dens. 0.07A From N23 3.29 eA-3
PLAT972_ALERT_2_B Check Calcd Resid. Dens. 0.24A From O62 -2.57 eA-3
PLAT973_ALERT_2_B Check Calcd Positive Resid. Density on Gd3 1.51 eA-3

Datablock: Comp3
Alert Level B

The following B-level alerts arise from the diffraction data being slightly weak.
PLAT084_ALERT_3_B High wR2 Value (i.e. > 0.25) ..... 0.37 Report
PLAT213_ALERT_2_B Atom C11 has ADP max/min Ratio ..... 4.1 prolat
PLAT213_ALERT_2_B Atom C27 has ADP max/min Ratio ..... 4.1 prolat

The lattice solvent molecule is disordered.
PLAT601_ALERT_2_B Unit Cell Contains Solvent Accessible VOIDS of . 168 Ang3**

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