Electronic Supplementary Material (ESI) for CrystEngComm
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Supporting Information for

Five intercalating coordination networks based on an identical anionic lamella and diverse hydrated cations

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Experimental Section

All of the chemicals were obtained from commercial sources and were used without further purification, except H_4**pdtc** was synthesized according to the literature method.[1] IR spectra were recorded from KBr pellets on a FTS-40 spectrophotometer. Thermogravimetric analyses (TGA) were carried out under N_2 atmosphere on a NETZSCH STA 409 PC/PG instrument at a heating rate of 10 ^oC min^{-1}. Powder X-ray diffraction data (PXRD) were recorded on a RIGAKU D/MAX 2550/PC for Cu-Kα (λ = 1.5406Å). Variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS(SQUID)-XL magnetometer. All data were corrected for diamagnetism of all constituents estimated by Pascal's constants.[2] The determinations of the unit cells and data collections for the crystals of compounds **1**, **2**, **3**, **4** and **5** were performed on a *CrysAlisPro*, Oxford Diffraction Ltd. The data of **1**, **2**, **3**, **4** and **5** were collected using graphite-monochromatic Mo-K_α radiation (λ = 0.71073 Å) at 293 K. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.[3] All structures were solved by direct methods, and refined by full-matrix least-square methods with the **SHELX-97** program package.[4] All non-hydrogen atoms including solvent molecules were located successfully from Fourier maps and were refined anisotropically. The H atoms on C atoms were generated geometrically. The H atoms of the water molecules were clearly visible in difference maps and were handled in the subsequent refinement with fixed isotropic displacement parameters.

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The spin-coupled Gd^{III} dimer equation deduced from the isotropic spin Hamiltonian $H = -JS_{Gd1} \cdot S_{Gd2}$ with the quantum numbers $S_{Gd1} = S_{Gd2} = 7/2$ as following:

$$x_{Mb} = \left(\frac{2N\beta^2 g^2}{kT}\right) \times \left(\frac{e^x + 5e^{3x} + 14e^{6x} + 30e^{10x} + 55e^{15x} + 91e^{21x} + 140e^{28x}}{1 + 3e^x + 5e^{3x} + 7e^{6x} + 9e^{10x} + 11e^{15x} + 13e^{21x} + 15e^{28x}}\right)$$

$x_{Mb} = J/kT$

$$x_M = \frac{x_{Mb}}{1 - \frac{2zJ'}{N\beta^2 g^2} x_{Mb}}$$

$$x_{MT} = \left(\frac{N\beta_T^2 g_T^2}{3k(T-\theta)}\right) \times S_T(S_T + 1)$$

Synthesis of $[H_3O][Gd(H_2O)_2(pdtc)] \cdot H_2O$ (1)

H_4**pdtc** (0.128 g, 0.5 mmol) was dissolved in 50 mL H_2O and the pH was adjusted to 1.5 by 1.0 M HCl aqueous solution. $Gd(NO_3)_3 \cdot 6H_2O$ (0.203 g, 0.45 mmol) was added into the mixture under stirring for 5 min at room temperature, which was subsequently sealed in a screw vial and heated at 95 ^oC for 12 h. Colorless crystals were collected by filtration, washed with water for several times and dried at room temperature (Yield: 73%). TGA showed that a weight loss of 15.0% occurred between 30 and 177 ^oC, corresponding to the loss of water molecules and aqua ligands (expected 15.0%). IR (KBr) cm^{-1}: 500 (w), 541 (w), 563 (w), 646 (s) , 841 (s), 885 (s), 1161 (s), 1263 (w), 1336 (s), 1410 (s), 1470 (s), 1555 (s), 1599 (s), 1645 (s).

Synthesis of $[Zn(H_2O)_6][Gd(H_2O)_2(pdtc)]_2 \cdot 4H_2O$ (2)

H_4**pdtc** (0.128 g, 0.5 mmol) was dissolved in 50 mL H_2O and the pH was adjusted to 1.5 by 1.0 M HCl aqueous solution. $Gd(NO_3)_3 \cdot 6H_2O$ (0.203 g, 0.45 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.297 g, 1.0 mmol) were added under stirring for 5 min at room temperature. The resulting solution in a screw vial and heated at 95 ^oC for 12 h. Colorless crystals were collected by filtration, washed with water for several times and dried at room temperature (Yield: 73%). TGA showed that the

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release of water molecules occurred between 30 and 248 ^{o}C (calculated: 22.2%; found: 22.0%). IR (KBr) cm^{-1}: 498 (w), 645 (s), 709 (w), 842 (s), 886 (w), 1161 (s), 1261 (w), 1336 (s), 1407 (s), 1468 (s), 1561 (s), 1604 (s), 1648 (s).

Synthesis of $[Cu(H_2O)_6][Gd(H_2O)_2(pdtc)]_2 \cdot 4H_2O$ (3)

The preparation procedure of **3** is similar to that of **2**, except $Cu(NO_3)_2 \cdot 3H_2O$ (0.242 g, 1.0 mmol) was used instead of $Zn(NO_3)_2 \cdot 6H_2O$ (Yield: 77%). TGA showed that the release of water molecules occurred between 30 and 245 ^{o}C (calculated: 22.3%; found: 20.7%). IR (KBr) cm^{-1}: 490 (w), 556 (w), 638 (w), 839 (w), 1160 (s), 1337 (s), 1385 (s), 1425 (s), 1473 (w), 1551 (s), 1597 (s), 1637 (s).

Synthesis of $[Co(H_2O)_6][Gd(H_2O)_2(pdtc)]_2 \cdot 3H_2O$ (4)

The preparation procedure of **4** is similar to that of **2**, except $Co(NO_3)_2 \cdot 6H_2O$ (0.291 g, 1.0 mmol) was used instead of $Zn(NO_3)_2 \cdot 6H_2O$ (Yield: 83%). TGA showed that the release of water molecules occurred between 30 and 268 ^{o}C (calculated: 21.1%; found: 21.0%). IR (KBr) cm^{-1}: 558 (w), 646 (w), 709 (w), 841 (w), 881 (w), 1160 (s), 1261 (w), 1337 (s), 1385 (s), 1406 (s), 1467 (w), 1560(s), 1578 (s), 1637 (s).

Synthesis of $[Mn(H_2O)_6][Gd(H_2O)_2(pdtc)]_2 \cdot 3H_2O$ (5)

The preparation procedure of **3** is similar to that of **2**, except $MnCl_2 \cdot 4H_2O$ (0.198 g, 1.0 mmol) was used instead of $Zn(NO_3)_2 \cdot 6H_2O$ (Yield: 71%). TGA showed that the release of water molecules occurred between 30 and 256 ^{o}C (calculated: 21.2%; found: 20.9%). IR (KBr) cm^{-1}: 501 (w), 541 (w), 562 (w), 645 (s), 709 (w), 840 (s), 883 (s), 1161 (s), 1262 (w), 1357 (s), 1408 (s), 1466 (s), 1552 (s), 1587 (s).

References

1. N. J. Babu, A. Nangia, *Cryst. Growth Des*., 2006, **6**, 1753.
2. P. Pascal, *Ann. Chim. Phys.*, 1910, **19**, 5.
3. Oxford Diffraction Ltd. CrysAlisPro, Version 1.171.33.56, **2010**.

4. G. M. Sheldrick, Program for Structure Refinement, University of Göttingen, Germany, **1997**.

Figures:

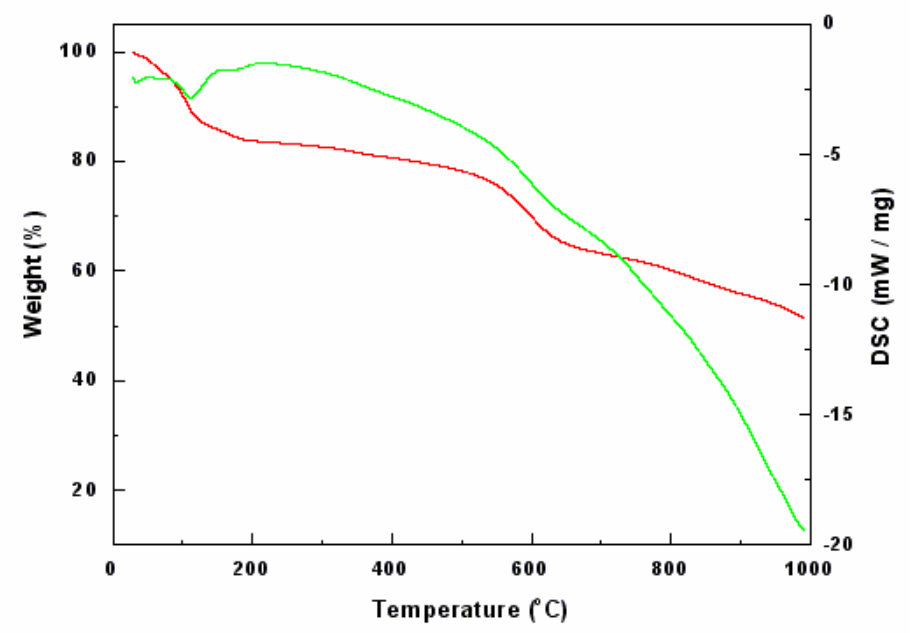

Fig. S1. TGA result of **1**.

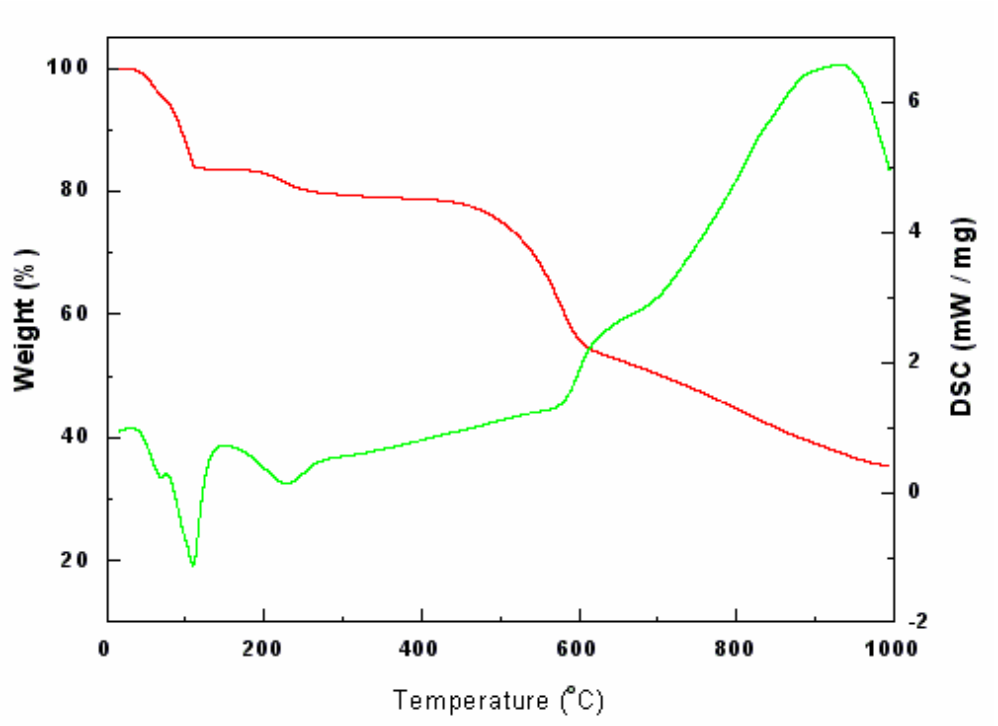

Fig. S2. TGA result of **2**.

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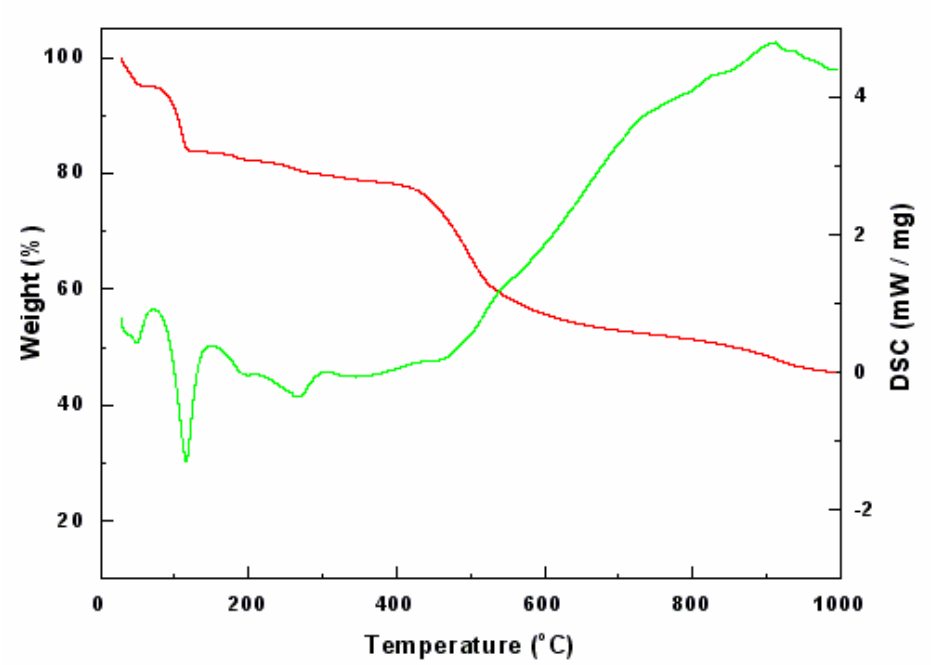

Fig. S3. TGA result of **3**.

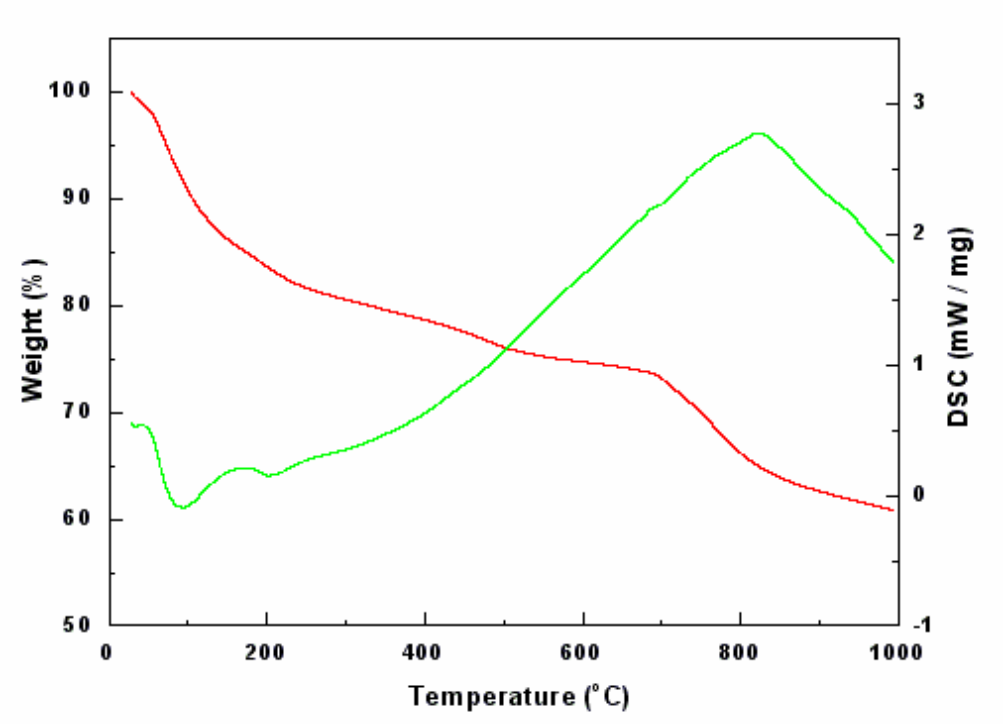

Fig. S4. TGA result of **4**.

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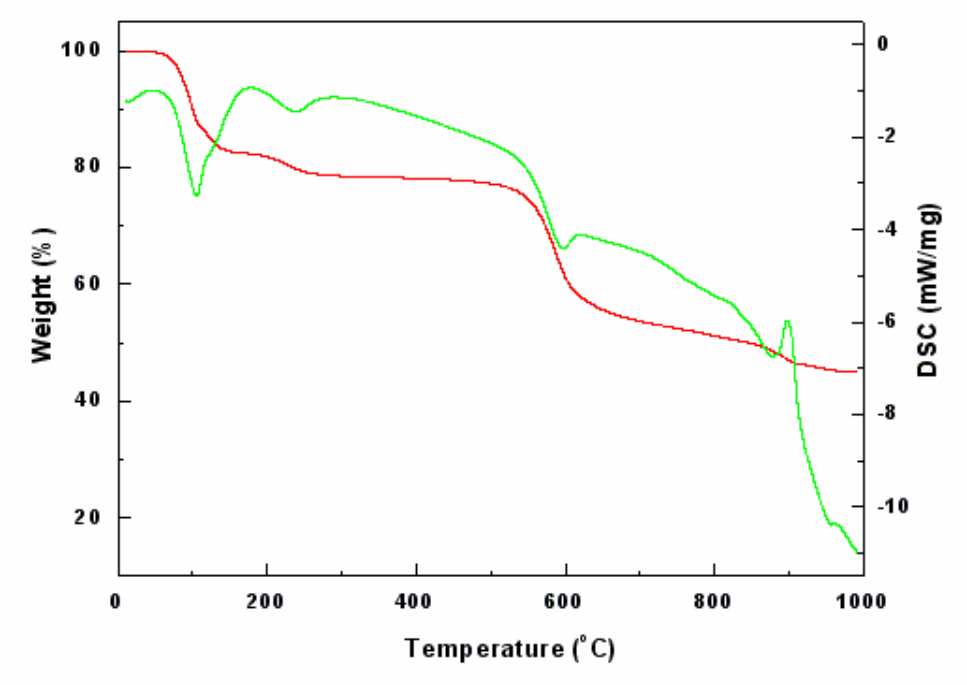

Fig. S5. TGA result of **5**.

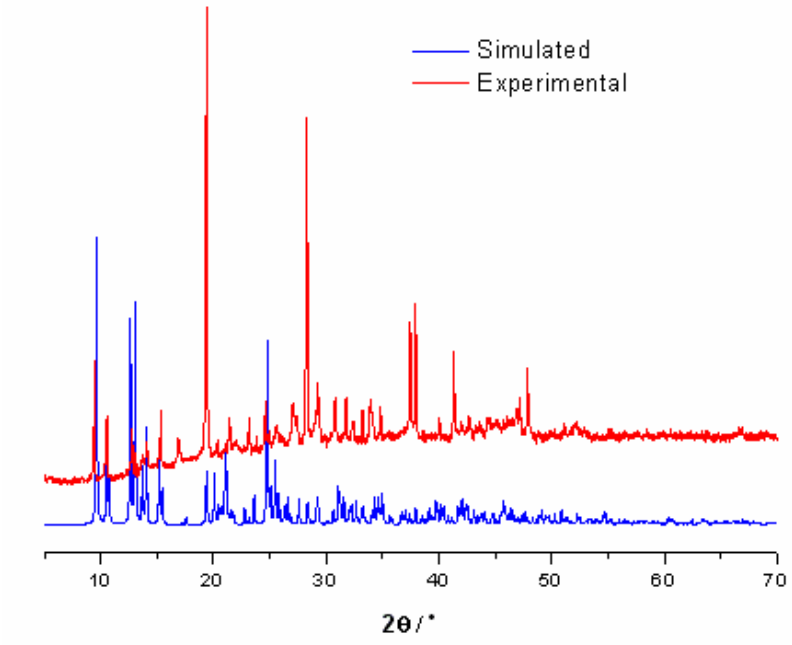

Fig. S6.Powder X-ray diffraction patterns for compound **1**.

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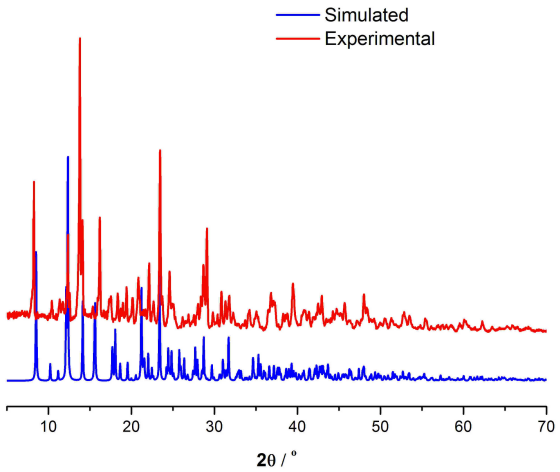

Fig. S7. Powder X-ray diffraction patterns for compound **2**.

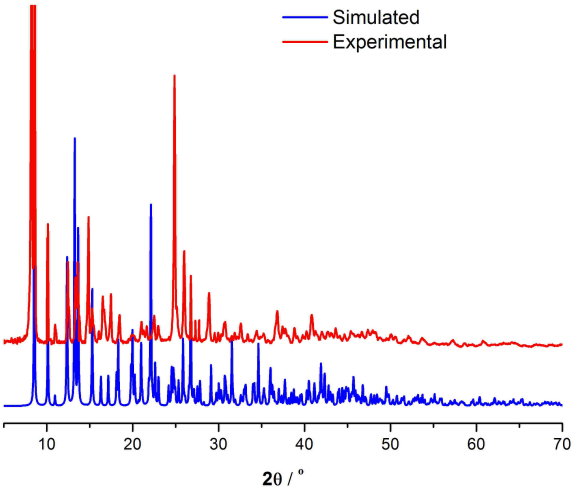

Fig. S8. Powder X-ray diffraction patterns for compound **3**.

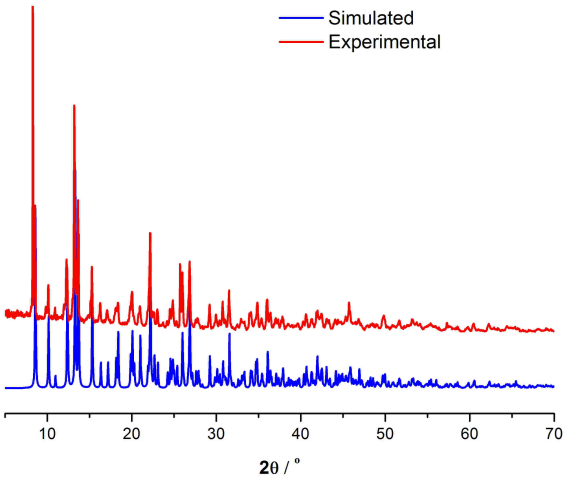

Fig. S9. Powder X-ray diffraction patterns for compound **4**.

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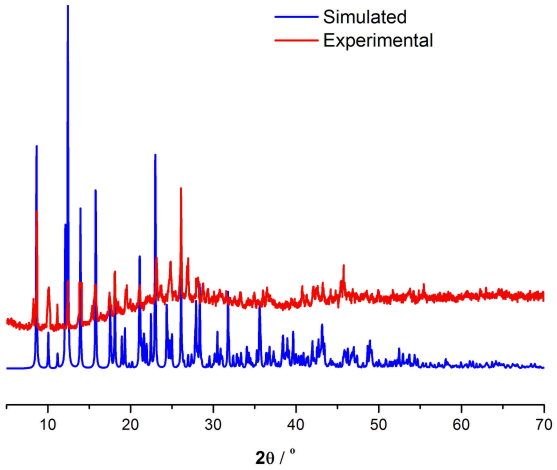

Fig. S10. Powder X-ray diffraction patterns for compound **5**.

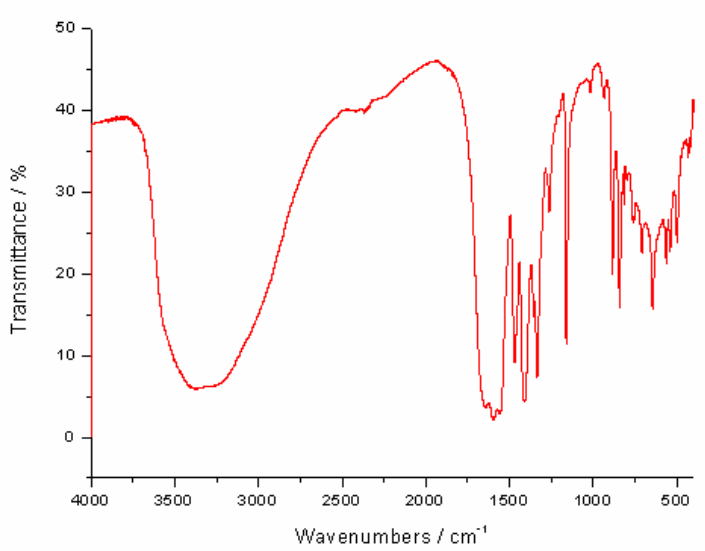

Fig. S11. IR spectrum of compound **1**.

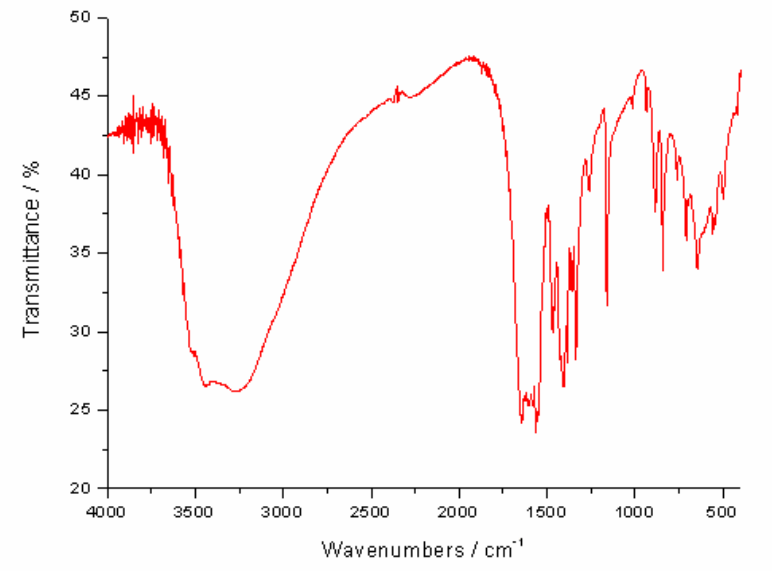

Fig. S12. IR spectrum of compound **2**.

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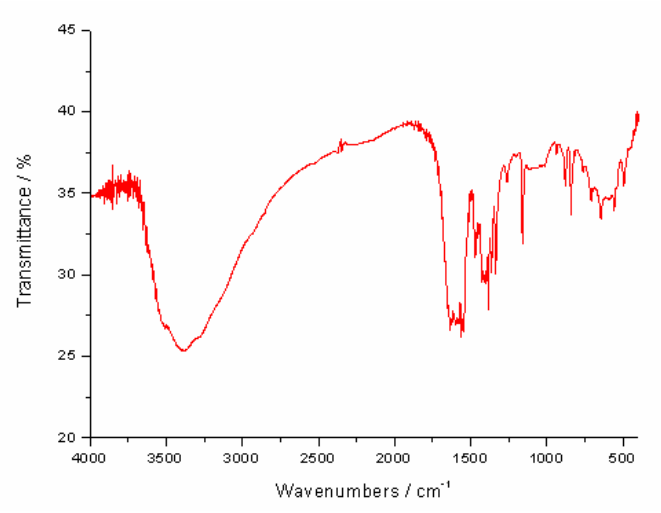

Fig. S13. IR spectrum of compound **3**.

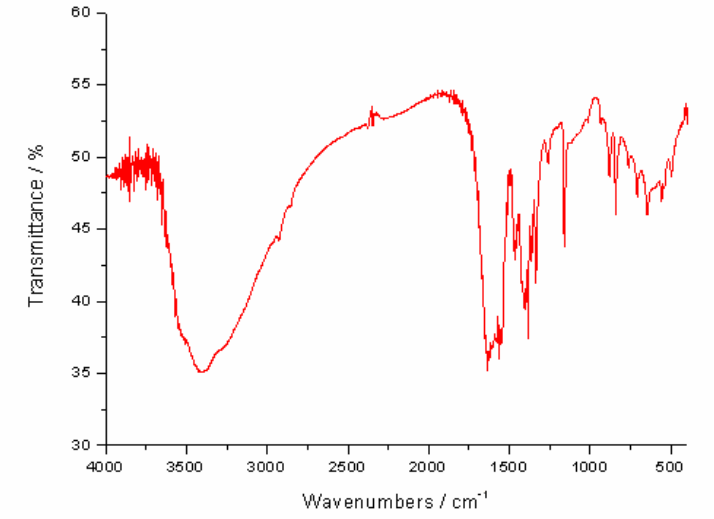

Fig. S14. IR spectrum of compound **4**.

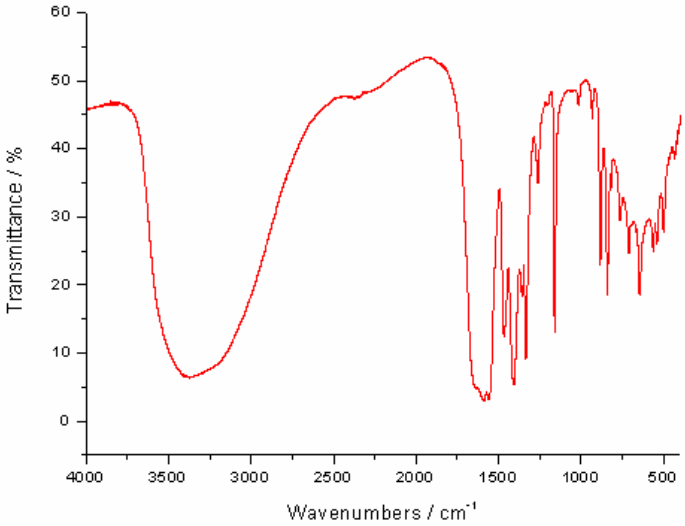

Fig. S15. IR spectrum of compound **5**.

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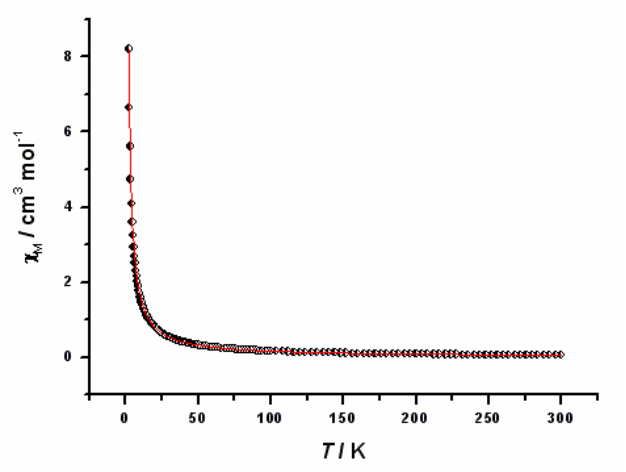

Fig. S16. The χ_M *vs.* T plot for compound **1** (The red line represents the best fit).

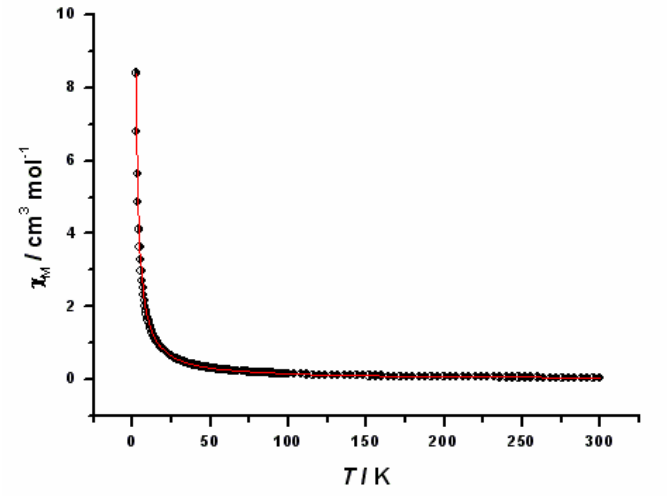

Fig. S17. The χ_M *vs.* T plot for compound **2** (The red line represents the best fit).

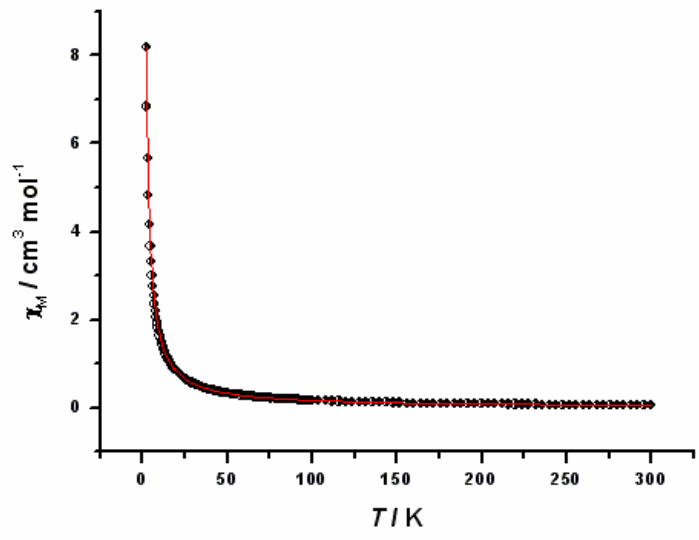

Fig. S18. The χ_M *vs.* T plot for compound **3** (The red line represents the best fit).

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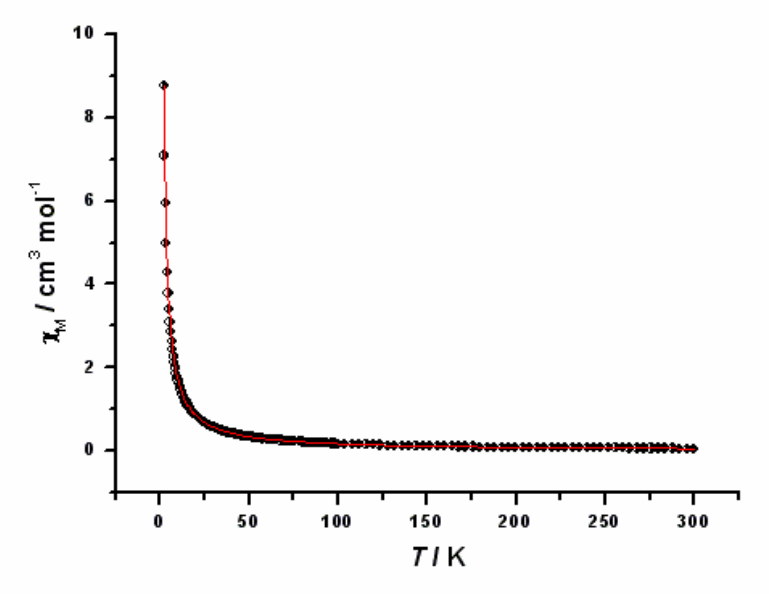

Fig. S19. The χ_M *vs.* T plot for compound **4** (The red line represents the best fit).

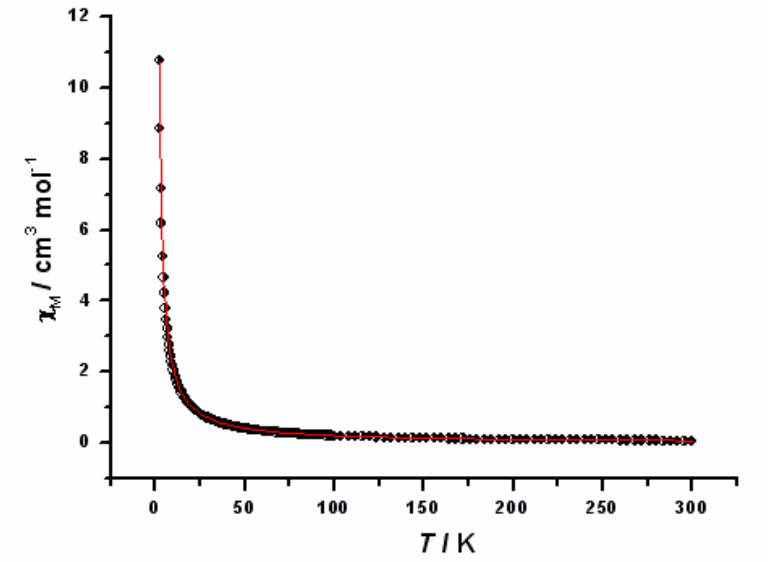

Fig. S20. The χ_M *vs.* T plot for compound **5** (The red line represents the best fit).

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Tables

Table **S1**. Crystal data and structure refinements for **1**, **2** and **3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_9H_{10}O_{12}NGd$	$C_{18}H_{30}O_{30}N_2ZnGd_2$	$C_{18}H_{30}O_{30}N_2CuGd_2$
Formula weight	481.43	1134.31	1132.48
Crystal size /mm^3	0.35 × 0.10 × 0.07	0.21 × 0.05 × 0.05	0.19 × 0.06 × 0.05
Crystal color	Colorless	Colorless	Light blue
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
a /Å	8.7200(10)	8.6761(12)	8.6552(10)
b / Å	8.9690(12)	9.3984(14)	9.2760(11)
c / Å	9.4220(12)	10.5809(17)	10.6950(11)
α /^{o}	77.951(11)	92.225(11)	93.603(6)
β /^{o}	80.690(10)	102.987(10)	101.819(6)
γ /^{o}	71.308(11)	109.636(9)	109.742(6)
Volume /Å^3	679.06(15)	785.7(2)	782.89(15)
Z	2	1	1
ρ_{calcd} /g cm^{-3}	2.355	2.397	2.402
μ /mm^{-1}	4.954	5.053	4.984
F(000)	462	550	549
θ range /^{o}	3.16 to 26.37	1.99 to 25.06	1.97 to 25.05
Limiting indices	-10 ≤ h ≤ 10 -11 ≤ k ≤ 6 -10 ≤ l ≤ 11	-10 ≤ h ≤ 10 -11 ≤ k ≤ 11 -12 ≤ l ≤ 12	-10 ≤ h ≤ 10 -11 ≤ k ≤ 11 -12 ≤ l ≤ 12
Reflections collected	4394	9100	7707
R(int)	0.0776	0.0976	0.0511
Data / parameters	2729 / 208	2772 / 241	2661 / 241
GOF on F^2	1.023	1.013	1.048
$R_1(wR_2)$ [$I > 2\sigma(I)$]	0.0845 (0.1945)	0.0837 (0.1813)	0.0457 (0.1089)
$R_1(wR_2)$ [all data]	0.0955 (0.2034)	0.1160 (0.1968)	0.0571 (0.1144)

$R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{0.5}$.

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Table **S2**. Crystal data and structure refinements for **4** and **5**.

Compound	**4**	**5**
Empirical formula	$C_{18}H_{28}O_{29}N_2CoGd_2$	$C_{18}H_{28}O_{29}N_2MnGd_2$
Formula weight	1109.85	1105.86
Crystal size /mm^3	0.27 × 0.11 × 0.08	0.18 × 0.065 × 0.015
Crystal color	Light red	Colorless
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a /Å	8.7113(3)	8.71960(10)
b / Å	9.1913(4)	9.2220(2)
c / Å	10.5321(4)	10.5926(2)
α /^{o}	86.054(2)	86.0030(10)
β /^{o}	77.189(2)	77.1680(10)
γ /^{o}	71.101(2)	71.0900(10)
Volume /Å^3	777.96(5)	785.68(2)
Z	1	1
ρ_{calcd} /g cm^{-3}	2.369	2.337
μ /mm^{-1}	4.861	4.687
F(000)	537	535
θ range /^{o}	1.98 to 25.06	1.97 to 25.05
Limiting indices	-10 ≤ h ≤ 10 -10 ≤ k ≤ 10 -12 ≤ l ≤ 12	-10 ≤ h ≤ 10 -10 ≤ k ≤ 10 -12 ≤ l ≤ 12
Reflections collected	7342	10334
R(int)	0.0248	0.0263
Data / parameters	2690 / 241	2787 / 241
GOF on F^2	1.047	1.048
$R_1(wR_2)$ [$I > 2\sigma(I)$]	0.0250 (0.0639)	0.0184 (0.0440)
$R_1(wR_2)$ [all data]	0.0279 (0.0659)	0.0208 (0.0449)

$R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{0.5}$.

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Table S3. Selected bond lengths and angles for **1**.

Bond length	**(Å)**	**Bond length**	**(Å)**
Gd(1)-O(5)^{i}	2.367(10)	Gd(1)-O(8)^{ii}	2.433(11)
Gd(1)-O(1)^{ii}	2.374(11)	Gd(1)-O(4)	2.505(12)
Gd(1)-O(3)^{iii}	2.408(11)	Gd(1)-N(1)^{ii}	2.549(13)
Gd(1)-O(9)	2.419(11)	Gd(1)-O(3)	2.706(11)
Gd(1)-O(10)	2.424(13)		

Bond angles	**(°)**	**Bond angles**	**(°)**
O(5)^{i}-Gd(1)-O(1)^{ii}	87.1(4)	O(10)-Gd(1)-O(4)	73.2(4)
O(5)^{i}-Gd(1)-O(3)^{iii}	149.4(4)	O(8)^{ii}-Gd(1)-O(4)	71.8(4)
O(1)^{ii}-Gd(1)-O(3)^{iii}	91.2(4)	O(5)^{i}-Gd(1)-N(1)^{ii}	74.3(4)
O(5)^{i}-Gd(1)-O(9)	137.5(4)	O(1)^{ii}-Gd(1)-N(1)^{ii}	63.1(4)
O(1)^{ii}-Gd(1)-O(9)	77.9(4)	O(3)^{iii}-Gd(1)-N(1)^{ii}	77.8(4)
O(3)^{iii}-Gd(1)-O(9)	71.2(4)	O(9)-Gd(1)-N(1)^{ii}	129.0(4)
O(5)^{i}-Gd(1)-O(10)	69.1(4)	O(10)-Gd(1)-N(1)^{ii}	129.7(4)
O(1)^{ii}-Gd(1)-O(10)	81.5(4)	O(8)^{ii}-Gd(1)-N(1)^{ii}	63.7(4)
O(3)^{iii}-Gd(1)-O(10)	140.7(4)	O(4)-Gd(1)-N(1)^{ii}	130.7(4)
O(9)-Gd(1)-O(10)	69.5(4)	O(5)^{i}-Gd(1)-O(3)	125.3(4)
O(5)^{i}-Gd(1)-O(8)^{ii}	79.4(4)	O(1)^{ii}-Gd(1)-O(3)	147.3(4)
O(1)^{ii}-Gd(1)-O(8)^{ii}	126.8(4)	O(3)^{iii}-Gd(1)-O(3)	63.6(4)
O(3)^{iii}-Gd(1)-O(8)^{ii}	77.4(4)	O(9)-Gd(1)-O(3)	74.3(4)
O(9)-Gd(1)-O(8)^{ii}	140.5(4)	O(10)-Gd(1)-O(3)	104.3(4)
O(10)-Gd(1)-O(8)^{ii}	136.6(4)	O(8)^{ii}-Gd(1)-O(3)	70.5(3)
O(5)^{i}-Gd(1)-O(4)	78.1(4)	O(4)-Gd(1)-O(3)	49.9(3)
O(1)^{ii}-Gd(1)-O(4)	153.9(4)	N(1)^{ii}-Gd(1)-O(3)	125.0(4)
O(3)^{iii}-Gd(1)-O(4)	112.5(4)	O(5)^{i}-Gd(1)-C(7)	101.0(4)
O(9)-Gd(1)-O(4)	98.6(4)		

Symmetry transformations used to generate equivalent atoms: i: -x+1, -y+2, -z+2; ii: x-1, y, z; iii: -x+1, -y+1, -z+2; iv: x+1, y, z.

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Table S4. Selected bond lengths and angles for **2**.

Bond angles	(°)	**Bond angles**	(°)
Gd(1)-O(4)^{i}	2.313(14)	Gd(1)-O(5)^{iii}	2.651(12)
Gd(1)-O(8)^{ii}	2.354(12)	Gd(1)-C(8)^{iii}	2.955(16)
Gd(1)-O(10)	2.416(16)	Zn(1)-O(12)	2.059(19)
Gd(1)-O(9)	2.422(13)	Zn(1)-O(12)^{iv}	2.059(19)
Gd(1)-O(1)^{ii}	2.437(12)	Zn(1)-O(13)	2.076(17)
Gd(1)-O(5)	2.478(13)	Zn(1)-O(13)^{iv}	2.076(17)
Gd(1)-O(6)^{iii}	2.505(11)	Zn(1)-O(11)^{iv}	2.141(15)
Gd(1)-N(1)^{ii}	2.528(12)	Zn(1)-O(11)	2.141(15)

Bond angles	(°)	**Bond angles**	(°)
O(1)^{ii}-Gd(1)-N(1)^{ii}	63.0(4)	O(5)-Gd(1)-N(1)^{ii}	79.6(4)
O(4)^{i}-Gd(1)-O(8)^{ii}	94.7(5)	O(6)^{iii}-Gd(1)-N(1)^{ii}	132.0(4)
O(4)^{i}-Gd(1)-O(10)	70.4(5)	O(4)^{i}-Gd(1)-O(5)^{iii}	122.6(4)
O(8)^{ii}-Gd(1)-O(10)	78.1(5)	O(8)^{ii}-Gd(1)-O(5)^{iii}	142.6(4)
O(4)^{i}-Gd(1)-O(9)	139.6(5)	O(10)-Gd(1)-O(5)^{iii}	110.0(5)
O(8)^{ii}-Gd(1)-O(9)	75.3(5)	O(9)-Gd(1)-O(5)^{iii}	74.1(4)
O(10)-Gd(1)-O(9)	69.3(5)	O(1)^{ii}-Gd(1)-O(5)^{iii}	70.2(4)
O(4)^{i}-Gd(1)-O(1)^{ii}	76.8(5)	O(5)-Gd(1)-O(5)^{iii}	63.3(4)
O(8)^{ii}-Gd(1)-O(1)^{ii}	127.1(4)	O(6)^{iii}-Gd(1)-O(5)^{iii}	50.1(4)
O(10)-Gd(1)-O(1)^{ii}	140.4(5)	N(1)^{ii}-Gd(1)-O(5)^{iii}	125.1(4)
O(9)-Gd(1)-O(1)^{ii}	140.1(5)	O(12)-Zn(1)-O(12)^{iv}	179.999(2)
O(4)^{i}-Gd(1)-O(5)	148.6(4)	O(12)-Zn(1)-O(13)	94.5(7)
O(8)^{ii}-Gd(1)-O(5)	86.7(4)	O(12)^{iv}-Zn(1)-O(13)	85.5(7)
O(10)-Gd(1)-O(5)	139.8(4)	O(12)-Zn(1)-O(13)^{iv}	85.5(7)
O(9)-Gd(1)-O(5)	70.9(4)	O(12)^{iv}-Zn(1)-O(13)^{iv}	94.5(7)
O(1)^{ii}-Gd(1)-O(5)	77.5(4)	O(13)-Zn(1)-O(13)^{iv}	180.0(10)
O(4)^{i}-Gd(1)-O(6)^{iii}	76.8(5)	O(12)-Zn(1)-O(11)^{iv}	90.0(8)
O(8)^{ii}-Gd(1)-O(6)^{iii}	154.9(4)	O(12)^{iv}-Zn(1)-O(11)^{iv}	90.0(8)
O(10)-Gd(1)-O(6)^{iii}	76.8(5)	O(13)-Zn(1)-O(11)^{iv}	91.4(6)
O(9)-Gd(1)-O(6)^{iii}	95.8(5)	O(13)^{iv}-Zn(1)-O(11)^{iv}	88.6(6)
O(1)^{ii}-Gd(1)-O(6)^{iii}	74.5(4)	O(12)-Zn(1)-O(11)	90.0(8)
O(5)-Gd(1)-O(6)^{iii}	113.0(4)	O(12)^{iv}-Zn(1)-O(11)	90.0(8)
O(4)^{i}-Gd(1)-N(1)^{ii}	72.9(5)	O(13)-Zn(1)-O(11)	88.6(6)
O(8)^{ii}-Gd(1)-N(1)^{ii}	64.6(4)	O(13)^{iv}-Zn(1)-O(11)	91.4(6)
O(10)-Gd(1)-N(1)^{ii}	124.2(5)	O(11)^{iv}-Zn(1)-O(11)	180.000(1)
O(9)-Gd(1)-N(1)^{ii}	131.1(5)		

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Symmetry transformations used to generate equivalent atoms: i: -x, -y+1, -z+2; ii: -x, -y+2, -z+2; iii: x+1, y, z; iv: -x+1, -y+1, -z+3; v: x-1, y, z.

Table S5. Selected bond lengths and angles for **3**.

Bond length	**(Å)**	**Bond length**	**(Å)**
Gd(1)-O(4)^{i}	2.328(6)	Gd(1)-O(5)^{iii}	2.644(6)
Gd(1)-O(8)^{ii}	2.352(6)	Cu(1)-O(12)^{iv}	1.973(8)
Gd(1)-O(9)	2.411(6)	Cu(1)-O(12)	1.973(8)
Gd(1)-O(10)	2.417(7)	Cu(1)-O(13)^{iv}	1.991(7)
Gd(1)-O(1)^{ii}	2.438(5)	Cu(1)-O(13)	1.991(7)
Gd(1)-O(5)	2.470(6)	Cu(1)-O(11)	2.398(8)
Gd(1)-O(6)^{iii}	2.499(6)	Cu(1)-O(11)^{iv}	2.398(8)
Gd(1)-N(1)^{ii}	2.521(6)		

Bond angles	**(°)**	**Bond angles**	**(°)**
O(4)^{i}-Gd(1)-O(8)^{ii}	91.4(2)	O(5)-Gd(1)-N(1)^{ii}	77.67(19)
O(4)^{i}-Gd(1)-O(9)	137.9(2)	O(6)^{iii}-Gd(1)-N(1)^{ii}	131.8(2)
O(8)^{ii}-Gd(1)-O(9)	74.9(2)	O(4)^{i}-Gd(1)-O(5)^{iii}	124.1(2)
O(4)^{i}-Gd(1)-O(10)	70.5(2)	O(8)^{ii}-Gd(1)-O(5)^{iii}	144.25(19)
O(8)^{ii}-Gd(1)-O(10)	78.8(2)	O(9)-Gd(1)-O(5)^{iii}	75.1(2)
O(9)-Gd(1)-O(10)	67.9(2)	O(10)-Gd(1)-O(5)^{iii}	107.1(2)
O(4)^{i}-Gd(1)-O(1)^{ii}	78.6(2)	O(1)^{ii}-Gd(1)-O(5)^{iii}	70.61(18)
O(8)^{ii}-Gd(1)-O(1)^{ii}	127.07(19)	O(5)-Gd(1)-O(5)^{iii}	64.1(2)
O(9)-Gd(1)-O(1)^{ii}	141.0(2)	O(6)^{iii}-Gd(1)-O(5)^{iii}	50.16(18)
O(10)-Gd(1)-O(1)^{ii}	140.3(2)	N(1)^{ii}-Gd(1)-O(5)^{iii}	124.65(19)
O(4)^{i}-Gd(1)-O(5)	149.3(2)	O(12)^{iv}-Cu(1)-O(12)	180.0(6)
O(8)^{ii}-Gd(1)-O(5)	87.9(2)	O(12)^{iv}-Cu(1)-O(13)^{iv}	93.7(3)
O(9)-Gd(1)-O(5)	71.2(2)	O(12)-Cu(1)-O(13)^{iv}	86.3(3)
O(10)-Gd(1)-O(5)	138.9(2)	O(12)^{iv}-Cu(1)-O(13)	86.3(3)
O(1)^{ii}-Gd(1)-O(5)	77.47(19)	O(12)-Cu(1)-O(13)	93.7(3)
O(4)^{i}-Gd(1)-O(6)^{iii}	77.3(2)	O(13)^{iv}-Cu(1)-O(13)	180
O(8)^{ii}-Gd(1)-O(6)^{iii}	154.1(2)	O(12)^{iv}-Cu(1)-O(11)	89.3(3)
O(9)-Gd(1)-O(6)^{iii}	97.9(3)	O(12)-Cu(1)-O(11)	90.7(3)
O(10)-Gd(1)-O(6)^{iii}	75.5(3)	O(13)^{iv}-Cu(1)-O(11)	91.4(3)
O(1)^{ii}-Gd(1)-O(6)^{iii}	73.9(2)	O(13)-Cu(1)-O(11)	88.6(3)
O(5)-Gd(1)-O(6)^{iii}	113.66(19)	O(12)^{iv}-Cu(1)-O(11)^{iv}	90.7(3)
O(4)^{i}-Gd(1)-N(1)^{ii}	74.4(2)	O(12)-Cu(1)-O(11)^{iv}	89.3(3)
O(8)^{ii}-Gd(1)-N(1)^{ii}	64.4(2)	O(13)^{iv}-Cu(1)-O(11)^{iv}	88.6(3)
O(9)-Gd(1)-N(1)^{ii}	129.0(2)	O(13)-Cu(1)-O(11)^{iv}	91.4(3)
O(10)-Gd(1)-N(1)^{ii}	127.6(3)	O(11)-Cu(1)-O(11)^{iv}	180
O(1)^{ii}-Gd(1)-N(1)^{ii}	62.81(19)		

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Symmetry transformations used to generate equivalent atoms: i: x, y-1, z; ii: -x, -y+2, -z+1; iii: -x+1, -y+2, -z+1; iv: -x-1, -y+1, -z; v: x, y+1, z.

Table S6. Selected bond lengths and angles for **4**.

Bond length	**(Å)**	**Bond length**	**(Å)**
Gd(1)-O(3)	2.287(3)	Gd(1)-O(6)^{iii}	2.671(3)
Gd(1)-O(7)^{i}	2.375(3)	Co(1)-O(11)	2.069(3)
Gd(1)-O(10)	2.405(3)	Co(1)-O(11)^{iv}	2.069(3)
Gd(1)-O(1)^{i}	2.431(3)	Co(1)-O(13)	2.116(4)
Gd(1)-O(6)^{ii}	2.456(3)	Co(1)-O(13)^{iv}	2.116(4)
Gd(1)-O(9)	2.465(3)	Co(1)-O(12)	2.120(3)
Gd(1)-O(5)^{iii}	2.514(3)	Co(1)-O(12)^{iv}	2.120(3)
Gd(1)-N(1)^{i}	2.526(3)		

Bond angles	**(°)**	**Bond angles**	
O(3)-Gd(1)-O(7)^{i}	93.04(12)	O(9)-Gd(1)-N(1)^{i}	122.62(11)
O(3)-Gd(1)-O(10)	142.81(12)	O(5)^{iii}-Gd(1)-N(1)^{i}	134.10(11)
O(7)^{i}-Gd(1)-O(10)	76.78(12)	O(3)-Gd(1)-O(6)^{iii}	120.26(11)
O(3)-Gd(1)-O(1)^{i}	75.21(11)	O(7)^{i}-Gd(1)-O(6)^{iii}	146.40(10)
O(7)^{i}-Gd(1)-O(1)^{i}	127.44(10)	O(10)-Gd(1)-O(6)^{iii}	73.64(11)
O(10)-Gd(1)-O(1)^{i}	138.81(11)	O(1)^{i}-Gd(1)-O(6)^{iii}	70.76(9)
O(3)-Gd(1)-O(6)^{ii}	145.22(11)	O(6)^{ii}-Gd(1)-O(6)^{iii}	62.66(10)
O(7)^{i}-Gd(1)-O(6)^{ii}	93.18(10)	O(9)-Gd(1)-O(6)^{iii}	109.64(10)
O(10)-Gd(1)-O(6)^{ii}	71.77(11)	O(5)^{iii}-Gd(1)-O(6)^{iii}	49.77(9)
O(1)^{i}-Gd(1)-O(6)^{ii}	73.89(10)	N(1)^{i}-Gd(1)-O(6)^{iii}	127.18(10)
O(3)-Gd(1)-O(9)	73.23(12)	O(11)-Co(1)-O(11)^{iv}	180.0(2)
O(7)^{i}-Gd(1)-O(9)	73.67(11)	O(11)-Co(1)-O(13)	93.06(14)
O(10)-Gd(1)-O(9)	69.58(12)	O(11)^{iv}-Co(1)-O(13)	86.94(14)
O(1)^{i}-Gd(1)-O(9)	142.81(11)	O(11)-Co(1)-O(13)^{iv}	86.94(14)
O(6)^{ii}-Gd(1)-O(9)	141.06(11)	O(11)^{iv}-Co(1)-O(13)^{iv}	93.06(14)
O(3)-Gd(1)-O(5)^{iii}	75.85(12)	O(13)-Co(1)-O(13)^{iv}	180
O(7)^{i}-Gd(1)-O(5)^{iii}	150.17(11)	O(11)-Co(1)-O(12)	94.91(13)
O(10)-Gd(1)-O(5)^{iii}	95.30(13)	O(11)^{iv}-Co(1)-O(12)	85.09(13)
O(1)^{i}-Gd(1)-O(5)^{iii}	77.04(10)	O(13)-Co(1)-O(12)	92.73(14)
O(6)^{ii}-Gd(1)-O(5)^{iii}	111.84(10)	O(13)^{iv}-Co(1)-O(12)	87.27(14)
O(9)-Gd(1)-O(5)^{iii}	76.61(11)	O(11)-Co(1)-O(12)^{iv}	85.09(13)
O(3)-Gd(1)-N(1)^{i}	72.24(12)	O(11)^{iv}-Co(1)-O(12)^{iv}	94.91(13)
O(7)^{i}-Gd(1)-N(1)^{i}	64.05(10)	O(13)-Co(1)-O(12)^{iv}	87.27(14)
O(10)-Gd(1)-N(1)^{i}	129.75(12)	O(13)^{iv}-Co(1)-O(12)^{iv}	92.73(14)
O(1)^{i}-Gd(1)-N(1)^{i}	63.57(10)	O(12)-Co(1)-O(12)^{iv}	180
O(6)^{ii}-Gd(1)-N(1)^{i}	79.95(10)		

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Symmetry transformations used to generate equivalent atoms: i: -x-1, -y+3, -z+2; ii: x, y-1, z; iii: -x, -y+3, -z+2; iv: -x-2, -y+3, -z+3; v: x, y+1, z; vi: -x-2, -y+2, -z+3.

Table S7. Selected bond lengths and angles for **5**.

Bond length	(Å)	Bond length	(Å)
Gd(1)-O(3)	2.298(2)	Gd(1)-O(6)^{iii}	2.692(2)
Gd(1)-O(7)^{i}	2.378(2)	Mn(1)-O(11)	2.161(2)
Gd(1)-O(10)	2.402(2)	Mn(1)-O(11)^{iv}	2.161(2)
Gd(1)-O(1)^{i}	2.429(2)	Mn(1)-O(12)^{iv}	2.193(2)
Gd(1)-O(6)^{ii}	2.445(2)	Mn(1)-O(12)	2.193(2)
Gd(1)-O(9)	2.469(2)	Mn(1)-O(13)^{iv}	2.228(3)
Gd(1)-O(5)^{iii}	2.508(2)	Mn(1)-O(13)	2.228(3)
Gd(1)-N(1)^{i}	2.525(2)		

Bond angles	(°)	Bond angles	(°)
O(3)-Gd(1)-O(7)^{i}	93.07(8)	O(9)-Gd(1)-N(1)^{i}	122.79(8)
O(3)-Gd(1)-O(10)	142.64(9)	O(5)^{iii}-Gd(1)-N(1)^{i}	134.33(8)
O(7)^{i}-Gd(1)-O(10)	76.94(8)	O(3)-Gd(1)-O(6)^{iii}	120.39(7)
O(3)-Gd(1)-O(1)^{i}	75.45(8)	O(7)^{i}-Gd(1)-O(6)^{iii}	146.21(7)
O(7)^{i}-Gd(1)-O(1)^{i}	127.53(7)	O(10)-Gd(1)-O(6)^{iii}	73.29(7)
O(10)-Gd(1)-O(1)^{i}	138.60(7)	O(1)^{i}-Gd(1)-O(6)^{iii}	70.81(7)
O(3)-Gd(1)-O(6)^{ii}	145.50(8)	O(6)^{ii}-Gd(1)-O(6)^{iii}	62.46(7)
O(7)^{i}-Gd(1)-O(6)^{ii}	93.27(7)	O(9)-Gd(1)-O(6)^{iii}	109.62(7)
O(10)-Gd(1)-O(6)^{ii}	71.69(8)	O(5)^{iii}-Gd(1)-O(6)^{iii}	49.68(7)
O(1)^{i}-Gd(1)-O(6)^{ii}	73.86(7)	N(1)^{i}-Gd(1)-O(6)^{iii}	127.09(7)
O(3)-Gd(1)-O(9)	73.12(8)	O(11)-Mn(1)-O(11)^{iv}	179.999(6)
O(7)^{i}-Gd(1)-O(9)	73.57(8)	O(11)-Mn(1)-O(12)^{iv}	84.68(9)
O(10)-Gd(1)-O(9)	69.52(8)	O(11)^{iv}-Mn(1)-O(12)^{iv}	95.32(9)
O(1)^{i}-Gd(1)-O(9)	142.96(8)	O(11)-Mn(1)-O(12)	95.32(9)
O(6)^{ii}-Gd(1)-O(9)	140.91(7)	O(11)^{iv}-Mn(1)-O(12)	84.68(9)
O(3)-Gd(1)-O(5)^{iii}	75.98(8)	O(12)^{iv}-Mn(1)-O(12)	180
O(7)^{i}-Gd(1)-O(5)^{iii}	150.19(8)	O(11)-Mn(1)-O(13)^{iv}	86.85(10)
O(10)-Gd(1)-O(5)^{iii}	94.91(9)	O(11)^{iv}-Mn(1)-O(13)^{iv}	93.15(10)
O(1)^{i}-Gd(1)-O(5)^{iii}	77.09(7)	O(12)^{iv}-Mn(1)-O(13)^{iv}	91.64(10)
O(6)^{ii}-Gd(1)-O(5)^{iii}	111.57(7)	O(12)-Mn(1)-O(13)^{iv}	88.36(10)
O(9)-Gd(1)-O(5)^{iii}	76.72(8)	O(11)-Mn(1)-O(13)	93.15(10)
O(3)-Gd(1)-N(1)^{i}	72.60(8)	O(11)^{iv}-Mn(1)-O(13)	86.85(10)
O(7)^{i}-Gd(1)-N(1)^{i}	64.14(7)	O(12)^{iv}-Mn(1)-O(13)	88.36(10)
O(10)-Gd(1)-N(1)^{i}	129.82(8)	O(12)-Mn(1)-O(13)	91.64(10)
O(1)^{i}-Gd(1)-N(1)^{i}	63.56(7)	O(13)^{iv}-Mn(1)-O(13)	180
O(6)^{ii}-Gd(1)-N(1)^{i}	79.87(7)		

Symmetry transformations used to generate equivalent atoms: i: x, y-1, z; ii: -x+1,

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-y+1, -z+2; iii: -x, -y+1, -z+2; iv: -x, -y, -z+1; v: x, y+1, z; vi: -x, -y+1, -z+3.

Table S8. Selected hydrogen bond lengths (Å) and angles (°) for **1**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O9-H9A...OW1	0.82	1.87	2.669(18)	164.00
O9-H9B...O8^{i}	0.82	1.91	2.712(17)	166.00
OW2-H10A...O4^{ii}	0.82	1.94	2.743(17)	166.00
OW2-H10B...O7^{iii}	0.82	1.86	2.677(18)	171.00
O10-H10C...OW1	0.83	2.09	2.679(19)	128.00
OW1-H10E...O2	0.82	1.98	2.781(18)	165.00
OW1-H10F...O1^{iv}	0.82	1.96	2.759(17)	163.00
OW2-H10G...O10	0.82	2.3	2.834(18)	124.00
OW2-H10G...O5^{v}	0.82	2.58	3.180(16)	132.00

Symmetry transformations used to generate equivalent atoms: i: 2-x, 1-y, 2-z; ii: 1-x, 2-y, 1-z; iii: -1+x, y, -1+z; iv: 2-x, 1-y, 1-z; v: 1-x, 2-y, 2-z.

Table S9. Selected hydrogen bond lengths (Å) and angles (°) for **2**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O9-H9A...O1^{i}	0.8700	1.9400	2.718(19)	148.00
O9-H9B...OW1^{ii}	0.7900	2.4000	3.15(3)	160.00
O10-H10A...OW1	0.9300	1.9300	2.68(3)	136.00
O10-H10B...O11^{iii}	0.8600	2.3700	3.09(2)	142.00
OW1-H10D...O2^{iv}	0.8600	2.4500	3.27(2)	160.00
OW2-H10F...O12	0.9200	2.1500	2.76(4)	122.00
O11-H11A...O3^{iv}	0.9000	1.9800	2.80(3)	150.00
O11-H11B...O2^{v}	0.9600	2.5400	2.87(2)	100.00
O11-H11B...O3^{v}	0.9600	2.3400	3.20(3)	150.00
O12-H12A...O7^{vi}	0.8700	2.2100	2.91(2)	138.00
O13-H13A...O6^{vi}	0.7700	1.9600	2.70(2)	164.00
O13-H13B...O2^{vii}	0.8400	1.8300	2.65(2)	162.00

Symmetry transformations used to generate equivalent atoms: i: 1+x, y, z; ii: 1-x, 2-y, -z; iii: -x, 1-y, -z; iv: -x, 2-y, -z; v: x, -1+y, z; vi: -1+x, -1+y, -1+z; vii: -1-x, 2-y, -z.

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Table S10. Selected hydrogen bond lengths (Å) and angles (°) for **3**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O9-H9A..O1^{i}	0.8200	1.9900	2.719(9)	148.00
O9-H9B...OW1^{ii}	0.8200	2.3200	3.077(14)	155.00
O10-H10A...OW1	0.8200	2.0800	2.764(12)	140.00
O10-H10B...O11^{iii}	0.8200	2.1700	2.839(11)	139.00
OW1-H10C...O7^{iv}	0.8500	2.1800	2.749(13)	124.00
OW1-H10D...O2^{v}	0.8200	2.4500	3.189(12)	151.00
OW2-H10F...O12	0.8200	2.2100	2.692(16)	118.00
O11-H11A...O3^{v}	0.8200	2.1100	2.756(12)	135.00
O11-H11B...O2^{vi}	0.8200	2.5900	3.036(10)	115.00
O11-H11B...O3^{vi}	0.8200	2.4200	3.091(14)	139.00
O12-H12A...O7^{vii}	0.8300	2.1600	2.832(10)	137.00
O12-H12B...OW1^{iii}	0.8700	2.5100	3.341(15)	160.00
O13-H13A...O6^{vii}	0.8200	1.8700	2.685(10)	171.00
O13-H13B...O2^{viii}	0.8200	1.8600	2.660(11)	166.00

Symmetry transformations used to generate equivalent atoms: i: 1+x, y, z; ii: 1-x, 2-y, -z; iii: -x, 1-y, -z; iv: x, y, -1+z; v: -x, 2-y, -z; vi: x, -1+y, z; vii: -1+x, -1+y, -1+z; viii: -1-x, 2-y, -z.

Table S11. Selected hydrogen bond lengths (Å) and angles (°) for **4**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O9-H9A...OW2^{i}	0.8100	2.0700	2.822(10)	153.00
O9-H9A...OW2^{ii}	0.8100	1.9800	2.739(9)	155.00
O9-H9B...OW1	0.8200	1.9700	2.779(6)	172.00
O10-H10A...O1^{iii}	0.8200	1.8800	2.680(5)	165.00
O10-H10B...O13^{ii}	0.8200	2.1700	2.988(5)	170.00
OW1-H10C...O7^{iv}	0.8200	2.0500	2.819(5)	157.00
OW1-H10D...O4^{v}	0.8200	1.8600	2.658(5)	164.00
O11-H11A...O5^{vi}	0.8200	1.9600	2.766(5)	171.00
O11-H11B...O2	0.8200	1.8400	2.640(5)	167.00
O12-H12A...O2	0.8200	2.0300	2.789(4)	154.00
O12-H12B...O4^{v}	0.8200	1.9500	2.758(5)	168.00
O13-H13A...OW1	0.8200	1.8900	2.707(6)	171.00
O13-H13B...OW2	0.8200	1.9800	2.663(10)	141.00

Symmetry transformations used to generate equivalent atoms: i: 1+x, y, z; ii: 1-x, -y, 1-z; iii: 1+x, -1+y, z; iv: x, -1+y, 1+z; v: 1-x, 1-y, 1-z; vi: 1-x, 1-y, -z.

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Table S12. Selected hydrogen bond lengths (Å) and angles (°) for **5**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O9-H9A...OW2^{i}	0.8200	2.1000	2.846(7)	151.00
O9-H9A...OW2^{ii}	0.8200	1.9700	2.746(6)	157.00
O9-H9B...OW1	0.8300	1.9500	2.776(4)	172.00
O10-H10A...O1^{iii}	0.8300	1.8800	2.687(3)	164.00
O10-H10B...O13^{ii}	0.8500	2.1400	2.973(4)	168.00
OW1-H10C...O7^{iv}	0.8000	2.0700	2.816(3)	157.00
OW1-H10D...O4^{v}	0.8200	1.8700	2.676(4)	167.00
O11-H11A...O5^{vi}	0.7700	1.9900	2.748(4)	168.00
O11-H11B...O2	0.8100	1.8300	2.640(4)	173.00
O12-H12A...O2	0.8000	2.0500	2.812(3)	159.00
O12-H12B...O4^{v}	0.7600	1.9900	2.751(4)	173.00
O13-H13A...OW1	0.7700	1.9500	2.707(4)	168.00
O13-H13B...OW2	0.7900	2.0400	2.677(7)	137.00

Symmetry transformations used to generate equivalent atoms: i: 1+x, y, z; ii: 1-x, -y, 1-z; iii: 1+x, -1+y, z; iv: x, -1+y, 1+z; v: 1-x, 1-y, 1-z; vi: 1-x, 1-y, -z.