ELECTRONIC SUPPLEMENTARY INFORMATION

to

Unusual coordination modes, field-induced slow magnetic relaxation and luminescence properties in the chemistry of lanthanide(III)/4-bromo-2-[(phenylimino)methyl]phenol complexes†

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Table S1 Crystallographic data for compounds **1**·MeCN, **3**·MeCN, **5**·MeCN, **7**·MeCN and **9**·MeCN

Parameter	**1**·MeCN	**3**·MeCN	**5**·MeCN	**7**·MeCN	**9**·MeCN
Formula	$C_{28}H_{25}PrN_6O_{12}Br_2$	$C_{28}H_{25}SmN_6O_{12}Br_2$	$C_{28}H_{25}GdN_6O_{12}Br_2$	$C_{28}H_{25}DyN_6O_{12}Br_2$	$C_{28}H_{25}ErN_6O_{12}Br_2$
F_w	938.27	947.71	954.61	959.86	964.62
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/m$	$P2_1/m$	$P2_1/m$	$P2_1/m$
a/Å	7.4940(2)	7.4805(1)	7.4712(1)	7.4676(1)	7.4579(1)
b/Å	17.6204(4)	17.5672(3)	17.5324(4)	17.4621(3)	17.4427(3)
c/Å	12.3858(3)	12.3748(2)	12.3673(3)	12.3690(2)	12.3564(2)
α/°	90.00	90.00	90.00	90.00	90.00
β/°	91.668(1)	91.784(1)	91.817(1)	91.821(1)	91.846(1)
γ/°	90.00	90.00	90.00	90.00	90.00
V/Å^3	1634.82(7)	1625.40(4)	1619.15(6)	1612.10(4)	1606.56(4)
Z	2	2	2	2	2
ρ_{calcd}/g cm^{-3}	1.906	1.936	1.958	1.977	1.994
T/°C	-93	-113	-113	-113	-103
Radiation/μ (mm^{-1})	Mo Kα/4.01	Mo Kα/4.34	Mo Kα/4.59	Mo Kα/4.87	Mo Kα/5.17
$2\theta_{max}$/°	54	54	54	54	54
Reflections collected	15927	14599	15643	16632	15700
Reflections unique (R_{int})	3690(0.028)	3663(0.038)	3646(0.053)	3637(0.032)	3621(0.031)
Reflections with $I>2\sigma(I)$	3457	3432	3421	3440	3441
No. of parameters	293	294	293	293	293
$R_1[I>2\sigma(I)]$, w$R_2[I>2\sigma(I)]$	0.0241,0.0580	0.0190,0.0444	0.0230,0.0540	0.0194,0.0408	0.0173,0.0403
R_1(all data), wR_2(all data)	0.0262,0.0591	0.0210,0.0452	0.0254,0.0550	0.0212,0.0415	0.0188,0.0409
GOF(F^2)	1.03	1.05	1.05	1.04	1.07
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	1.22/-0.91	0.61/-0.66	0.83/-0.89	0.78/-1.05	0.62/-0.47
CCDC	1833552	1833555	1833553	1833556	1833554

Table S2 Continuous Shape Measures (CShM) values for the potential coordination polyhedra of the Ln^{III} centre in the structures of complexes $[Ln(NO_3)_3(5BrsalanH)_2(H_2O)]\cdot MeCN$ (Ln=Pr, Sm, Gd, Dy and Er)[a]

Ideal coordination polyhedron	**1**·MeCN (Ln=Pr)	**3**·MeCN (Ln=Sm)	**5**·MeCN (Ln=Gd)	**7**·MeCN (Ln=Dy)	**9**·MeCN (Ln=Er)
Enneagon (EP-9)	34.044	34.362	34.575	34.730	34.915
Octagonal pyramid (OPY-9)	24.468	24.311	24.218	24.133	24.086
Heptagonal bipyramid (HBPY-9)	16.822	17.162	17.348	17.569	17.710
Johnson triangular cupola (JTC-9)	15.048	15.095	15.119	15.161	16.000
Capped cube (JCCU-9)	10.797	10.791	10.780	10.800	10.787
Spherical-relaxed capped cube (CCU-9)	9.052	9.065	9.078	9.108	9.115
Capped square antiprism (JCSAPR-9)	4.05249	3.765	3.597	3.459	3.340
Spherical capped square antiprism (CSAPR-9)	**3.154**	**2.828**	**2.647**	**2.530**	**2.377**
Tricapped trigonal prism (JTCTPR-9)	5.541	5.263	5.100	4.968	4.848
Spherical tricapped trigonal prism (TCTPR-9)	4.471	4.134	3.940	3.816	3.655

[a] The polyhedron with the CShM value in bold is the real coordination polyhedron of the Ln^{III} centre for each compound.

Table S3 H-bonding interactions in the crystal structures of **1**·MeCN, **3**·MeCN, **5**·MeCN and **9**·MeCN

D-H···A (Å)	D···A (Å)	H···A (Å)	D-H···A (°)	Symmetry of A
		Complex **1**·MeCN		
C2-H2···O2	3.265(2)	2.45(3)	149(2)	*x*, *y*, *z*
N1-H(N1)···O1	2.656(3)	1.95(3)	138(2)	*x*, *y*, *z*
C13-H13···O7	3.329(3)	2.45(3)	158(2)	*x*, *y*, *z*
C9-H9···O5	3.445(4)	2.61(3)	159(3)	-*x*+1, -*y*, -*z*+2
O1W-HA(O1W)···N5	2.799(5)	2.04(5)	177(5)	*x*, *y*, *z*+1
O1W-HB(O1W)···O4	2.753(4)	2.08(5)	152(4)	*x*+1, *y*, *z*
		Complex **3**·MeCN		
C2-H2···O2	3.231(2)	2.39(2)	147(2)	*x*, *y*, *z*
N1-H(N1)···O1	2.664(2)	1.94(3)	139(2)	*x*, *y*, *z*
C13-H13···O7	3.323(3)	2.48(3)	158(2)	*x*, *y*, *z*
C9-H9···O5	3.453(3)	2.59(3)	157(2)	-*x*+1, -*y*, -*z*+2
O1W-HA(O1W)···N5	2.810(5)	2.06(5)	166(5)	*x*, *y*, *z*+1
O1W-HB(O1W)···O4	2.746(3)	2.06(4)	159(4)	*x*+1, *y*, *z*
		Complex **5**·MeCN		
C2-H2···O2	3.212(2)	2.38(3)	150(2)	*x*, *y*, *z*
N1-H(N1)···O1	2.662(3)	1.96(3)	136(3)	*x*, *y*, *z*
C13-H13···O7	3.317(3)	2.45(3)	155(3)	*x*, *y*, *z*
C9-H9···O5	3.454(4)	2.61(3)	158(3)	-*x*+1, -*y*, -*z*+2
O1W-HA(O1W)···N5	2.822(5)	2.03(6)	169(5)	*x*, *y*, *z*+1
O1W-HB(O1W)···O4	2.744(4)	2.01(5)	160(5)	*x*+1, *y*, *z*
		Complex **9**·MeCN		
C2-H2···O2	3.173(2)	2.39(3)	144(2)	*x*, *y*, *z*
N1-H(N1)···O1	2.669(2)	2.00(3)	138(2)	*x*, *y*, *z*
C13-H13···O7	3.304(3)	2.44(3)	155(2)	*x*, *y*, *z*
C9-H9···O5	3.458(3)	2.62(3)	156(2)	-*x*+1, -*y*, -*z*+2
O1W-HA(O1W)···N5	2.817(4)	2.12(5)	166(6)	*x*, *y*, *z*+1
O1W-HB(O1W)···O4	2.743(3)	2.02(4)	155(4)	*x*+1, *y*, *z*

D=donor, A=acceptor.

Table S4 Nitrato-nitrato contacts(Å) in the crystal structures of **1**·MeCN, **3**·MeCN, **5**·MeCN and **9**·MeCN

O6···N4(Å)		Symmetry of N
	Complex **1**·MeCN	
2.876(4)		*x*+1, *y*, *z*
	Complex **3**·MeCN	
2.904(3)		*x*+1, *y*, *z*
	Complex **5**·MeCN	
2.921(4)		*x*+1, *y*, *z*
	Complex **9**·MeCN	
2.967(3)		*x*+1, *y*, *z*

Table S5 Stacking interactions in the crystal structures of **1**·MeCN, **3**·MeCN, **5**·MeCN and **9**·MeCN

Type[a]	Centroid-centroid (Å)	Symmetry operation
	Complex **1**·MeCN	
E1	3.805	-*x*+1, -*y*, -*z*+2
E2	3.723	-*x*, -*y*, -*z*+2
	Complex **3**·MeCN	
E1	3.795	-*x*+1, -*y*, -*z*+2
E2	3.713	-*x*, -*y*, -*z*+2
	Complex **5**·MeCN	
E1	3.791	-*x*+1, -*y*, -*z*+2
E2	3.708	-*x*, -*y*, -*z*+2
	Complex **9**·MeCN	
E1	3.783	-*x*+1, -*y*, -*z*+2
E2	3.697	-*x*, -*y*, -*z*+2

[a] For descriptions, see main body of the ms.

Table S6 Percentage values for all types of atomic contacts (based on 2D FP plots) in the crystal structures of complexes **1**·MeCN, **3**·MeCN, **5**·MeCN, **7**·MeCN and **9**·MeCN

Contact	Percentage (%)				
	1·MeCN	**3**·MeCN	**5**·MeCN	**7**·MeCN	**9**·MeCN
O···H	25.9	25.7	25.8	25.8	25.6
H···H	21.4	21.1	21.3	21.2	21.3
C···H	13.2	13.3	13.5	13.5	13.4
C···C	11.4	11.5	11.4	11.5	11.6
Br···H	10.3	10.6	10.7	11.0	11.2
N···H	4.2	4.3	4.1	4.2	4.3
O···Br	4.8	4.6	4.2	4.1	4.0
O···N	1.7	1.7	1.7	1.7	1.6
O···O	1.6	1.5	1.5	1.5	1.5
N···C	1.4	1.5	1.6	1.5	1.5
Br···Br	1.3	1.4	1.5	1.5	1.5
Br···C	1.1	1.2	1.1	1.1	1.1
O···C	0.8	0.8	0.7	0.6	0.7
N···Br	0.7	0.7	0.7	0.6	0.6
N···N	0.2	0.2	0.2	0.2	0.2

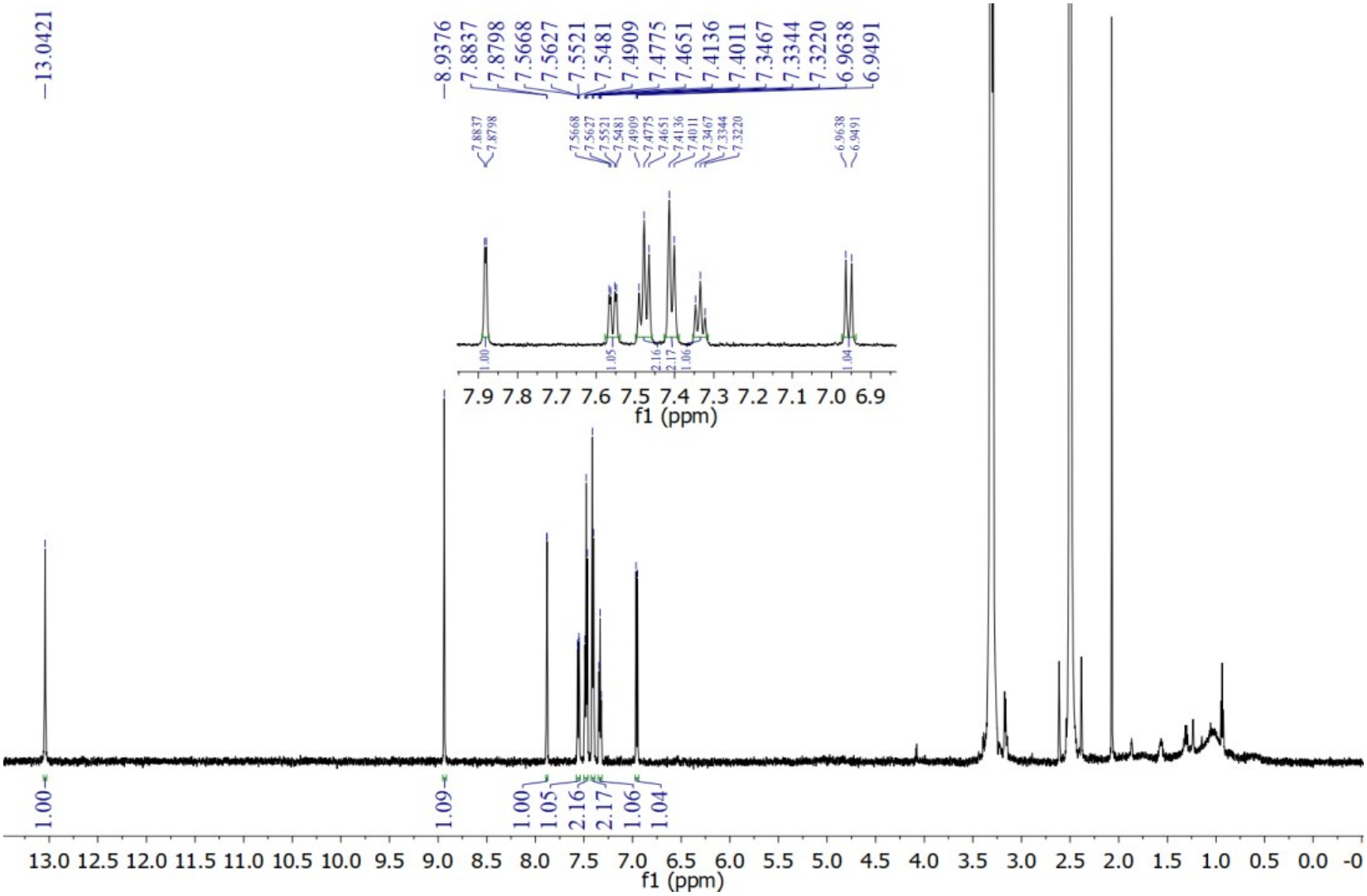

Fig. S1 The ^{1}H NMR spectrum (DMSO-d_6, δ/ppm) of complex [$Y(NO_3)_3(5BrsalanH)_2(H_2O)$] (**11**).

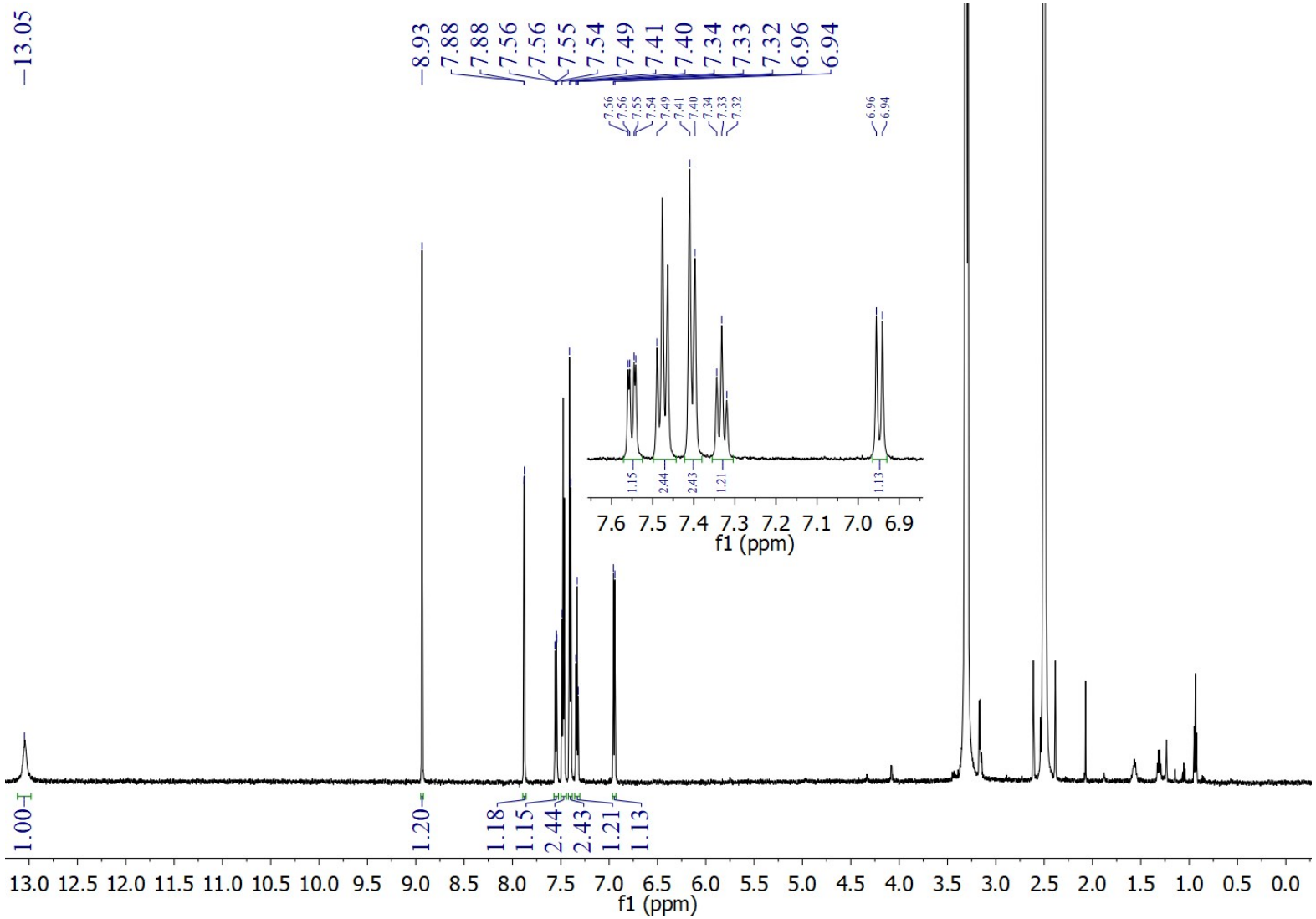

Fig. S2 The ^{1}H NMR spectrum (DMSO-d_6, δ/ppm) of the free ligand 5BrsalanH.

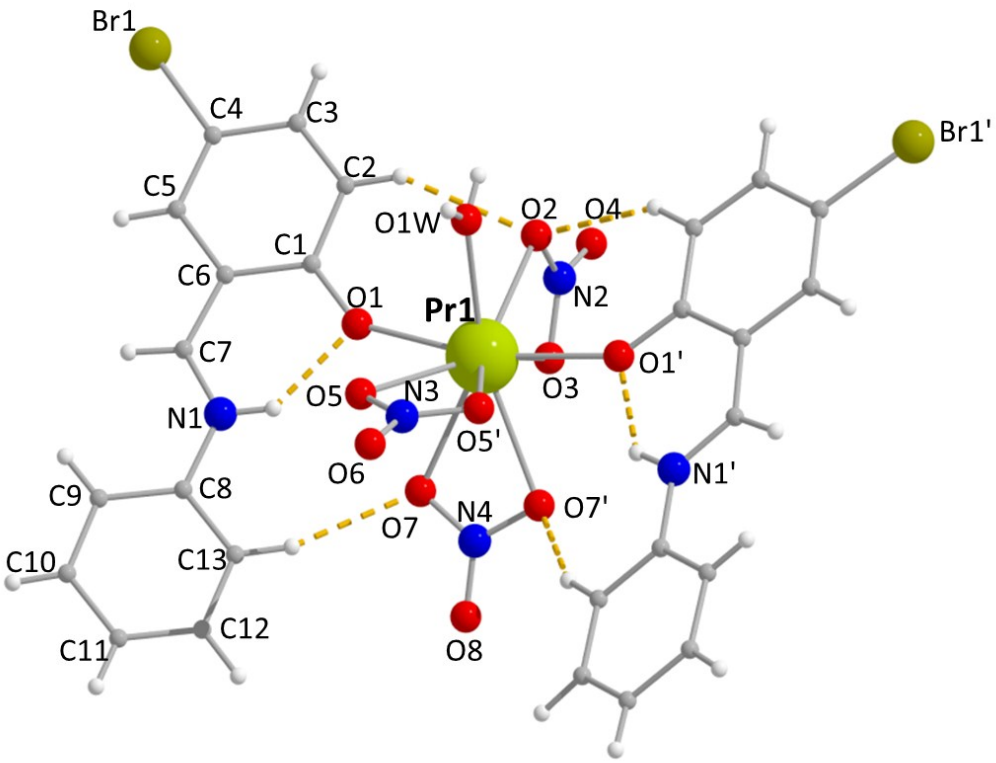

Fig. S3 Partially labelled plot of the molecular structure of complex $[Pr(NO_3)_3(5BrsalanH)_2(H_2O)]\cdot MeCN$ (**1**·MeCN); the lattice MeCN molecule is not shown. Symmetry operation used to generate equivalent atoms: (') *x*, -*y*+1/2, *z*. Dashed thick orange lines represent intramolecular H bonds.

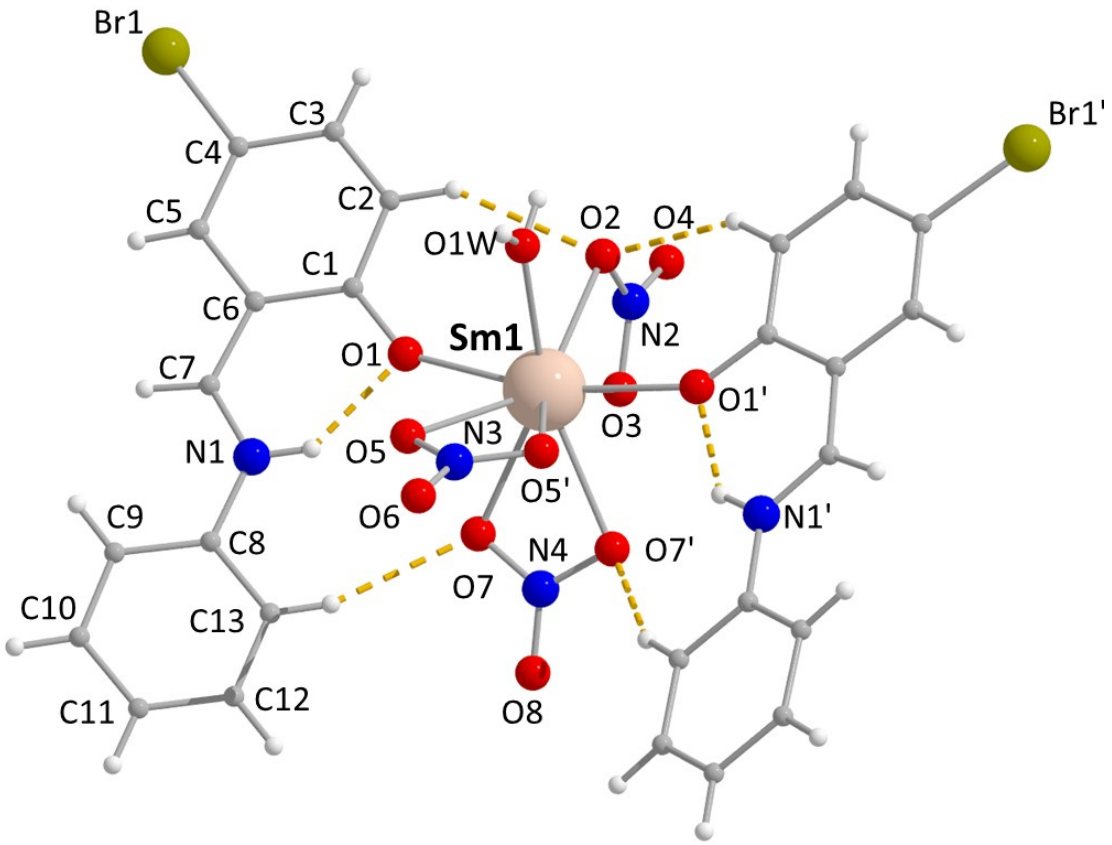

Fig. S4 Partially labelled plot of the molecular structure of complex $[Sm(NO_3)_3(5BrsalanH)_2(H_2O)]\cdot MeCN$ (**3**·MeCN); the lattice MeCN molecule is not shown. Symmetry operation used to generate equivalent atoms: (') *x*, -*y*+1/2, *z*. Dashed thick orange lines represent intramolecular H bonds.

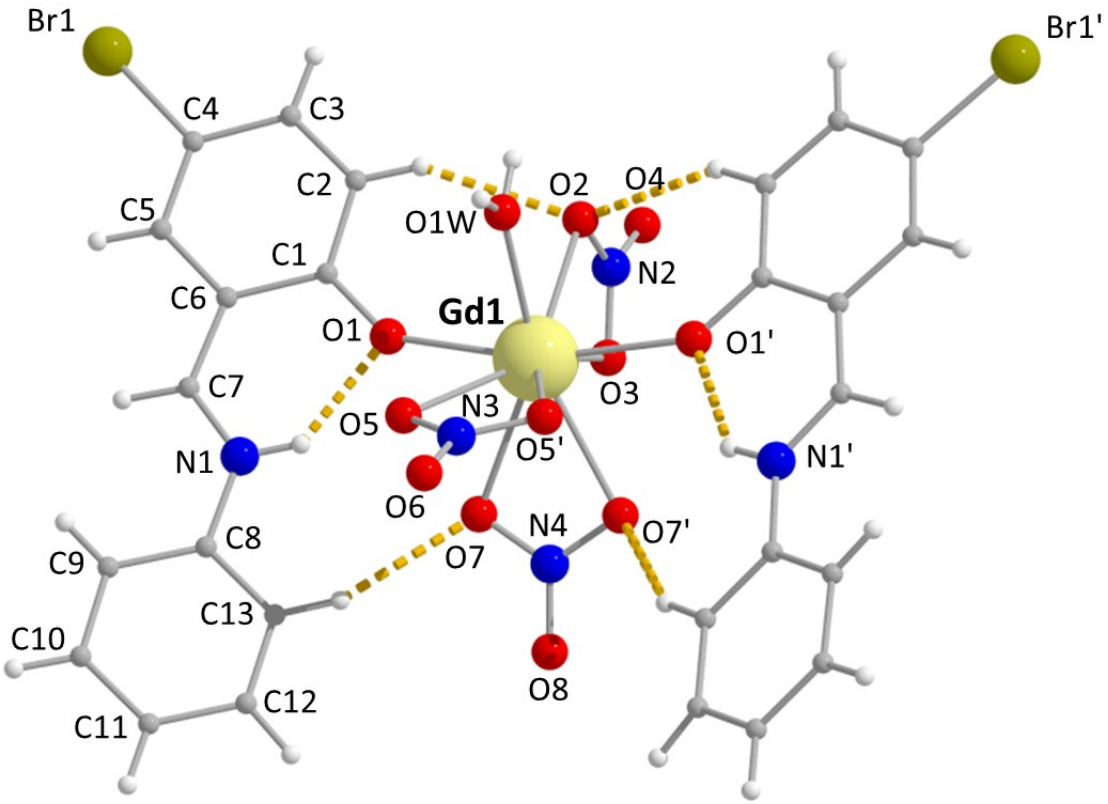

Fig. S5 Partially labelled plot of the molecular structure of complex $[Gd(NO_3)_3(5BrsalanH)_2(H_2O)]\cdot MeCN$ (**5**·MeCN); the lattice MeCN molecule is not shown. Symmetry operation used to generate equivalent atoms: (') *x*, -*y*+1/2, *z*. Dashed thick orange lines represent intramolecular H bonds.

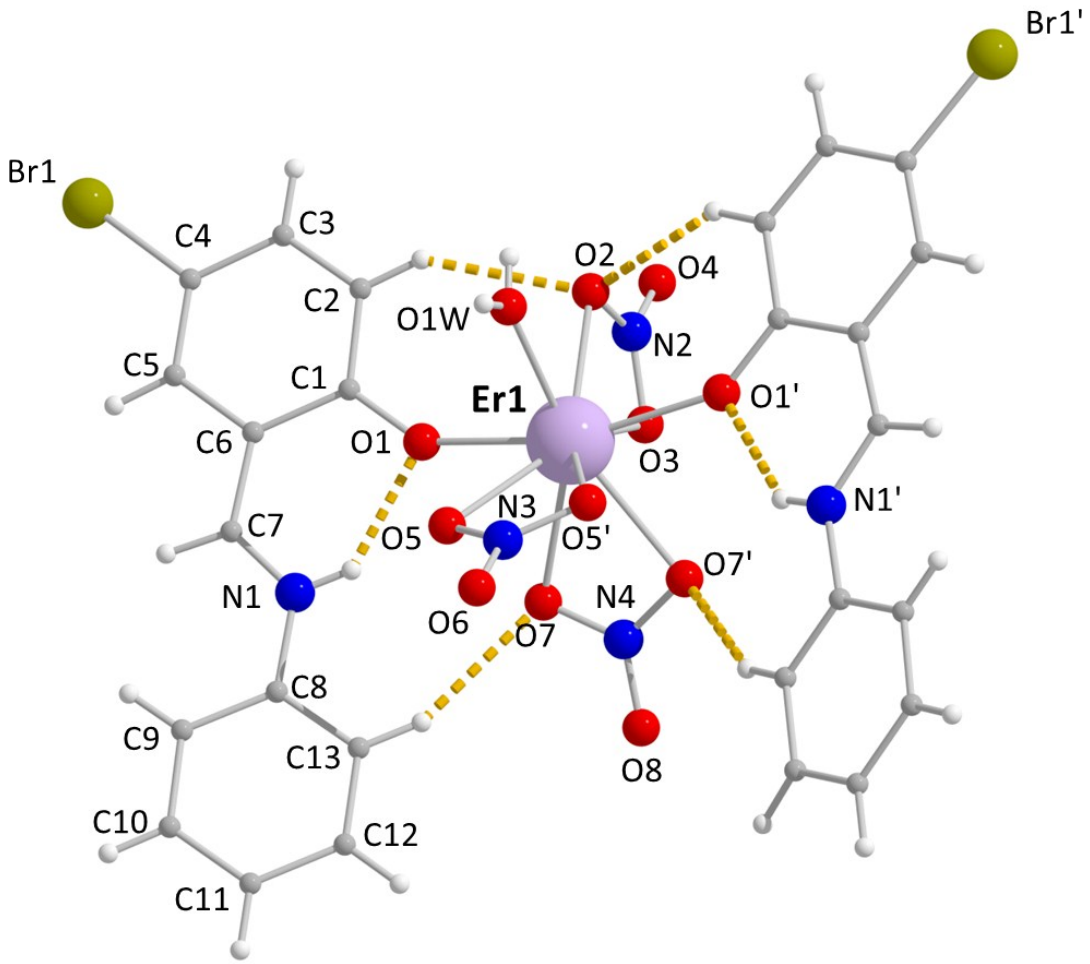

Fig. S6 Partially labelled plot of the molecular structure of complex $[Er(NO_3)_3(5BrsalanH)_2(H_2O)]\cdot MeCN$ (**9**·MeCN); the lattice MeCN molecule is not shown. Symmetry operation used to generate equivalent atoms: (') *x*, -*y*+1/2, *z*. Dashed thick orange lines represent intramolecular H bonds.

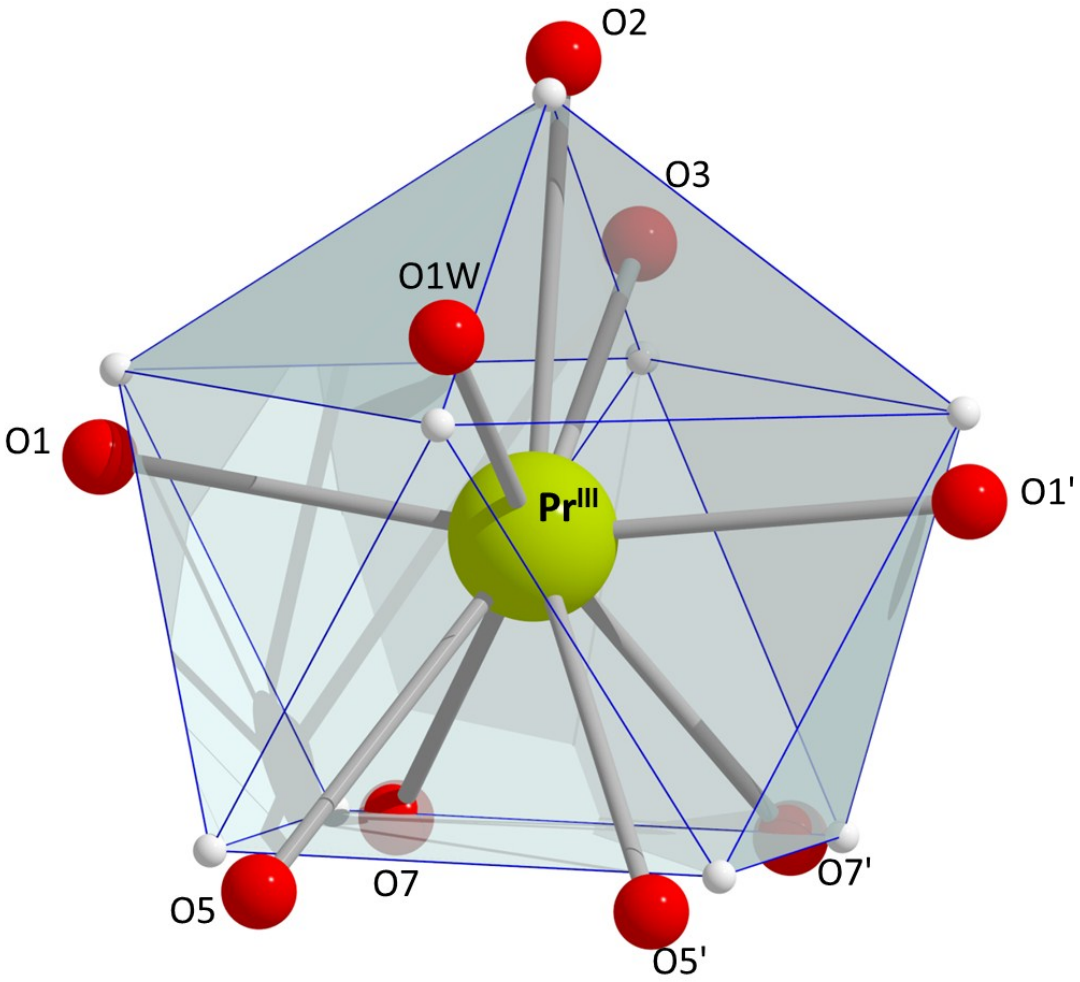

Fig. S7 The spherical capped square antiprismatic coordination polyhedron of Pr^{III} in complex **1**·MeCN. The smaller cream spheres define the vertices of the ideal polyhedron. Symmetry operation used to generate equivalent atoms: (') *x*, -*y*+1/2, *z*.

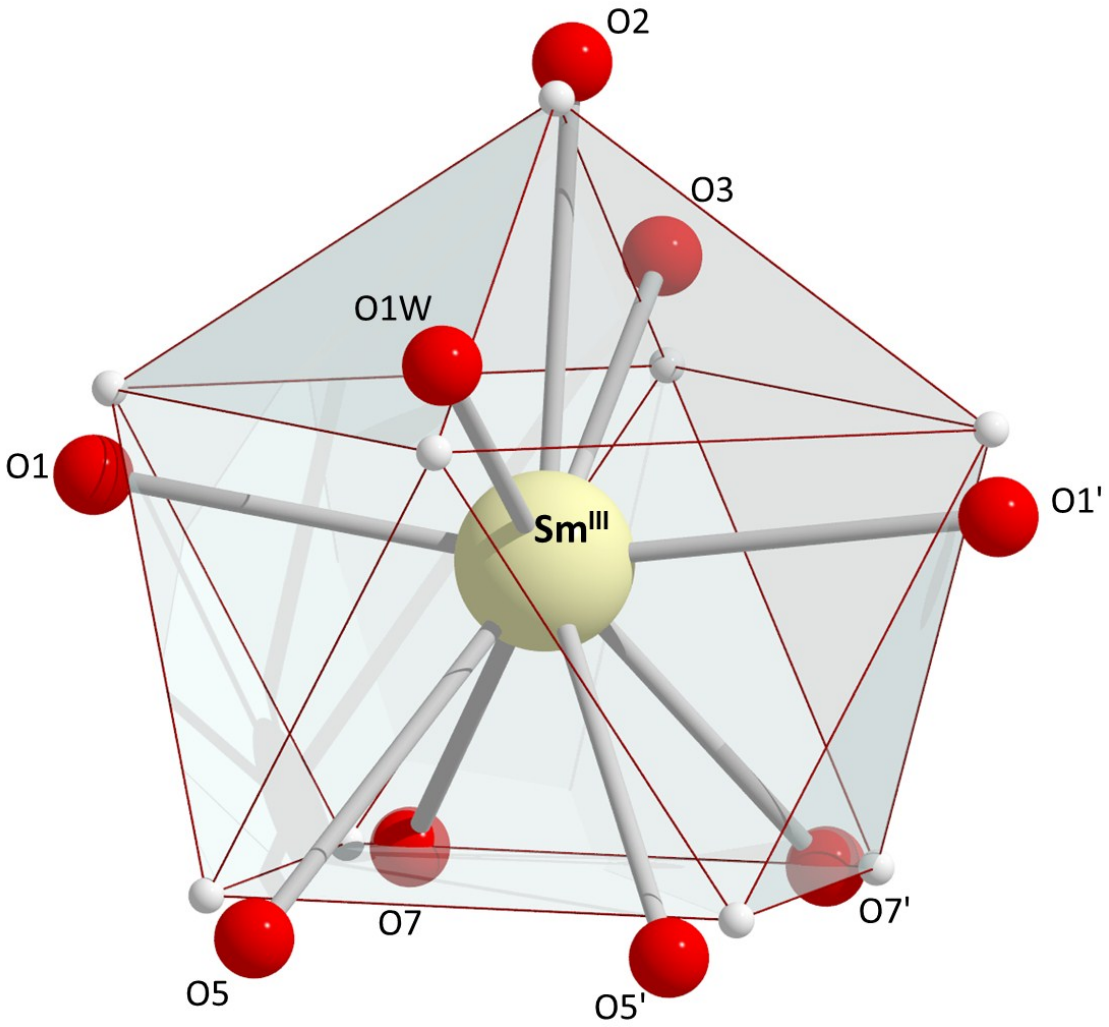

Fig. S8 The spherical capped square antiprismatic coordination polyhedron of Sm^{III} in complex **3**·MeCN. The smaller cream spheres define the vertices of the ideal polyhedron. Symmetry operation used to generate equivalent atoms: (') *x*, -*y*+1/2, *z*.

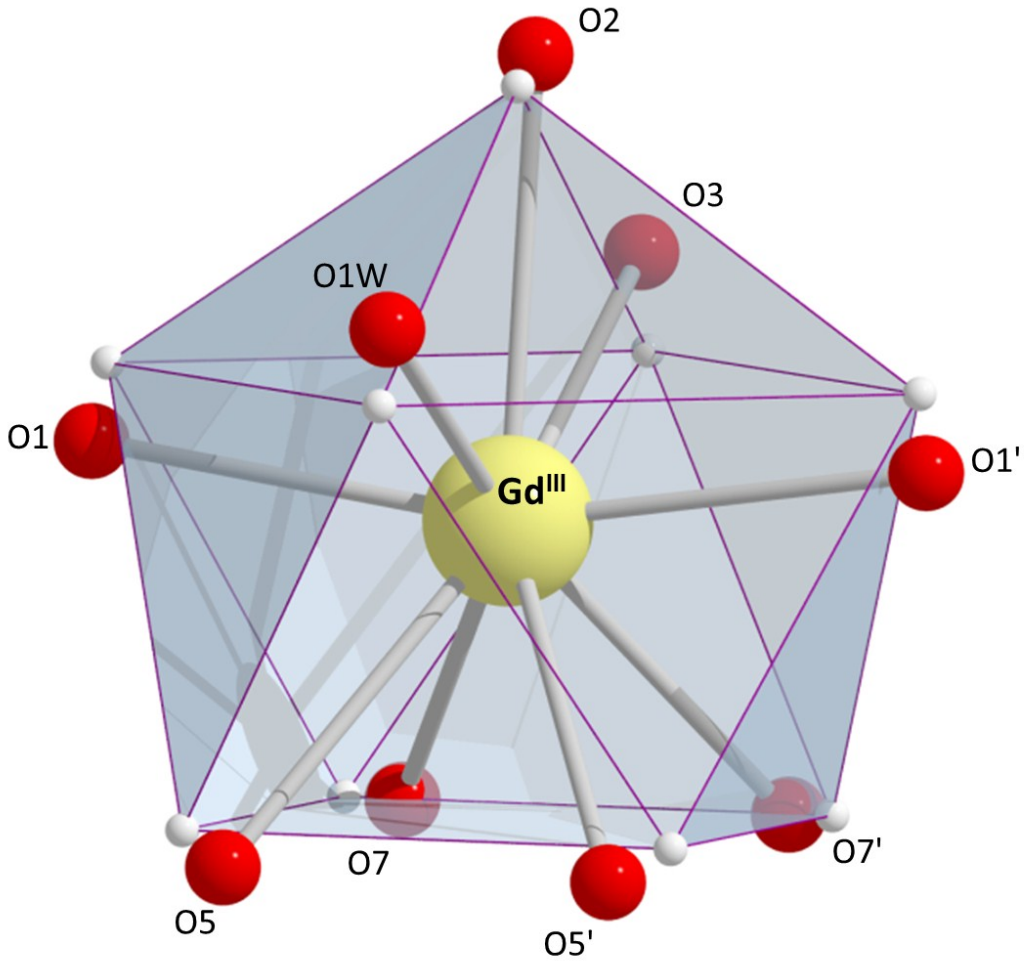

Fig. S9 The spherical capped square antiprismatic coordination polyhedron of Gd^{III} in complex **5**·MeCN. The smaller cream spheres define the vertices of the ideal polyhedron. Symmetry operation used to generate equivalent atoms: (') *x*, -*y*+1/2, *z*.

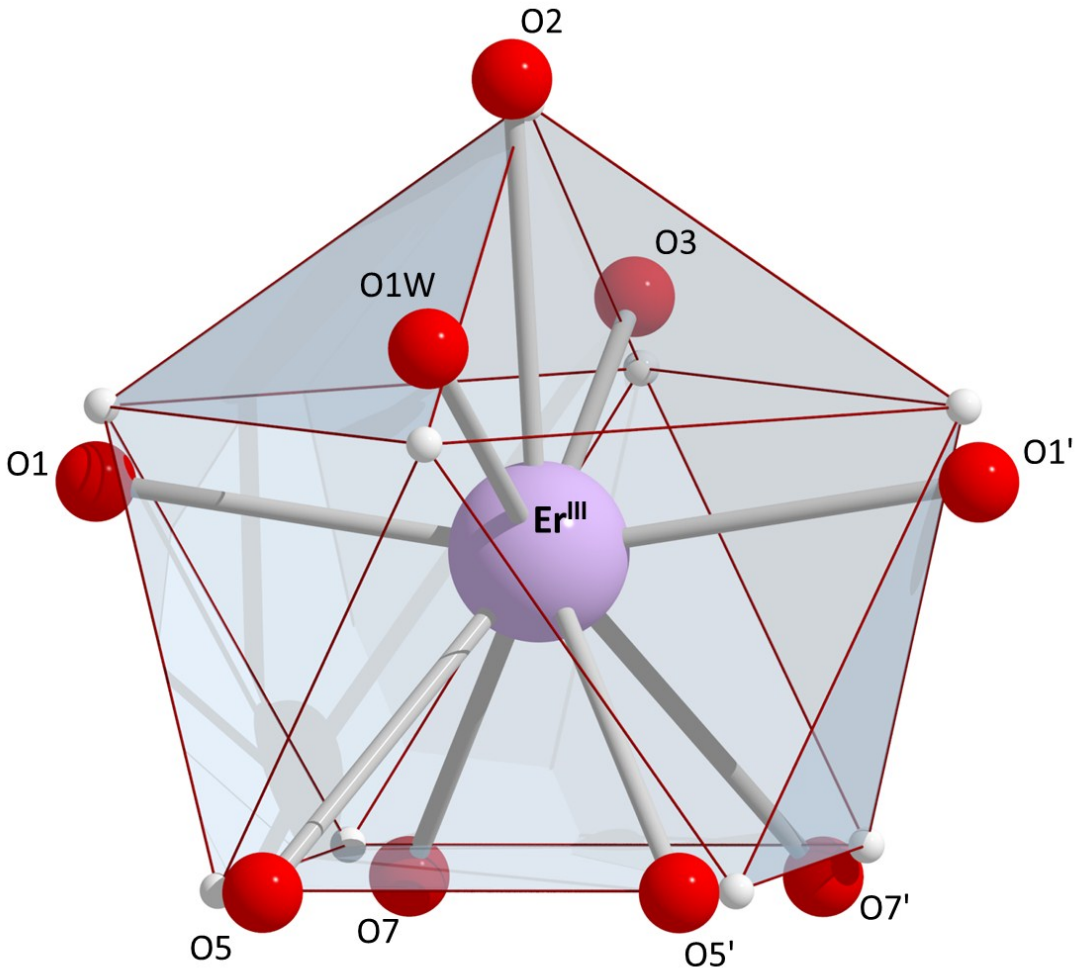

Fig. S10 The spherical capped square antiprismatic coordination polyhedron of Er^{III} in complex **9**·MeCN. The smaller cream spheres define the vertices of the ideal polyhedron. Symmetry operation used to generate equivalent atoms: (') *x*, -*y*+1/2, *z*.

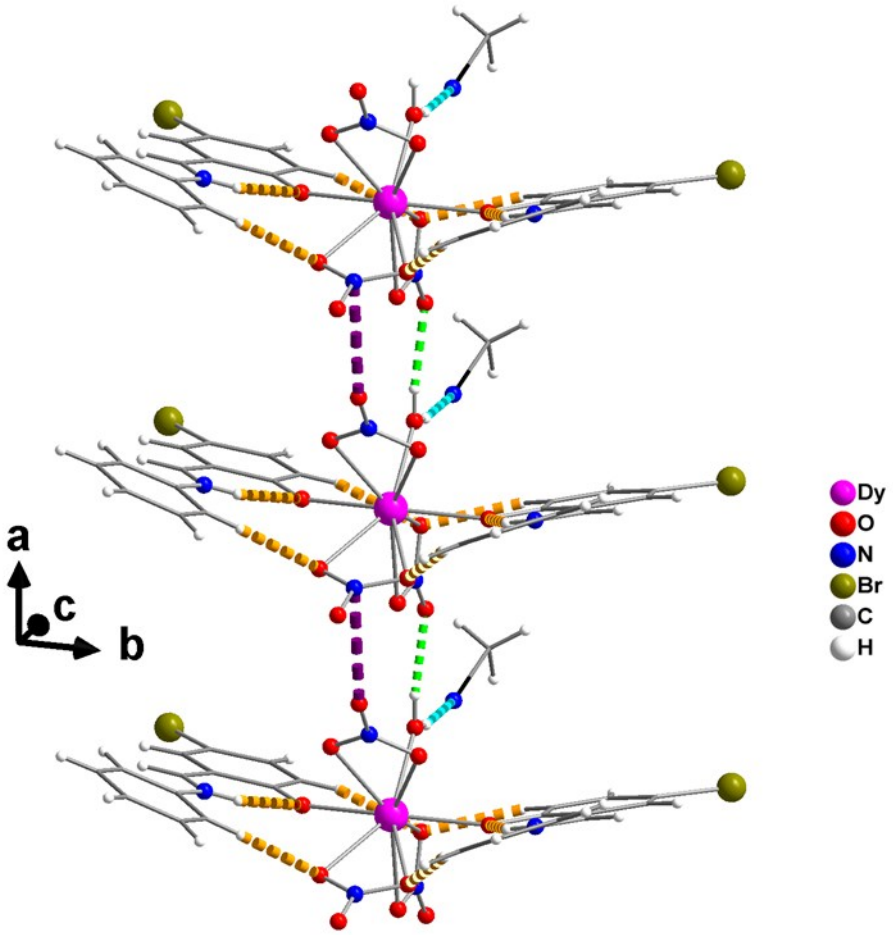

Fig. S11 A chain in the crystal structure of **7**·MeCN along the crystallographic axis *a*, formed through aquo oxygen-H···non-coordinated nitrato oxygen H bonds and nitrato-nitrato contacts. Dashed thick orange lines represent intramolecular H bonds (see caption of Fig. 2). The dashed thick cyan lines represent the H bonds with the aqua ligands as donors and the lattice MeCN molecules as acceptors; the dashed thick light green and violet lines indicate the aquo-H···non-coordinated nitrato oxygen H bonds and the nitrato-nitrato contacts, respectively.

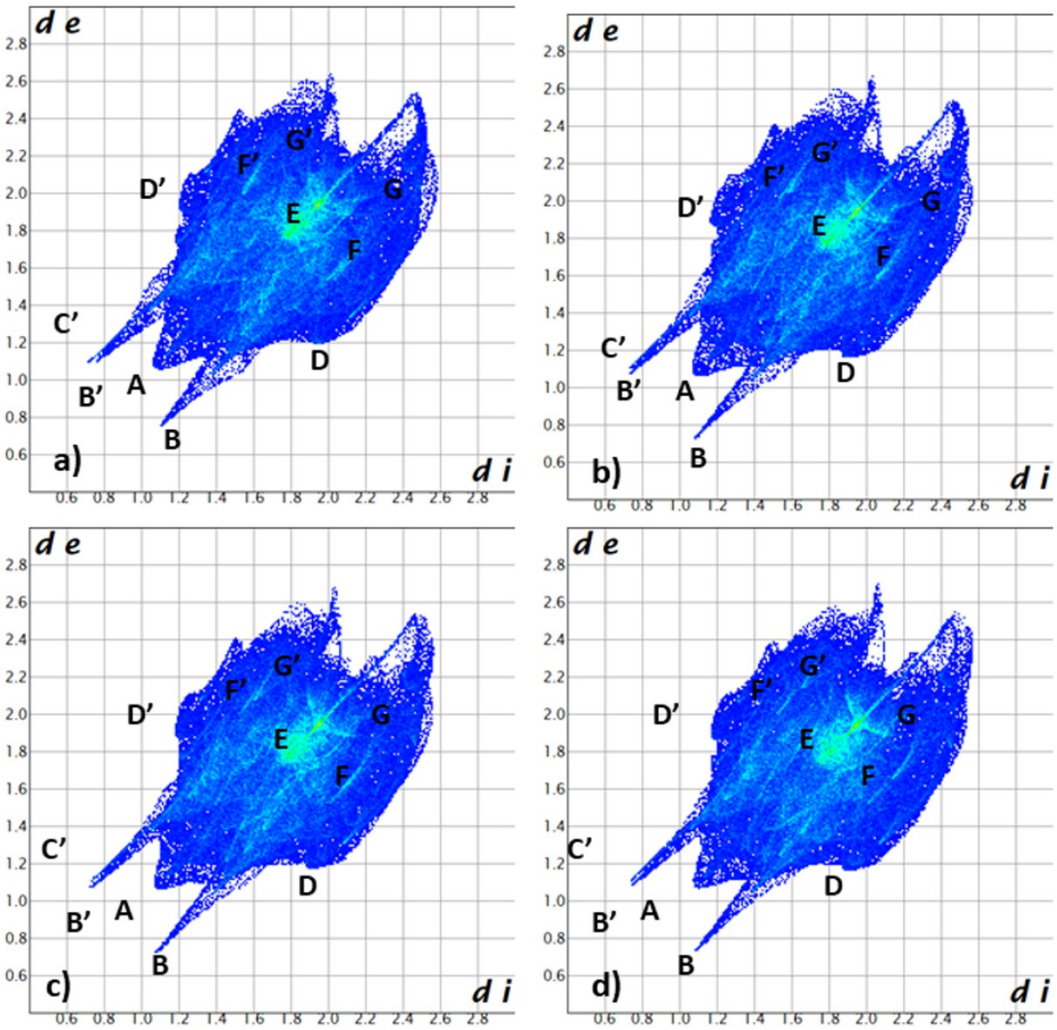

Fig. S12 FP plots for all types of interactions in the crystal structures of (a) **1**·MeCN, (b) **3**·MeCN, (c) **5**·MeCN and (d) **9**·MeCN. Symbols B, D, F and G indicate acceptor point contributions for the O···H, Br···H, N···O and Br···O interactions, respectively, while B', D', F' and G' stand for the corresponding donor points. C', A and E correspond to the H···N, H···H and C···C interactions, respectively.

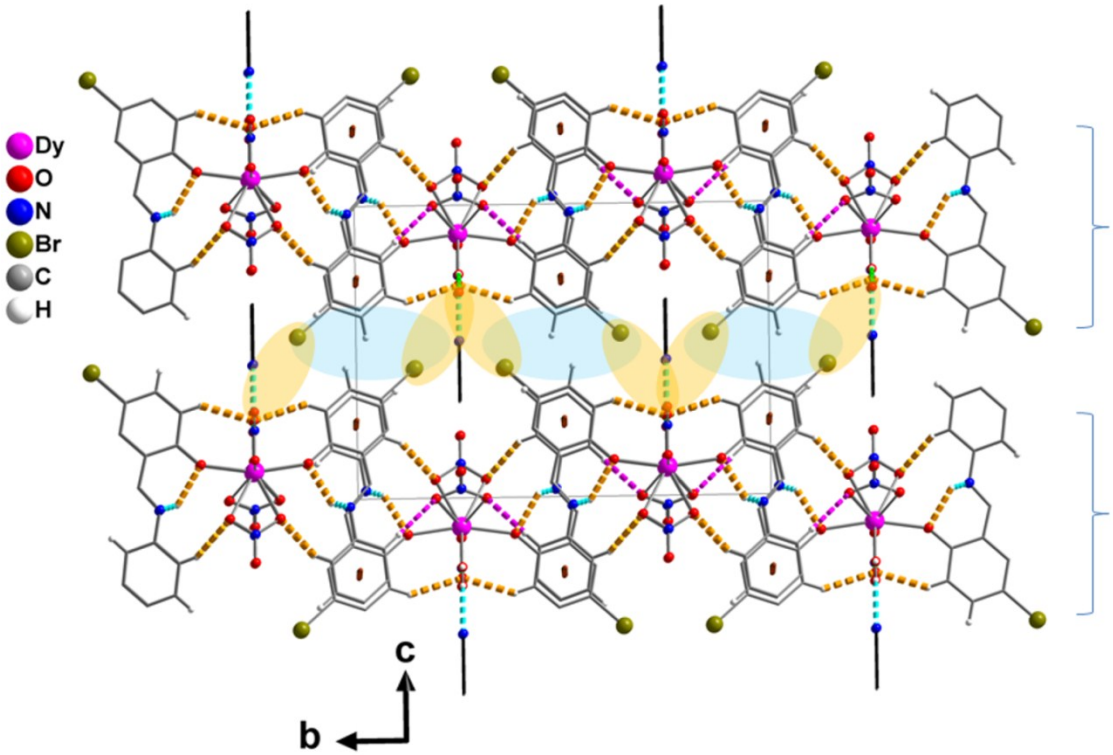

Fig. S13 Stacking of layers along the *c* axis in the crystal structure of **7**·MeCN. The stacking (and the consequent formation of the 3D architecture) is formed through C-H···Br H bonds and Br···O contacts indicated by faint cyan and orange shaded areas, respectively.

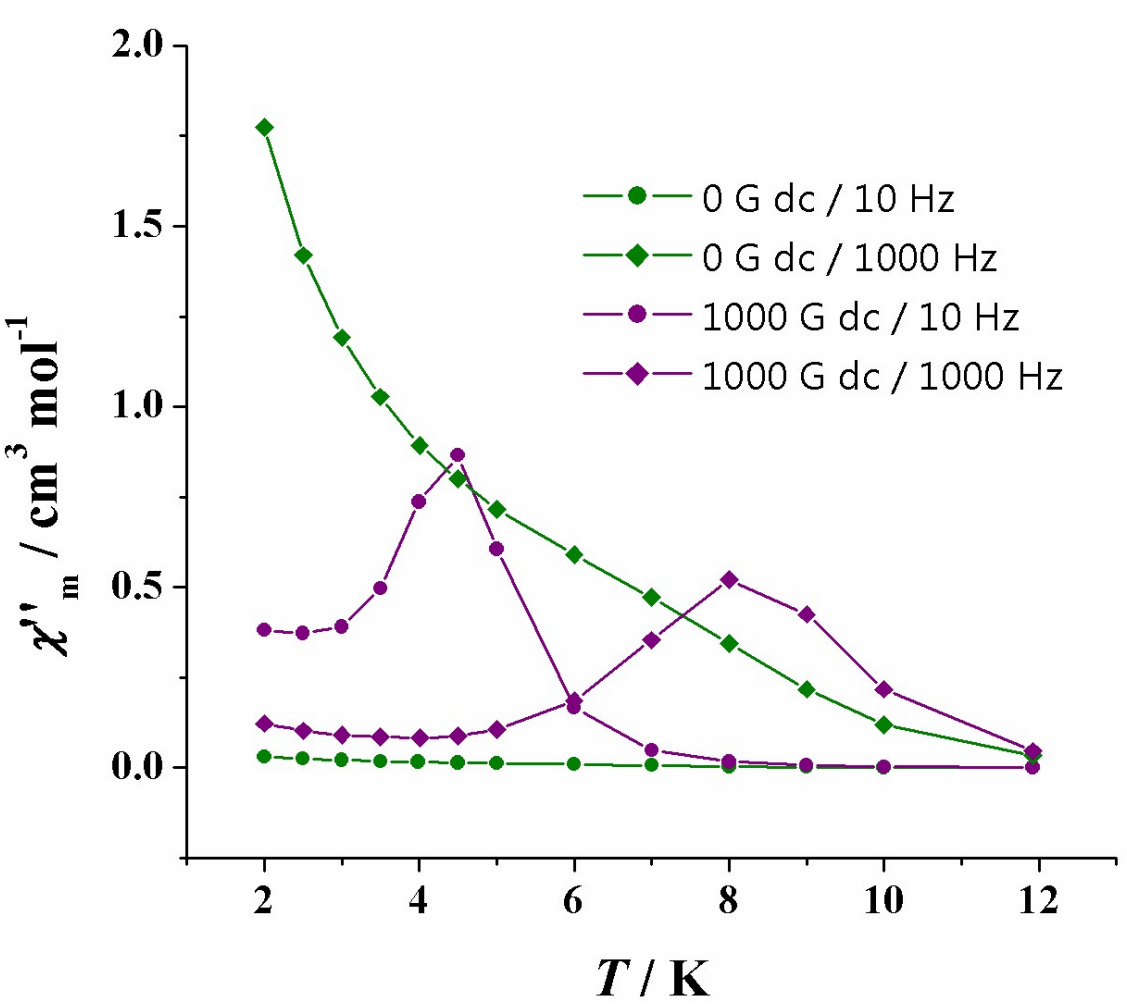

Fig. S14 χ''_M *versus T* plots at 0 and 1000 G dc fields for complex $[Dy(NO_3)_3(5BrsalanH)_2(H_2O)]$ (**7**) at ac frequencies of 10 and 1000 Hz.