Supplementary Information

Novel Fe_4 cluster topology from a new hexadentate chelate: magnetic analysis by experimental, DFT, and magnetostructural correlation methods

Alexander Diodati,[1] Christianna L. Brantley,[1] Amelia Figueroa,[1] Juan E. Peralta,[2] Lukasz Dobrzycki,[1] Khalil A. Abboud,[1] and George Christou *[1]

(christou@chem.ufl.edu)

[1] *Department of Chemistry, University of Florida, Gainesville, Florida 32611, USA.*

[2] *Department of Physics, Central Michigan University, Mount Pleasant, Michigan 48859, USA*

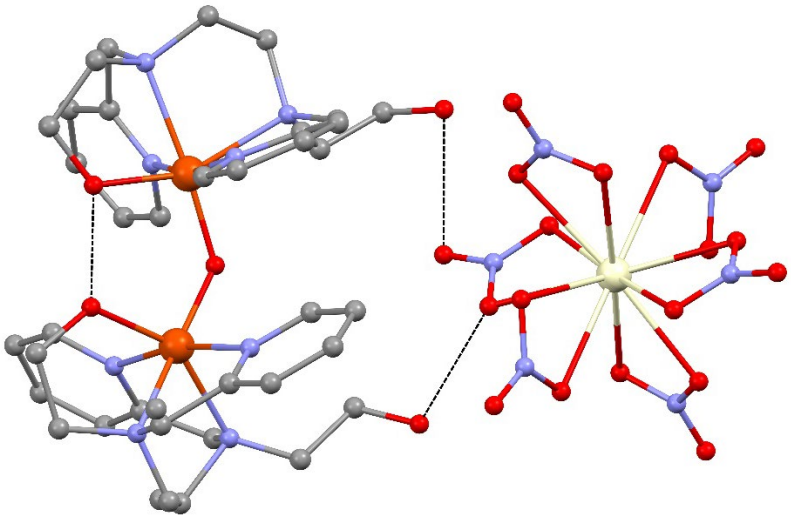

Figure S1. Hydrogen-bonding within the cation of **1**, and between it and the $[Ce(NO_3)_6]^{3-}$ anion.

Table S1. Bond valence Sum Calculations for Fe and Ce atoms in **1** and **2**

Complex	Atom	Fe^{II}	Fe^{III}	Assignment[a]
1	Fe1	2.52	**2.93**	Fe^{III}
	Fe2	2.50	**2.90**	Fe^{III}
2	Fe1	2.38	**2.75**	Fe^{III}
	Fe2	2.42	**2.80**	Fe^{III}
	Fe3	2.78	**3.31**	Fe^{III}
	Fe4	2.55	**3.04**	Fe^{III}
Complex	Atom	Ce^{III}	Ce^{IV}	Assignment
1	Ce1	**2.78**	2.52	Ce^{III}

[a] The value in bold is the oxidation state closest to the one for which it was calculated. The oxidation state of the metal is the nearest integer to the bold value.

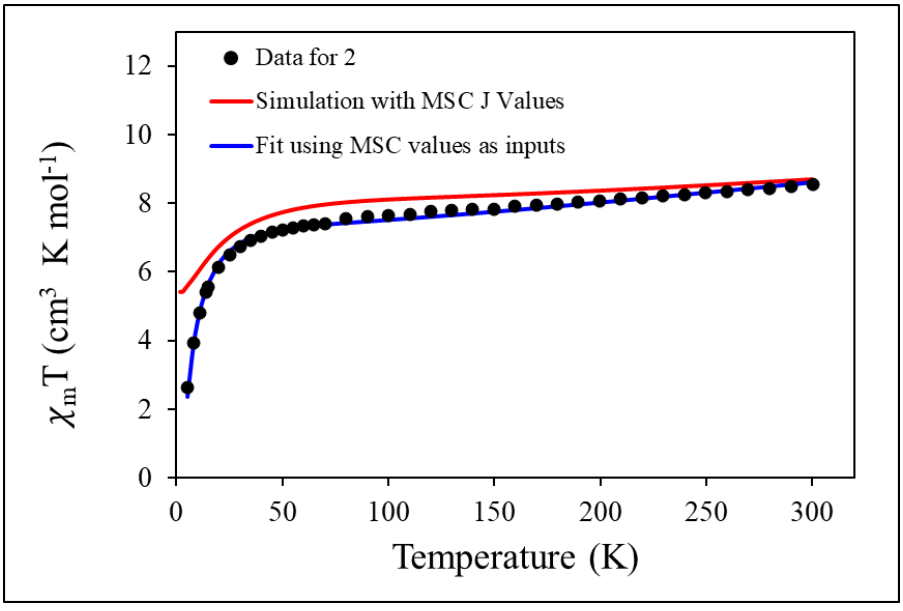

Figure S2. Plot of experimental $\chi_m T$ *vs* T data (●) for complex **2** in the 5.0 - 300 K range in a 0.1 T DC field, as in Figure 5. The red line is now the simulation using the MSC values as inputs, and the blue line is the fit using the MSC or DFT inputs.

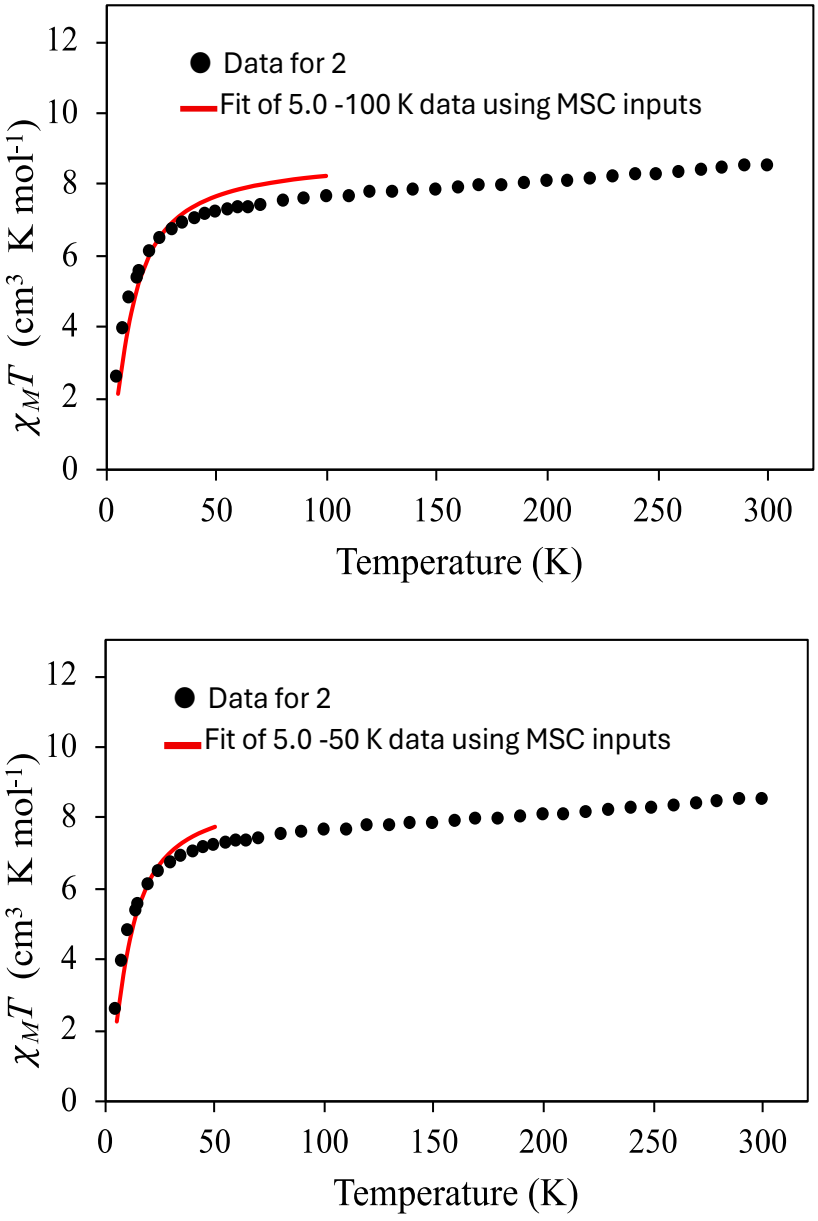

Figure S3. Plot of experimental $\chi_m T$ *vs* T data (●) for complex **2** in the 5.0 - 300 K range in a 0.1 T dc field. The red line is the fit of the (top) 5.0-100 K data and (bottom) 5.0-50 K data to *J*″ using its MSC value as input.

Table S2. Exchange interactions *J, J′,* and *J″* for **2** (not symmetry-averaged) from MSC calculations, DFT computations, and PHI fits of experimental data in the 5.0 K – 300 K range with various inputs. $J_{1,2}$ values reported were fit independently from the other *J*-couplings present.

J_{ij}	Fe-O (av, Å)	Fe-O-Fe (deg)	J_{MSC}	J_{DFT}	$J_{FIT, MSC}$	$J_{FIT, DFT}$	$J_{FIT, 0}$	$J_{FIT, -10}$	$J_{FIT, -20}$
$J_{1,3}$	1.976	117.0	-14.9	-7.1	3.0	-23.5	-121.1	-0.1	4.2
$J_{3,2}$	1.974	114.6	-13.6	-4.8	-28.9	0.9	-139.1	-0.7	-34.1
$J_{2,4}$	1.979	113.5	-14.6	-7.9	-22.8	-0.1	-197.4	-0.2	-31.0
$J_{1,4}$	1.976	117.7	-14.9	-9.4	1.2	-23.7	-182.0	-0.2	-1.2
$J_{3,4}$	1.977	175.9	-75.6	-78.4	-91.8	-91.8	-103.6	-0.8	-151.8
$J_{1,2}$	2.819	179.8	-0.01	-0.6	-0.6	-0.7	-	-	-
TIP					400	400	400	400	400

[a] Using J_{MSC} inputs.

Table S3. Exchange interactions *J* and *J′* for **2** (not symmetry-averaged) from MSC calculations, DFT computations, and PHI fits of experimental data in the 70 K – 300 K range with various inputs

J_{ij}	Fe-O (av, Å)	Fe-O-Fe (deg)	J_{MSC}	J_{DFT}	$J_{FIT, MSC}$	$J_{FIT, DFT}$	$J_{FIT, 0}$	$J_{FIT, -10}$	$J_{FIT, -20}$
$J_{1,3}$	1.976	117.02	-14.9	-7.1	-7.0	+1.26	-9.1	+18.3	-7.1
$J_{3,2}$	1.974	114.64	-13.6	-4.8	-17.3	-23.4	-152.5	-25.9	-10.0
$J_{2,4}$	1.979	113.54	-14.6	-7.9	-15.1	-29.6	-191.0	-91.3	-9.8
$J_{1,4}$	1.976	117.74	-14.9	-9.4	-11.6	+3.0	-200.8	+25.4	-26.4
$J_{3,4}$	1.977	175.94	-75.6	-78.4	-63.9	-93.7	388.2	-69.1	-44.5
TIP					400	400	400	400	400

[a] Using J_{MSC} inputs.

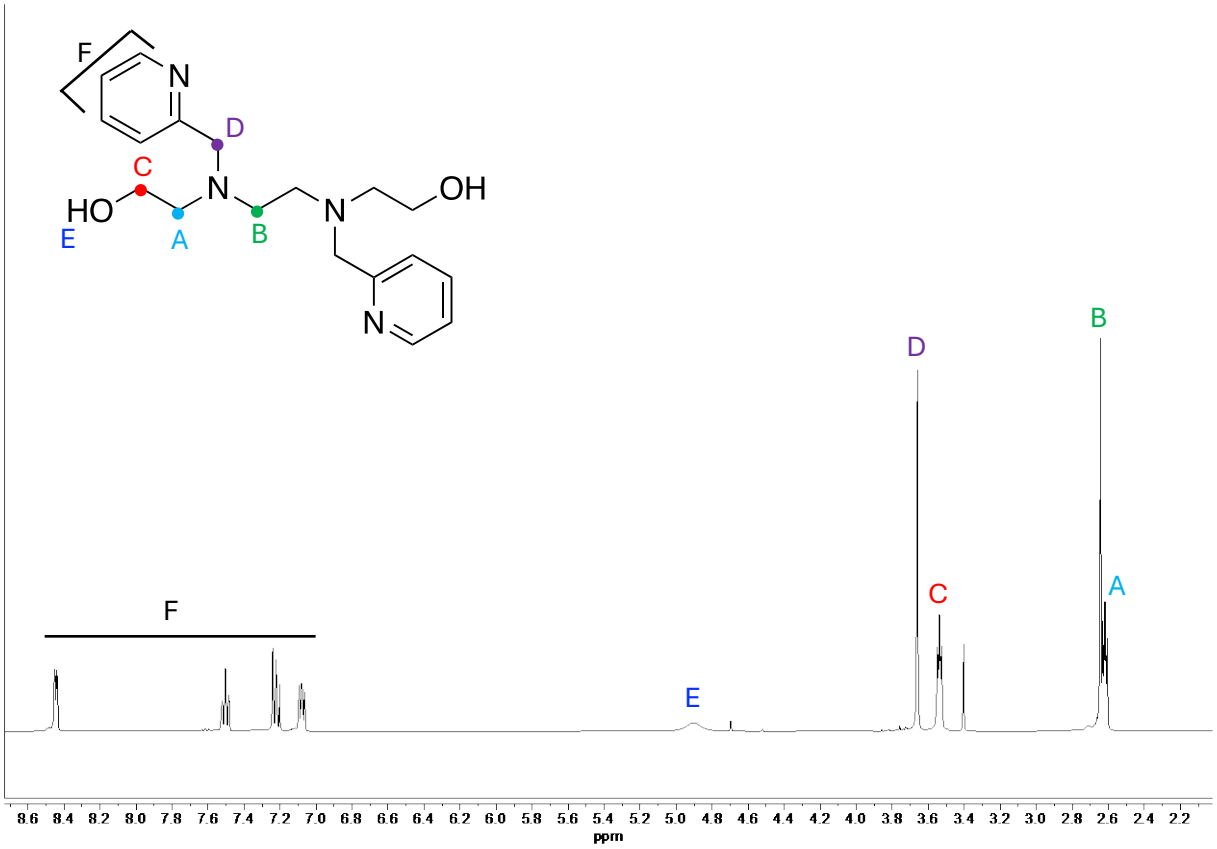

Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N,N'*-bis(2-pyridylmethyl)-*N,N'*-bis(2-hydroxyethyl)ethylenediamine ($bphnH_2$). See main text for specific details.

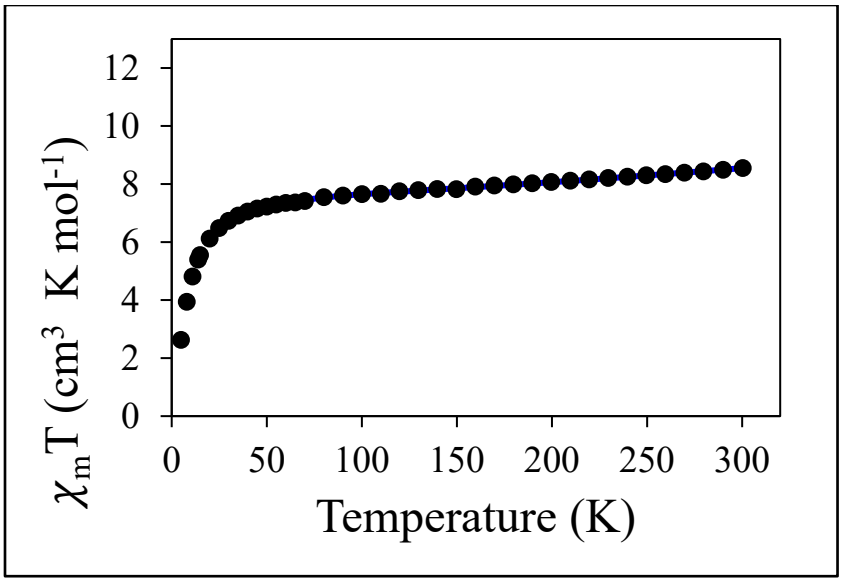

Figure S5. Plot of experimental $\chi_m T$ *vs* T data (●) for complex **2** in the 5.0 - 300 K range in a 0.1 T dc field. The blue line is the 5-J fit (excluding J_{12}) in Table S3 of the 70.0-300 K data using its MSC values as inputs.