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Filling tricompartmental ligands with Gd^{III} and Zn^{II} ions: some structural and MRI studies

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Contents

Table S1. X-ray crystallographic data for **Gd** and **Zn_2Gd**

Formula	$C_{33}H_{38}GdN_7O_{20}$	$C_{126}H_{183}Br_{12}Gd_4N_{31}O_{89}Zn_8$
M_r	1009.95	5666.90
Crystal dimensions (mm)	0.20 × 0.15 × 0.04	0.18 × 0.12 × 0.04
Crystal System	Monoclinic	Triclinic,
Space group	$P2_1/m$	P-1
a, b, c (Å)	10.0285(3), 17.8274(6), 11.8469(3)	12.7030(9), 17.5773 (11), 22.5949 (14)
α, β, γ (°)	90, 109.744(2), 90	107.655 (3), 94.421 (3), 101.334(3)
θ Ranges (°)	1.8 - 30.5	1.24 – 25.25
V(Å^3), μ/ mm^{-1}	1993.50(11), 1.755	4664.1(9), 5.084
Z	2	1
F(000)	1016	2784
D_x / g·cm^{-3}	1.682	2.018
-h, h / -k, k / -l, l	-14, 14 / -25, 25 / -16, 16	-14, 15 / -21, 18 / -26, 27
Total, unique, [$I > 2\sigma(I)$] reflec.	38749, 6256, 5454	66747, 16866, 9074
No. of reflect., restraints, param.	6256, 0, 328	16866, 1593, 1222
R_{int}	0.051	0.0984
Final R, wR	0.0376, 0.824	0.07443, 0.1272
R, wR (all data)	0.481, 0.854	0.1587, 0.2150
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/Å^3)	0.967, -1.559	4.589, -3.033

Table S2. Main geometric parameters for **Gd**

Atoms	Distance (Å)	Atoms	Distance (Å)
Gd(1)-O(3)	2.315(3)	N(1)-C(7)	1.299(4)
Gd(1)-O(1)	2.363(2)	N(1)-C(8)	1.465(5)
Gd(1)-O(1)$^{\#1}$	2.363(2)	N(2)-C(11)	1.478(4)
Gd(1)-O(4)	2.398(3)	N(2)-C(9)	1.480(4)
Gd(1)-O(1W)	2.408(3)	N(2)-C(10)	1.485(4)
Gd(1)-O(2)$^{\#1}$	2.487(2)	O(1)-C(1)	1.291(4)
Gd(1)-O(2)	2.487(2)	O(2)-C(2A)	1.232(4)
Gd(1)-O(11)	2.535(2)	O(3)-C(13)	1.290(5)
Gd(1)-O(11)$^{\#1}$	2.535(2)	O(4)-C(14A)	1.234(5)
Gd(1)-N(10)	2.959(4)	N(10)-O(12)	1.233(5)
		N(10)-O(11)$^{\#1}$	1.261(3)
Atoms	Angle (°)	Atoms	Angle (°)
O(3)-Gd(1)-O(1)	74.26(8)	O(1)$^{\#1}$-Gd(1)-O(11)	65.49(8)
O(3)-Gd(1)-O(1)$^{\#1}$	74.26(8)	O(4)-Gd(1)-O(11)	139.81(8)
O(1)-Gd(1)-O(1)$^{\#1}$	147.59(17)	O(1W)-Gd(1)-O(11)	73.20(9)
O(3)-Gd(1)-O(4)	72.99(11)	O(2)$^{\#1}$-Gd(1)-O(11)	112.00(8)
O(1)-Gd(1)-O(4)	81.85(8)	O(2)-Gd(1)-O(11)	146.10(8)
O(1)$^{\#1}$-Gd(1)-O(4)	81.85(8)	O(3)-Gd(1)-O(11)$^{\#1}$	75.94(10)
O(3)-Gd(1)-O(1W)	145.86(12)	O(1)-Gd(1)-O(11)$^{\#1}$	65.49(8)
O(1)-Gd(1)-O(1W)	105.14(8)	O(1)$^{\#1}$-Gd(1)-O(11)$^{\#1}$	113.40(8)
O(1)$^{\#1}$-Gd(1)-O(1W)	105.14(8)	O(4)-Gd(1)-O(11)$^{\#1}$	139.81(8)
O(4)-Gd(1)-O(1W)	141.15(11)	O(1W)-Gd(1)-O(11)$^{\#1}$	73.20(9)
O(3)-Gd(1)-O(2)$^{\#1}$	132.61(8)	O(2)$^{\#1}$-Gd(1)-O(11)$^{\#1}$	146.10(8)
O(1)-Gd(1)-O(2)$^{\#1}$	131.93(8)	O(2)-Gd(1)-O(11)$^{\#1}$	111.99(8)
O(1)$^{\#1}$-Gd(1)-O(2)$^{\#1}$	68.51(9)	O(11)-Gd(1)-O(11)$^{\#1}$	50.02(11)
O(4)-Gd(1)-O(2)$^{\#1}$	73.64(8)	O(3)-Gd(1)-N(10)	75.80(11)
O(1W)-Gd(1)-O(2)$^{\#1}$	73.81(9)	O(1)-Gd(1)-N(10)	89.81(6)
O(3)-Gd(1)-O(2)	132.60(8)	O(1)$^{\#1}$-Gd(1)-N(10)	89.82(6)
O(1)-Gd(1)-O(2)	68.51(9)	O(4)-Gd(1)-N(10)	148.80(10)
O(1)$^{\#1}$-Gd(1)-O(2)	131.93(8)	O(1W)-Gd(1)-N(10)	70.05(11)
O(4)-Gd(1)-O(2)	73.64(8)	O(2)$^{\#1}$-Gd(1)-N(10)	130.71(8)
O(1W)-Gd(1)-O(2)	73.81(9)	O(2)-Gd(1)-N(10)	130.71(7)
O(2)$^{\#1}$-Gd(1)-O(2)	65.19(11)	O(11)-Gd(1)-N(10)	25.04(5)
O(3)-Gd(1)-O(11)	75.94(10)	O(11)$^{\#1}$-Gd(1)-N(10)	25.04(5)
O(1)-Gd(1)-O(11)	113.40(8)		

$^{\#1}$ x,-y+1/2,z

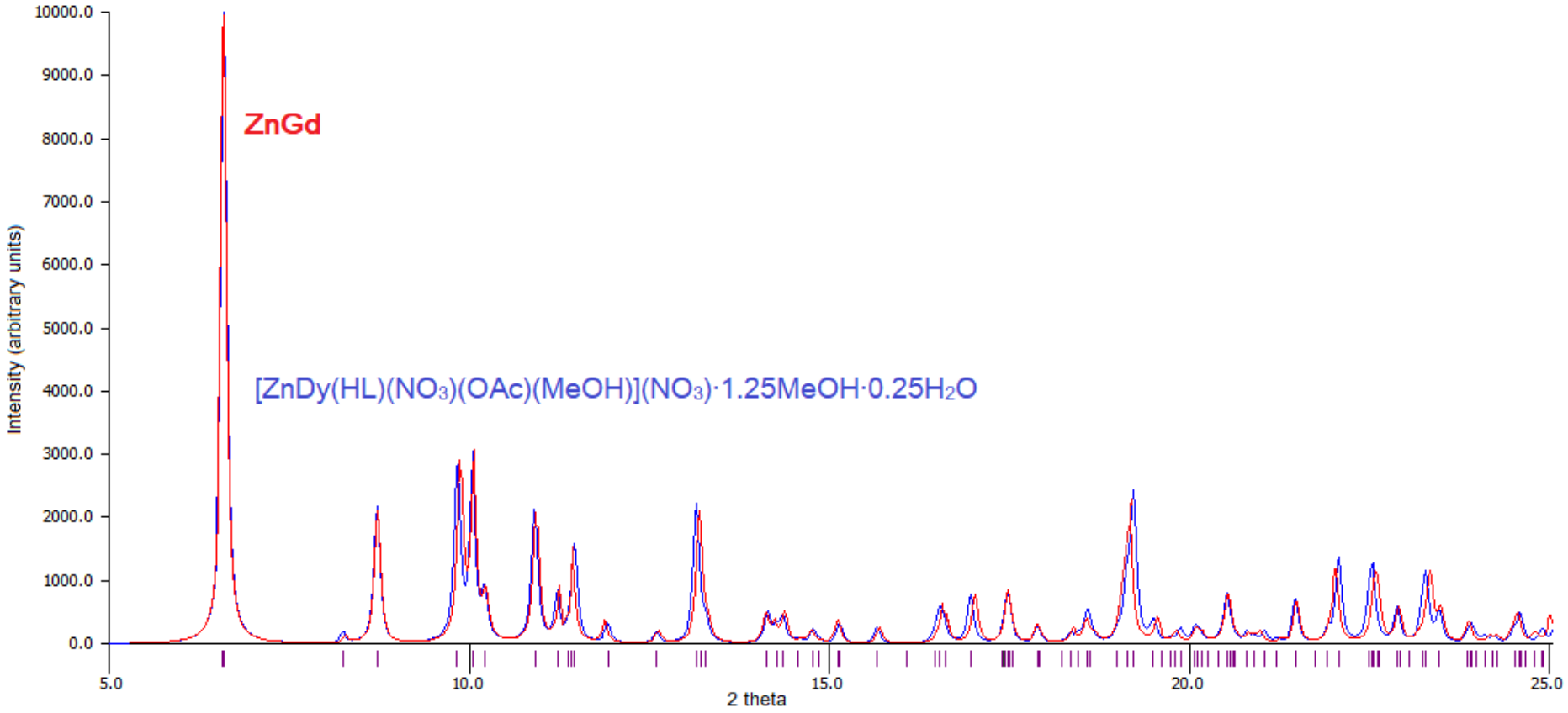

Figure S1. Powder XRD patterns for **ZnGd** (red) and [ZnDy(HL)(NO_3)(OAc)(MeOH)](NO_3)·1.25MeOH·0.25H_2O (blue) [ref 15 in the text]

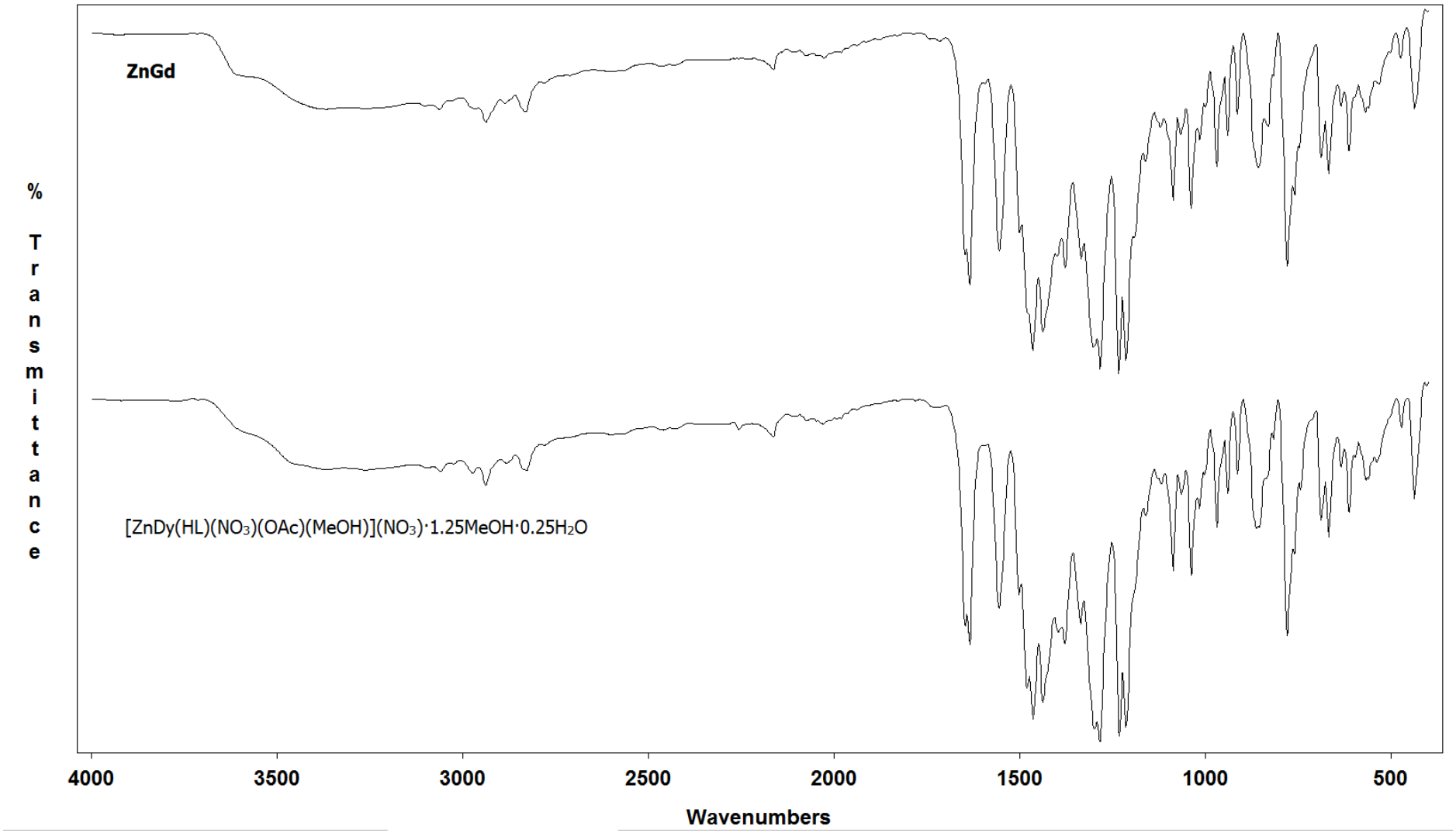

Figure S2. IR spectra for **ZnGd** and [ZnDy(HL)(NO_3)(OAc)(MeOH)](NO_3)·1.25MeOH·0.25H_2O [15]

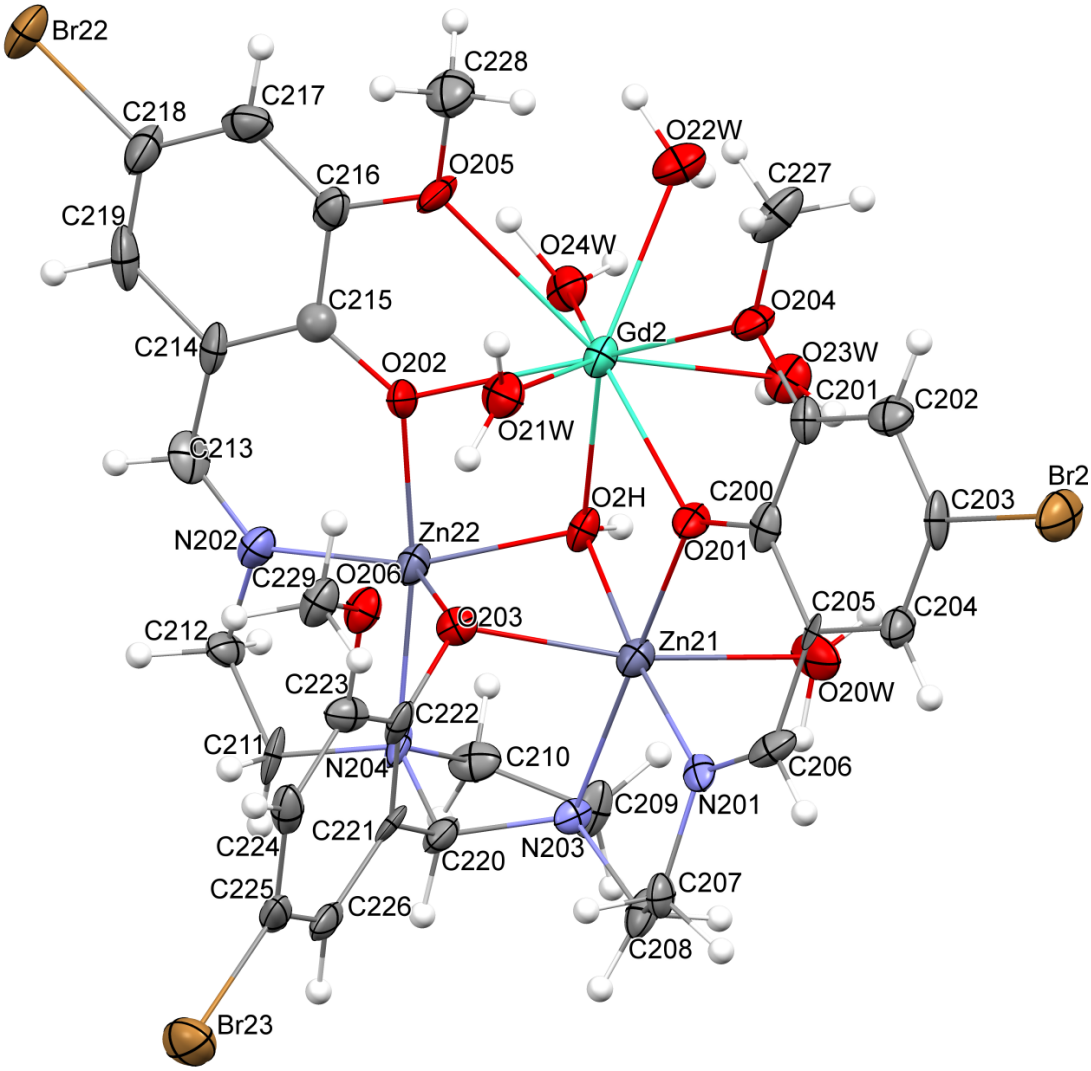

Figure S3. Ellipsoid diagram for a second $[Zn_2Gd(L)(OH)(H_2O)_5]^{3+}$ moiety present in (**Zn_2Gd**). This unit can be considered as unit 2, so all the atoms contain a 2 as first figure in the numbering scheme. It also corresponds to the (*S*,*S*,*S*) enantiomer

Table S3. Main geometric parameters for **Zn_2Gd**

Atoms	Distance (Å)	Atoms	Distance (Å)
Gd1-O101	2.374(9)	Gd2-O201	2.357(8)
Gd1-O102	2.386(9)	Gd2-O202	2.364(8)
Gd1-O11W	2.445(8)	Gd2-O21W	2.475(8)
Gd1-O12W	2.432(9)	Gd2-O22W	2.356(9)
Gd1-O13W	2.387(9)	Gd2-O23W	2.390(8)
Gd1-O14W	2.412(9)	Gd2-O24W	2.438(8)
Gd1-O1H	2.452(10)	Gd2-O2H	2.426(8)
Gd1-O104	2.587(11)	Gd2-O204	2.653(6)
Gd1-O105	2.721(9)	Gd2-O205	2.656(8)
Zn11-O101	1.967(12)	Zn21-O201	2.037(8)
Zn11-N101	1.996(12)	Zn21-N201	2.010(10)
Zn11-O1H	2.050(9)	Zn21-O2H	2.002(8)
Zn11-O10W	2.144(9)	Zn21-O20W	2.322(8)
Zn11-N103	2.219(14)	Zn21-N203	2.181(10)
Zn11-O103	2.224(9)	Zn21-O203	2.182(8)
Zn12-O1H	1.979(10)	Zn22-O2H	1.971(8)
Zn12-N102	2.006(12)	Zn22-N202	2.011(10)
Zn12-O102	2.051(10)	Zn22-O202	2.037(8)
Zn12-O103	2.057(9)	Zn22-O203	2.052(8)
Zn12-N104	2.238(13)	Zn22-N204	2.196(10)
Gd1···Zn11	3.4921(19)	Gd2···Zn21	3.4486(16)
Gd1···Zn12	3.460(2)	Gd2···Zn22	3.4358(17)
Zn11···Zn12	2.987(2)	Zn21···Zn22	2.972(2)

Atoms	Angle (°)	Atoms	Angle (°)
O102-Gd1-O105	60.2(3)	O202-Gd2-O205	60.(3)
O14W-Gd1-O11W	142.7(3)	O24W-Gd2-O21W	143.6(3)
O102-Gd1-O104	142.3(3)	O202-Gd2-O204	145.1(3)
N101-Zn11-O1H	174.3(5)	N201-Zn21-O2H	174.0(4)
O101-Zn11-N103	170.1(4)	O201-Zn21-N203	172.7(3)
O10W-Zn11-O103	166.2(4)	O20W-Zn21-O203	167.5(3)
O102-Zn12-N104	169.3(4)	O202-Zn22-N204	172.0(3)
O1H-Zn12-N102	146.1(4)	O2H-Zn22-N202	145.9(4)

Table S4. Continuous Shape measures calculations for **Gd** and **Zn_2Gd**

Geometries for coordination number 9

MFF-9	13 Cs	Muffin
HH-9	12 C2v	Hula-hoop
JTDIC-9	11 C3v	Tridiminished icosahedron J63
TCTPR-9	10 D3h	Spherical tricapped trigonal prism
JTCTPR-9	9 D3h	Tricapped trigonal prism J51
CSAPR-9	8 C4v	Spherical capped square antiprism
JCSAPR-9	7 C4v	Capped square antiprism J10
CCU-9	6 C4v	Spherical-relaxed capped cube
JCCU-9	5 C4v	Capped cube J8
JTC-9	4 C3v	Johnson triangular cupola J3
HBPY-9	3 D7h	Heptagonal bipyramid
OPY-9	2 C8v	Octagonal pyramid
EP-9	1 D9h	Enneagon

Gd

Structure [ML9]	MFF-9	HH-9	JTDIC-9	TCTPR-9	JTCTPR-9	CSAPR-9	JCSAPR-9
	2.284,	6.730,	13.437,	3.582,	5.478,	3.251,	4.507
CCU-9	JCCU-9	JTC-9	HBPY-9	OPY-9	EP-9		
7.751,	9.109,	14.575,	14.718,	22.452,	32.929		

Zn_2Gd

Unit 1

Structure [ML9]	MFF-9	HH-9	JTDIC-9	TCTPR-9	JTCTPR-9	CSAPR-9	JCSAPR-9
	1.130,	8.455,	12.429,	2.055	4.655,	1.480,	2.994,
CCU-9	JCCU-9	JTC-9	HBPY-9	OPY-9	EP-9		
9.048,	10.545,	14.827	17.452,	21.197,	34.494		

Unit 2

Structure [ML9]	MFF-9	HH-9	JTDIC-9	TCTPR-9	JTCTPR-9	CSAPR-9	JCSAPR-9
	1.387,	8.884,	13.105,	1.959,	4.798,	1.564,	3.005,
CCU-9	JCCU-9	JTC-9	HBPY-9	OPY-9	EP-9		
9.146	10.706,	15.472,	18.570,	20.177,	33.896		

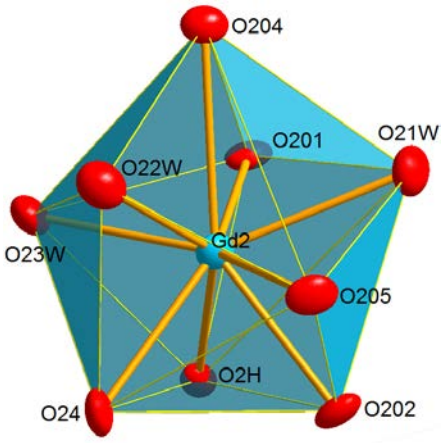

Figure S4. Coordination polyhedra for the Gd^{III} centre present in unit 2 of **Zn_2Gd** (left) and the Ho^{III} corresponding to **Zn_2Ho** (right).

Table S5. H bonds found for **Zn_2Gd**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)	D-H···A	d(D-H)	d(H···A)	d(D···A)	D-H···A
O(1H)-H(1H)···O(50)	1.00	2.16	3.138(14)	166.1	O(2H)-H(2H)···O(1W)	1.00	1.89	2.828(12)	154.9
O(10W)-H(1W1)···O20W#1	0.89	1.81	2.650(14)	156.6	O(20W)-H(2W1)···O(2H)	0.88	2.60	3.031(11)	111.2
O(10W)-H(1W2)···O(52)	0.90	1.97	2.872(15)	173.8	O(20W)-H(2W1)···O(1W)	0.88	1.94	2.766(13)	157.0
O(11W)-H(1W3)···O(103)	0.99	2.28	2.976(14)	126.1	O(20W)-H(2W2)···O30#8	0.96	1.73	2.691(18)	176.6
O(11W)-H(1W3)···O(106)	0.99	1.97	2.915(12)	157.6	O(21W)-H(2W3)···O(203)	0.85	2.63	3.123(12)	118.2
O(11W)-H(1W4)···O(60)	0.90	1.91	2.787(13)	164.1	O(21W)-H(2W3)···O(206)	0.85	2.17	3.022(12)	174.4
O(12W)-H(1W5)···O(14W)	0.98	2.26	2.850(15)	117.4	O(21W)-H(2W4)···O(62)	0.91	1.93	2.821(13)	169.8
O(12W)-H(1W5)···O51#2	0.98	1.97	2.782(13)	139.2	O(22W)-H(2W5)···O(11)	0.94	1.87	2.768(13)	159.1
O(12W)-H(1W6)···O(41)	0.89	1.92	2.752(14)	155.1	O(22W)-H(2W6)···O(2W)	0.85	1.91	2.706(13)	154.3
O(13W)-H(1W7)···O(40)	0.98	1.82	2.769(14)	162.6	O(23W)-H(2W7)···O30#8	1.01	2.56	3.465(15)	148.7
O(13W)-H(1W8)···O(30)	1.03	1.69	2.686(16)	162.6	O(23W)-H(2W7)···O31#8	1.01	1.95	2.569(16)	116.4
O(14W)-H(1W9)···O50#2	0.87	1.98	2.817(13)	161.1	O(23W)-H(2W8)···O(24W)	0.99	2.45	2.970(12)	112.2
O(14W)-H(1W9)···O50#2	0.87	1.98	2.817(13)	161.1	O(23W)-H(2W8)···O22#9	0.99	1.87	2.788(12)	152.0
O(14W)-H(1WA)···O(50)	1.03	2.42	3.356(14)	150.0	O(24W)-H(2W9)···O20#9	1.05	2.52	3.302(13)	130.2
C(104)-H(104)···O22#3	0.95	2.63	3.185(17)	117.6	O(24W)-H(2W9)···O21#9	1.05	2.33	3.382(12)	176.6
C(109)-H(10E)···BR21#4	0.99	3.10	4.001(16)	152.1	O(24W)-H(2WA)···O(10)	1.03	1.89	2.751(13)	139.1
C(109)-H(10F)···O(10W)	0.99	2.53	3.19(2)	124.4	C(207)-H(20A)···BR23#10	0.99	3.02	3.506(12)	111.2
C(109)-H(10F)···O(52)	0.99	2.42	3.386(19)	164.2	C(207)-H(20B)···O52#8	0.99	2.59	3.275(15	126.4
C(110)-H(11A)···O42#2	0.99	2.28	3.170(19)	149.1	C(208)-H(20C)···O10W#8	0.99	2.64	3.587(16)	159.6
C(111)-H(11D)···O51#5	0.99	2.60	3.56(2)	162.6	C(208)-H(20C)···O10W#8	0.99	2.64	3.587(16)	159.6
C(112)-H(11E)···BR23	0.99	2.88	3.713(17)	142.2	C(209)-H(20E)···BR21#11	0.99	2.92	3.890(14)	167.5
C(112)-H(11F)···BR21#6	0.99	3.01	3.629(15)	121.5	C(209)-H(20F)···O(20W)	0.99	2.63	3.352(16)	129.9
C(112)-H(11F)···BR21#6	0.99	3.01	3.629(15)	121.5	C(209)-H(20F)···O(1W)	0.99	2.66	3.570(17)	153.0
C(127)-H(12B)···O(12W)	0.98	2.55	3.09(2)	114.9	C(210)-H(21A)···O21$#11	0.99	2.52	3.425(16)	151.4
C(127)-H(12C)···O(3Wa)	0.98	2.55	3.48(4)	159.0	C(212)-H(21E)···O20#11	0.99	2.47	3.384(16)	153.4
C(128)-H(12E)···BR13#7	0.98	3.11	3.861(16)	134.2	C(212)-H(21F)···BR13	0.99	2.97	3.574(13)	120.3
C(129)-H(12G)···O(21W)	0.98	2.64	3.455(16)	140.8	C(212)-H(21F)···O61#11	0.99	2.53	3.453(17)	154.8
C(2S)-H(2S2)···O(60)	0.98	2.48	3.309(18)	142.2	C(213)-H(213)···BR11#12	0.95	2.98	3.661(12)	129.6
C(2S)-H(2S2)···O(62)	0.98	2.60	3.55(2)	164.5	C(220)-H(220)···N1S#11	1.00	2.55	3.536(19)	167.1
C(4S)-H(4S1)···O61#3	0.98	2.57	3.51(4)	161.0	C(227)-H(22B)···O(22W)	0.98	2.45	3.071(15)	121.2

O(1W)-H(1WC)···O10#13	0.96	1.86	2.734(14)	151.0	C(227)-H(22C)···O11#9	0.98	2.48	3.384(18)	153.6
O(2W)-H(2WF)···BR11#8	0.99	3.08	3.648(9)	117.6	C(228)-H(22D)···O(11)	0.98	2.66	3.401(17)	132.7
O(3W)-H(3W1)···O(32)	0.98	1.76	2.73(4)	173.8	C(229)-H(22H)···O(60)	0.98	2.38	3.362(18)	177.0
O(3W)-H(3W2)···N(2S)	0.88	2.49	3.30(4)	153.5	C(229)-H(22I)···BR12#6	0.98	3.07	3.854(13)	137.7

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z ; #2 -x+1,- y+1, -z+1; #3 x+1, y+1, z; #4 -x+2, -y+1, -z; #5 -x+1, -y, -z #6 x-1, y, z; #7 x, y-1, z; #8 -x+1, -y ,-z+1; #9 -x+2, -y, -z; #10 x+1, y, z; #11 -x+2, -y+1, -z+1; #12 -x+2, -y, -z+1; #13 -x+2,-y,-z+1

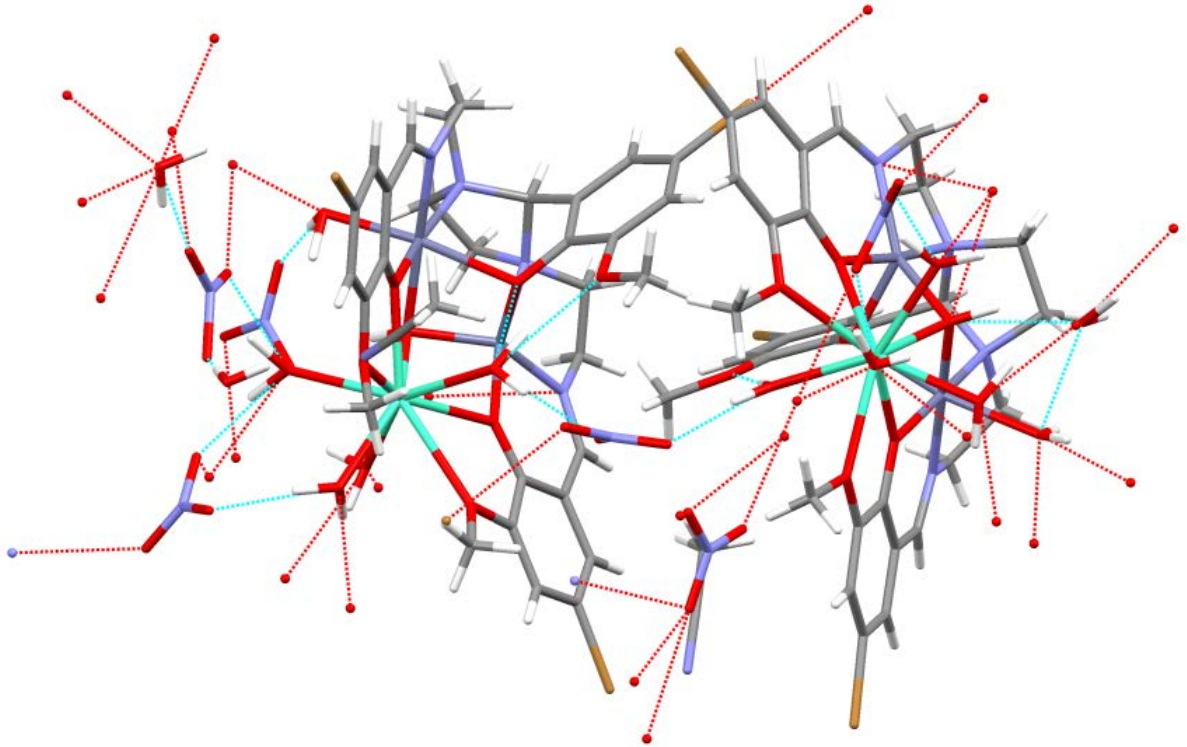

Figure S5. Sticks view of the asymmetric unit of **Zn_2Gd** showing the multiple H-bonds between cations, anions and occluded solvent molecules.

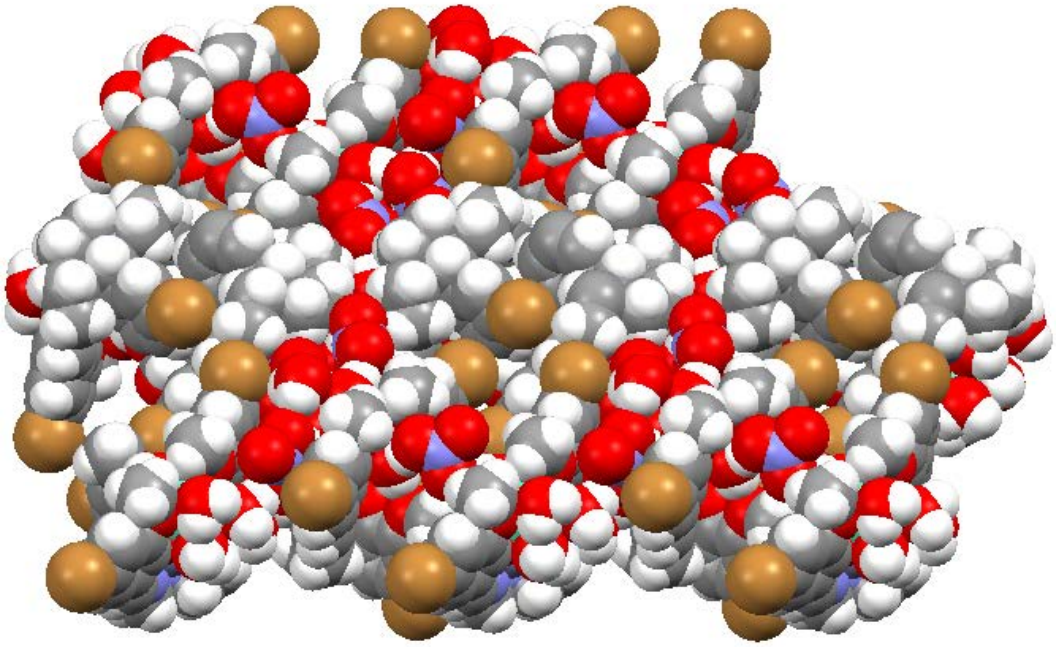

Figure S6. Space-filled views of a portion of one of the 2D-H-bonded layers formed by **Zn_2Gd**