Supporting Information for

Nine members of a family nine-membered cyclic coordination clusters; Fe_6Ln_3 wheels (Ln = Gd to Lu and Y)

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Table of Contents

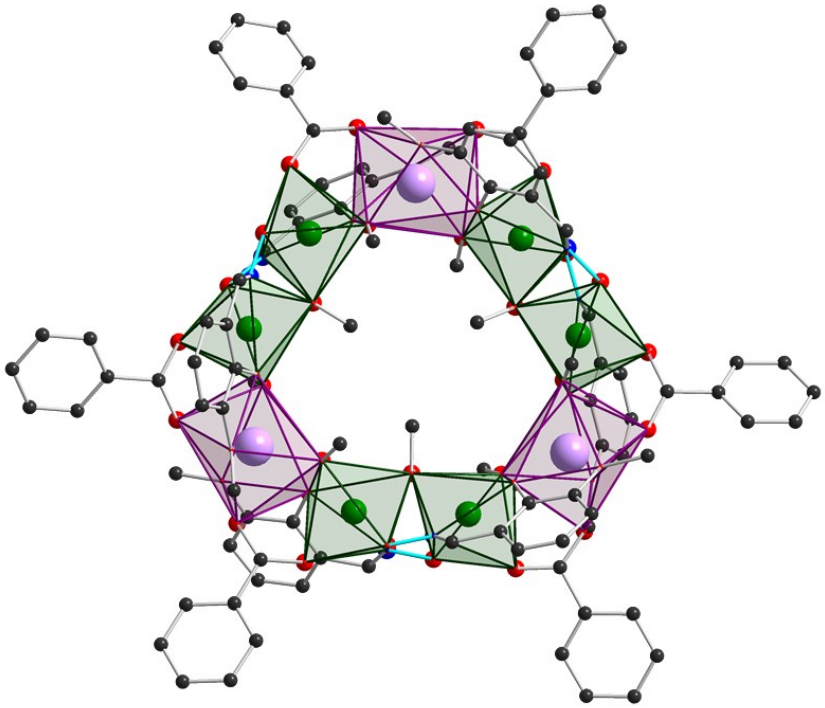
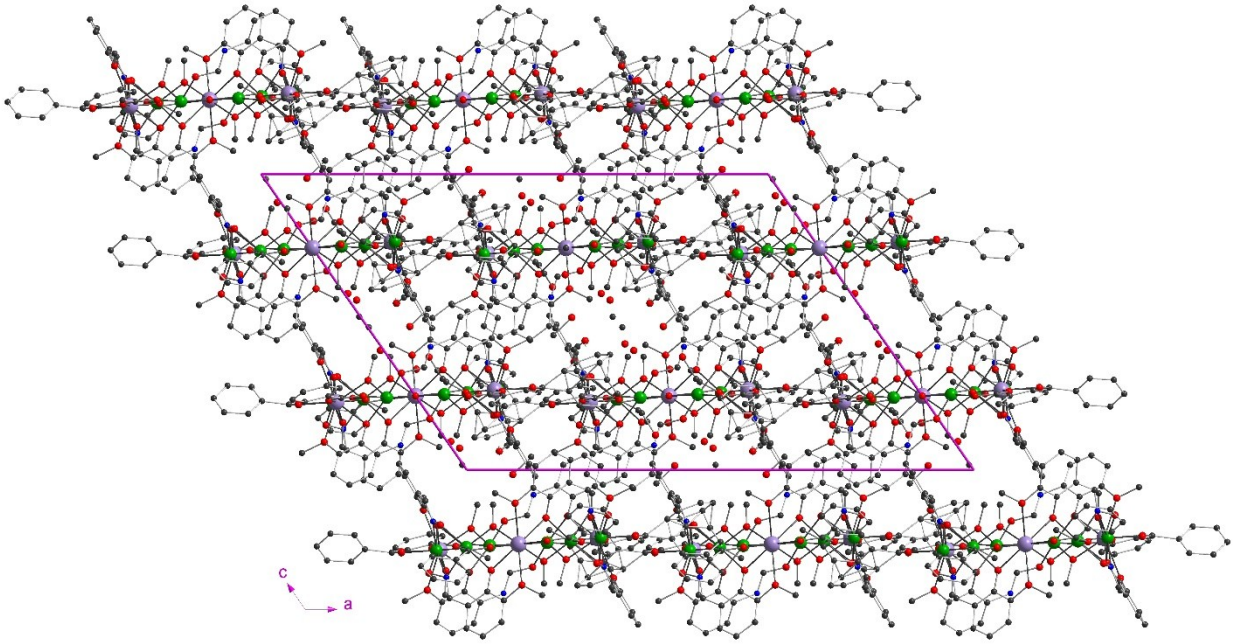


Fig. S1: Structure of Fe_6Dy_3 (**2**) with polyhedra around the metal center to emphasize the distorted bicapped trigonal-prismatic geometry of the Ln^{III} and the distorted octahedral environment of the Fe^{III} ions.



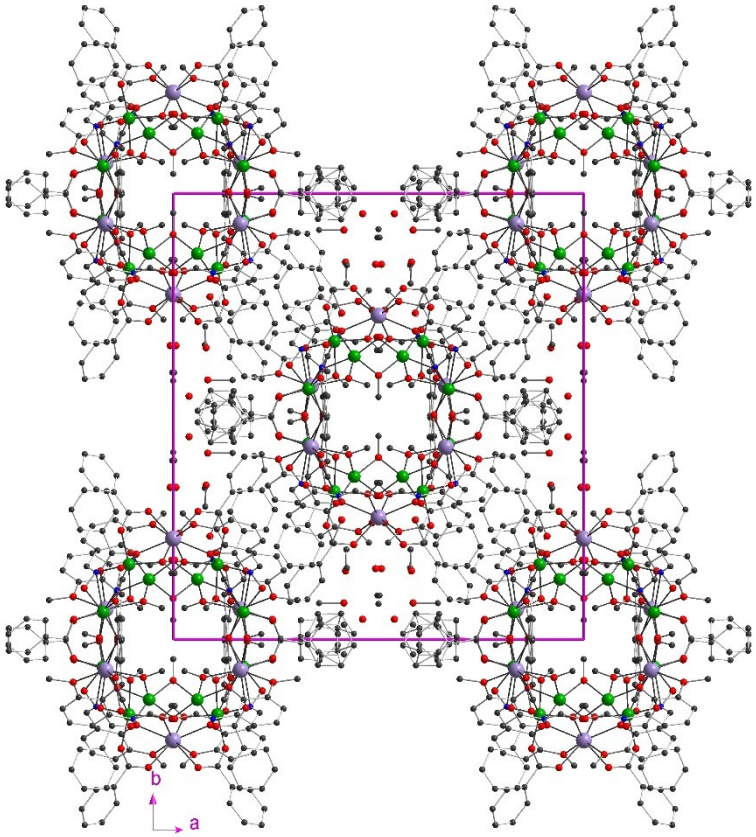
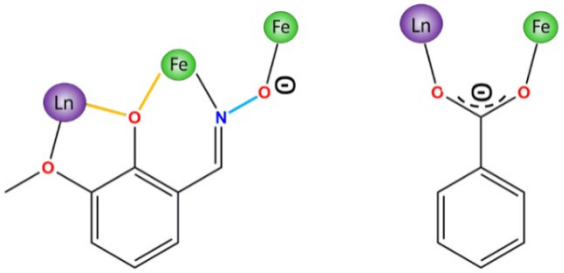


Fig. S2: Packing arrangement of **1** along *a*-axis (top) and *c*-axis (bottom).

Scheme 1. Coordination modes of the deprotonated vanox^{2-} ligand, (η^1:η^2:η^1:η^1:μ_3) (left) and the benzoic acid (η^1:η^1:μ_2) (right).



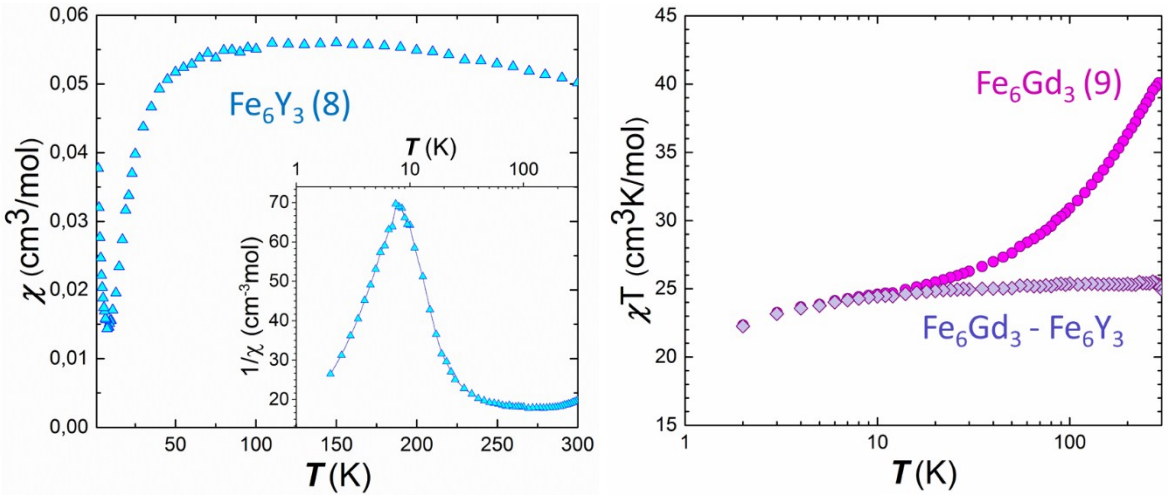


Fig. S3: Temperature dependence of the χ plot at 1000 Oe for complexes Fe_6Y_3 (**8**) (blue triangles) and the $1/\chi$ plot with logarithmic *x*-axis (inset) (left) and χT plot of Fe_6Gd_3 (**9**) and the substituted χT plot (Fe_6Gd_3 - Fe_6Y_3) on a logarithmic temperature scale (right).

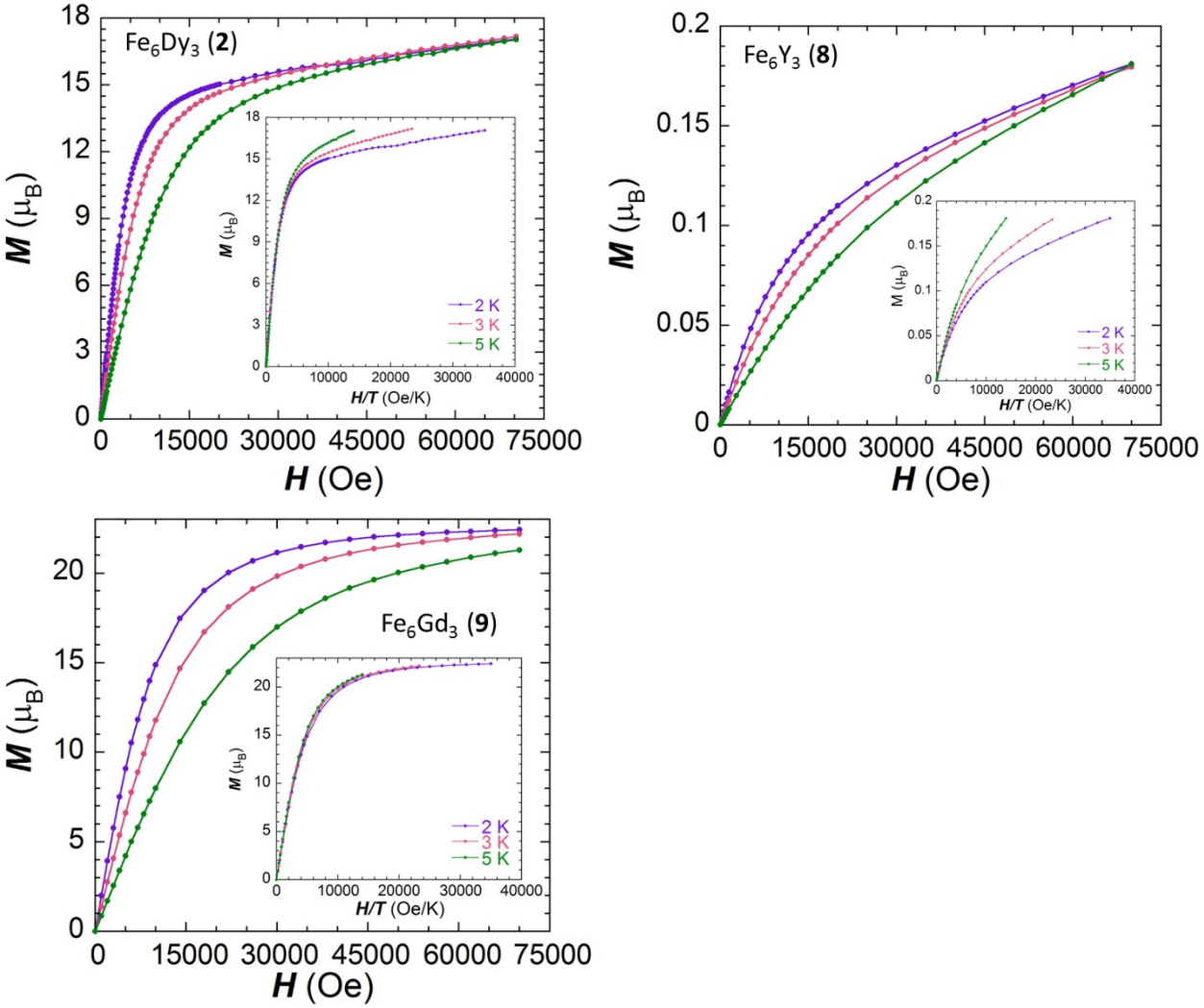


Fig. S4: Field dependence of Magnetization for Fe_6Dy_3 (**2**) (left), Fe_6Y_3 (**8**) (right) and Fe_6Gd_3 (**9**) at different temperatures; reduced magnetization (inset).

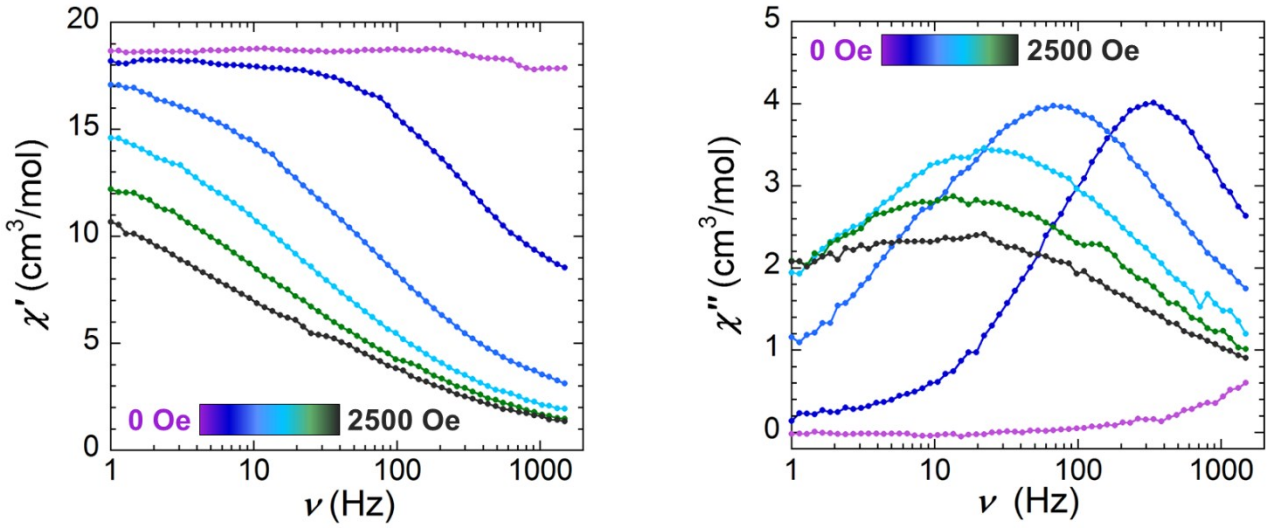


Fig. S5: In-phase (left) and out-of-phase susceptibility of Fe_6Dy_3 (**2**) at varying field.

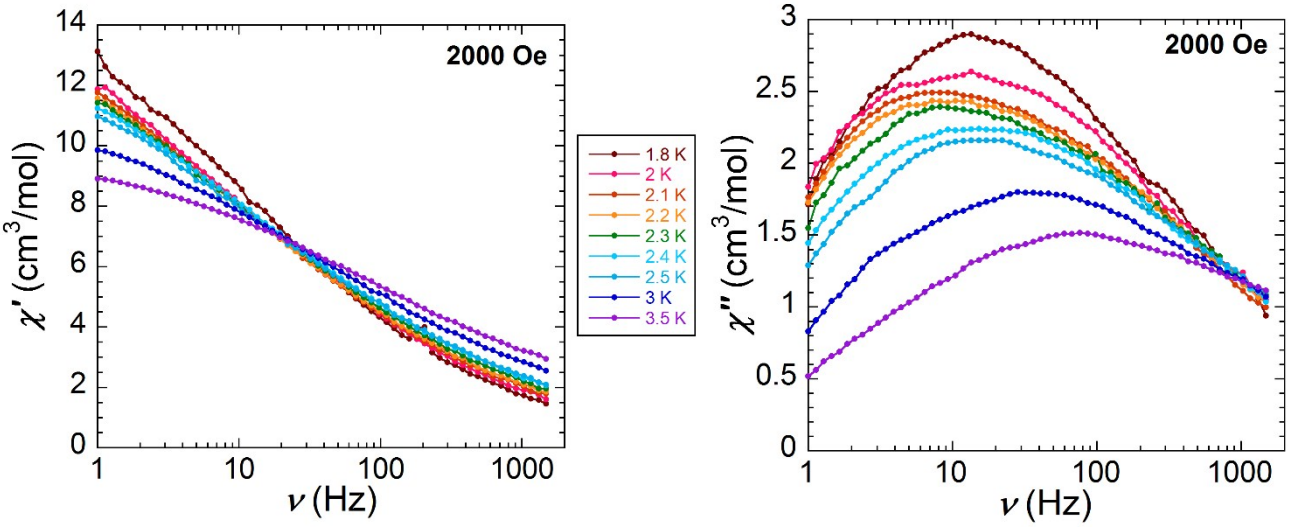


Fig. S6: In-phase (left) and out-of-phase susceptibility (right) of Fe_6Dy_3 (**2**) under an applied field of 2000 Oe.

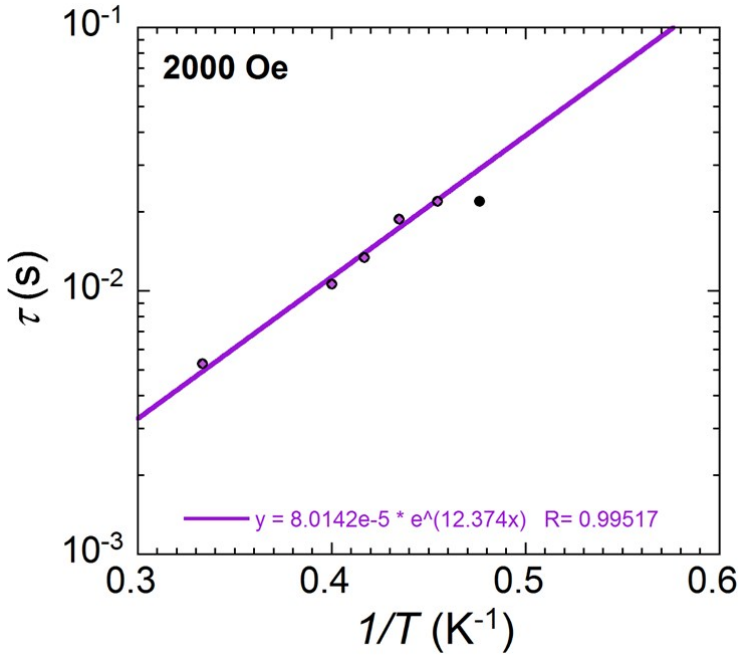


Fig. S7: Arrhenius fit for Fe_6Dy_3 (**2**).

S3. Chemicals and Instrumentation.

Commercially available reagents were used without further purification unless otherwise stated.

o-Vanillinoxime (Hvanox) was prepared according to the procedures described in the literature.[1]
A suspension of 3.31g (24.2 mmol) of *o*-vanillin in 11ml H_2O was stirred while heating to 45°C. A solution containing 1.80g (26.1 mmol) $NH_2OH{\cdot}HCl$ and 1.78g (21.8 mmol) CH_3CO_2Na was added and the reaction was heated with stirring at 80°C for 2h. Upon cooling to room temperature the resulting white microcrystalline precipitate was filtered and washed with cold H_2O and recrystallized from EtOH. The resulting compound is light sensitive.

Elemental analysis (C, H and N) was performed by Vario EL (Elementar Analysen System GmbH) from Perkin Elmer. Fourier transform infrared spectra (FT-IR) were recorded as KBr pellets on a Perkin Elmer Spectrum GX in the range of 4000 to 400 cm^{-1}.
Magnetic susceptibility measurements were obtained with a Quantum Design SQUID magnetometer MPMS-XL. The measurements were performed of a polycrystalline powder.

[1] I. J. Hewitt, Y. Lan, C. E. Anson, J. Luzon, R. Sessoli, and A. K. Powell, *Chem. Commun.*, 2009, **3**, 6765–7.

S4. Synthesis and characterization of **1-9**.

The syntheses have been optimised for the production of single crystals rather than bulk microcrysalline products.

(**1**) $[Fe_6Tb_3(\mu\text{-}OMe)_9(vanox)_6(benzoate)_6]\cdot 7MeOH\cdot 4H_2O$: 0.066 g (0.4 mmol) H_2vanox, 0.054 g (1.0 mmol) NaOMe were solved in 10.0 ml MeOH and put to a solution of 0.040 g (0.2 mmol) $FeCl_2\cdot 4H_2O$, 0.114 g (0.25 mmol) $Tb(NO_3)_3\cdot 6H_2O$ and 0.048 g (0.4 mmol) benzoic acid in 10.0 ml MeOH. The dark red almost black solution is stirred for 10 minutes at room temperature, and without any filtering left to stand for crystallisation. After one week complex **1** crystallises as dark red-black cubes suitable for single crytsal X-ray analysis.
The use of $FeCl_3\cdot 6H_2O$ instead of $FeCl_2\cdot 4H_2O$ leads to microcrystalline precipitate in much lower yield.
Yield: 0.048 g (19.6% related to Tb)
Elemental analysis for $C_{99}H_{113}Fe_6Tb_3N_6O_{46}$ (%): calculated: C: 40.51, H: 3.88; N: 2.86; found: C: 40.36; H: 4.01; N: 2.97.

IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3436 (m), 1598 (m), 1539 (s), 1492 (w), 1458 (m), 1438 (s), 1405 (s), 1268 (m), 1241 (m), 1220 (m), 1170 (w), 1095 (w), 1057 (s), 966 (m), 853 (m), 764 (w), 721 (m), 673 (m), 657 (m), 559 (w), 453 (m).

(**2**)-(**8**): The complexes were synthesized in a similar fashion to complex **1**, but using the relevant lanthanide nitrate in place of $Tb(NO_3)_3\cdot 6H_2O$.
Yield $[Fe_6Dy_3]$ (**2**): 0.037 g (15.1 % related to Dy)
Elemental analysis for $C_{99}H_{113}Fe_6Dy_3N_6O_{46}$ (%): calculated: C: 40.36, H: 3.86; N: 2.85; found: C: 40.52; H: 3.61; N: 2.89.
IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3429 (m), 3060 (w), 2932 (m), 2851 (w), 2822 (w), 1740 (w), 1591 (m), 1541 (s), 1452 (s), 1399 (s), 1268 (m), 1236 (m), 1215 (m), 1172 (w), 1055 (s), 966 (m), 846 (w), 718 (m), 658 (w), 562 (w), 448 (m).

Yield $[Fe_6Ho_3]$ (**3**): 0.044 g (17.8 % related to Ho)
Elemental analysis for $C_{99}H_{115}Fe_6Ho_3N_6O_{47}$ (%): calculated: C: 40.02, H: 3.90; N: 2.82; found: C: 40.12; H: 3.83; N: 3.04.
IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3431 (m), 3064 (w), 1596 (m), 1541 (s), 1491 (w), 1455 (s), 1399 (s), 1268 (m), 1238 (m), 1217 (m), 1172 (w), 1096 (m), 1057 (s), 966 (m), 849 (w), 723 (m), 664 (w), 589 (w), 449 (m).

Yield $[Fe_6Er_3]$ (**4**): 0.029 g (11.8 % related to Er)
Elemental analysis for $C_{99}H_{109}Fe_6Er_3N_6O_{44}$ (%): calculated: C: 40.76, H: 3.76; N: 2.88; found: C: 40.58; H: 3.66; N: 2.84.
IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3439 (m), 1598 (s), 1540 (s), 1492 (w), 1459 (m), 1438 (w), 1407 (m), 1269 (m), 1242 (m), 1219 (w), 1173 (w), 1095 (m), 1059 (m), 965 (w), 855 (m), 766 (w), 725 (m), 687 (w), 675 (w), 643 (w), 452 (w).

Yield $[Fe_6Tm_3]$ (**5**): 0.032 g (13.1 % related to Tm)
Elemental analysis for $C_{99}H_{109}Fe_6Tm_3N_6O_{44}$ (%): calculated: C: 40.59, H: 3.75; N: 2.86; found: C: 40.44; H: 3.68; N: 2.62.
IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3444 (m), 1597 (s), 1539 (s), 1492 (w), 1458 (m), 1438 (w), 1406 (m), 1268 (m), 1241 (m), 1221 (w), 1170 (w), 1094 (m), 1058 (m), 967 (w), 856 (m), 763 (w), 722 (m), 680 (w), 674 (w), 626 (w) 456 (w).

Yield $[Fe_6Yb_3]$ (**6**): 0.038 g (15.1 % related to Yb)
Elemental analysis for $C_{102}H_{133}Fe_6Yb_3N_6O_{53}$ (%): calculated: C: 39.10, H: 4.27; N: 2.68; found: C: 39.32; H: 4.11; N: 2.56.
IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3455 (m), 2928 (w), 1598 (s), 1541 (s), 1491 (w), 1458 (m), 1437 (w), 1408 (m), 1268 (m), 1240 (m), 1221 (w), 1095 (m), 1059 (m), 968 (w), 858 (m), 762 (w), 724 (m), 689 (w), 672 (w), 631 (w), 457 (w).

Yield $[Fe_6Lu_3]$ (**7**): 0.036 g (14.3 % related to Lu)
Elemental analysis for $C_{99}H_{117}Fe_6Lu_3N_6O_{48}$ (%): calculated: C: 39.38, H: 3.90; N: 2.78; found: C: 39.15; H: 4.01; N: 2.82.

IR (KBr): $\tilde{\nu}$/cm^{-1} = 3450 (m), 2931 (w), 1597 (m), 1540 (m), 1493 (w), 1459 (m), 1438 (w), 1409 (m), 1269 (m), 1242 (m), 1221 (m), 1175 (w), 1095 (w), 1060 (m), 966 (m), 853 (m), 764 (m), 721 (m), 689 (w), 674 (m), 657 (m), 577 (w), 456 (m).

Yield [Fe_6Y_3] (**8**): 0.073 g (39.4 % related to Y)
Elemental analysis for $C_{99}H_{117}Fe_6Y_3N_6O_{48}$ (%): calculated: C: 43.07, H: 4.27; N: 3.04; found: C: 42.95; H: 4.19; N: 3.07.
IR (KBr): $\tilde{\nu}$/cm^{-1} = 3423 (m), 2911 (w), 1594 (s), 1536 (s), 1488 (w), 1457 (m), 1439 (w), 1409 (m), 1267 (m), 1242 (m), 1223 (m), 1176 (w), 1094 (w), 1062 (m), 967 (m), 854 (m), 765 (w), 720 (m), 674 (m), 643 (w), 436 (w).

(**9**) [$Fe_6Gd_3(\mu$-OMe)$_9$(vanox)$_6$(4-Cl-benzoate)$_6$]·9MeOH: 0.066 g (0.4 mmol) H_2vanox, 0.081 g (1.5 mmol) NaOMe were solved in 10.0 ml MeOH and put to a solution of 0.040 g (0.2 mmol) $FeCl_2·4H_2O$, 0.114 g (0.25 mmol) $Gd(NO_3)_3·6H_2O$ and 0.063 g (0.4 mmol) 4-Chlorobenzoic acid in 10.0 ml MeOH. The dark red almost black solution is stirred for 10 minutes at room temperature, and without any filtering left to stand for crytalization. After 4 days complex **9** crystallizes as dark red-black cubes suitable for single crytsal X-ray analysis.
Yield (**9**): 0.025 g (10.7 % related to Gd)
Elemental analysis for $C_{102}H_{123}Fe_6Gd_3N_6O_{48}Cl_6$ (%): calculated: C: 37.85, H: 3.83; N: 2.59; found: C: 37.78; H: 3.64; N: 2.44.
IR (KBr): $\tilde{\nu}$/cm^{-1} = 3439 (m), 1600 (s), 1541 (s), 1501 (w), 1459 (s), 1438 (m), 1444 (s), 1358 (w), 1270 (m), 1240 (w), 1221 (m), 1167 (m), 1094 (w), 1056 (m), 1010 (w), 966 (m), 855 (m), 779 (w), 735 (w), 683 (w), 608 (w), 564 (w), 502 (w), 461 (m).

S5. Crystal data for **1-9**.

Compound	Fe_6Tb_3 **1**	Fe_6Ho_3 **3**	Fe_6Er_3 **4**
Empirical formula	$C_{106}H_{135}Fe_6N_6O_{50}Tb_3$	$C_{107}H_{135}Fe_6Ho_3N_6O_{49}$	
Formula weight	3105.05	3119.09	
Crystal system	monoclinic	monoclinic	
Space group	*C2/c*	*C2/c*	
Crystal size (nm)	0.280 x 0.090 x 0.070	0.370 x 0.110 x 0.090	
a (Å)	29.189(3)	29.211(2)	
b (Å)	26.117(3)	25.894(2)	
c (Å)	20.479(2)	20.7929(16)	
α (°)	90	90	
β (°)	124.572(2)	124.970(5)	
γ (°)	90	90	
V (Å^3)	12854(2)	12888.1(19)	
Z	4	4	
d_{calc} (g cm^{-3})	1.604	1.607	
T (K)	100(2)	150(2)	
μ (mm^{-1})	2.371	2.559	
F(000)	6256	6272	
Limiting indices	h = ± 38, k = ± 33, l = ± 27	h = ± 36, k = ± 32, l = ± 26	h = ± 12, k = ± 14, l = ± 15
Reflections collected / unique	30941 / 14288	41101 / 13580	4842 / 4842
R(int)	0.00426	0.1006	
Completeness to Θ (%)	99.7	99.4	88.8
Data / restraints / parameters	14288 / 32 / 770	13580 / 25 / 703	4440 / 0 / 291
GooF on F^2	1.035	1.009	1.016
Final R indices [I > 2σ(I)][a]	R_1 = 0.0476; wR_2 = 0.1259	R_1 = 0.0661; wR_2 = 0.1604	R_1 = 0.0715; wR_2 = 0.1572
R indices (all data)	R_1 = 0.0679; wR_2 = 0.1373	R_1 = 0.0952; wR_2 = 0.1719	R_1 = 0.1191; wR_2 = 0.1810
Largest diff. peak/hole (e·Å^{-3})	2.875 / -1.523	0.942 / -3.548	1.294 / -1.437
CCDC no.			

Compound	Fe_6Tm_3 **5**	Fe_6Yb_3**6**	Fe_6Lu_3 **7**
Empirical formula	$C_{108}H_{139}Fe_6N_6O_{50}Tm_3$		$C_{108}H_{139}Fe_6Lu_3N_6O_{50}$
Formula weight	3163.14		3181.25
Crystal system	monoclinic		monoclinic
Space group	*C2/c*		*C2/c*
Crystal size (nm)	0.48 x 0.04 x. 0.03		0.42 x 0.07 x 0.04
a (Å)	29.069(4)		29.1226(16)
b (Å)	25.935(4)		25.811(2)
c (Å)	20.683(3)		20.8572(12)
α (°)	90		90
β (°)	124.822(2)		125.126(4)
γ (°)	90		90
V (Å^3)	12801(3)		12823.0(15)
Z	4		4
d_{calc} (g cm^{-3})	1.641		1.648
T (K)	100(2)		150(2)
μ (mm^{-1})	2.803		3.032
F(000)	6368		6392
Limiting indices	h = ± 35, k = ± 32, l = ± 25		h = ± 36, k = ± 32, l = ± 26
Reflections collected / unique	29204 / 12537		41722 / 13630
R(int)	0.0707		0.0869
Completeness to Θ (%)			99.9
Data / restraints / parameters	12537 / 29 / 747		13630 / 49 / 698
GooF on F^2	1.036		1.047
Final R indices [I > 2σ(I)][a]	R_1 = 0.0626; wR_2 = 0.1426		R_1 = 0.0654; wR_2 = 0.1600
R indices (all data)	R_1 = 0.0992; wR_2 = 0.1594		R_1 = 0.0866; wR_2 = 0.1694
Largest diff. peak/hole (e·Å^{-3})	2.981 / -1.900		0878 / -3.134
CCDC no.			

S5. PHI report for Fe_6Y_3 **8**.

PHI Report generated on 28/07/2015 at 16:16:13

Job: FeY1

Name:

Input:

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****ion fe(iii)oh(w)
fe(iii)oh(w)
****gfactors
1 2.0
2 2.0
****exchange
1 2 -10
****fit
simplex
10
ex 1 2 4
----
1.9 2.0 2.1
gf 1 4 0
gf 2 4 0
----
****sus
bsus 0.1
****params
opmode fit s
imp 1 0
****end
```

Output:

```
================================================
Finished Simplex with         247 iterations
------------------------------------------------
```

```
-16.504536635286755
EX   1  2  4
-----------------------------------------
1.9508748984356066
GF   1  4  0
GF   2  4  0
-----------------------------------------
Residual: 0.04210139550604808
Residual reduced by:   0.53585383680019504E+004
                     or: 99.999214318124984%

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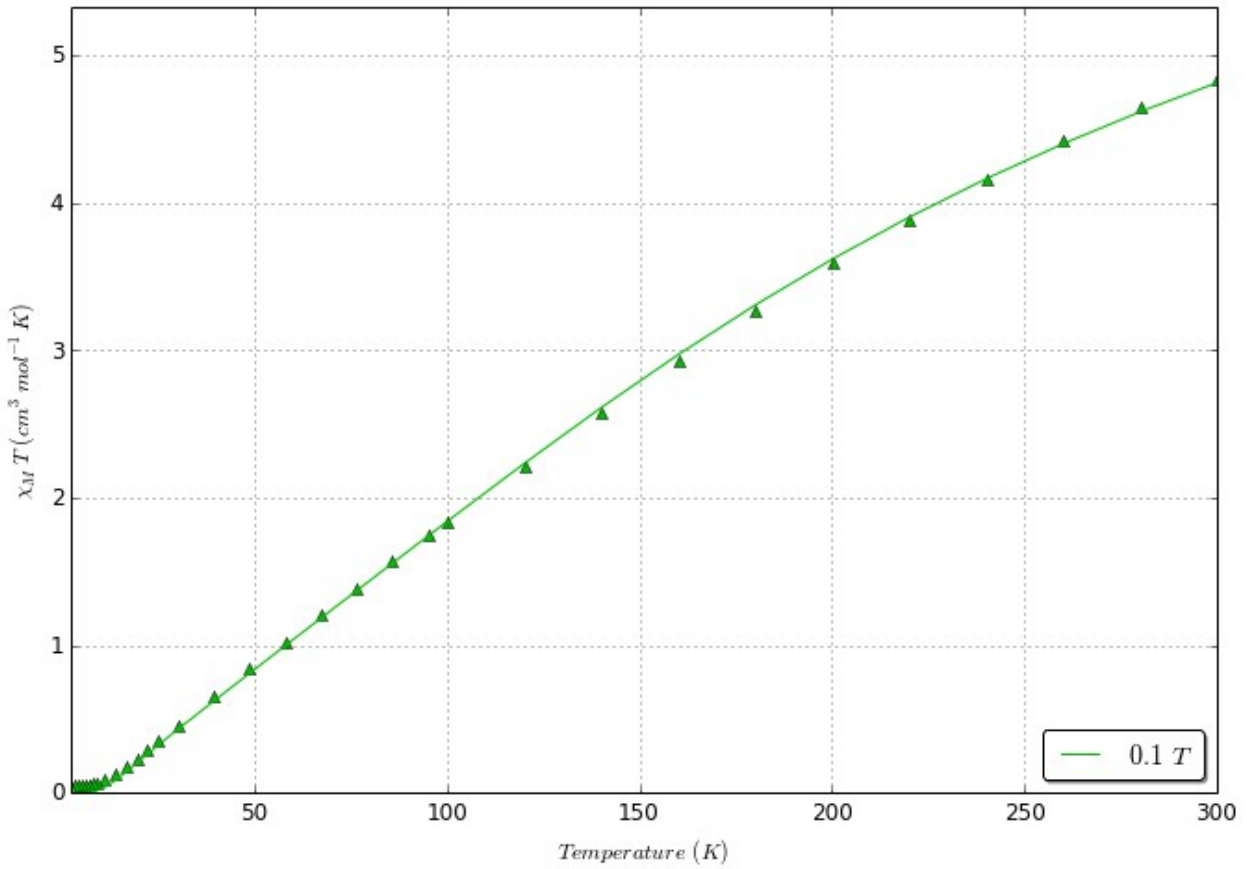
Susceptibility: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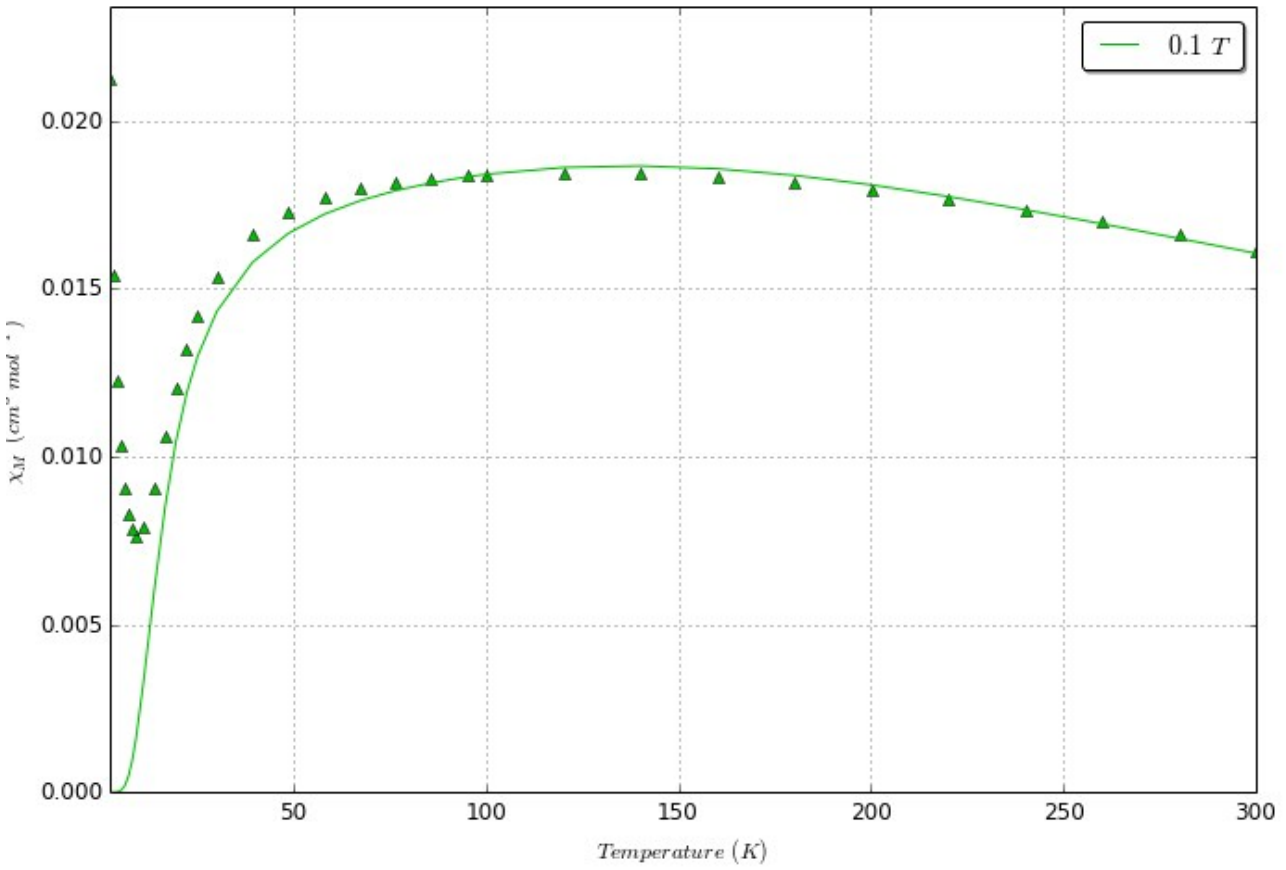
Temperature (K)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Temperature (K)