Supporting Information

Triple-stranded ferric helices: a π - π interaction-driven structural

hierarchy of Fe5, Fe7, and Fe17 clusters

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$[Fe^{III}_{17}(L)_{9}(\mu_{3}-O)_{13}(\mu_{3}-OH)](PF_{6})_{6}\cdot 2H_{2}O\cdot 8CH_{3}CN (3\cdot 2H_{2}O\cdot 8CH_{3}CN):$

A methanolic solution (3 mL) of H₂L (21.9 mg, 0.06 mmol) and triethylamine (16.5 μ L, 0.12 mmol) was added to a solution of FeCl₂·4H₂O (23.9 mg, 0.12 mmol) in methanol (7 mL). The reaction mixture was stirred and a solution of triazole (4.0 mg, 0.06 mmol) in methanol (2.5 mL) was added and the resultant mixture heated for 10 minutes. After cooling, the solution was filtered and evaporated to yield a brown solid. The dried brown solid was dissolved with NH₄PF₆ (19.6 mg, 0.12 mmol) in methanol/acetonitrile (4:1) and left for slow evaporation. The recrystallization was repeated several times to give dark-brown crystals of [Fe^{III}₁₇(L)₉(μ ₃·O)₁₃(μ ₃·OH)](PF₆)₆·2H₂O·8CH₃CN (**3**) and a pentanuclear triazole bridged [Fe5] cluster, [Fe₅(L)₃(m₃-O)(trz)₃]Cl₅^[1] in extremely low yield. The crystals were visually indistinguishable, so while a single crystal structure could be determined for compound **3**, full analyses were impossible at this time.

[1] Triazole bridged [Fe5] cluster, T. Shiga, M. Noguchi, G. N. Newton, H. Oshio, unpublished result.



Figure S1. Mössbauer spectra of **2** at 20 K (top) and 300 K (bottom). Fitting parameters given in Table S1.

Table S1. Mössbauer parameters of **2**. Least-square-fit parameters; δ_{IS} , ΔE_Q , Γ , and A are the isomer shifts compared to metallic iron, quadrupole splitting, Lorentzian linewidth, area ratio, respectively.

Temp.	Spin state	$\delta_{\rm IS} \ ({\rm mm \ s^{-1}})$	$\Delta E_{\rm Q} \ ({\rm mm \ s^{-1}})$	Γ (mm s ⁻¹)	A (%)
20 K	Fe(III)HS ^[a]	0.534	0.304	0.479	48
	Fe(II)HS	1.212	3.278	0.309	31
	Fe(II)HS	0.994	1.698	0.213	21
300 K	Fe(III)HS	0.535	0.262	0.524	52
	Fe(II)HS	1.136	2.701	0.267	27
	Fe(II)HS	0.770	1.366	0.208	21

Parameters were calculated relative to metallic iron.[a] HS = High-Spin