SUPPLEMENTARY MATERIAL TO THE ARTICLE:

Direct Observation of the Role of Lanthanides in Stabilizing a Ferromagnetic Spin Orientation in a Weak Fe^{III}-Fe^{III} Antiferromagnet

Authors: Hua Xiang, Valeriu Mereacre, Yanhua Lan, Tong-Bu Lu, Christopher E. Anson and Annie K. Powell

Synthesis of [Fe^{III}₂Dy^{III}₂(OH)₂(L¹)₂(HL²)₂(NO₃)₄(H₂O)_{1/2}(MeOH)_{1/2}]·6MeCN (2·6MeCN)

The addition of Fe^{II}(ClO₄)₂·6H₂O (363 mg, 1.0 mmol) and Dy(NO₃)₃·6H₂O (457 mg, 1.0 mmol) to a stirred solution of 2,3-dihydroxybenzaldehyde (138 mg, 1.0 mmol), furfurylamine (98 mg, 1.0 mmol), and triethylamine (101mg, 1.0 mmol) in CH₃OH/MeCN (40 mL) produce black solution. After stirring at room temperature for 40 minutes, the solution was filtered and the filtrate was evaporated slowly at room temperature. After one week, black block-shaped crystals of **2**isolated from the solution, yield: 128 mg, 16% based on Dy(NO₃)₃. Found: C 33.21, H 2.79, N 7.96; C₄₄H₄₃N₉O₂₈Fe₂Dy₂ (loss of three MeCN) requires C 33.62, H 2.79, N 7.93%. v_{max} (KBr)/cm⁻¹: 3436 (s, br), 1646 (s), 1590 (m), 1549 (m), 1484 (s), 1446 (s), 1385 (vs), 1288 (s), 1252 (s), 1211 (s), 1172 (m), 1084 (w), 1030 (m), 869 (m), 786 (m), 744 (s), and 587 (m).

 $[Fe^{III}_{2}Y^{III}_{2}(OH)_{2}(L^{1})_{2}(HL^{2})_{2}(NO_{3})_{4}(H_{2}O)_{1\frac{1}{2}}(MeOH)_{\frac{1}{2}}]$ •6MeCN (1·6MeCN) Compound 1was obtained by the same procedure using $Y(NO_{3})_{3}$ •6H₂O in place of Dy(NO₃)₃ •6H₂O. Black crystals (547 mg, 25% based on $Y(NO_{3})_{3}$) were formed after about one week.

Found: C 35.06, H 2.91, N 7.60; $C_{38.5}H_{35}N_6O_{28}Fe_2Y_2$ (loss of six MeCN) requires C 35.05, H 2.67, N 6.37%. v_{max} (KBr)/cm⁻¹: 3440 (s, br), 1641 (s), 1588 (m), 1551 (m), 1482 (s), 1450 (s), 1385 (s), 1286 (s), 1245 (s), 1210 (s), 1173 (m), 1084 (w), 1033 (m), 870 (m), 788 (m), 746 (s), and 582 (m).

Physical measurements: Magnetic susceptibility data (1.8-300K) were collected on powdered samples of a SQUID-based sample magnetometer on Quantum Design model MPMS-XL instrument in a 0.1 T applied magnetic field. Magnetization isotherm was collected at 2, 3 - 5K between 0 and 7 T. All data were corrected for the contribution of the sample holder and diamagnetism of the samples estimated from Pascal's constants.

The Mössbauer spectra were required using a conventional spectrometer in the constant – acceleration mode equipped with ⁵⁷Co source (3.7 GBq) in rhodium matrix. Isomer shifts are given relative to α -Fe at room temperature. The sample was inserted inside an Oxford Instruments Mössbauer-Spectromag 4000 Cryostat which has a split- pair superconducting magnet system for applied fields up to 5 T, with the field of the sample oriented perpendicular to the gamma-ray direction, while the sample temperature can be varied between 3.0 and 300 K.



Figure S1. Field dependence of magnetization at low temperatures for 1 (Fe₂Y₂).

Electronic Supplementary Material (ESI) for Chemical Communications This journal is O The Royal Society of Chemistry 2013



Figure S2. Field dependence of magnetization at low temperatures for 2 (Fe₂Dy₂).



Figure S3. Plots of in-phase (left) and out-of-phase (right) ac susceptibility signals vs. temperature for 2 (Fe₂Dy₂) at the indicated oscillation frequencies.



Figure S4. Plots of in-phase (left) and out-of-phase (right) ac susceptibility signals vs. frequency for 2 (Fe₂Dy₂) at 1.8 K under the indicated external dc fields.

Table 1. Mössbauer parameters for 1 at 3K in zero- and applied external magnetic field 5 T.

T, K; B _{appl}	δ , mm/s	$\Delta E_{\rm Q}$ or ε , mm/s	<i>Г</i> , mm/s	B _{eff} , T
3; 0 T	0.51(1)	0.95(1)	0.41(2)	
3; 5 T	0.51(2)	0.13(1)	0.81(1)	47.6



Figure S5. ⁵⁷Fe Mössbauer spectra for **2** at 20 K and 3K in zero- and applied external magnetic fields.

T, K; B _{appl}	$\delta^{[a]}$, mm/s	$\Delta E_{\rm Q}$ or ϵ , ^[b] mm/s	Г, mm/s	B _{eff} , T
20	0.513(1)	0.89(8)	0.63(1)	
3, 0T	0.513	0.17(1)	0.47(3)	52.2
3K, 1T	0.513	0.19(1)	0.42(2)	51.7
3K, 3T	0.513	0.13(1)	0.45(1)	49.8
3K, 5T	0.513	0.10(1)	0.43(1)	48.0

Table 2. Mössbauer parameters for 2 at various temperatures and applied external magnetic fields.

^[a]Relative to α -Fe at room temperature; δ - isomer shift. ^[b]For magnetically-split spectra the quadrupole shifts, $\varepsilon = \frac{1}{2}\Delta E_Q(3\cos^2\varphi - 1)$. φ - angle between the internal hyperfine field, B_{hf} and the main electrical field gradient (EFG) principal axis (V_{zz}), ΔE_Q – quadrupole splitting. B_{eff} – effective hyperfine field. The statistical errors are given in parentheses. $B_{eff} = B_{hf} + B_{appl}$

Electronic Supplementary Material (ESI) for Chemical Communications This journal is The Royal Society of Chemistry 2013



Figure S6. X - ray powder diffraction patterns measured at room temperature for complexes 1 and 2.