Electronic Supporting Information

A Thioether-decorated {$Mn_{11}Tb_4$} Coordination Cluster with Slow Magnetic Relaxation

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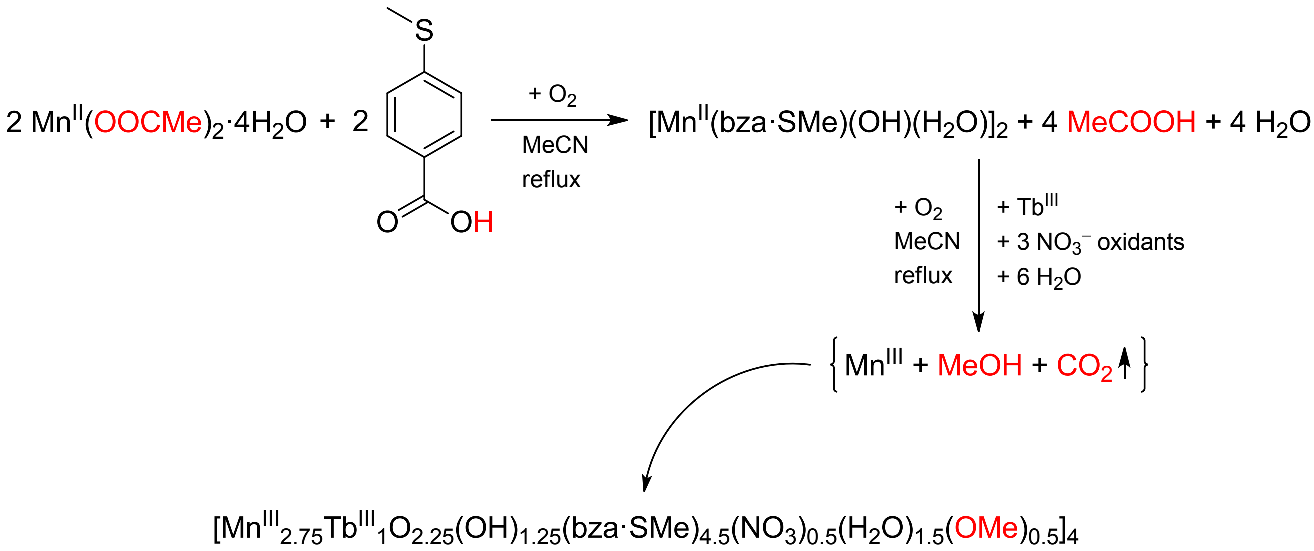
1. Proposed formation of methoxide anions in compound 1



Scheme S1.

2. IR spectrum of compound 1

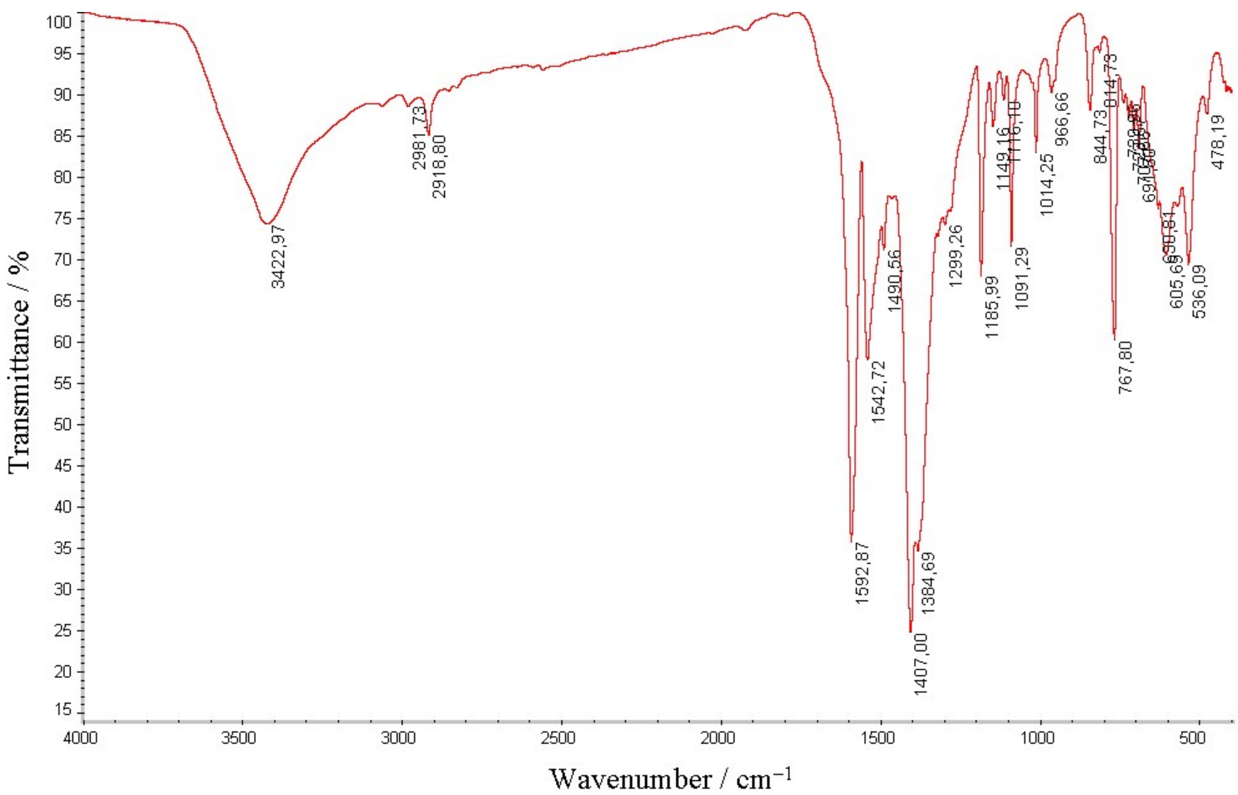


Figure S1. IR spectrum of $[Mn^{III}_{11}Tb^{III}_4O_9(OH)_5(bza\cdot SMe)_{18}(NO_3)_2(H_2O)_6(OMe)_2]$ (**1**) in the 4000–400 cm^{-1} region (KBr pellet).

3. Crystal data and structure refinement details for compound 1

Table S1. Crystallographical details.

Chemical formula	$C_{146}H_{144}Mn_{11}N_2O_{64}S_{18}Tb_4 \cdot 13(C_2H_3N)$
M_r (g mol^{-1})	5306.46
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	153
a, *b*, *c* (Å)	17.7970 (4), 18.4077 (6), 18.4319 (5)
α, β, γ (°)	61.520 (3), 66.702 (3), 78.020 (2)
V (Å^3)	4873.4 (3)
Z	1
Radiation type	Mo *K*α
μ (mm^{-1})	2.40
Crystal size (mm)	0.29 × 0.12 × 0.03
Diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer
Absorption correction	Multi-scan
T_{min}, T_{max}	0.687, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	64195, 22423, 11171
R_{int}	0.088
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.673
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.084, 0.296, 0.91
No. of reflections	22423
No. of parameters	1093
No. of restraints	1233
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.1678P)^2 + 31.6174P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	3.18, −2.03

Refinement

The positions of all metal atoms were found by the direct methods. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. A half of the centrosymmetric dimer was found in the asymmetric unit of the triclinic cell. All non-hydrogen atoms were refined in full-matrix anisotropic approximation. The majority of hydrogen atoms were placed in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. H atoms of six water ligands were placed and fixed at calculated positions. To be charge neutral neutral the coordination cluster should have five out of eight μ_3-oxygens protonated. It was not possible to assign the positions of those H atoms objectively. Therefore, they were not included in the calculation, but were included in the final formula. Oxo-carboxylate ligands are highly disordered; therefore SIMU, DELU, *DFIX* restraints were applied to obtain reasonable geometrical parameters and thermal displacement coefficients. As typical for this family of coordination clusters, the crystal structures have huge voids accessible for solvents but not all of them were objectively located on a difference Fourier map and refined. The SQUEEZE[1] was applied to treat electron density of disordered and diffused solvents and observed electron density was assigned to thirteen MeCN solvent molecules per cell. They were included in the final moiety and brutto formula. Crystal was twinned and diffracted very poorly, however the results are sufficient to obtain reasonable geometry of the coordination cluster.

Table S2. Fractional atomic coordinates (Å) and isotropic or equivalent isotropic displacement parameters (Å^2).

[1] A.L. Spek, *J. Appl. Cryst.*, 36 (2003), 7–13.

	x	y	z	U_{eq}
Tb1	1.06053 (3)	0.34539 (3)	0.42420 (4)	0.04337 (17)
Tb2	0.67991 (3)	0.44238 (4)	0.52828 (4)	0.04757 (18)
Mn1	1.0000	0.5000	0.5000	0.0382 (5)
Mn2	0.77822 (10)	0.52042 (11)	0.60035 (11)	0.0419 (4)
Mn3	0.87474 (10)	0.51325 (10)	0.39444 (10)	0.0396 (4)
Mn4	1.01424 (10)	0.33747 (10)	0.64104 (11)	0.0415 (4)
Mn5	0.86409 (10)	0.35705 (11)	0.56730 (11)	0.0431 (4)
Mn6	0.83669 (11)	0.32494 (11)	0.44281 (12)	0.0480 (4)
C1	1.2649 (10)	−0.0589 (8)	0.9937 (11)	0.092 (6)
S1	1.3214 (3)	0.0300 (3)	0.9410 (3)	0.0832 (12)
C2	1.2632 (7)	0.1068 (6)	0.8809 (8)	0.064 (2)
C3	1.1920 (7)	0.0926 (7)	0.8782 (9)	0.066 (2)
C4	1.1510 (7)	0.1565 (6)	0.8262 (8)	0.058 (2)
C5	1.1817 (7)	0.2349 (6)	0.7794 (7)	0.0507 (19)
C6	1.2547 (7)	0.2492 (7)	0.7807 (8)	0.056 (2)
C7	1.2938 (8)	0.1852 (7)	0.8327 (8)	0.063 (2)
C8	1.1439 (7)	0.3016 (7)	0.7162 (7)	0.048 (2)
C9	0.6042 (16)	0.250 (2)	1.1718 (16)	0.36 (4)
S2	0.5656 (4)	0.2516 (3)	1.1017 (3)	0.1114 (19)
C10	0.6429 (6)	0.2774 (8)	0.9986 (6)	0.060 (2)
C11	0.7217 (6)	0.2868 (8)	0.9859 (7)	0.062 (2)
C12	0.7822 (7)	0.3100 (8)	0.9030 (6)	0.058 (2)
C13	0.7619 (6)	0.3247 (8)	0.8322 (6)	0.0512 (19)
C14	0.6821 (6)	0.3145 (8)	0.8453 (7)	0.054 (2)
C15	0.6228 (7)	0.2921 (8)	0.9278 (6)	0.057 (2)
C16	0.8260 (7)	0.3515 (8)	0.7435 (7)	0.053 (2)
C17	0.5926 (9)	1.0231 (12)	0.2626 (15)	0.126 (8)
S3	0.6901 (3)	1.0382 (2)	0.2499 (3)	0.0879 (13)
C18	0.7220 (7)	0.9375 (6)	0.3135 (8)	0.061 (2)
C19	0.6717 (7)	0.8712 (6)	0.3604 (8)	0.058 (2)
C20	0.7000 (7)	0.7945 (7)	0.4118 (8)	0.055 (2)
C21	0.7769 (6)	0.7854 (6)	0.4158 (8)	0.0522 (19)
C22	0.8275 (7)	0.8531 (6)	0.3659 (8)	0.057 (2)
C23	0.8005 (7)	0.9293 (7)	0.3157 (8)	0.062 (2)
C24	0.8056 (8)	0.7026 (6)	0.4725 (8)	0.049 (2)
C25	0.3773 (10)	0.2369 (11)	0.3522 (13)	0.102 (6)
S4	0.4576 (3)	0.1665 (4)	0.3703 (5)	0.131 (3)
C26	0.5181 (7)	0.2144 (8)	0.3904 (10)	0.069 (2)
C27	0.5954 (7)	0.1802 (9)	0.3902 (10)	0.072 (2)
C28	0.6468 (8)	0.2146 (8)	0.4056 (10)	0.070 (2)
C29	0.6210 (7)	0.2814 (8)	0.4228 (9)	0.0602 (19)
C30	0.5436 (7)	0.3150 (8)	0.4247 (9)	0.062 (2)
C31	0.4934 (7)	0.2840 (8)	0.4051 (9)	0.065 (2)
C32	0.6743 (8)	0.3152 (9)	0.4444 (9)	0.059 (2)
C33	0.4480 (14)	0.0492 (14)	1.1492 (12)	0.146 (10)
S5	0.3885 (3)	0.1153 (4)	1.0880 (3)	0.1103 (18)

C34	0.4573 (7)	0.1506 (8)	0.9780 (7)	0.074 (3)
C35	0.5289 (7)	0.1097 (9)	0.9507 (8)	0.077 (3)
C36	0.5821 (7)	0.1445 (8)	0.8633 (7)	0.071 (3)
C37	0.5624 (7)	0.2199 (7)	0.8047 (7)	0.065 (2)
C38	0.4902 (7)	0.2608 (8)	0.8325 (7)	0.067 (3)
C39	0.4380 (8)	0.2264 (8)	0.9184 (7)	0.069 (3)
C40	0.6203 (7)	0.2609 (9)	0.7132 (7)	0.063 (3)
C41	0.5479 (14)	0.4537 (9)	1.1568 (10)	0.127 (8)
S6	0.5583 (3)	0.5582 (3)	1.0898 (3)	0.1007 (15)
C42	0.6136 (9)	0.5628 (8)	0.9844 (7)	0.070 (2)
C43	0.6151 (8)	0.4994 (8)	0.9647 (7)	0.067 (2)
C44	0.6570 (7)	0.5072 (7)	0.8806 (7)	0.060 (2)
C45	0.7012 (7)	0.5757 (7)	0.8161 (7)	0.056 (2)
C46	0.6981 (8)	0.6418 (8)	0.8348 (8)	0.065 (2)
C47	0.6530 (8)	0.6350 (8)	0.9181 (7)	0.071 (2)
C48	0.7515 (6)	0.5822 (7)	0.7252 (7)	0.045 (2)
C49	1.2518 (9)	0.397 (2)	−0.1032 (17)	0.215 (12)
S7	1.1503 (4)	0.4226 (5)	−0.0857 (3)	0.1412 (19)
C50	1.1048 (8)	0.3891 (11)	0.0286 (7)	0.089 (3)
C51	1.1468 (8)	0.3451 (11)	0.0861 (8)	0.087 (3)
C52	1.1051 (7)	0.3186 (11)	0.1762 (8)	0.084 (3)
C53	1.0230 (7)	0.3376 (10)	0.2067 (8)	0.076 (2)
C54	0.9818 (8)	0.3819 (10)	0.1481 (8)	0.083 (3)
C55	1.0223 (8)	0.4058 (11)	0.0598 (8)	0.090 (3)
C56	0.9818 (8)	0.3186 (10)	0.3009 (8)	0.069 (3)
C57	1.1572 (15)	0.7642 (14)	−0.1884 (16)	0.215 (12)
S8	1.2047 (4)	0.6735 (5)	−0.1434 (3)	0.1412 (19)
C58	1.1458 (8)	0.6307 (9)	−0.0300 (7)	0.083 (3)
C59	1.1741 (8)	0.5578 (9)	0.0237 (7)	0.081 (3)
C60	1.1317 (7)	0.5219 (9)	0.1125 (7)	0.072 (3)
C61	1.0594 (7)	0.5562 (8)	0.1492 (6)	0.062 (2)
C62	1.0309 (8)	0.6308 (8)	0.0947 (7)	0.071 (3)
C63	1.0751 (8)	0.6678 (9)	0.0052 (7)	0.080 (3)
C64	1.0153 (7)	0.5158 (8)	0.2454 (6)	0.054 (2)
C65	0.9141 (12)	−0.2028 (12)	0.9751 (16)	0.153 (11)
S9	0.8381 (8)	−0.1623 (4)	0.9380 (5)	0.187 (4)
C66	0.8698 (10)	−0.0588 (7)	0.8687 (10)	0.091 (3)
C67	0.9410 (10)	−0.0282 (8)	0.8547 (10)	0.092 (3)
C68	0.9589 (9)	0.0549 (7)	0.7970 (10)	0.083 (3)
C69	0.9062 (8)	0.1033 (7)	0.7549 (9)	0.071 (2)
C70	0.8342 (9)	0.0722 (7)	0.7705 (9)	0.076 (3)
C71	0.8159 (10)	−0.0096 (7)	0.8269 (10)	0.087 (3)
C72	0.9204 (9)	0.1932 (6)	0.6955 (8)	0.061 (3)
C73	0.6026 (13)	0.5016 (14)	0.6856 (15)	0.117 (7)
N1	1.0734 (8)	0.1653 (8)	0.4985 (8)	0.068 (3)
O1	0.9405 (4)	0.5381 (5)	0.2733 (5)	0.0455 (18)
O2	0.8027 (5)	0.3718 (5)	0.6778 (5)	0.0491 (19)

O3	0.8179 (5)	0.6337 (5)	0.3409 (5)	0.0478 (19)
O4	0.8984 (4)	0.3539 (5)	0.7358 (5)	0.0498 (19)
O5	0.9166 (4)	0.3677 (5)	0.4533 (5)	0.0426 (17)
O6	0.7717 (5)	0.3273 (5)	0.5550 (5)	0.050 (2)
O7	0.9696 (4)	0.3852 (4)	0.5484 (5)	0.0377 (16)
O8	1.0440 (4)	0.4471 (4)	0.5923 (5)	0.0397 (17)
O9	0.7542 (5)	0.6478 (5)	0.5254 (5)	0.0454 (18)
O10	0.7465 (5)	0.2904 (5)	0.4325 (6)	0.052 (2)
O11	0.7383 (5)	0.5267 (5)	0.7107 (5)	0.0501 (19)
O12	1.0713 (5)	0.2890 (5)	0.7267 (5)	0.0467 (18)
O13	0.8664 (6)	0.1918 (6)	0.5087 (6)	0.067 (2)
O14	0.8071 (5)	0.4830 (5)	0.5132 (5)	0.0460 (18)
O15	0.7929 (5)	0.4610 (5)	0.3905 (5)	0.0445 (18)
O16	0.9801 (5)	0.2244 (5)	0.6926 (5)	0.050 (2)
O17	0.9047 (5)	0.3337 (5)	0.3277 (6)	0.056 (2)
O18	1.0259 (5)	0.2920 (5)	0.3489 (6)	0.057 (2)
O19	0.6432 (5)	0.3671 (6)	0.4760 (6)	0.062 (2)
O20	0.8906 (4)	0.5289 (5)	0.5912 (5)	0.0421 (17)
O21	0.6054 (5)	0.3351 (6)	0.6667 (6)	0.061 (2)
O22	1.1183 (5)	0.3063 (5)	0.5362 (5)	0.0487 (19)
O23	1.0521 (5)	0.4627 (5)	0.2940 (5)	0.0490 (19)
O24	1.1966 (5)	0.3607 (5)	0.3258 (5)	0.0486 (19)
O25	0.6723 (5)	0.4920 (5)	0.6233 (5)	0.0499 (19)
O26	0.8724 (5)	0.2324 (5)	0.6549 (5)	0.055 (2)
O27	1.0098 (5)	0.2033 (5)	0.5290 (6)	0.059 (2)
O28	1.1355 (6)	0.2092 (5)	0.4417 (6)	0.062 (2)
O29	0.5340 (6)	0.4726 (6)	0.5629 (6)	0.071 (3)
O30	0.6626 (6)	0.5830 (6)	0.4338 (7)	0.081 (3)
O31	0.6837 (6)	0.2182 (6)	0.6896 (6)	0.070 (3)
O32	1.0746 (8)	0.0898 (6)	0.5250 (9)	0.099 (4)

Table S3. Atomic displacement parameters (Å^2).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tb1	0.0435 (3)	0.0462 (3)	0.0431 (3)	−0.0029 (2)	−0.0204 (2)	−0.0166 (3)
Tb2	0.0421 (3)	0.0545 (4)	0.0489 (3)	−0.0058 (3)	−0.0206 (3)	−0.0191 (3)
Mn1	0.0370 (12)	0.0416 (13)	0.0358 (12)	−0.0038 (10)	−0.0203 (10)	−0.0097 (10)
Mn2	0.0388 (9)	0.0495 (10)	0.0368 (9)	−0.0044 (7)	−0.0162 (7)	−0.0146 (8)
Mn3	0.0396 (9)	0.0450 (9)	0.0350 (8)	−0.0053 (7)	−0.0184 (7)	−0.0122 (7)
Mn4	0.0433 (9)	0.0411 (9)	0.0389 (9)	−0.0052 (7)	−0.0217 (7)	−0.0089 (7)
Mn5	0.0423 (9)	0.0484 (10)	0.0390 (9)	−0.0077 (8)	−0.0200 (7)	−0.0123 (8)
Mn6	0.0478 (10)	0.0529 (11)	0.0500 (10)	−0.0073 (8)	−0.0235 (8)	−0.0201 (9)
C1	0.112 (14)	0.067 (10)	0.105 (13)	0.005 (9)	−0.078 (12)	−0.014 (9)
S1	0.091 (3)	0.074 (3)	0.091 (3)	0.013 (2)	−0.060 (3)	−0.024 (2)
C2	0.066 (4)	0.062 (4)	0.061 (4)	−0.004 (4)	−0.030 (4)	−0.016 (4)
C3	0.068 (4)	0.060 (4)	0.062 (4)	−0.005 (4)	−0.032 (4)	−0.013 (4)
C4	0.065 (4)	0.056 (4)	0.056 (4)	−0.006 (3)	−0.031 (4)	−0.017 (3)

C5	0.058 (4)	0.053 (4)	0.047 (4)	−0.004 (3)	−0.029 (3)	−0.018 (3)
C6	0.061 (4)	0.057 (4)	0.052 (4)	−0.008 (3)	−0.027 (3)	−0.016 (3)
C7	0.063 (4)	0.064 (4)	0.057 (4)	−0.007 (4)	−0.029 (4)	−0.013 (4)
C8	0.056 (5)	0.049 (5)	0.045 (4)	−0.001 (4)	−0.025 (4)	−0.019 (4)
C9	0.08 (2)	0.27 (5)	0.36 (7)	0.01 (2)	−0.01 (3)	0.08 (4)
S2	0.121 (4)	0.083 (3)	0.067 (3)	−0.022 (3)	0.020 (3)	−0.018 (2)
C10	0.056 (4)	0.062 (4)	0.049 (4)	−0.007 (4)	−0.017 (3)	−0.015 (4)
C11	0.060 (4)	0.070 (4)	0.045 (4)	−0.011 (4)	−0.019 (3)	−0.013 (4)
C12	0.056 (4)	0.070 (4)	0.043 (3)	−0.014 (4)	−0.021 (3)	−0.012 (4)
C13	0.051 (4)	0.058 (4)	0.044 (3)	−0.009 (3)	−0.021 (3)	−0.016 (3)
C14	0.050 (4)	0.056 (4)	0.051 (4)	−0.007 (4)	−0.021 (3)	−0.016 (4)
C15	0.052 (4)	0.058 (4)	0.055 (4)	−0.009 (4)	−0.019 (3)	−0.016 (4)
C16	0.052 (5)	0.054 (5)	0.046 (4)	−0.006 (4)	−0.019 (4)	−0.014 (4)
C17	0.138 (19)	0.113 (16)	0.18 (2)	0.055 (14)	−0.112 (18)	−0.078 (16)
S3	0.112 (4)	0.059 (2)	0.099 (3)	0.028 (2)	−0.064 (3)	−0.029 (2)
C18	0.063 (4)	0.052 (4)	0.063 (4)	0.012 (3)	−0.032 (4)	−0.020 (4)
C19	0.060 (4)	0.057 (4)	0.061 (4)	0.009 (3)	−0.035 (4)	−0.021 (4)
C20	0.057 (4)	0.055 (4)	0.058 (4)	0.007 (3)	−0.032 (4)	−0.022 (3)
C21	0.056 (4)	0.051 (4)	0.058 (4)	0.005 (3)	−0.032 (3)	−0.023 (3)
C22	0.060 (4)	0.050 (4)	0.063 (4)	0.005 (3)	−0.031 (4)	−0.019 (4)
C23	0.065 (4)	0.051 (4)	0.066 (4)	0.006 (4)	−0.032 (4)	−0.018 (4)
C24	0.058 (5)	0.050 (4)	0.055 (5)	0.002 (4)	−0.032 (4)	−0.025 (4)
C25	0.088 (13)	0.140 (17)	0.112 (15)	0.005 (12)	−0.048 (11)	−0.075 (14)
S4	0.069 (3)	0.184 (6)	0.250 (8)	0.030 (3)	−0.076 (4)	−0.174 (6)
C26	0.058 (4)	0.087 (5)	0.086 (5)	−0.005 (4)	−0.029 (4)	−0.051 (4)
C27	0.059 (4)	0.087 (5)	0.091 (5)	−0.005 (4)	−0.027 (4)	−0.051 (4)
C28	0.058 (4)	0.085 (5)	0.083 (5)	−0.007 (4)	−0.026 (4)	−0.046 (4)
C29	0.056 (4)	0.081 (5)	0.066 (4)	−0.005 (4)	−0.032 (3)	−0.038 (4)
C30	0.059 (4)	0.082 (5)	0.067 (4)	−0.003 (4)	−0.032 (4)	−0.041 (4)
C31	0.057 (4)	0.083 (5)	0.076 (5)	−0.004 (4)	−0.030 (4)	−0.045 (4)
C32	0.053 (5)	0.079 (6)	0.061 (5)	−0.003 (4)	−0.031 (4)	−0.033 (5)
C33	0.19 (3)	0.15 (2)	0.080 (14)	0.012 (18)	−0.069 (16)	−0.019 (14)
S5	0.082 (3)	0.161 (5)	0.059 (2)	−0.037 (3)	−0.018 (2)	−0.017 (3)
C34	0.060 (4)	0.082 (5)	0.068 (5)	−0.011 (4)	−0.025 (4)	−0.017 (4)
C35	0.062 (5)	0.081 (5)	0.068 (4)	−0.008 (4)	−0.025 (4)	−0.014 (4)
C36	0.057 (4)	0.075 (5)	0.067 (4)	−0.007 (4)	−0.026 (4)	−0.016 (4)
C37	0.055 (4)	0.073 (5)	0.063 (4)	−0.008 (3)	−0.027 (3)	−0.019 (4)
C38	0.057 (4)	0.077 (5)	0.063 (4)	−0.008 (4)	−0.026 (4)	−0.020 (4)
C39	0.059 (4)	0.079 (5)	0.064 (4)	−0.010 (4)	−0.025 (4)	−0.021 (4)
C40	0.053 (5)	0.071 (6)	0.063 (5)	−0.009 (5)	−0.027 (4)	−0.020 (4)
C41	0.139 (19)	0.17 (2)	0.070 (12)	0.025 (16)	−0.029 (12)	−0.073 (15)
S6	0.109 (4)	0.119 (4)	0.069 (3)	−0.016 (3)	0.001 (3)	−0.057 (3)
C42	0.070 (5)	0.077 (5)	0.060 (4)	0.000 (4)	−0.013 (4)	−0.035 (4)
C43	0.065 (5)	0.074 (5)	0.058 (4)	0.001 (4)	−0.016 (4)	−0.030 (4)
C44	0.059 (4)	0.069 (4)	0.056 (4)	0.000 (4)	−0.019 (4)	−0.031 (4)
C45	0.051 (4)	0.063 (4)	0.057 (4)	0.003 (3)	−0.017 (3)	−0.031 (3)
C46	0.062 (4)	0.072 (4)	0.062 (4)	−0.004 (4)	−0.012 (4)	−0.036 (4)

C47	0.072 (5)	0.078 (5)	0.063 (4)	−0.005 (4)	−0.010 (4)	−0.040 (4)
C48	0.034 (4)	0.046 (5)	0.054 (4)	0.008 (4)	−0.017 (4)	−0.025 (4)
C49	0.114 (14)	0.37 (4)	0.128 (16)	−0.068 (19)	−0.023 (13)	−0.08 (2)
S7	0.108 (3)	0.236 (6)	0.066 (2)	−0.061 (3)	−0.014 (2)	−0.046 (3)
C50	0.076 (5)	0.117 (6)	0.087 (5)	0.004 (5)	−0.034 (4)	−0.051 (5)
C51	0.073 (5)	0.117 (6)	0.086 (5)	0.002 (5)	−0.032 (4)	−0.054 (5)
C52	0.071 (5)	0.114 (6)	0.085 (5)	0.004 (5)	−0.033 (4)	−0.056 (5)
C53	0.068 (4)	0.106 (6)	0.081 (5)	0.005 (4)	−0.034 (4)	−0.058 (5)
C54	0.072 (5)	0.112 (6)	0.082 (5)	0.003 (5)	−0.034 (4)	−0.052 (5)
C55	0.076 (5)	0.116 (6)	0.084 (5)	0.007 (5)	−0.034 (4)	−0.048 (5)
C56	0.066 (6)	0.097 (6)	0.082 (5)	0.008 (5)	−0.034 (5)	−0.064 (5)
C57	0.114 (14)	0.37 (4)	0.128 (16)	−0.068 (19)	−0.023 (13)	−0.08 (2)
S8	0.108 (3)	0.236 (6)	0.066 (2)	−0.061 (3)	−0.014 (2)	−0.046 (3)
C58	0.071 (5)	0.113 (6)	0.053 (4)	−0.029 (4)	−0.014 (4)	−0.022 (4)
C59	0.066 (5)	0.111 (6)	0.055 (4)	−0.024 (4)	−0.012 (4)	−0.027 (4)
C60	0.061 (4)	0.101 (5)	0.053 (4)	−0.020 (4)	−0.016 (4)	−0.029 (4)
C61	0.058 (4)	0.089 (5)	0.046 (4)	−0.020 (4)	−0.021 (3)	−0.027 (3)
C62	0.067 (5)	0.097 (5)	0.047 (4)	−0.021 (4)	−0.021 (4)	−0.021 (4)
C63	0.072 (5)	0.107 (6)	0.049 (4)	−0.026 (4)	−0.019 (4)	−0.018 (4)
C64	0.052 (5)	0.077 (6)	0.043 (4)	−0.016 (5)	−0.021 (4)	−0.024 (4)
C65	0.13 (2)	0.14 (2)	0.19 (3)	−0.088 (17)	0.013 (19)	−0.09 (2)
S9	0.333 (14)	0.080 (4)	0.101 (5)	−0.065 (6)	−0.033 (7)	−0.014 (3)
C66	0.123 (6)	0.064 (5)	0.073 (5)	−0.024 (4)	−0.031 (5)	−0.014 (4)
C67	0.117 (6)	0.064 (5)	0.074 (5)	−0.017 (4)	−0.037 (5)	−0.005 (4)
C68	0.107 (6)	0.059 (4)	0.071 (5)	−0.015 (4)	−0.042 (4)	−0.005 (4)
C69	0.100 (5)	0.054 (4)	0.063 (4)	−0.016 (4)	−0.041 (4)	−0.015 (4)
C70	0.107 (6)	0.061 (4)	0.066 (5)	−0.024 (4)	−0.036 (4)	−0.019 (4)
C71	0.117 (6)	0.067 (5)	0.072 (5)	−0.028 (4)	−0.032 (5)	−0.017 (4)
C72	0.092 (6)	0.047 (4)	0.056 (5)	−0.008 (4)	−0.043 (5)	−0.017 (4)
C73	0.122 (18)	0.129 (18)	0.134 (19)	0.020 (14)	−0.076 (16)	−0.067 (15)
N1	0.066 (8)	0.069 (8)	0.073 (8)	−0.009 (7)	−0.034 (7)	−0.025 (7)
O1	0.039 (4)	0.058 (5)	0.038 (4)	−0.006 (4)	−0.015 (3)	−0.017 (4)
O2	0.049 (5)	0.055 (5)	0.035 (4)	−0.016 (4)	−0.016 (3)	−0.006 (4)
O3	0.055 (5)	0.045 (4)	0.042 (4)	−0.004 (4)	−0.024 (4)	−0.010 (4)
O4	0.037 (4)	0.069 (5)	0.041 (4)	−0.004 (4)	−0.014 (3)	−0.020 (4)
O5	0.042 (4)	0.047 (4)	0.045 (4)	−0.004 (3)	−0.021 (3)	−0.019 (4)
O6	0.048 (5)	0.064 (5)	0.042 (4)	−0.012 (4)	−0.020 (4)	−0.018 (4)
O7	0.039 (4)	0.035 (4)	0.044 (4)	−0.007 (3)	−0.021 (3)	−0.012 (3)
O8	0.040 (4)	0.037 (4)	0.040 (4)	−0.005 (3)	−0.022 (3)	−0.009 (3)
O9	0.050 (5)	0.050 (5)	0.037 (4)	0.003 (4)	−0.017 (4)	−0.019 (4)
O10	0.055 (5)	0.041 (4)	0.076 (6)	−0.008 (4)	−0.036 (4)	−0.023 (4)
O11	0.050 (5)	0.055 (5)	0.047 (5)	−0.011 (4)	−0.015 (4)	−0.021 (4)
O12	0.043 (4)	0.051 (5)	0.042 (4)	−0.009 (4)	−0.021 (4)	−0.010 (4)
O13	0.074 (6)	0.064 (6)	0.073 (6)	−0.009 (5)	−0.034 (5)	−0.028 (5)
O14	0.045 (4)	0.051 (5)	0.044 (4)	−0.001 (4)	−0.018 (4)	−0.021 (4)
O15	0.044 (4)	0.048 (4)	0.051 (5)	−0.009 (3)	−0.023 (4)	−0.021 (4)
O16	0.059 (5)	0.044 (4)	0.052 (5)	−0.005 (4)	−0.032 (4)	−0.012 (4)

O17	0.057 (5)	0.064 (5)	0.061 (5)	0.000 (4)	−0.031 (4)	−0.031 (5)
O18	0.055 (5)	0.066 (6)	0.067 (6)	0.000 (4)	−0.028 (4)	−0.038 (5)
O19	0.049 (5)	0.078 (6)	0.061 (6)	−0.022 (4)	−0.017 (4)	−0.026 (5)
O20	0.035 (4)	0.051 (4)	0.039 (4)	−0.003 (3)	−0.016 (3)	−0.015 (4)
O21	0.057 (5)	0.065 (6)	0.054 (5)	−0.013 (4)	−0.020 (4)	−0.017 (5)
O22	0.048 (5)	0.047 (4)	0.060 (5)	−0.004 (4)	−0.037 (4)	−0.014 (4)
O23	0.045 (4)	0.064 (5)	0.046 (4)	−0.004 (4)	−0.022 (4)	−0.024 (4)
O24	0.052 (5)	0.051 (5)	0.046 (4)	0.000 (4)	−0.021 (4)	−0.021 (4)
O25	0.035 (4)	0.073 (6)	0.046 (4)	−0.005 (4)	−0.009 (4)	−0.031 (4)
O26	0.057 (5)	0.055 (5)	0.054 (5)	−0.010 (4)	−0.031 (4)	−0.013 (4)
O27	0.050 (5)	0.060 (5)	0.066 (6)	0.000 (4)	−0.020 (4)	−0.029 (5)
O28	0.062 (6)	0.052 (5)	0.071 (6)	0.006 (5)	−0.031 (5)	−0.024 (5)
O29	0.061 (6)	0.072 (6)	0.072 (6)	0.000 (5)	−0.031 (5)	−0.019 (5)
O30	0.059 (6)	0.075 (7)	0.089 (7)	0.000 (5)	−0.035 (6)	−0.014 (6)
O31	0.062 (6)	0.065 (6)	0.063 (6)	−0.005 (5)	−0.015 (5)	−0.017 (5)
O32	0.115 (10)	0.044 (6)	0.149 (12)	0.002 (6)	−0.073 (9)	−0.030 (7)

Table S4. Geometric parameters for compound **1** (Å, º).

Tb1—O18	2.346 (8)	O20—Mn1—Tb1	135.9 (2)
Tb1—O24	2.357 (8)	Mn4^{i}—Mn1—Tb1	111.34 (4)
Tb1—O23	2.377 (8)	O14—Mn2—O25	82.5 (3)
Tb1—O5	2.388 (7)	O14—Mn2—O11	163.6 (4)
Tb1—O22	2.405 (7)	O14—Mn2—O9	99.4 (3)
Tb1—O27	2.484 (9)	O25—Mn2—O9	91.4 (3)
Tb1—O20^{i}	2.492 (8)	O11—Mn2—O9	94.9 (3)
Tb1—O28	2.519 (8)	O20—Mn2—O9	98.9 (3)
Tb1—O7	2.565 (7)	O14—Mn2—O2	76.2 (3)
Tb1—N1	2.918 (13)	O25—Mn2—O2	85.9 (3)
Tb1—Mn5	3.4871 (18)	O8^{i}—Mn3—O1	91.5 (3)
Tb1—Mn1	3.5414 (6)	O14—Mn3—O1	176.0 (3)
Tb2—O25	2.282 (8)	O8^{i}—Mn3—O15	173.9 (3)
Tb2—O19	2.329 (9)	O14—Mn3—O15	84.9 (3)
Tb2—O6	2.366 (8)	O1—Mn3—O15	91.4 (3)
Tb2—O30	2.371 (10)	O22—Mn4—Mn1	87.74 (19)
Tb2—O21	2.403 (9)	O5—Mn5—O7	81.5 (3)
Tb2—O14	2.402 (8)	O5—Mn5—O6	82.6 (3)
Tb2—O29	2.427 (9)	O7—Mn5—O6	164.0 (3)
Tb2—O15	2.455 (8)	O5—Mn5—O2	167.7 (3)
Tb2—Mn2	3.4045 (18)	O7—Mn5—O2	97.6 (3)
Tb2—Mn3	3.4427 (18)	O6—Mn5—O2	98.3 (3)
Tb2—Mn6	3.494 (2)	O5—Mn5—O26	108.2 (3)
Tb2—Mn5	3.5184 (17)	O7—Mn5—O26	95.7 (3)
Mn1—O8	1.901 (6)	O6—Mn5—O26	87.5 (3)
Mn1—O8^{i}	1.901 (6)	O2—Mn5—O26	84.1 (3)
Mn1—O7^{i}	1.961 (7)	O5—Mn5—O14	89.1 (3)

Mn1—O7	1.961 (7)	O7—Mn5—O14	100.7 (3)
Mn1—O20^{i}	2.176 (7)	O6—Mn5—O14	80.9 (3)
Mn1—O20	2.176 (7)	O2—Mn5—O14	79.0 (3)
Mn1—Mn4^{i}	2.9261 (16)	O26—Mn5—O14	157.8 (3)
Mn1—Mn4	2.9261 (16)	O5—Mn5—Mn6	40.3 (2)
Mn1—Tb1^{i}	3.5413 (6)	O7—Mn5—Mn6	121.1 (2)
Mn2—O14	1.890 (8)	O6—Mn5—Mn6	42.9 (2)
Mn2—O25	1.891 (8)	O2—Mn5—Mn6	141.0 (2)
Mn2—O11	1.924 (8)	O26—Mn5—Mn6	95.7 (2)
Mn2—O20	1.972 (7)	O14—Mn5—Mn6	88.6 (2)
Mn2—O9	2.133 (8)	O5—Mn5—Mn3	52.5 (2)
Mn2—O2	2.446 (8)	O7—Mn5—Mn3	85.7 (2)
Mn3—O8^{i}	1.890 (7)	O6—Mn5—Mn3	86.1 (2)
Mn3—O14	1.893 (8)	O2—Mn5—Mn3	115.3 (2)
Mn3—O1	1.935 (7)	O26—Mn5—Mn3	160.3 (3)
Mn3—O15	1.945 (7)	O14—Mn5—Mn3	37.7 (2)
Mn3—O3	2.164 (7)	Mn6—Mn5—Mn3	67.23 (6)
Mn3—O5	2.440 (7)	O5—Mn5—Tb1	40.1 (2)
Mn3—Mn5	3.077 (2)	O7—Mn5—Tb1	46.1 (2)
Mn4—O8	1.870 (7)	O6—Mn5—Tb1	118.3 (2)
Mn4—O7	1.916 (7)	O2—Mn5—Tb1	142.8 (2)
Mn4—O16	1.946 (8)	O26—Mn5—Tb1	91.0 (2)
Mn4—O12	1.967 (7)	O14—Mn5—Tb1	111.2 (2)
Mn4—O4	2.189 (8)	Mn6—Mn5—Tb1	76.16 (5)
Mn4—O22	2.297 (9)	Mn3—Mn5—Tb1	75.79 (5)
Mn5—O5	1.860 (7)	O5—Mn5—Tb2	92.3 (2)
Mn5—O7	1.905 (7)	O7—Mn5—Tb2	143.0 (2)
Mn5—O6	1.961 (8)	O6—Mn5—Tb2	39.7 (2)
Mn5—O2	2.015 (8)	O2—Mn5—Tb2	81.0 (2)
Mn5—O26	2.099 (8)	O26—Mn5—Tb2	120.8 (2)
Mn5—O14	2.240 (8)	O14—Mn5—Tb2	42.5 (2)
Mn5—Mn6	2.855 (2)	Mn6—Mn5—Tb2	65.53 (5)
Mn6—O5	1.873 (7)	Mn3—Mn5—Tb2	62.51 (4)
Mn6—O17	1.927 (9)	Tb1—Mn5—Tb2	131.26 (5)
Mn6—O6	1.947 (8)	O5—Mn6—O17	93.1 (3)
Mn6—O10	1.949 (7)	O5—Mn6—O6	82.7 (3)
Mn6—O13	2.212 (9)	O17—Mn6—O6	174.1 (4)
Mn6—O15	2.300 (8)	O5—Mn6—O10	174.1 (3)
C1—S1	1.740 (12)	O17—Mn6—O10	89.5 (4)
S1—C2	1.763 (9)	O6—Mn6—O10	94.3 (4)
C2—C3	1.368 (12)	O5—Mn6—O13	98.7 (3)
C2—C7	1.375 (12)	O17—Mn6—O13	93.0 (4)
C3—C4	1.399 (12)	O6—Mn6—O13	91.7 (4)
C4—C5	1.376 (11)	O10—Mn6—O13	86.4 (3)
C5—C6	1.388 (11)	O5—Mn6—O15	82.6 (3)
C5—C8	1.493 (11)	O17—Mn6—O15	93.9 (3)
C6—C7	1.380 (11)	O6—Mn6—O15	81.5 (3)

C8—O3^{i}	1.251 (13)	O10—Mn6—O15	92.0 (3)
C8—O12	1.282 (13)	O13—Mn6—O15	172.9 (3)
C9—S2	1.668 (16)	O5—Mn6—Mn5	39.9 (2)
S2—C10	1.753 (10)	O17—Mn6—Mn5	133.0 (3)
C10—C11	1.362 (12)	O6—Mn6—Mn5	43.3 (2)
C10—C15	1.377 (12)	O10—Mn6—Mn5	137.5 (3)
C11—C12	1.394 (12)	O13—Mn6—Mn5	92.0 (2)
C12—C13	1.379 (11)	O15—Mn6—Mn5	84.56 (19)
C13—C14	1.380 (11)	O5—Mn6—Tb2	92.8 (2)
C13—C16	1.486 (11)	O17—Mn6—Tb2	136.6 (3)
C14—C15	1.382 (11)	O6—Mn6—Tb2	40.2 (2)
C16—O4	1.247 (13)	O10—Mn6—Tb2	81.7 (3)
C16—O2	1.296 (13)	O13—Mn6—Tb2	128.4 (3)
C17—S3	1.721 (14)	O15—Mn6—Tb2	44.5 (2)
S3—C18	1.774 (9)	Mn5—Mn6—Tb2	66.42 (5)
C18—C19	1.369 (12)	O12—C8—C5	116.3 (10)
C18—C23	1.389 (12)	C9—S2—C10	109.1 (10)
C19—C20	1.396 (11)	C11—C10—C15	119.1 (9)
C20—C21	1.371 (11)	C11—C10—S2	121.7 (8)
C21—C22	1.387 (12)	C15—C10—S2	119.1 (8)
C21—C24	1.503 (11)	C10—C11—C12	121.1 (10)
C22—C23	1.374 (11)	C13—C12—C11	119.6 (10)
C24—O9	1.243 (14)	C12—C13—C14	119.2 (9)
C24—O22^{i}	1.284 (13)	C12—C13—C16	119.4 (9)
C25—S4	1.741 (13)	C14—C13—C16	121.4 (9)
		C15—C14—C13	120.4 (10)
O18—Tb1—O24	90.0 (3)	C10—C15—C14	120.5 (10)
O18—Tb1—O23	75.3 (3)	O4—C16—O2	123.6 (9)
O24—Tb1—O23	76.6 (3)	O4—C16—C13	119.1 (10)
O18—Tb1—O5	72.9 (3)	O2—C16—C13	117.3 (9)
O24—Tb1—O5	151.2 (3)	C17—S3—C18	102.7 (7)
O23—Tb1—O5	76.7 (3)	C19—C18—C23	120.9 (9)
O18—Tb1—O22	142.3 (3)	C19—C18—S3	122.5 (8)
O24—Tb1—O22	86.2 (3)	C23—C18—S3	116.6 (8)
O23—Tb1—O22	139.1 (3)	C18—C19—C20	119.1 (10)
O5—Tb1—O22	121.5 (3)	C21—C20—C19	120.7 (10)
O18—Tb1—O27	71.9 (3)	C20—C21—C22	119.1 (9)
O24—Tb1—O27	118.3 (3)	C20—C21—C24	119.8 (9)
O23—Tb1—O27	143.5 (3)	C22—C21—C24	121.1 (9)
O5—Tb1—O27	78.8 (3)	C23—C22—C21	121.1 (10)
O22—Tb1—O27	77.2 (3)	C22—C23—C18	119.0 (10)
O18—Tb1—O20^{i}	143.5 (3)	O9—C24—O22^{i}	124.4 (9)
O24—Tb1—O20^{i}	74.7 (3)	O9—C24—C21	118.1 (10)
O23—Tb1—O20^{i}	69.0 (2)	O22^{i}—C24—C21	117.5 (10)
O5—Tb1—O20^{i}	105.4 (2)	C25—S4—C26	104.3 (7)
O22—Tb1—O20^{i}	70.7 (2)	C31—C26—C27	118.9 (9)
O27—Tb1—O20^{i}	144.5 (3)	C31—C26—S4	123.7 (8)

O18—Tb1—O28	70.8 (3)	C27—C26—S4	117.4 (8)
O24—Tb1—O28	67.0 (3)	C28—C27—C26	120.7 (11)
O23—Tb1—O28	129.3 (3)	C29—C28—C27	120.1 (11)
O5—Tb1—O28	125.0 (3)	C28—C29—C30	119.6 (9)
O22—Tb1—O28	73.3 (3)	C28—C29—C32	120.1 (10)
O27—Tb1—O28	51.3 (3)	C30—C29—C32	120.3 (10)
O20^{i}—Tb1—O28	128.3 (3)	C29—C30—C31	120.9 (10)
O18—Tb1—O7	130.3 (3)	C26—C31—C30	119.6 (10)
O24—Tb1—O7	139.0 (2)	O10—C32—O19	122.8 (10)
O23—Tb1—O7	104.2 (2)	O10—C32—C29	118.7 (11)
O5—Tb1—O7	59.4 (2)	O19—C32—C29	118.5 (11)
O22—Tb1—O7	66.3 (2)	C33—S5—C34	103.7 (8)
O27—Tb1—O7	85.7 (3)	C35—C34—C39	119.5 (10)
O20^{i}—Tb1—O7	68.0 (2)	C35—C34—S5	124.3 (9)
O28—Tb1—O7	126.4 (3)	C39—C34—S5	116.1 (9)
O18—Tb1—N1	66.9 (3)	C34—C35—C36	120.5 (11)
O24—Tb1—N1	92.7 (3)	C37—C36—C35	119.4 (11)
O23—Tb1—N1	140.7 (3)	C36—C37—C38	119.8 (10)
O5—Tb1—N1	101.2 (3)	C36—C37—C40	120.6 (10)
O22—Tb1—N1	75.9 (3)	C38—C37—C40	119.5 (10)
O27—Tb1—N1	25.8 (3)	C39—C38—C37	120.6 (11)
O20^{i}—Tb1—N1	144.8 (3)	C38—C39—C34	120.1 (11)
O28—Tb1—N1	25.8 (3)	O21—C40—O31	125.4 (11)
O7—Tb1—N1	108.1 (3)	O21—C40—C37	117.8 (12)
O18—Tb1—Mn5	98.0 (2)	O31—C40—C37	116.7 (11)
O24—Tb1—Mn5	169.6 (2)	C41—S6—C42	103.1 (7)
O23—Tb1—Mn5	98.90 (19)	C43—C42—C47	118.8 (10)
O5—Tb1—Mn5	30.13 (17)	C43—C42—S6	122.5 (9)
O22—Tb1—Mn5	91.4 (2)	C47—C42—S6	118.6 (9)
O27—Tb1—Mn5	70.8 (2)	C42—C43—C44	120.3 (11)
O20^{i}—Tb1—Mn5	94.97 (17)	C45—C44—C43	121.4 (11)
O28—Tb1—Mn5	121.9 (2)	C44—C45—C46	118.6 (9)
O7—Tb1—Mn5	32.37 (15)	C44—C45—C48	121.6 (9)
N1—Tb1—Mn5	96.6 (3)	C46—C45—C48	119.8 (9)
O18—Tb1—Mn1	141.6 (2)	C47—C46—C45	119.4 (11)
O24—Tb1—Mn1	112.05 (19)	C46—C47—C42	121.1 (11)
O23—Tb1—Mn1	79.68 (19)	O11—C48—O24^{i}	127.5 (9)
O5—Tb1—Mn1	73.31 (18)	O11—C48—C45	114.3 (10)
O22—Tb1—Mn1	72.87 (19)	O24^{i}—C48—C45	118.2 (10)
O27—Tb1—Mn1	118.2 (2)	C49—S7—C50	105.0 (10)
O20^{i}—Tb1—Mn1	37.42 (16)	C55—C50—C51	120.3 (11)
O28—Tb1—Mn1	146.1 (2)	C55—C50—S7	116.5 (9)
O7—Tb1—Mn1	32.78 (15)	C51—C50—S7	123.1 (9)
N1—Tb1—Mn1	138.1 (3)	C50—C51—C52	119.3 (11)
Mn5—Tb1—Mn1	57.60 (3)	C53—C52—C51	120.0 (12)
O25—Tb2—O19	158.0 (3)	C52—C53—C54	119.9 (11)
O25—Tb2—O6	104.8 (3)	C52—C53—C56	119.5 (10)

O19—Tb2—O6	78.4 (3)	C54—C53—C56	120.2 (11)
O25—Tb2—O30	84.6 (4)	C55—C54—C53	119.9 (12)
O19—Tb2—O30	105.1 (4)	C54—C55—C50	120.4 (12)
O6—Tb2—O30	145.9 (3)	O18—C56—O17	124.3 (10)
O25—Tb2—O21	78.9 (3)	O18—C56—C53	117.8 (11)
O19—Tb2—O21	81.1 (3)	O17—C56—C53	117.8 (11)
O6—Tb2—O21	74.3 (3)	C57—S8—C58	104.9 (10)
O30—Tb2—O21	139.6 (3)	C59—C58—C63	120.0 (10)
O25—Tb2—O14	64.2 (3)	C59—C58—S8	117.1 (9)
O19—Tb2—O14	135.0 (3)	C63—C58—S8	123.0 (9)
O6—Tb2—O14	69.9 (3)	C60—C59—C58	120.0 (12)
O30—Tb2—O14	85.9 (3)	C59—C60—C61	121.3 (11)
O21—Tb2—O14	118.1 (3)	C60—C61—C62	118.7 (10)
O25—Tb2—O29	86.1 (3)	C60—C61—C64	119.9 (10)
O19—Tb2—O29	78.5 (3)	C62—C61—C64	121.3 (10)
O6—Tb2—O29	139.7 (3)	C63—C62—C61	119.6 (11)
O30—Tb2—O29	72.5 (3)	C58—C63—C62	120.4 (11)
O21—Tb2—O29	69.9 (3)	O23—C64—O1	124.0 (9)
O14—Tb2—O29	144.9 (3)	O23—C64—C61	119.1 (10)
O25—Tb2—O15	126.4 (3)	O1—C64—C61	117.0 (10)
O19—Tb2—O15	75.4 (3)	C65—S9—C66	100.7 (10)
O6—Tb2—O15	70.5 (3)	C67—C66—C71	121.6 (10)
O30—Tb2—O15	77.5 (3)	C67—C66—S9	125.3 (10)
O21—Tb2—O15	140.8 (3)	C71—C66—S9	113.1 (10)
O14—Tb2—O15	64.5 (2)	C66—C67—C68	119.2 (12)
O29—Tb2—O15	132.9 (3)	C69—C68—C67	119.2 (12)
O25—Tb2—Mn2	31.67 (19)	C68—C69—C70	121.0 (10)
O19—Tb2—Mn2	165.0 (2)	C68—C69—C72	121.6 (10)
O6—Tb2—Mn2	87.30 (19)	C70—C69—C72	117.3 (10)
O30—Tb2—Mn2	84.3 (3)	C71—C70—C69	120.5 (12)
O21—Tb2—Mn2	99.3 (2)	C70—C71—C66	118.5 (12)
O14—Tb2—Mn2	32.54 (18)	O26—C72—O16	125.1 (10)
O29—Tb2—Mn2	115.8 (3)	O26—C72—C69	117.9 (11)
O15—Tb2—Mn2	95.91 (17)	O16—C72—C69	116.9 (10)
O25—Tb2—Mn3	93.1 (2)	O32—N1—O28	122.4 (13)
O19—Tb2—Mn3	108.4 (2)	O32—N1—O27	121.2 (13)
O6—Tb2—Mn3	72.27 (19)	O28—N1—O27	116.4 (12)
O30—Tb2—Mn3	74.6 (2)	O32—N1—Tb1	173.8 (10)
O21—Tb2—Mn3	142.3 (2)	O28—N1—Tb1	59.3 (6)
O14—Tb2—Mn3	31.91 (18)	O27—N1—Tb1	57.7 (6)
O29—Tb2—Mn3	147.0 (2)	C64—O1—Mn3	125.9 (7)
O15—Tb2—Mn3	33.49 (17)	C16—O2—Mn5	128.5 (7)
Mn2—Tb2—Mn3	62.44 (4)	C16—O2—Mn2	113.7 (7)
O25—Tb2—Mn6	128.8 (2)	Mn5—O2—Mn2	94.7 (3)
O19—Tb2—Mn6	64.1 (2)	C8^{i}—O3—Mn3	124.6 (7)
O6—Tb2—Mn6	32.03 (19)	C16—O4—Mn4	131.4 (7)
O30—Tb2—Mn6	118.5 (3)	Mn5—O5—Mn6	99.8 (4)

O21—Tb2—Mn6	100.3 (2)	Mn5—O5—Tb1	109.7 (3)
O14—Tb2—Mn6	72.23 (18)	Mn6—O5—Tb1	135.1 (4)
O29—Tb2—Mn6	142.4 (3)	Mn5—O5—Mn3	90.4 (3)
O15—Tb2—Mn6	41.03 (18)	Mn6—O5—Mn3	98.6 (3)
Mn2—Tb2—Mn6	101.36 (4)	Tb1—O5—Mn3	113.8 (3)
Mn3—Tb2—Mn6	56.61 (4)	Mn6—O6—Mn5	93.9 (3)
O25—Tb2—Mn5	80.8 (2)	Mn6—O6—Tb2	107.8 (3)
O19—Tb2—Mn5	108.3 (2)	Mn5—O6—Tb2	108.4 (4)
O6—Tb2—Mn5	31.92 (19)	Mn5—O7—Mn4	121.6 (4)
O30—Tb2—Mn5	123.6 (2)	Mn5—O7—Mn1	122.3 (3)
O21—Tb2—Mn5	89.9 (2)	Mn4—O7—Mn1	98.0 (3)
O14—Tb2—Mn5	39.03 (18)	Mn5—O7—Tb1	101.5 (3)
O29—Tb2—Mn5	157.7 (2)	Mn4—O7—Tb1	109.7 (3)
O15—Tb2—Mn5	68.94 (17)	Mn1—O7—Tb1	102.1 (3)
Mn2—Tb2—Mn5	56.80 (4)	Mn4—O8—Mn3^{i}	127.8 (4)
Mn3—Tb2—Mn5	52.45 (4)	Mn4—O8—Mn1	101.8 (3)
Mn6—Tb2—Mn5	48.05 (4)	Mn3^{i}—O8—Mn1	127.6 (4)
O8—Mn1—O8^{i}	180.0	C24—O9—Mn2	126.7 (7)
O8—Mn1—O7^{i}	100.9 (3)	C32—O10—Mn6	131.3 (8)
O8^{i}—Mn1—O7^{i}	79.1 (3)	C48—O11—Mn2	127.4 (7)
O8—Mn1—O7	79.1 (3)	C8—O12—Mn4	129.3 (7)
O8^{i}—Mn1—O7	100.9 (3)	Mn2—O14—Mn3	139.6 (5)
O7^{i}—Mn1—O7	180.0	Mn2—O14—Mn5	105.5 (3)
O8—Mn1—O20^{i}	92.2 (3)	Mn3—O14—Mn5	95.9 (3)
O8^{i}—Mn1—O20^{i}	87.8 (3)	Mn2—O14—Tb2	104.3 (3)
O7^{i}—Mn1—O20^{i}	93.9 (3)	Mn3—O14—Tb2	105.9 (3)
O7—Mn1—O20^{i}	86.1 (3)	Mn5—O14—Tb2	98.5 (3)
O8—Mn1—O20	87.8 (3)	Mn3—O15—Mn6	101.2 (3)
O8^{i}—Mn1—O20	92.2 (3)	Mn3—O15—Tb2	102.4 (3)
O7^{i}—Mn1—O20	86.1 (3)	Mn6—O15—Tb2	94.5 (3)
O7—Mn1—O20	93.9 (3)	C72—O16—Mn4	132.9 (7)
O20^{i}—Mn1—O20	180.0	C56—O17—Mn6	127.3 (7)
O8—Mn1—Mn4^{i}	141.3 (2)	C56—O18—Tb1	133.8 (8)
O8^{i}—Mn1—Mn4^{i}	38.7 (2)	C32—O19—Tb2	139.7 (7)
O7^{i}—Mn1—Mn4^{i}	40.42 (19)	Mn2—O20—Mn1	124.0 (4)
O7—Mn1—Mn4^{i}	139.58 (19)	Mn2—O20—Tb1^{i}	122.6 (3)
O20^{i}—Mn1—Mn4^{i}	90.47 (19)	Mn1—O20—Tb1^{i}	98.5 (3)
O20—Mn1—Mn4^{i}	89.53 (19)	C40—O21—Tb2	135.3 (8)
O8—Mn1—Mn4	38.7 (2)	C24^{i}—O22—Mn4	125.9 (7)
O8^{i}—Mn1—Mn4	141.3 (2)	C24^{i}—O22—Tb1	127.4 (7)
O7^{i}—Mn1—Mn4	139.58 (19)	Mn4—O22—Tb1	103.1 (3)
O7—Mn1—Mn4	40.42 (19)	C64—O23—Tb1	154.3 (7)
O20^{i}—Mn1—Mn4	89.53 (19)	C48^{i}—O24—Tb1	137.9 (7)
O20—Mn1—Mn4	90.47 (19)	C73—O25—Mn2	125.1 (10)
Mn4^{i}—Mn1—Mn4	180.0	C73—O25—Tb2	125.9 (10)
O8—Mn1—Tb1^{i}	83.1 (2)	Mn2—O25—Tb2	109.0 (3)
O8^{i}—Mn1—Tb1^{i}	96.9 (2)	C72—O26—Mn5	132.9 (8)

O7^{i}—Mn1—Tb1^{i}	45.1 (2)	N1—O27—Tb1	96.5 (8)
O7—Mn1—Tb1^{i}	134.9 (2)	N1—O28—Tb1	94.9 (8)
O7^{i}—Mn1—Tb1	134.9 (2)		
O7—Mn1—Tb1	45.1 (2)		
O20^{i}—Mn1—Tb1	44.1 (2)		

Symmetry code: (i) $-x+2, -y+1, -z+1$.

4. TGA thermogram of compound 1

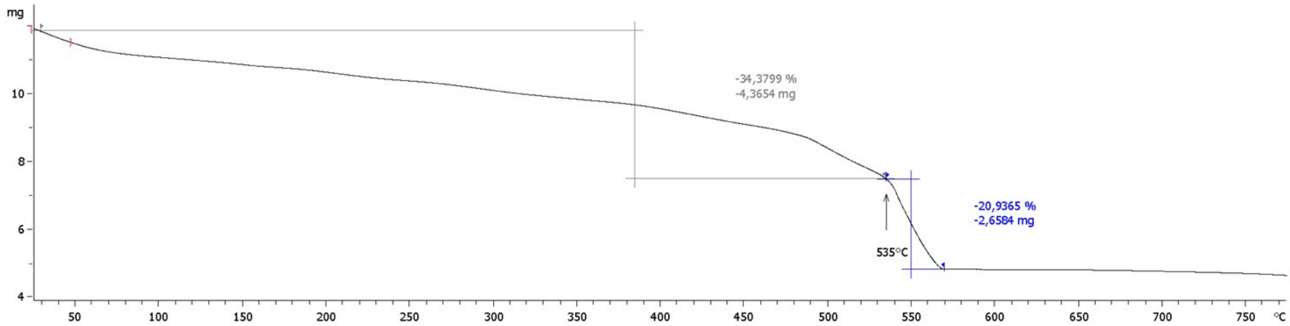


Figure S2. TGA curve for $[Mn^{III}_{11}Tb^{III}_4O_9(OH)_5(bza{\cdot}SMe)_{18}(NO_3)_2(H_2O)_6(OMe)_2]$ (**1**) under air in the range 25–800 °C.

5. Comparison of $\chi_m T$ vs. T data of compound 1 and single ion contributions

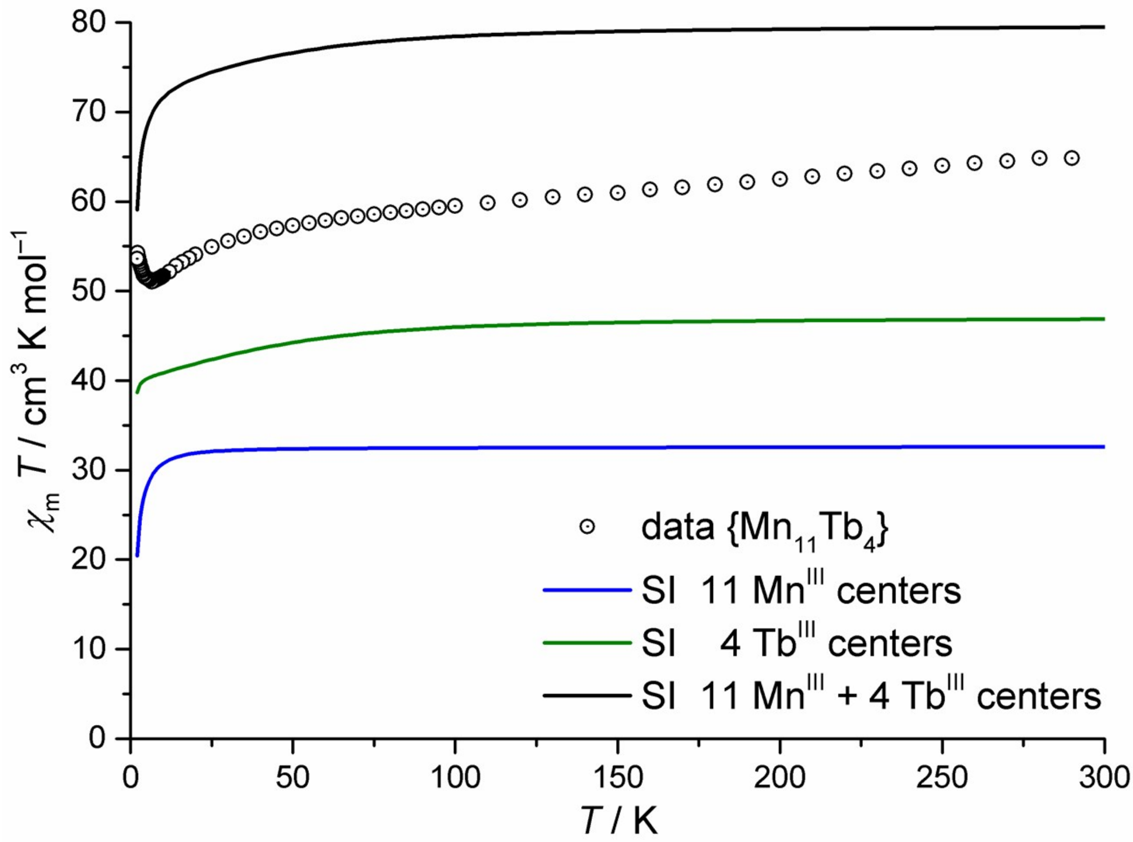


Figure S3. Experimental $\chi_m T$ vs. T (open circles) and calculated single ion (SI) contributions of non-interacting M^{III} centers (lines) at 0.1 Tesla; contributions of single centers were computed using CONDON[2] for representative ligand field parameters ($Mn^{III}(D_{4h})$,[3] $Tb^{III}(D_{3h})$,[4] assuming an oxide ligand environment), one electron spin-orbit coupling parameters ($\xi_{3d(Mn)}$, $\xi_{4f(Tb)}$),[5] Racah and Slater-Condon parameters,[5] respectively. The significant deviation of measured $\chi_m T$ and SI contributions of 11 Mn^{III} and 4 Tb^{III} non-interacting centers at 290 K and, to a lesser extent, the distinct decrease of $\chi_m T$ from 290 K to 6.5 K reveal dominant antiferromagnetic exchange interactions within the compound, while the subsequent increase for T < 6.5 K hints at minor ferromagnetic interactions.

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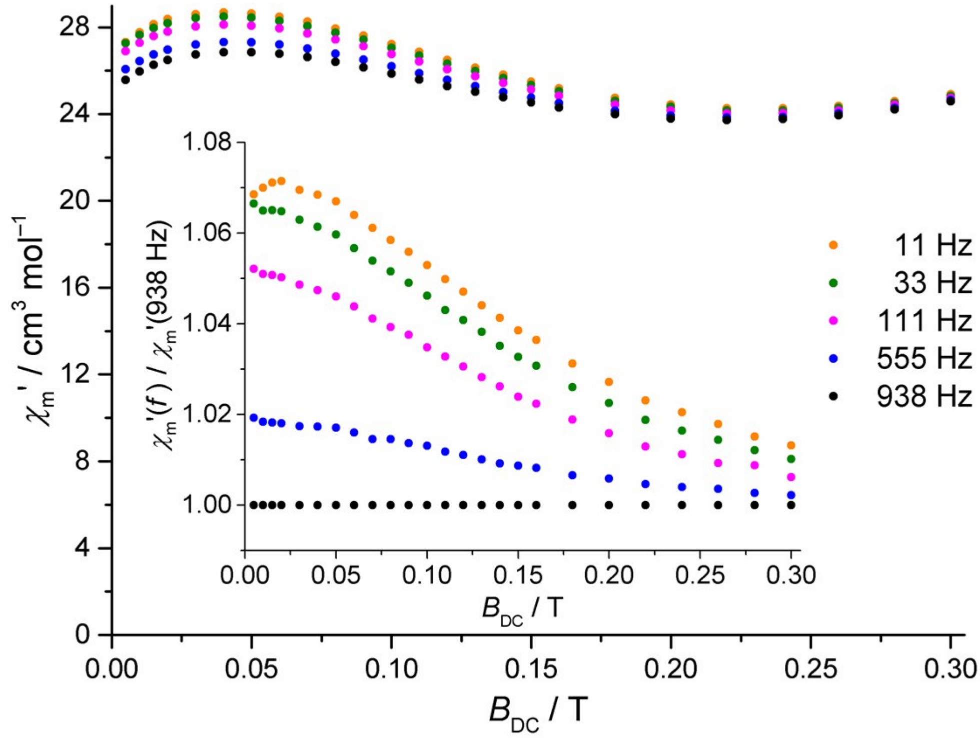
[2] (a) H. Schilder, H. Lueken, *J. Magn. Magn. Mater.*, 281 (2004), 17–26; (b) M. Speldrich, H. Schilder, H. Lueken, P. Kögerler, *Isr. J. Chem.*, 51 (2011), 215–227.
[3] A. Grigoropoulos, M. Pissas, P. Papatolis, V. Psycharis, P. Kyritsis, Y. Sanakis, *Inorg. Chem.*, 52 (2013), 12869–12871.
[4] C. Görller-Walrand, K. Binnemans, *Rationalization of Crystal-Field Parametrization*, in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 23 (1996), K.A. Gschneidner, Jr., L. Eyring (Eds.), Elsevier, Amsterdam.
[5] J.S. Griffith, *The Theory of Transition-Metal Ions*, Cambridge University Press, Cambridge (1971).

6. Variation of static bias field B_{DC} in ac susceptibility measurements of compound 1



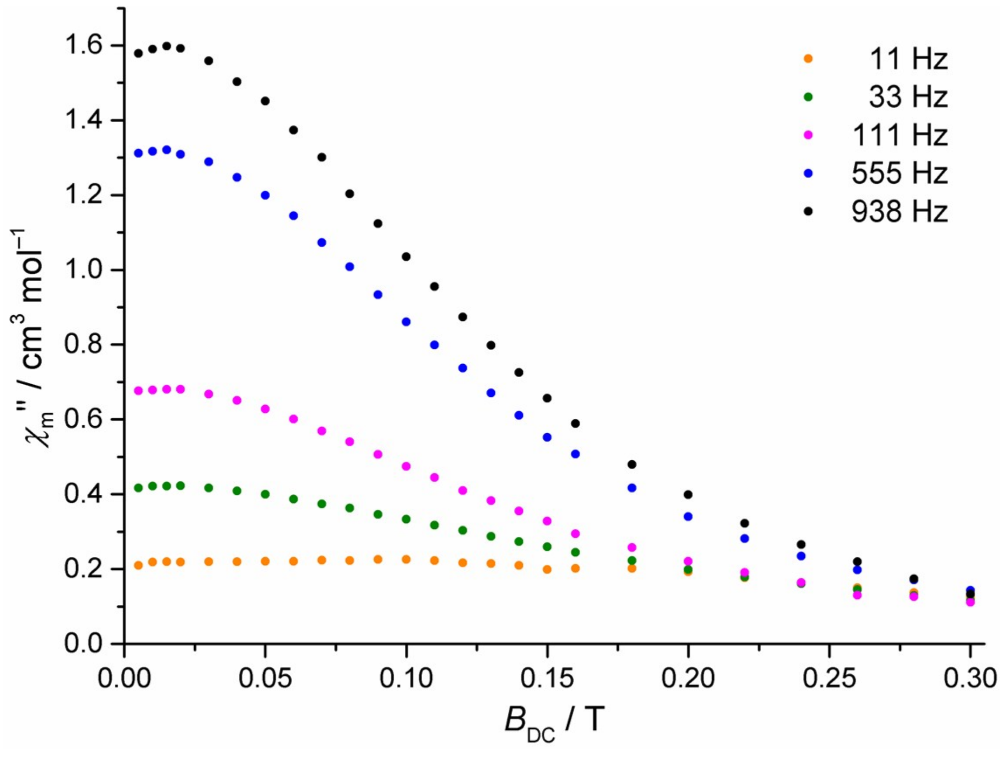


Figure S4. In-phase (χ_m', top) and out-of-phase (χ_m'', bottom) ac magnetic susceptibility data at T = 2.0 K as a function of the applied static bias field B_{DC} at various frequencies. The spread of the frequency-dependent χ_m' and χ_m'' components as well as the amplitude of χ_m'' reaches a small maximum at B_{DC} = 0.015 T and then decreases with increasing static bias field, therefore improving neither the curvature of the corresponding Cole-Cole plot nor the amplitude of the out-of-phase signal for a more specific analysis. The inset (top) illustrates the relative frequency dependence of χ_m', normalized against the data for f = 938 Hz (i.e. the highest possible frequency in our experimental setup).

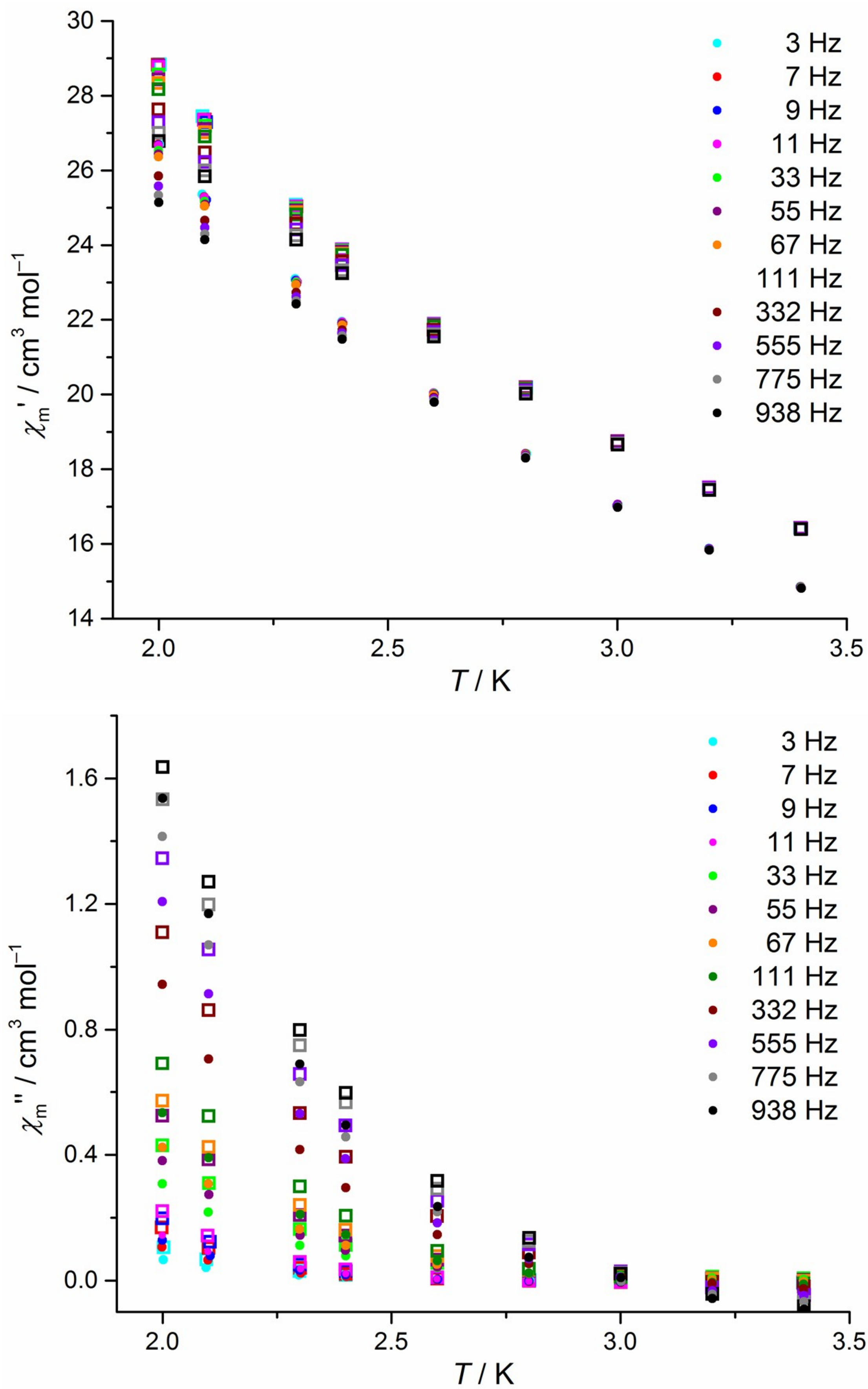


Figure S5. Comparison of the out-of-phase ac susceptibility component of compound **1** for a static bias field of B_{DC} = 0.015 T (open squares) and B_{DC} = 0 T (filled circles).

7. Synthesis of the dysprosium analogue

$Mn(OOCMe)_2 \cdot 4H_2O$ (0.245 g, 1.0 mmol), 4-(methylthio)benzoic acid (0.168 g, 1.0 mmol) and $Dy(NO_3)_3 \cdot 6H_2O$ (0.228 g, 0.5 mmol) were solved in 7 mL of MeCN and stirred for 2.5 h under reflux. The colour change from light rose to dark brown was observed. The MeCN solution was filtered off and the filtrate was stored in a capped vial at ambient temperature. Dark-brown microcrystalline precipitate was obtained after *ca.* two weeks. IR, ν_{max} (KBr pellet) / cm^{-1}: 3426 (br, m), 2920 (w), 1593 (s), 1542 (m), 1492 (sh, vw), 1408 (s), 1384 (sh, w), 1186 (m), 1149 (w), 1116 (vw), 1091 (m), 1014 (w), 967 (w), 847 (w), 768 (m), 707 (w), 691 (w), 604 (m), 536 (m), 478 (w).

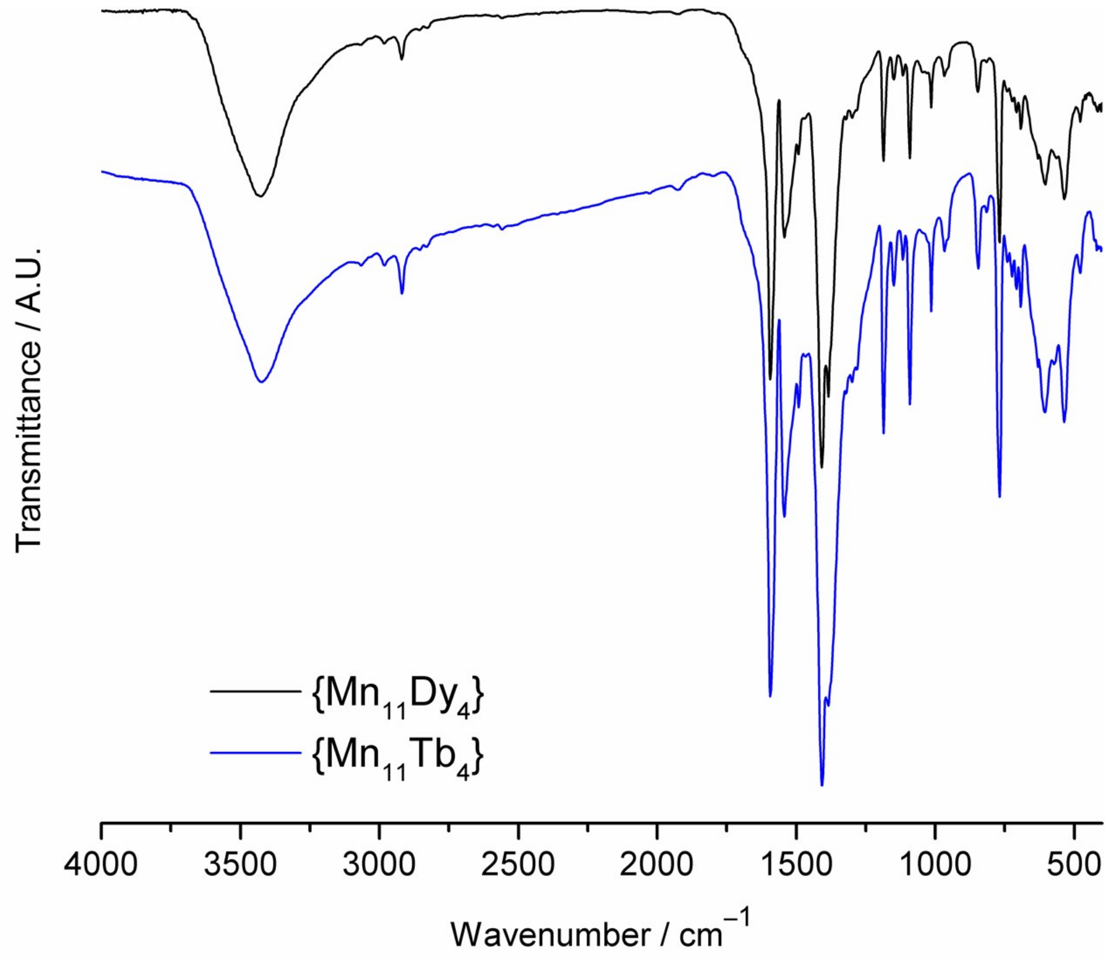


Figure S6. Comparison of the IR spectra of compound **1** (blue) and its dysprosium analogue (black) in the 4000–400 cm^{-1} region (KBr pellet).