Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Nitronyl nitroxide metal complexes as metalloligands for the construction of hetero-tri-spin (2p-3d-4f) chains

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CONTENTS

X-ray Crystallography: Diffraction intensity data of the single crystals of complexes **1a**, **1b**, **2a** and **2b**. were collected on a Rigaku Saturn CCD diffractometer at 113 K employing graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods by using the program SHELXS-97[1] and refined by full matrix least-squares methods on F^2 with the use of the SHELXL-97 [2] program package. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. For the four complexes disorders were observed for some fluorine atoms and the restraints with DELU, SIMU, EADP and ISOR were applied to keep the disordered fluorine atoms reasonable. In these compounds, the unit cells include large regions of disordered solvent molecules which are C_7H_{16} for **1a** and **1b**, and H_2O for **2a** and **2b**. When the lattice solvent molecules were too disordered and could not be modelled properly the SQUEEZE[3] option of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. The pertinent crystallographic data and structure refinement parameters for complexes are listed in Table S1.

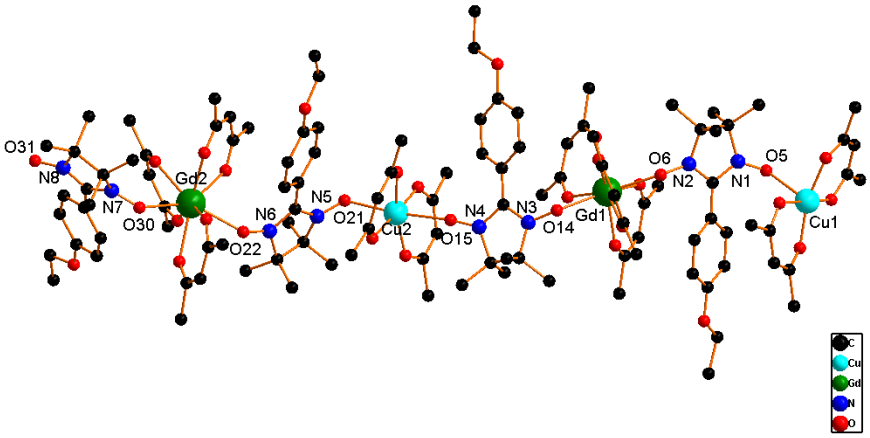
Table S1 Crystal Data and Structure Refinement for complexes **1a**, **1b**, **2a** and **2b**.

	1a	**1b**	**2a**	**2b**
empirical formula	$C_{117}H_{110}Cu_2F_{60}N_8O_{32}Gd_2$	$C_{117}H_{110}Cu_2F_{60}N_8O_{32}Tb_2$	$C_{115}H_{97}CuF_{66}N_8O_{35}Gd_3$	$C_{115}H_{97}CuF_{66}N_8O_{35}Tb_3$
M_r	3721.71	3725.05	3940.31	3945.35
T, K	113(2)	113(2)	113(2)	113(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	21.860(2)	21.853(2)	20.014(4)	19.973(5)
b, Å	23.702(2)	23.682(2)	20.020(4)	19.983(4)
c, Å	28.848(3)	28.760(3)	21.717(4)	21.679(4)
α, deg	90	90	107.330(3)	90.959(2)
β, deg	100.829(2)	100.782(2)	91.043(2)	107.219(2)
γ, deg	90	90	114.9410(10)	114.941(4)
V, Å^3	14681(3)	14621(3)	7427(3)	7393(3)
Z	4	4	2	2
Dc, gcm^{-3}	1.692	1.692	1.762	1.772
μ, mm^{-1}	1.327	1.391	1.620	1.717
θ range, deg	1.12-25.01	1.12-25.01	1.63-27.86	1.19-25.01
Unique reflns /R_{int}	25855/0.0897	25744 /0.0487	34842/0.0684	25961/0.0566
GOF	1.055	1.043	1.096	1.090
$R1^a$ [$I > 2\sigma(I)$]	0.0537	0.0343	0.0606	0.0607
$wR2^b$[$I > 2\sigma(I)$]	0.1228	0.0836	0.1388	0.1243

[a] $R1 = = \sum(||F_0|-|F_c||)/\sum|F_0|$, [b] $wR2 = \{\sum w(|F_0|^2-|F_c|^2)^2/\sum w|F_0|^2)^2\}^{1/2}$

[1] G. M. Sheldrick, SHELXS-97: Program for the Solution of Crystal Structures, University of Göttingen, Germany, **1997**.
[2] G. M. Sheldrick, SHELXL-97: Program for the refinement of Crystal Structures, University of Göttingen, Germany, **1997**.
[3] A. L. Spek, *Acta Crystallogr.*, 2009, **D65**, 148-155.

Figure S1. $[(NitPhOEt)_2\{Cu(hfac)_2\}\{Gd(hfac)_3\}]_2 \cdot C_7H_{16}$, **1a**: *(top)* view of the one-dimensional chain structure of complex with the atom-labeling, and *(bottom)* their crystal packing. All hydrogen and fluorine atoms are omitted for clarity. Color scheme: Gd^{III}, green; Cu^{II}, light blue; O, red; N, blue; C, black.



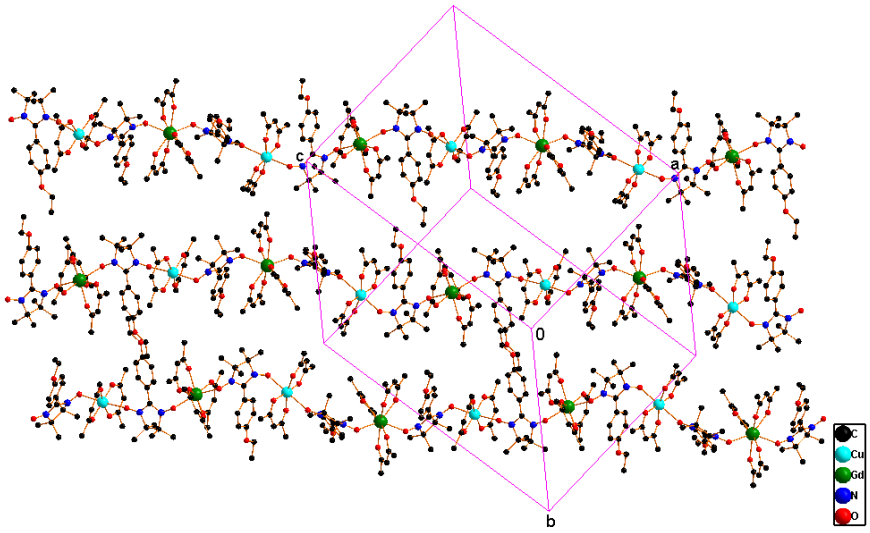


Table S2. Selected bond lengths (Å) and angles (°) for complex **1a**

Gd(1)-O(6)	2.354(3)	O(5)-N(1)	1.283(5)
Gd(1)-O(14)	2.359(3)	O(6)-N(2)	1.296(5)
Gd(2)-O(22)	2.380(3)	O(14)-N(3)	1.313(5)
Gd(2)-O(30)	2.358(3)	O(15)-N(4)	1.267(5)
Cu(1)-O(5)	2.383(3)	O(21)-N(5)	1.286(5)
Cu(1)-O(31)#1	2.653(3)	O(22)-N(6)	1.300(5)
Cu(2)-O(15)	2.471(4)	O(30)-N(7)	1.307(5)
Cu(2)-O(21)	2.337(3)	O(31)-N(8)	1.273(5)
O(9)-Gd(1)-O(14)	89.93(12)	O(25)-Gd(2)-O(30)	103.49(11)
O(11)-Gd(1)-O(14)	105.57(12)	O(28)-Gd(2)-O(30)	91.37(12)
O(6)-Gd(1)-O(13)	73.91(11)	O(30)-Gd(2)-O(27)	73.86(11)
O(6)-Gd(1)-O(8)	74.41(12)	O(30)-Gd(2)-O(22)	139.34(11)
O(6)-Gd(1)-O(14)	136.80(11)	O(27)-Gd(2)-O(22)	72.92(11)
O(14)-Gd(1)-O(12)	72.97(11)	O(24)-Gd(2)-O(22)	146.40(11)
O(6)-Gd(1)-O(10)	148.29(11)	O(26)-Gd(2)-O(22)	73.16(11)
N(2)-O(6)-Gd(1)	140.8(3)	N(6)-O(22)-Gd(2)	137.3(3)
N(3)-O(14)-Gd(1)	135.0(3)	N(7)-O(30)-Gd(2)	138.6(3)
O(4)-Cu(1)-O(5)	93.55(13)	O(20)-Cu(2)-O(21)	89.03(13)
O(1)-Cu(1)-O(5)	82.68(13)	O(18)-Cu(2)-O(21)	88.48(13)
O(3)-Cu(1)-O(5)	106.20(13)	O(17)-Cu(2)-O(21)	98.82(13)
O(2)-Cu(1)-O(5)	88.51(13)	O(19)-Cu(2)-O(21)	94.91(13)
O(5)-Cu(1)-O(31)#1	176.57(13)	O(21)-Cu(2)-O(15)	174.13(13)

Symmetry transformations used to generate equivalent atoms: #1: 1+x,y,1+z

Figure S2. $[(NitPhOEt)_2\{Cu(hfac)_2\}\{Tb(hfac)_3\}]_2 \cdot C_7H_{16}$, **1b**: view of the crystal packing for the one-dimensional chains All hydrogen and fluorine atoms are omitted for clarity. Color scheme: Tb^{III}, green; Cu^{II}, light blue; O, red; N, blue; C, black.

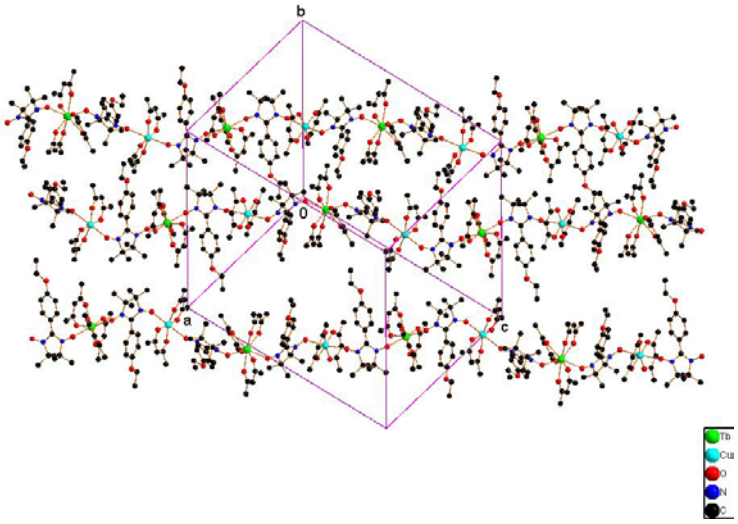


Table S3. Selected bond lengths (Å) and angles (°) for complex **1b**

Tb(1)-O(6)	2.3506(19)	O(5)-N(1)	1.285(3)
Tb(1)-O(14)	2.352(2)	O(6)-N(2)	1.298(3)
Tb(2)-O(22)	2.3768(19)	O(14)-N(3)	1.306(3)
Tb(2)-O(30)	2.355(2)	O(15)-N(4)	1.268(3)
Cu(1)-O(5)	2.3757(19)	O(21)-N(5)	1.286(3)
Cu(1)-O(31)#1	2.647(19)	O(22)-N(6)	1.302(3)
Cu(2)-O(15)	2.468(2)	O(30)-N(7)	1.306(3)
Cu(2)-O(21)	2.339(2)	O(31)-N(8)	1.273(3)
O(9)-Tb(1)-O(14)	89.86(7)	O(25)-Tb(2)-O(30)	103.93(7)
O(11)-Tb(1)-O(14)	105.45(7)	O(28)-Tb(2)-O(30)	91.12(8)
O(6)-Tb(1)-O(13)	74.05(7)	O(30)-Tb(2)-O(27)	73.63(7)
O(6)-Tb(1)-O(8)	74.42(7)	O(30)-Tb(2)-O(22)	139.10(7)
O(6)-Tb(1)-O(14)	136.72(7)	O(27)-Tb(2)-O(22)	73.00(7)
O(14)-Tb(1)-O(12)	73.29(7)	O(24)-Tb(2)-O(22)	146.33(7)
O(6)-Tb(1)-O(10)	148.17(7)	O(26)-Tb(2)-O(22)	73.15(7)
N(2)-O(6)-Tb(1)	140.18(17)	N(6)-O(22)-Tb(2)	137.54(16)
N(3)-O(14)-Tb(1)	135.00(17)	N(7)-O(30)-Tb(2)	137.67(18)
O(4)-Cu(1)-O(5)	93.80(8)	O(20)-Cu(2)-O(21)	89.16(8)
O(1)-Cu(1)-O(5)	82.71(8)	O(18)-Cu(2)-O(21)	88.34(8)
O(3)-Cu(1)-O(5)	106.46(8)	O(17)-Cu(2)-O(21)	98.81(8)
O(2)-Cu(1)-O(5)	88.60(8)	O(19)-Cu(2)-O(21)	95.18(8)
O(5)-Cu(1)-O(31)#1	176.56(8)	O(21)-Cu(2)-O(15)	173.71(8)

Symmetry transformations used to generate equivalent atoms: #1: 1+x,y,1+z

Figure S3. $[(NitPhOEt)_4\{Cu(hfac)_2\}\{Gd(hfac)_3\}_3]\ H_2O$, **2a**: *(top)* view of the one-dimensional chain structure of complex with the atom-labeling, and *(bottom)* their crystal packing. All hydrogen and fluorine atoms are omitted for clarity.

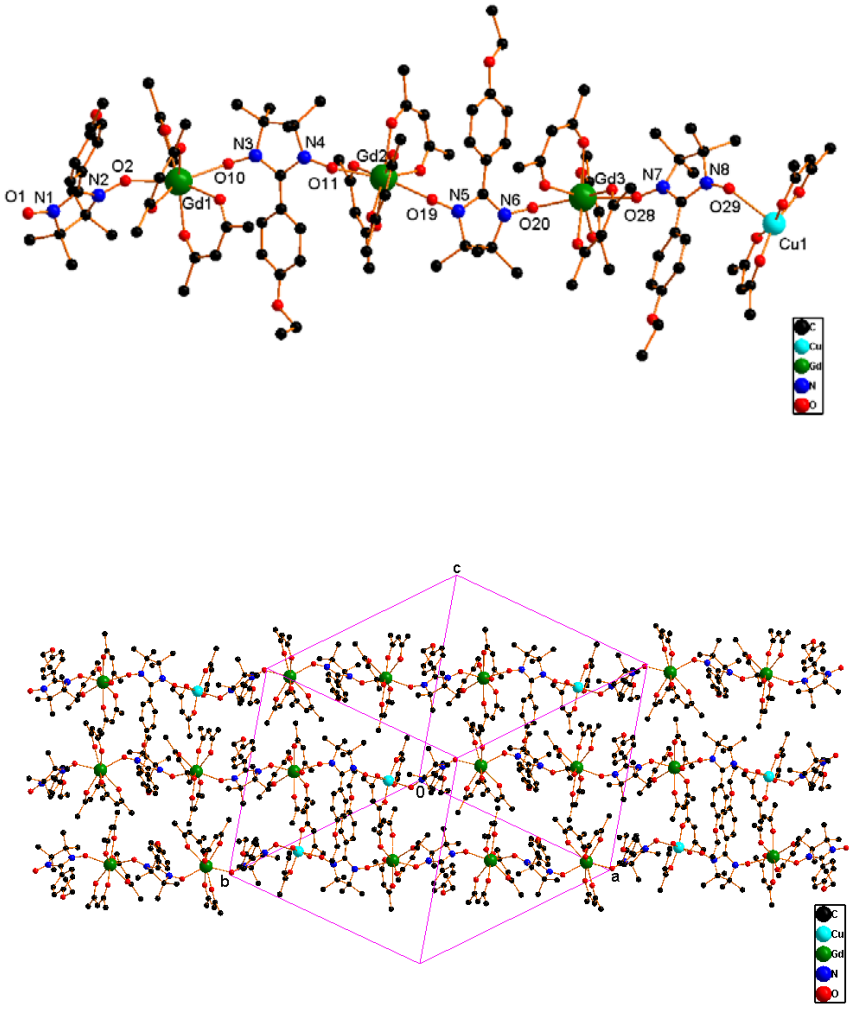


Table S4. Selected bond lengths (Å) and angles (°) for complex **2a**

Gd(1)-O(2)	2.363(4)	O(1)-N(1)	1.290(6)
Gd(1)-O(10)	2.410(4)	O(2)-N(2)	1.303(6)
Gd(2)-O(11)	2.345(4)	O(10)-N(3)	1.289(6)
Gd(2)-O(19)	2.388(4)	O(11)-N(4)	1.307(6)
Gd(3)-O(20)	2.403(4)	O(19)-N(5)	1.299(5)
Gd(3)-O(28)	2.366(4)	O(20)-N(6)	1.298(6)
Cu(1)-O(29)	2.426(4)	O(28)-N(7)	1.298(6)
Cu(1)-O(1)#1	2.488(4)	O(29)-N(8)	1.280(6)
O(8)-Gd(1)-O(2)	93.84(14)	N(5)-O(19)-Gd(2)	139.7(3)
O(4)-Gd(1)-O(2)	71.05(14)	O(23)-Gd(3)-O(28)	91.54(14)
O(7)-Gd(1)-O(2)	103.79(14)	O(24)-Gd(3)-O(28)	103.22(13)
O(2)-Gd(1)-O(10)	136.98(13)	O(26)-Gd(3)-O(28)	69.28(14)
O(6)-Gd(1)-O(10)	148.24(13)	O(28)-Gd(3)-O(20)	137.97(13)
O(9)-Gd(1)-O(10)	71.52(13)	O(25)-Gd(3)-O(20)	147.27(13)
O(5)-Gd(1)-O(10)	68.29(13)	O(27)-Gd(3)-O(20)	71.10(13)
N(2)-O(2)-Gd(1)	143.3(3)	O(22)-Gd(3)-O(20)	74.57(14)
N(3)-O(10)-Gd(1)	138.2(3)	N(6)-O(20)-Gd(3)	136.0(3)
O(11)-Gd(2)-O(18)	89.35(14)	N(7)-O(28)-Gd(3)	137.8(3)
O(11)-Gd(2)-O(14)	100.16(15)	O(31)-Cu(1)-O(29)	102.97(15)
O(11)-Gd(2)-O(16)	78.94(14)	O(33)-Cu(1)-O(29)	92.64(16)
O(11)-Gd(2)-O(15)	73.60(13)	O(29)-Cu(1)-O(1)#1	177.37(14)
O(11)-Gd(2)-O(19)	141.14(13)	O(32)-Cu(1)-O(1)#1	95.73(16)
O(17)-Gd(2)-O(19)	73.98(13)	O(34)-Cu(1)-O(1)#1	96.56(15)
O(13)-Gd(2)-O(19)	143.37(13)	N(8)-O(29)-Cu(1)	131.9(3)
N(4)-O(11)-Gd(2)	145.9(3)	N(1)-O(1)-Cu(1)#2	128.6(3)

Symmetry transformations used to generate equivalent atoms: #1: x-1,y+1,z; #2: x+1,y-1,z

Figure S4. $[(NitPhOEt)_4\{Cu(hfac)_2\}\{Tb(hfac)_3\}_3]\ H_2O$, **2b**: Crystal packing of the chains. All hydrogen and fluorine atoms are omitted for clarity.

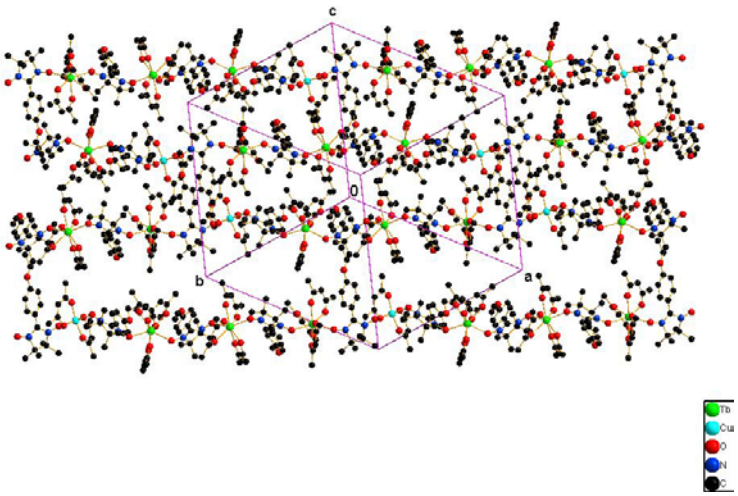
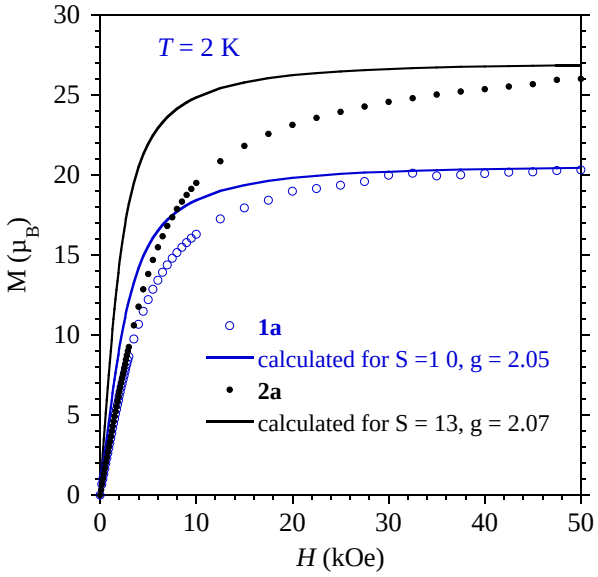


Table S5. Selected bond lengths (Å) and angles (°) for complex **2b**

Tb(1)-O(7)	2.346(4)	O(7)-N(1)	1.305(6)
Tb(1)-O(33)#1	2.385(4)	O(8)-N(2)	1.284(6)
Tb(2)-O(8)	2.409(4)	O(16)-N(3)	1.307(6)
Tb(2)-O(16)	2.349(4)	O(17)-N(4)	1.271(6)
Tb(3)-O(24)	2.360(4)	O(23)-N(5)	1.278(6)
Tb(3)-O(32)	2.389(4)	O(24)-N(6)	1.305(6)
Cu(1)-O(17)	2.498(4)	O(32)-N(7)	1.306(6)
Cu(1)-O(23)	2.423(4)	O(33)-N(8)	1.287(6)
O(6)-Tb(1)-O(7)	100.48(14)	N(3)-O(16)-Tb(2)	143.2(4)
O(7)-Tb(1)-O(4)	89.19(14)	O(26)-Tb(3)-O(24)	91.07(14)
O(7)-Tb(1)-O(3)	145.36(15)	O(28)-Tb(3)-O(24)	103.44(15)
O(7)-Tb(1)-O(33)#1	140.59(15)	O(30)-Tb(3)-O(24)	69.28(13)
O(1)-Tb(1)-O(33)#1	74.01(15)	O(24)-Tb(3)-O(32)	137.66(14)
O(5)-Tb(1)-O(33)#1	143.37(15)	O(29)-Tb(3)-O(32)	147.19(14)
O(33)#1-Tb(1)-O(2)	71.65(14)	O(31)-Tb(3)-O(32)	71.07(14)
N(1)-O(7)-Tb(1)	145.7(4)	O(31)-Tb(3)-O(27)	121.44(15)
N(8)-O(33)-Tb(1)#2	139.4(4)	N(6)-O(24)-Tb(3)	137.6(3)
O(10)-Tb(2)-O(16)	93.54(15)	N(7)-O(32)-Tb(3)	136.0(4)
O(13)-Tb(2)-O(16)	70.90(15)	O(22)-Cu(1)-O(23)	103.14(16)
O(14)-Tb(2)-O(16)	103.68(14)	O(21)-Cu(1)-O(23)	86.37(16)
O(16)-Tb(2)-O(8)	136.82(15)	O(20)-Cu(1)-O(17)	96.50(17)
O(15)-Tb(2)-O(8)	148.24(15)	O(19)-Cu(1)-O(17)	88.40(17)
O(11)-Tb(2)-O(8)	71.72(14)	O(23)-Cu(1)-O(17)	177.76(15)
O(12)-Tb(2)-O(8)	68.10(14)	N(5)-O(23)-Cu(1)	132.5(4)
N(2)-O(8)-Tb(2)	137.8(4)	N(4)-O(17)-Cu(1)	128.8(4)

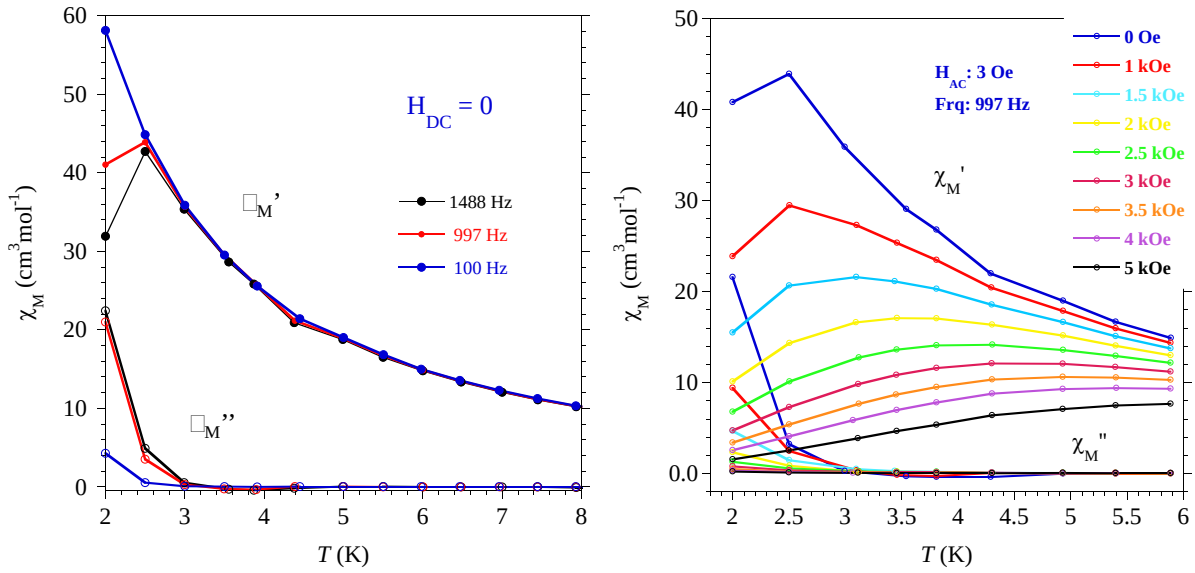
Symmetry transformations used to generate equivalent atoms: #1: x+1,y-1,z ; #2: x-1,y+1,z

Figure S5. Experimental (O/•) versus calculated (full lines) field dependence of the magnetization for **1a** and **2a** at 2 K



The Brillouin function has been used to calculated the M versus H behaviours for the S = 10 and S = 13 spin ground states.

Figure S6. AC susceptibility behaviour for **2b**



Compound **2b** exhibits a clear frequency-dependent out-of-phase (χ″) signal below 4.0 K (Fig. S10, left), in agreement with slow magnetic relaxation at low temperatures. The maxima of the χ″ peaks are not seen, which prevented an evaluation of the energy barrier for spin reversal. Application of a DC field did not change the outcome (Fig. S10, right), suggesting that the quantum tunnelling in zero-field is negligible.

Figure S7. Temperature dependence of the in-phase and out-of-phase components of the ac magnetic susceptibility for *(top)* **1a** and *(bottom)* **2a** (H_{AC} =2.5 Oe, H_{DC} =0)

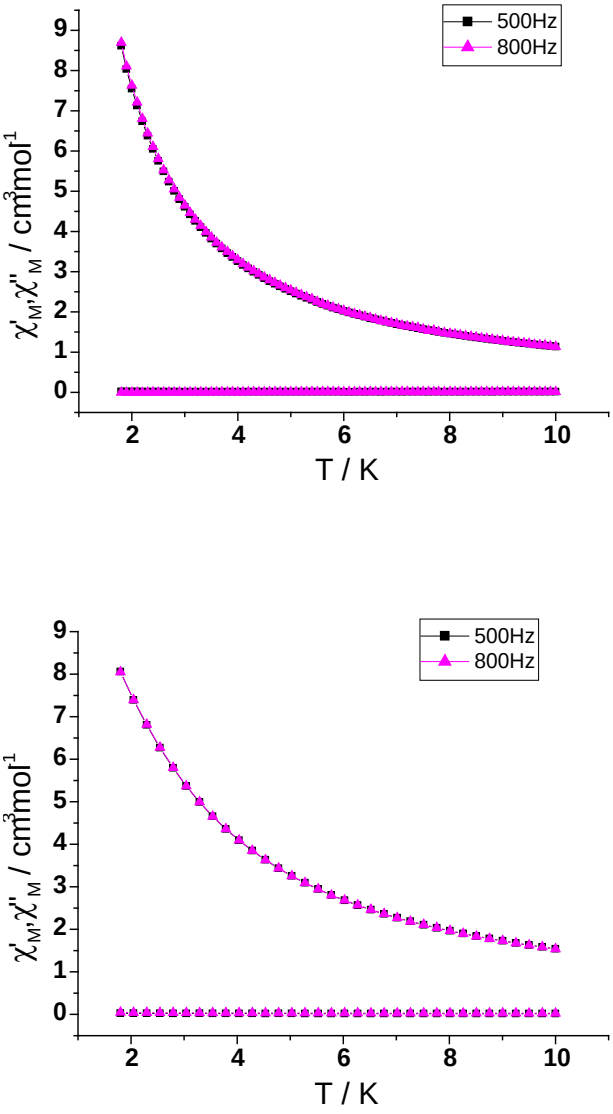


Figure S8. Powder X-ray diffractograms for the batches of **1b** (op) and **2b** (bottom) used for the magnetic studies. The diffractograms calculated from the corresponding single crystal X-ray structure data (cif) are shown for comparison.