Enterobactin Protonation and Iron Release: Structural Characterization of the Salicylate Coordination Shift in Ferric Enterobactin

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Supporting Information

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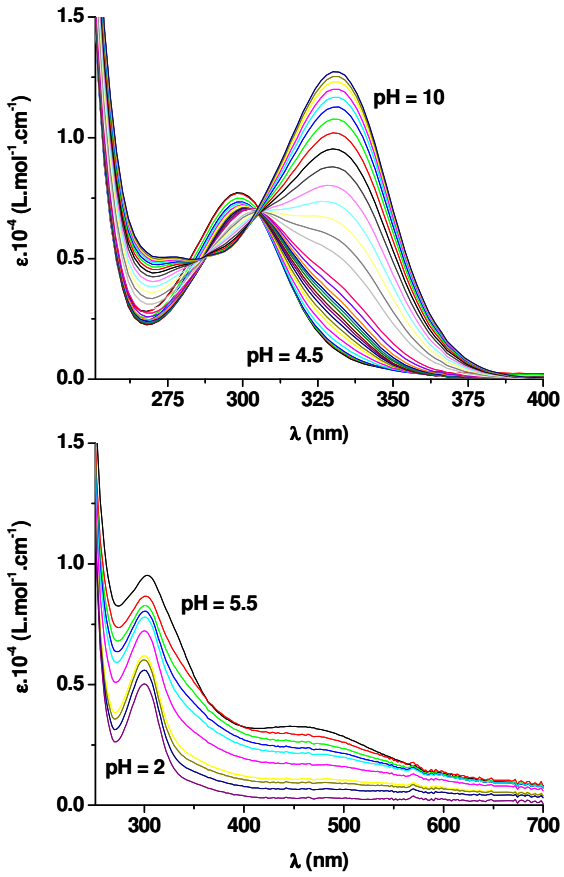

Figure S1. Spectrophotometric titrations of SERSAM by KOH (top) and $[Fe^{III}(SERSAM)]^0$ by HCl (bottom) in water. I = 0.1 (KCl), T = 25.0 °C, l = 1 cm.

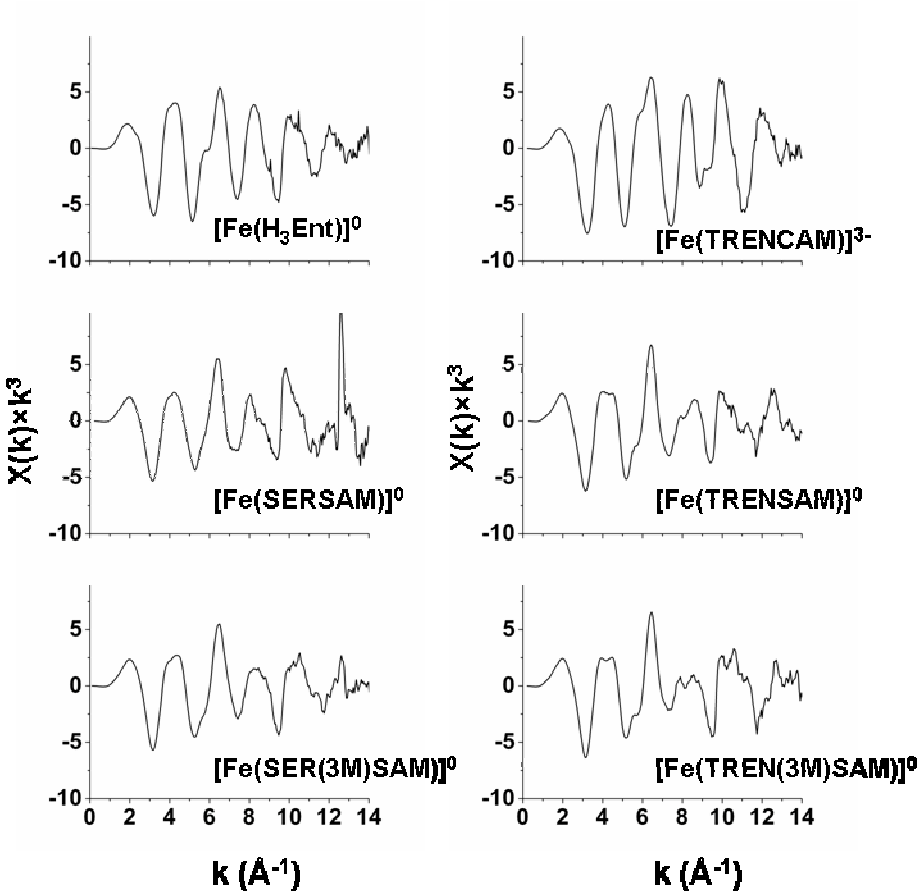

Figure S2. k-space spectra of the studied ferric complexes at 200 K.

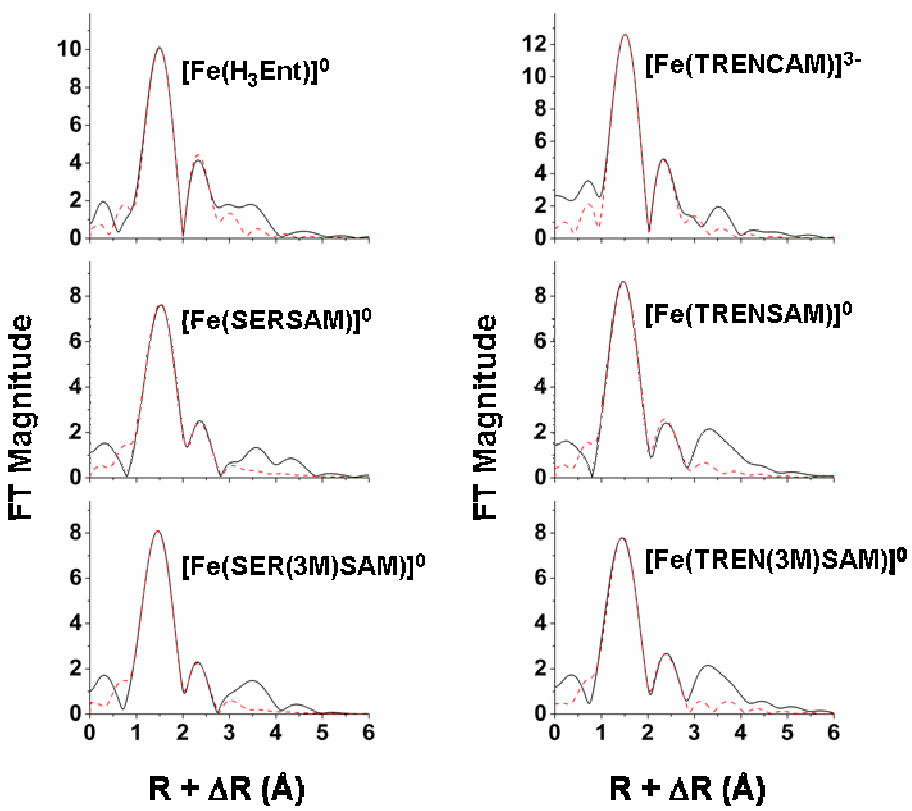

Figure S3. Fourier transforms (solid lines) and R-space fits (dashed lines) of the studied ferric complexes at 200 K.

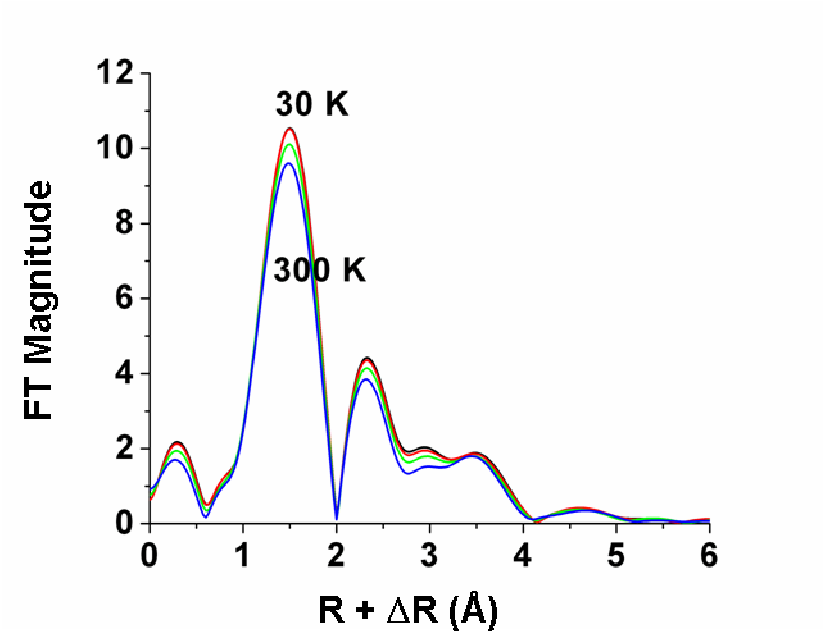

Figure S4. Fourier transforms temperature dependence for $[Fe^{III}(H_3Ent)]^0$.

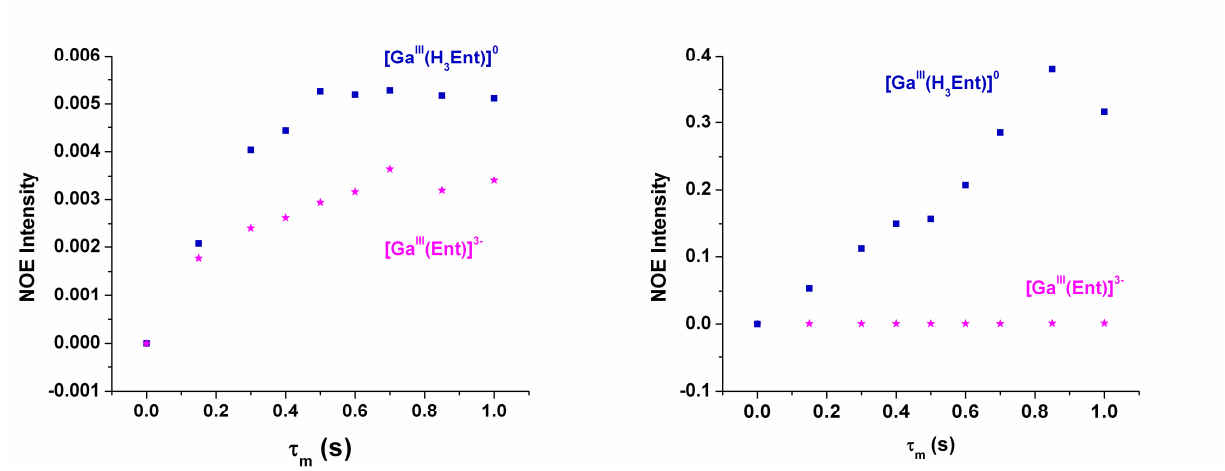

Figure S5. NOE intensities build up for the cross peaks between the amide proton and its two closest protons: the seryl β-proton (H_b, left) and the benzoyl *ortho*-proton (H_d, right).

Complex	N_{idp}	N_{vp}	*R* (30K)	*R* (100K)	*R* (200K)	*R* (300K)
$[Fe^{III}(Ent)]^{3-}$	18	6	6.0 %	6.3 %	6.1 %	6.4 %
$[Fe^{III}(H_3ent)]^0$	18	6	12.1 %	11.9 %	11.5 %	10.7 %
$[Fe^{III}(SERSAM)]^0$	18	6	5.4 %	3.9 %	3.4 %	4.7 %
$[Fe^{III}(SER(3M)SAM)]^0$	18	6	5.1 %	5.3 %	5.4 %	5.8 %
$[Fe^{III}(TRENCAM)]^{3-}$	18	6	10.1 %	10.2 %	10.5 %	10.0 %
$[Fe^{III}(TRENSAM)]^0$	18	4	8.2 %	8.3 %	8.6 %	8.2 %
$[Fe^{III}(TREN(3M)SAM)]^0$	18	6	6.3 %	5.8 %	5.8 %	5.4 %

Table S1. Fitting Parameters Used for EXAFS Spectral Analysis.[a]

[a]Number of independent parameters (N_{idp}), variable parameters (N_{vp}) and *R* factors for each studied complex. The *R* factors are averaged from at least two independent scans.

Complex	ΔH (hartrees)	ΔH (kcal/mol)	Ga-O_{ortho} distance (Å)	Ga-O_{meta} distance (Å)	Ga-$O_{carbonyl}$ distance (Å)	Average Ga-O length (Å)
$[Ga^{III}(Ent)]^{3-}$	-2450.775	-3905555	2.034	1.953	6.211	1.993
			2.029	1.953	6.211	
			2.033	1.956	6.200	
cat-$[Ga^{III}(H_3Ent)]^0$	-2452.536	-3908361	1.835	2.184	5.947	2.010
			1.835	2.185	5.957	
			1.834	2.186	5.945	
sal-$[Ga^{III}(H_3Ent)]^0$	-2452.551	-3908385	1.890	4.444	2.009	1.951
			1.893	4.443	2.013	
			1.893	4.440	2.010	

Table S2. Calculated Heats of Formation, Atomic Distances and Bond Lengths for Different Binding Modes of Gallic Enterobactin.

Complex	N**H**-$\mathbf{H_b}$ distance (Å)	Average N**H**-$\mathbf{H_b}$ distance (Å)	N**H**-$\mathbf{H_d}$ distance (Å)	Average N**H**-$\mathbf{H_d}$ distance (Å)
$[Ga^{III}(Ent)]^{3-}$	3.071	3.063	4.456	4.456
	3.052		4.458	
	3.067		4.456	
cat-$[Ga^{III}(H_3Ent)]^0$	3.440	3.438	4.448	4.449
	3.438		4.450	
	3.435		4.448	
sal-$[Ga^{III}(H_3Ent)]^0$	2.971	2.972	1.956	1.963
	2.972		1.963	
	2.973		1.969	

Table S3. Calculated Proton Distances for Different Binding Modes of Gallic Enterobactin.