SUPPORTING INFORMATION

Structural and Magnetic Analysis of a Family of Structurally Related Iron(III)-oxo Clusters of Metal Nuclearity Fe_8, $Fe_{12}Ca_4$, and $Fe_{12}La_4$

Alok P. Singh [1], ChristiAnna L. Brantley [1], Kenneth Hong Kit Lee [1], Khalil A. Abboud [1], Juan E. Peralta [2] and George Christou [1]

[1] Department of Chemistry, University of Florida, Gainesville, FL 32611, USA
[2] Department of Physics and Science of Advanced Materials, Central Michigan University, Mount Pleasant, MI 48859, USA

Table S1

Bond valence sums[a] and assignments for the Fe atoms in the asymmetric unit of **1**.

Atom	Fe^{2+}	Fe^{3+}
Fe1	2.89	3.08
Fe2	2.72	2.91
Fe3	2.85	3.05
Fe4	2.75	2.95
Fe5	2.86	3.05
Fe6	2.75	2.94
Fe7	2.88	3.08
Fe8	2.80	3.00

[a] For Fe, the metal oxidation state is the nearest integer to the underlined value, which is the closest to the charge for which it was calculated.

Table S2

Bond valence sums and assignments for O atoms in the cation of **1**.

Atom	BVS [a]	Assignment
O1	1.86	O^{2-}
O2	1.86	O^{2-}
O3	1.87	O^{2-}
O4	1.91	O^{2-}
O112	1.55 [b]	O^{2-}
O5	0.98	OH^{-}
O6	1.00	OH^{-}
O7	1.02	OH^{-}
O8	0.81	OH^{-}
O111	1.24	OH^{-}
O11	1.90	$PhPO_2^{-}$
O12	1.88	$PhPO_2^{-}$
O21	1.92	$PhPO_2^{-}$
O22	1.84	$PhPO_2^{-}$
O31	1.93	$PhPO_2^{-}$
O32	1.93	$PhPO_2^{-}$
O41	1.94	$PhPO_2^{-}$
O42	1.89	$PhPO_2^{-}$
O51	1.86	$PhPO_2^{-}$
O52	1.87	$PhPO_2^{-}$
O61	1.91	$PhPO_2^{-}$
O62	1.91	$PhPO_2^{-}$
O71	1.94	$PhPO_2^{-}$
O72	1.94	$PhPO_2^{-}$
O81	1.87	$PhPO_2^{-}$
O82	1.93	$PhPO_2^{-}$
O91	1.92	$PhPO_2^{-}$
O92	1.89	$PhPO_2^{-}$
O101	1.89	$PhPO_2^{-}$
O102	1.89	$PhPO_2^{-}$

[a] Non-, singly-, and doubly-protonated O atoms have BVS values of ~1.8 to 2.0, ~1.0 to 1.2, and ~0.2 to 0.4, although H-bonding can affect the ranges. [b] Decreased from a typical O^{2-} value due to hydrogen-bonding with the $NHEt_3^{+}$ cation.

Table S3

Bond valence sums[a] and assignments for the Fe and O atoms in the asymmetric unit of **2**.

Atom	Fe^{2+}	Fe^{3+}
Fe1	2.54	3.03
Fe2	2.67	3.18
Fe3	2.67	3.18
Fe4	2.56	2.05
Fe5	2.62	3.1
Fe6	2.60	2.96
Atom	BVS	Assignment
O1	1.94	O^{2-}
O2	1.92	O^{2-}
O3	1.96	O^{2-}
O4	1.99	O^{2-}
O5	2.06	RO^{-}
O6	1.96	O^{2-}
O7	1.94	RO^{-}
O14	2.12	RCO_2^{-}
O16	2.10	RCO_2^{-}
O23	2.16	RCO_2^{-}
O25	2.11	RCO_2^{-}

[a] For Fe, the metal oxidation state is the nearest integer to the underlined value, which is the closest to the charge for which it was calculated. For O, values in the ~1.8–2.0, ~1.0–1.2, and ~0.2-0.4 indicate non-, single-, and double-protonation, respectively.

Table S4

Bond valence sums[a] and assignments for the Fe and O atoms in the asymmetric unit of **3**.

Atom	Fe^{2+}	Fe^{3+}
Fe1	2.78	2.97
Fe2	2.79	2.99
Fe3	2.73	2.92
Fe4	2.73	2.92
Fe5	2.67	2.86
Fe6	2.74	2.94
Atom	BVS	Assignment
O1	1.72	O^{2-}
O2	1.73	O^{2-}
O3	1.83	O^{2-}
O4	2.07	O^{2-}
O5	1.14	OH^{-}
O6	2.01	O^{2-}
O7	1.15	OH^{-}

[a] For Fe, the metal oxidation state is the nearest integer to the underlined value, which is the closest to the charge for which it was calculated. For O, values in the ~1.8–2.0, ~1.0–1.2, and ~0.2-0.4 indicate non-, single-, and double-protonation, respectively.

Table S5

RMSD calculations for **1** with **2**.

Complex **1**	Complex **2**	Deviation (Å)
Fe3	Fe3	0.012
Fe2	Fe5	0.060
Fe4	Fe4	0.071
Fe1	Fe2	0.148
Fe5	Fe3	0.096
Fe6	Fe5	0.083
Fe8	Fe5	0.083
Fe7	Fe2	0.177
	Total	0.109

Table S6

RMSD calculations for **1** with **3**.

Complex **1**	Complex **2**	Deviation (Å)
Fe8	Fe2	0.047
Fe6	Fe3	0.133
Fe5	Fe4	0.070
Fe1	Fe1	0.086
Fe7	Fe1	0.127
Fe3	Fe4	0.103
Fe2	Fe2	0.075
Fe4	Fe3	0.100
	Total	0.096

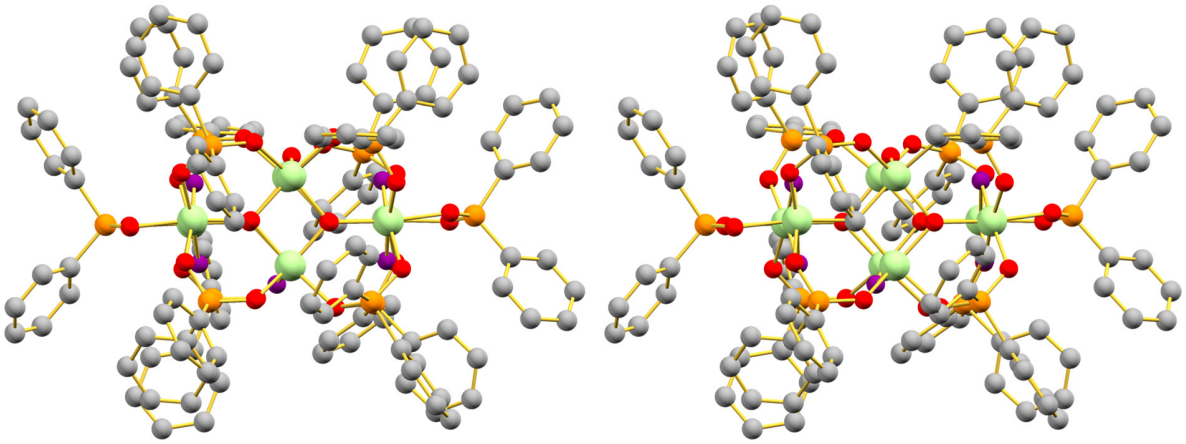

Figure S1. Stereopair of the complete anion of **1**. Color code: Fe^{3+} light green, O red, P orange, C gray (H atoms omitted for clarity).

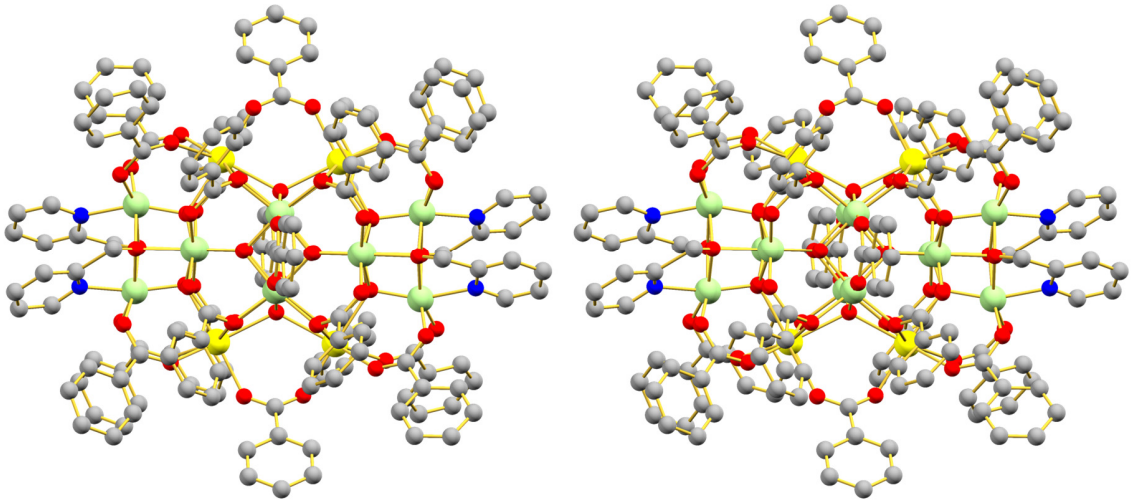

Figure S2. Stereopair of complex **2**. Color code: Fe^{3+} light green, Ca^{2+} yellow, O red, N blue, C gray (H atoms omitted for clarity).

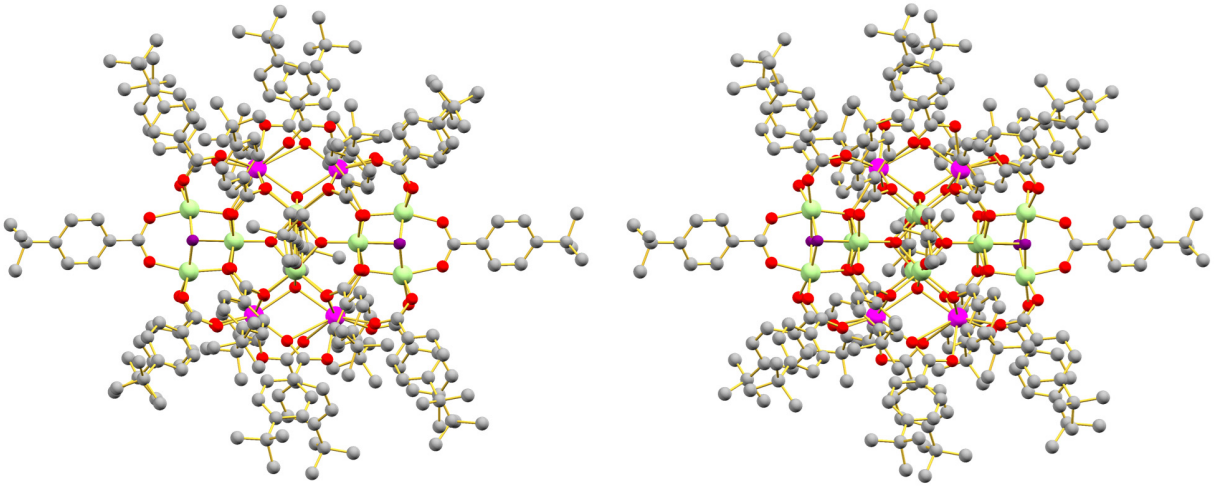

Figure S3. Stereopair of complex **3**. Color code: Fe^{3+} light green, La^{3+} magneta, O red, OH^- purple, C gray (H atoms omitted for clarity).

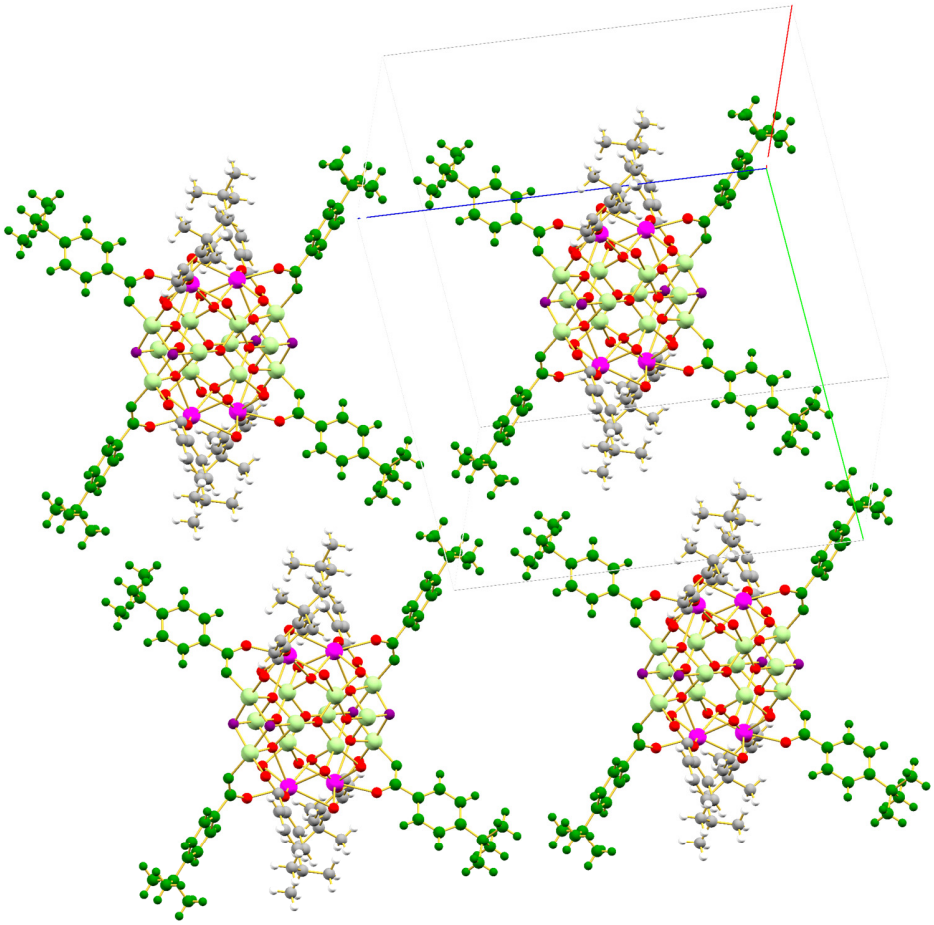

Figure S4. Expanded version of Figure 10 showing the near-perpendicular alignment of 4-^{t}Bu-benzoate ligands for four molecules of **3**. The *a* axis is the red line, *b* axis is the lime green line, and the *c* axis is the blue line. Color code: Fe^{3+} light green, La^{3+} magenta, O red, OH^{-} purple, C gray (some C and H atoms are omitted for clarity).

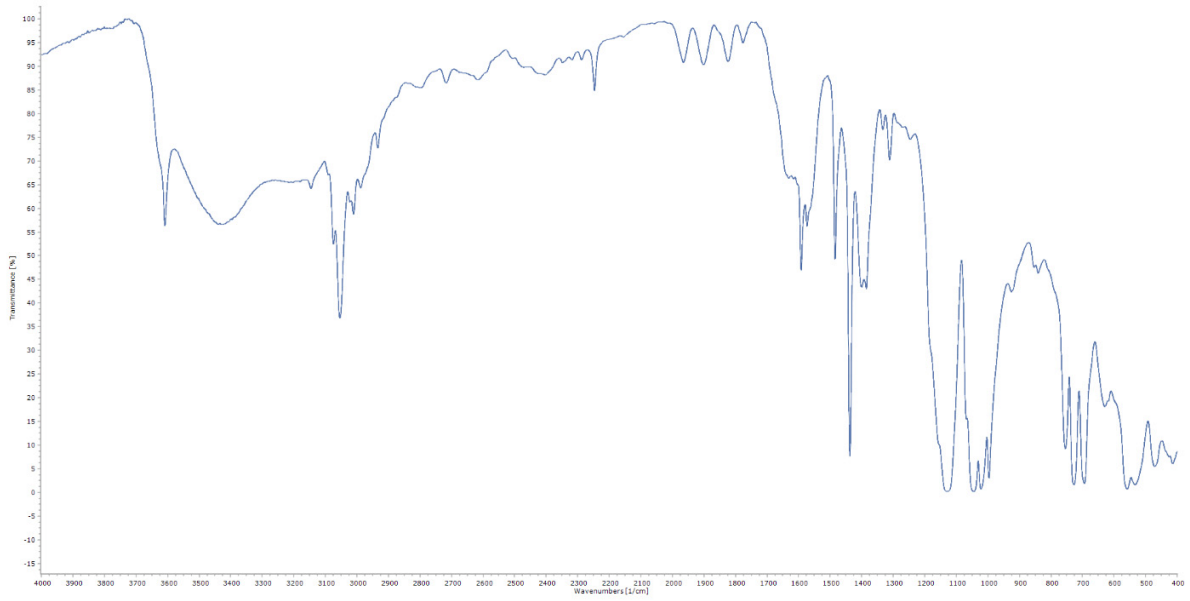

Figure S5. Infrared spectrum of **1**.

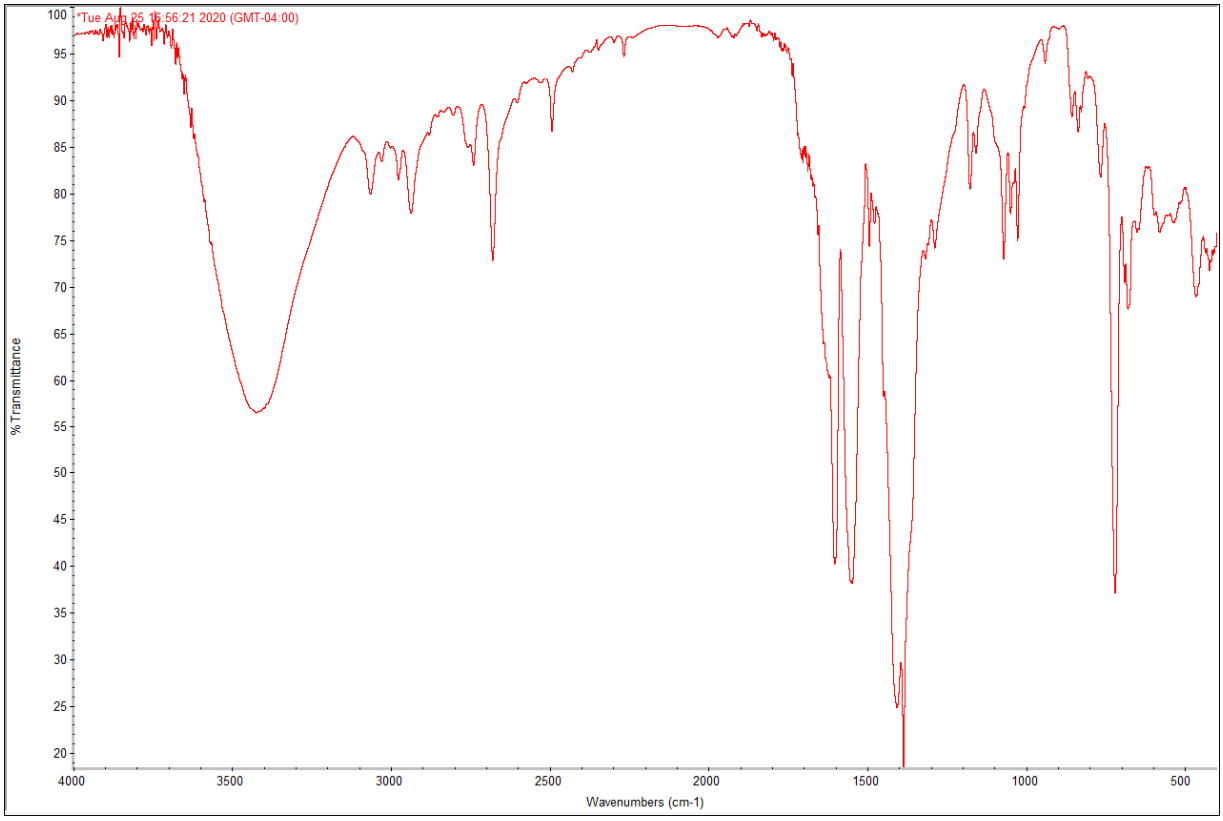

Figure S6. Infrared spectrum of **2**.

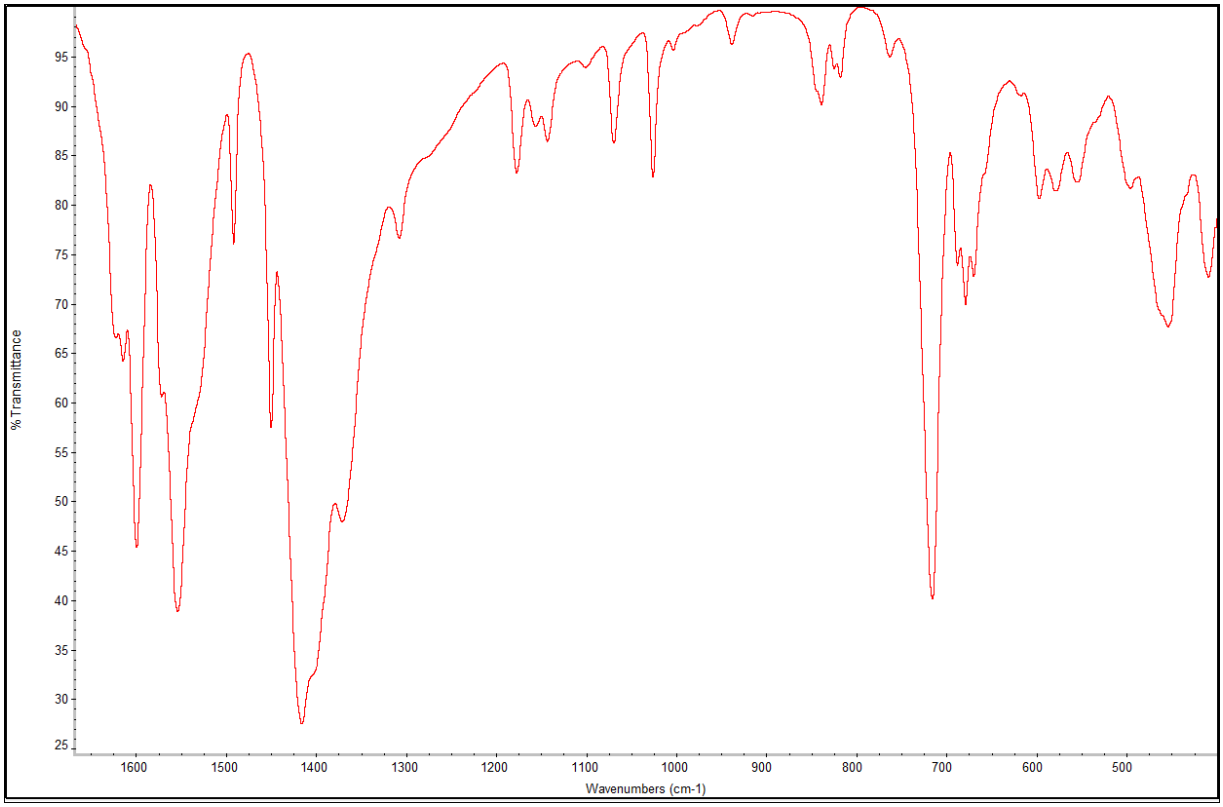

Figure S7. Infrared spectrum of **3**.