Supporting information to the article:

Influence of Lanthanides on Spin-Relaxation and Spin-Structure in a Family of Fe_7Ln_4 Single Molecule Magnets

Denis Prodius, Valeriu Mereacre,* Prashant Singh, Yanhua Lan, Samir Mameri, Duane D. Johnson, Wolfgang Wernsdorfer, Christopher E. Anson and Annie K. Powell

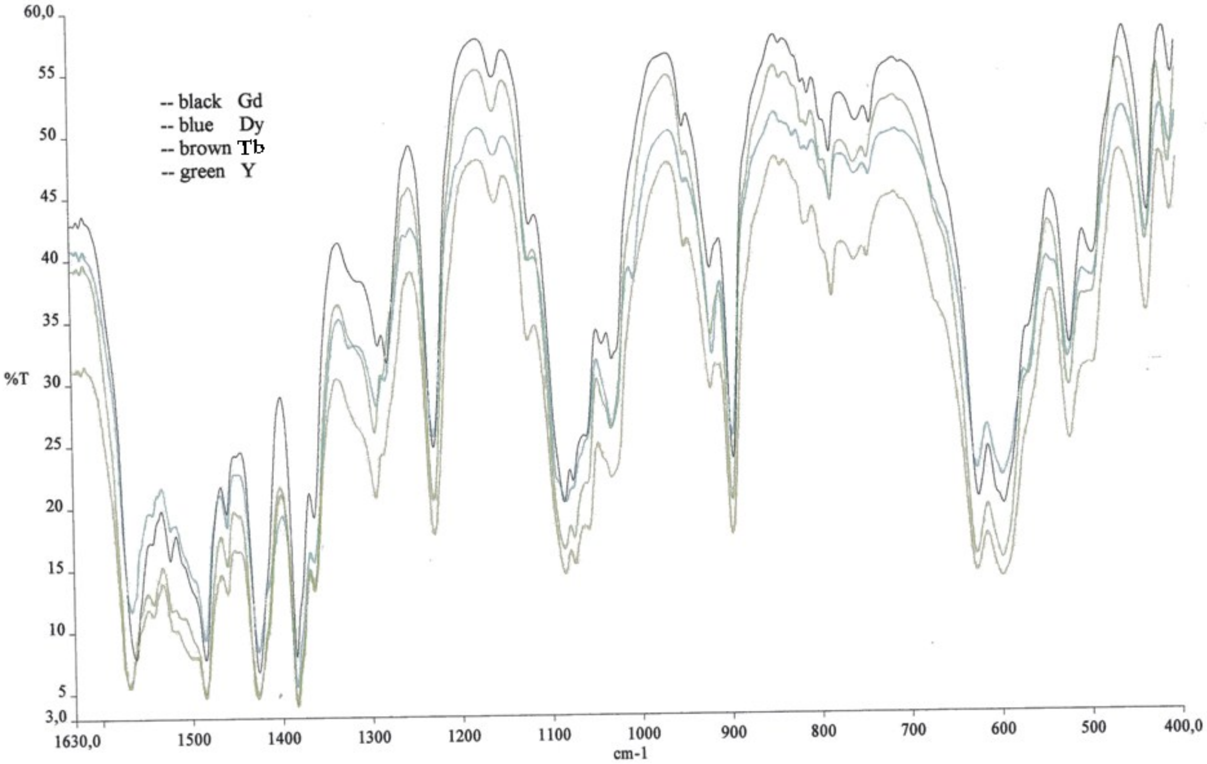


Figure S1: IR spectra for **1-4** clusters.

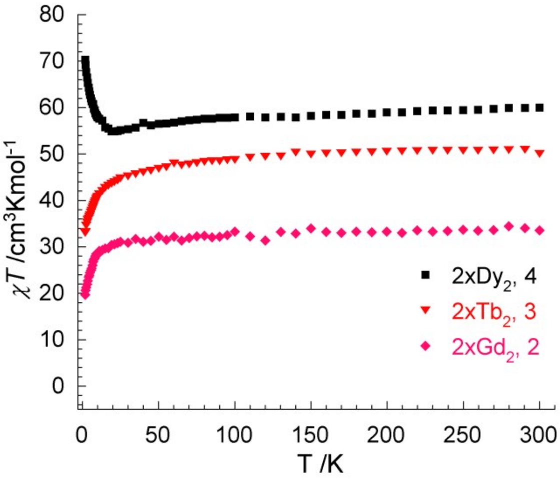


Fig. S2. The χT vs T plots for **2, 3** and **4** with the data for **1** subtracted, i.e. without the magnetic contribution of the Fe_7 unit.

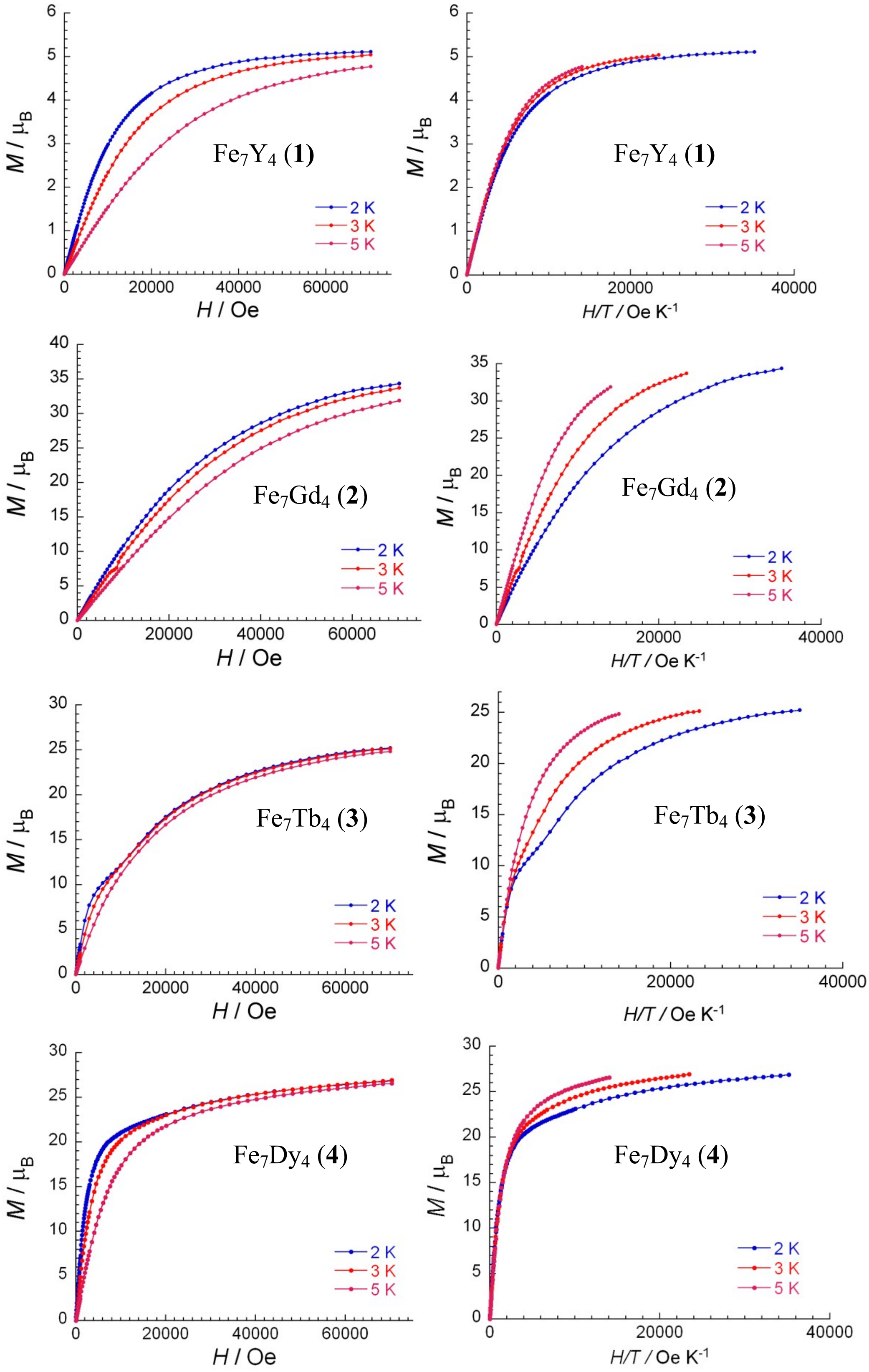
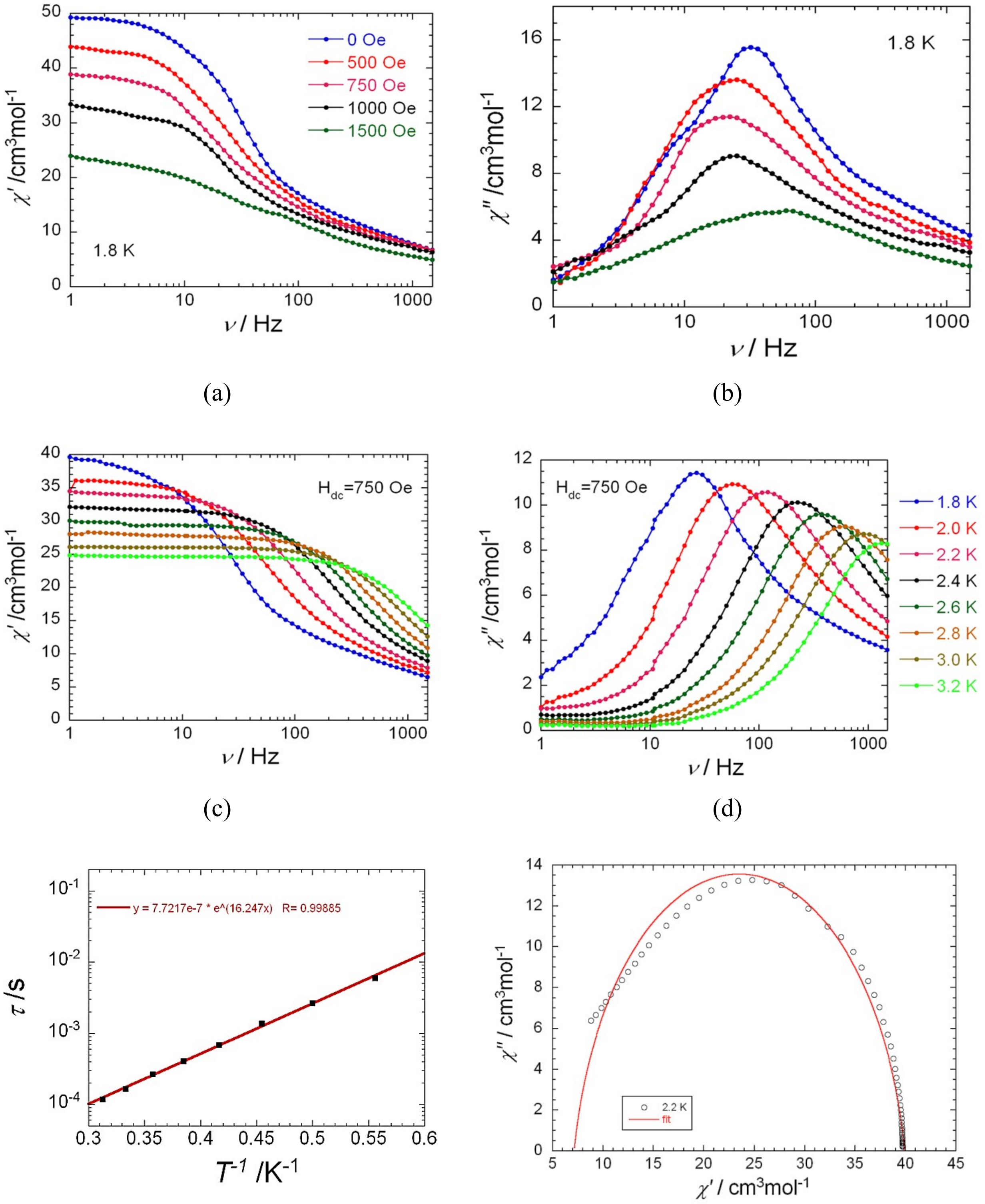


Figure S3: Field-dependence of magnetization of compounds **1**-**4.**



(a) (b)

(c) (d)

(e) (f)

Figure S4: (a and b) The frequency dependence of the in-phase (χ') and out-of-phase (χ'') signals under applied dc fields for **4;** (c and d) The frequency dependence of the in-phase (χ') and out-of-phase (χ'') signals in H_{dc} = 750 Oe at different temperatures for **4**; (e) plot of the magnetization relaxation rate *versus* the inverse of the absolute temperature for **4**. The solid line represents a least-squares fit of the data to the Arrhenius equation; (f) The Cole-Cole plot of χ'' vs χ' at 2.2K for **4**.

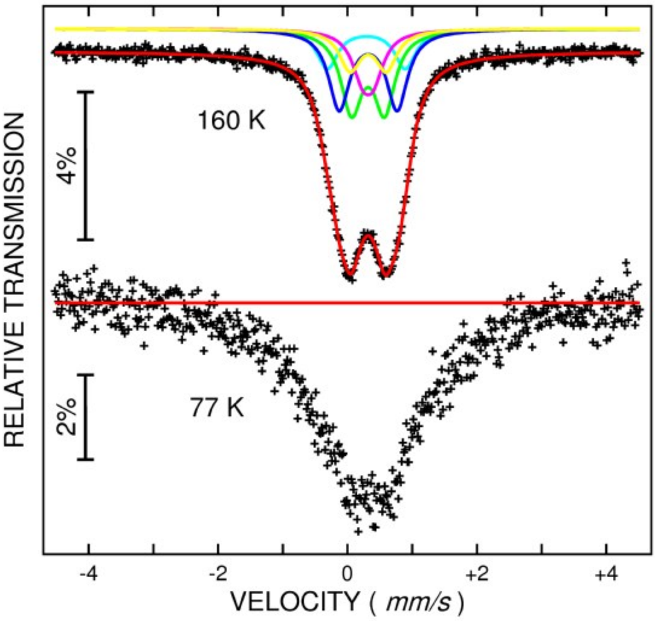


Figure S5: Mössbauer spectra for **1** (Fe_7Y_4) at 160 and 77 K in zero-field.

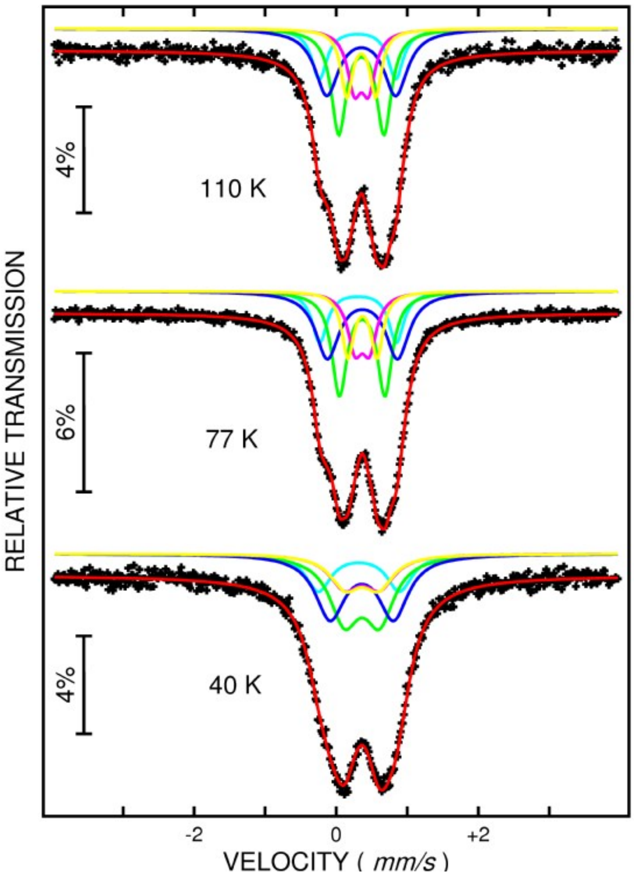


Figure S6: Mössbauer spectra for **3** (Fe_7Tb_4) at 110, 77 and 40 K in zero-field.

Table S1. Mössbauer data* for **1, 3** and **4** at 3 K in zero-field and at 3 K in applied magnetic fields of 6 or 6.5 T.

Compound, temperature, applied field	Fe sites	δ[a], mm/s	ΔE_Q or ε[c], mm/s	Γ[d], mm/s	θ[d], °	B_{eff}, T
(1) Fe_7Y_4 3K, 6.5T	Fe(1)	0.49(1)	-0.14(1)	0.34(1)	68.7	46.37
	Fe(2)	0.46(1)	-0.42(1)	0.34(1)	68.7	35.97
	Fe(3)	0.41(3)	-0.42(1)	0.34(1)	68.7	33.27
	Fe(4)	0.49(1)	0.10(1)	0.34(1)	68.7	45.84
	Fe(5)	0.49(1)	0.10(1)	0.34(1)	68.7	45.84
	Fe(6)	0.46(1)	-0.003(3)	0.34(1)	68.7	36.43
	Fe(7)	0.46(1)	-0.003(3)	0.34(1)	68.7	36.43
(3) Fe_7Tb_4 3 K	Fe(1)	0.49(1)	-0.23(1)	0.34(1)	57.6	42.45
	Fe(2)	0.46(1)	0.21(1)	0.34(1)	57.6	42.70
	Fe(3)	0.44(1)	0.06(1)	0.34(1)	57.6	41.92
	Fe(4)	0.50(1)	0.11(1)	0.34(1)	57.6	40.77
	Fe(5)	0.50(1)	0.11(1)	0.34(1)	57.6	40.77
	Fe(6)	0.50(2)	0.19(1)	0.34(1)	57.6	44.32
	Fe(7)	0.50(2)	0.19(1)	0.34(1)	57.6	44.32
(3) Fe_7Tb_4 3K, 6.5T	Fe(1)	0.49[b]	0.12(1)	0.43(1)	62.7	46.05
	Fe(2)	0.46[b]	0.19(1)	0.43(1)	62.7	39.84
	Fe(3)	0.44[b]	0.29(1)	0.43(1)	62.7	35.65
	Fe(4)	0.50[b]	-0.08(1)	0.43(1)	62.7	45.23
	Fe(5)	0.50[b]	-0.08(1)	0.43(1)	62.7	45.23
	Fe(6)	0.50[b]	0.17(1)	0.43(1)	62.7	37.40
	Fe(7)	0.50[b]	0.17(1)	0.43(1)	62.7	37.40
(4) Fe_7Dy_4 3 K	Fe(1)	0.50(1)	0.20(1)	0.43(1)	51.9	39.06
	Fe(2)	0.48(2)	0.15(1)	0.43(1)	51.9	42.52
	Fe(3)	0.45(1)	0.45(1)	0.43(1)	51.9	41.31
	Fe(4)	0.50(1)	0.09(1)	0.43(1)	51.9	39.02
	Fe(5)	0.50(1)	0.09(1)	0.43(1)	51.9	39.02
	Fe(6)	0.48(2)	0.04(1)	0.43(1)	51.9	41.15
	Fe(7)	0.48(2)	0.04(1)	0.43(1)	51.9	41.15
(4) Fe_7Dy_4 3K, 6T	Fe(1)	0.50[b]	0.09(1)	0.44(1)	64.1	44.53
	Fe(2)	0.48[b]	0.10(1)	0.44(1)	64.1	37.77
	Fe(3)	0.45[b]	0.11(1)	0.44(1)	64.1	35.53
	Fe(4)	0.50[b]	0.02(1)	0.44(1)	64.1	44.65
	Fe(5)	0.50[b]	0.02(1)	0.44(1)	64.1	44.65
	Fe(6)	0.48[b]	-0.02(1)	0.44(1)	64.1	37.59
	Fe(7)	0.48[b]	-0.02(1)	0.44(1)	64.1	37.59

[a] Relative to α-Fe at room temperature. [b] Fixed values. [c] For magnetically-split spectra the quadrupole shifts, $\varepsilon = \frac{1}{2}\Delta E_Q(3\cos^2\varphi - 1)$. φ - Euler angle between the B_{int} and the main electrical field gradient (EFG) principal axis (V_{zz}).[d] Constrained to the same value for all sites. δ is the isomer shift, ΔE_Q - quadrupolar splitting, θ - angle between B_{eff} and direction of γ-rays. B_{eff} - hyperfine field. The statistical errors are given in parentheses. The estimated absolute errors on B_{eff} are ± 0.05 mm/s. The relative areas for the doublets and sextets have been constrained to the 1:1:1:2:2 ratio.

*Given that spectra for all compounds at 40K and higher temperatures gave very similar hyperfine parameters to the published ones (V. Mereacre, et al., *Chem.-Eur. J.*, 2011, **17**, 123) (taking into consideration the compensation of isomeric shifts for second order Doppler shift), their parameters are not given.

Table S2: Calculated bond-lengths (Å) and bond-angles (°) of Fe7 core with oxygen in **2** (Fe7Gd4) polynuclear cluster show good agreement with experiments.

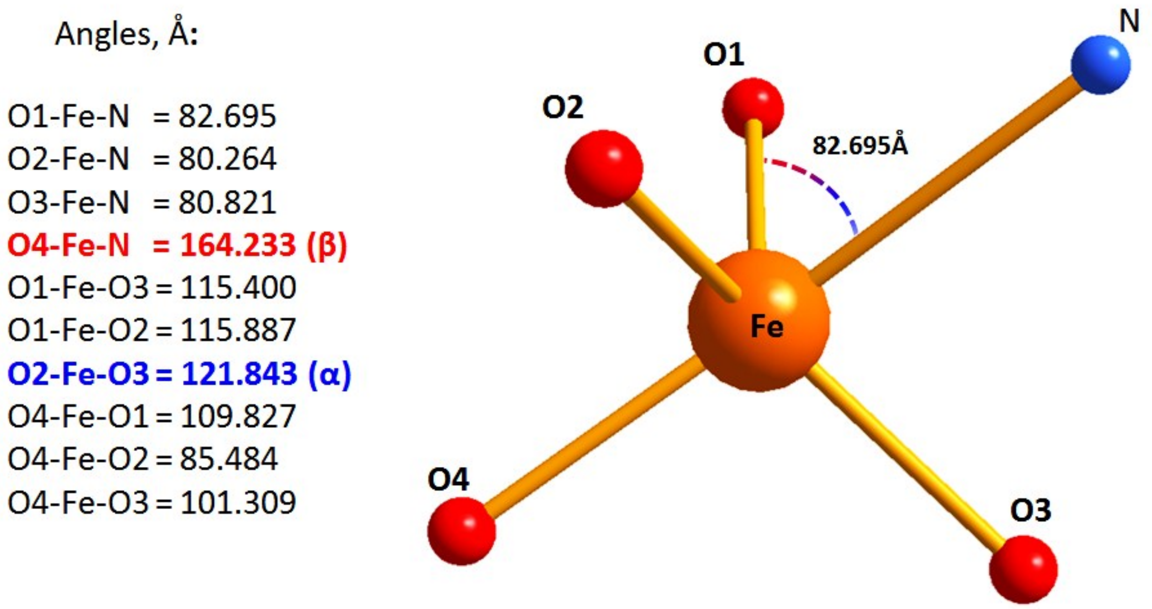
2 Gd4Fe7	**Avg. Bond-length (Å)**		**2** Gd4Fe7	**Bond-angle (°)**	
	Expt.	**Theory**		**Expt.**	**Theory**
Fe-O	2.06	2.01	**Fe1-O-Fe4** **Fe1-O-Fe5** **Fe1-O-Fe(2,3,6,7)/** **Fe4-O-Fe(2,3,6,7)/** **Fe5-O-Fe(2,3,6,7)/**	97.7º; 93.9º 94.5º; 94.9º 119.9º - 134.6º.	95.14º; 94.52º 97.88º; 96.56º 121.30º - 137.80º

Geometry index (τ) for 5-coordinated Fe(3) atom in {Fe_7Ln_4} complexes

To distinguish whether the geometry of the Fe(3) coordination center is trigonal bipyramidal or square pyramidal, the τ parameter was calculated according to Addison et al. [R1]:

$$\tau = \frac{\beta - \alpha}{60^\circ} \approx -0.01667\alpha + 0.01667\beta \qquad (1)$$

where: β > α are the two greatest valence angles of the coordination center (Fig. S8). When τ is close to 0 the geometry is similar to square pyramidal, while if τ is close to 1 the geometry is similar to trigonal bipyramidal.



Angles, Å:

O1-Fe-N = 82.695
O2-Fe-N = 80.264
O3-Fe-N = 80.821
O4-Fe-N = 164.233 (β)
O1-Fe-O3 = 115.400
O1-Fe-O2 = 115.887
O2-Fe-O3 = 121.843 (α)
O4-Fe-O1 = 109.827
O4-Fe-O2 = 85.484
O4-Fe-O3 = 101.309

Figure S7: Coordination environment of pentacoordinated Fe(3) atom in complex **2**.

τ = -0.01667*121.445 + 0.01667*164.013 = 0.7096 (for complex **1**, Fe_7Y_4)

τ = -0.01667*121.843 + 0.01667*164.233 = 0.7067 (for complex **2**, Fe_7Gd_4)

τ = -0.01667*121.816 + 0.01667*164.585 = 0.7129 (for complex **3**, Fe_7Tb_4)

τ = -0.01667*121.544 + 0.01667*164.221 = 0.7114 (for complex **4**, Fe_7Dy_4)

[R1] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.