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XAS Study of a Metal-Induced Phase Transition by a Microbial Surfactant

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Abstract

The metal-induced micelle-to-vesicle phase change that the ferric complex of the microbially produced amphiphile, marinobactin E (M_E), undergoes has been investigated by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). Marinobactin E is one member of the suite of siderophores, marinobactins A–E, that are used by the source bacterium to facilitate iron acquisition. $Fe(III)-M_E$ undergoes a micelle-to-multilamellar vesicle transition in the presence of $Cd(II)$ and $Zn(II)$. XRD measurements indicate the interlamellar repeat distance of the $Cd(II)$ - and $Zn(II)$ -induced multilamellar vesicles is ~ 5.3 nm. XAS spectra of the sedimented $Cd(II)$ - and $Zn(II)$ -induced multilamellar vesicles suggests hexadentate coordination of $Cd(II)$ and $Zn(II)$ consisting of two monodentate carboxylate ligands and four water ligands. This coordination environment supports the hypothesis that $Cd(II)$ and $Zn(II)$ bridge the terminal carboxylate moiety of two $Fe(III)-M_E$ headgroups, pulling the headgroups together in an arrangement that favors vesicle formation over the formation of micelles. XAS spectra of the $Fe(III)$ center in the sedimented $Cd(II)$ - and $Zn(II)$ -induced vesicles confirm the anticipated six-coordinate geometry of $Fe(III)$ by the M_E headgroup via the two hydroxamate groups and the α -hydroxy amide moiety.

Introduction

Metal chelating surfactants have attracted considerable attention for their ability to self-assemble, thereby presenting an organized interface of metal cations.^{1,2} Assemblies of metal-chelating surfactants have been utilized in a variety of fields such as catalysis,^{3,4} environmental remediation of toxic metals,^{5,6} and magnetic resonance imaging contrast agents.⁷ Some metal chelating surfactants undergo a change in aggregate morphology upon metal coordination.^{8–15} For example, micelles of 4,8-dioctyl-3,9-dioxo-6-hydroxy-4,8-diaza-1,11-undecanedicarboxylate undergo a phase transition to vesicles upon coordination of $Cu(II)$ to the dicarboxylate head group.¹⁶ The phospholipid cardiolipin assembles as a lamellar phase in the absence of metals and forms a reverse-hexagonal phase in the presence of certain divalent metal cations.¹⁷ Marinobactins A–E (M_A-M_E , Figure 1) are a suite of microbial surfactants known as siderophores that also undergo a change in aggregate morphology upon metal coordination.^{18–20} Each marinobactin is composed of the same peptidic headgroup that coordinates $Fe(III)$, and each marinobactin is appended by a different fatty acid tail that confers the amphiphilic properties to these molecules.

Apo-marinobactin E forms spherical micelles that are ca. 4.6 nm in diameter.¹⁸ Upon coordination of 1 equiv of $Fe(III)$, the micellar phase persists, although the diameter of the

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Fe(III)–M_E micelles decreases to ca. 3.5 nm.^{18,19} We recently reported that the addition of Cd(II), Zn(II), La(III), or excess Fe(III) to Fe(III)–M_E micelles induces the formation of ~100–200-nm-diameter multilamellar vesicles.^{18–20} We hypothesized that these metal cations induce vesicle formation by bridging the terminal carboxylate moiety of multiple Fe(III)–M_E headgroups, drawing the headgroups closer together in an arrangement that favors vesicle formation (Scheme 1).^{18,19} The proposed carboxylate–metal bridging mechanism is consistent with the coordination chemistry of these metals with carboxylate-based ligands.²¹ In this investigation, X-ray absorption spectroscopy (XAS) is used to probe the Cd(II), Zn(II), and Fe(III) sites in the Cd(II)- and Zn(II)-induced vesicles of Fe(III)–M_E. XAS results indicate that Cd(II) and Zn(II) are coordinated by two carboxylate ligands and thus function to bridge two Fe(III)–M_E headgroups in the vesicle phase.

Materials and Methods

Definitions

Fe(III)–M_E refers to the iron complex of marinobactin E. Apo-M_E refers to marinobactin E that is not coordinated to a metal.

Materials

Deuterium oxide, deuterium chloride, and sodium deuterioxide were purchased from Cambridge Isotope Laboratories, Inc. Triply deionized water (Barnstead NANOpure II) was used in all experiments. All other chemicals and organic solvents were purchased from EM Science. Apo-M_B, apo-M_D, and apo-M_E were isolated and purified as previously described.^{18,20}

Sample Preparation

D₂O was used as a solvent in place of H₂O for comparison to previous SANS measurements, which were also performed in D₂O.^{18,19} Samples analyzed by DLS consisted of 1.4 mM Fe(III)–M_E in D₂O at pD 6.0. Fe(III)–M_E was prepared by adding 0.9 equiv of Fe(III) to apo-M_E. The concentration of apo-M_E was determined by spectrophotometric titration at 400 nm (i.e., the λ_{max} of Fe(III)–M_E) with a standardized stock solution of Fe(III). Fe(III) was added to apo-M_E from a standardized stock solution of 0.073 M FeCl₃ in 0.05 M DCl in D₂O. The concentration of the Fe(III) stock solution was determined spectrophotometrically with 1,10-phenanthroline at pH 4 after the addition of hydroxylamine: Fe(phen)₃²⁺ with $\lambda_{\text{max}} = 510 \text{ nm}$ $\epsilon = 11\,000 \text{ M}^{-1} \text{ cm}^{-1}$.²³ pD adjustments were accomplished with NaOD and DCl. The standard correction of pD = pH + 0.4 was applied for all titrations in D₂O.

The metal cations were added to Fe(III)–M_E solutions at 25 °C from stock solutions of 1 M CdCl₂ or ZnCl₂ in 0.05 M DCl in 99.9% D₂O and then equilibrated at 37 °C for at least 3 days prior to DLS measurements. Specifically, 2.5 equiv of Cd(II) or Zn(II) per equivalent of Fe(III)–M_E (1.4 mM Fe(III)–M_E, pD 6.0, 37 °C) was added to induce multilamellar vesicle formation, followed by equilibration for 72 h at 37 °C. After equilibration, the Cd(II)- and Zn(II)-induced vesicles were sedimented by centrifugation at 13 200 rpm for 20 min (at 25 °C) in order to concentrate the vesicles for X-ray diffraction (XRD) and XAS measurements.

X-ray Diffraction

X-ray diffraction (XRD) measurements were performed in-house at the Materials Research Laboratory X-ray facility. X-rays were generated using an 18 kW Rigaku rotating anode generator. An average X-ray wavelength of 1.54 Å was used to analyze the sample. Scattered X-rays were collected by an 18-cm-diameter Mar image plate detector at a sample-

to-detector distance of 758 cm. This configuration allowed wavevector transfers (Q) in the range of $0.03 \text{ \AA}^{-1} < Q < 0.45 \text{ \AA}^{-1}$, where $Q = (4\pi/\lambda)\sin(\theta/2)$ and θ represents the X-ray scattering angle. The sedimented Cd(II)- and Zn(II)-induced vesicles were loaded into 2-mm-diameter quartz capillaries (Charles Supper Company) for XRD measurements.

Dynamic Light Scattering

DLS measurements were carried out on a Brookhaven BI-200SM goniometer with an AT9000 digital autocorrelator equipped with a Melles Griot 30 mW HeNe laser ($\lambda = 633 \text{ nm}$). The correlation function itself was calculated between delay times of 5 and $1 \times 10^5 \mu\text{s}$ and analyzed by the method of cumulants.²⁴ Measurements were taken in 12 mm round glass cells in a temperature-controlled toluene bath with the detector set perpendicular (90°) to the incident laser beam. The diffusion coefficient was calculated using values of the viscosity and refractive index of D_2O at the appropriate temperature, and a hydrodynamic diameter was calculated by assuming that the particle was spherical. Measurements of particle size by DLS were repeated several times to obtain a standard deviation of $\sim 5 \text{ nm}$ for the hydrodynamic diameter. The DLS instrument used for these experiments cannot be used to characterize particles with diameters of less than $\sim 7 \text{ nm}$ and thus cannot be used to size the micelles encountered in this work.

X-ray Absorption Spectroscopy

Fe, Zn, and Cd K-edge EXAFS spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL), beam line 11-2 under SPEAR3. Samples in capillary tubes were placed directly in the beam at room temperature with a beam aperture illuminating only the sample area. The X-ray energy was selected using a Si(220) double-crystal monochromator with a collimating mirror for harmonic rejection. Energy was calibrated by defining the first derivative peak of the Fe, Zn, or Cd metal foils to be 7112, 9659, or 26 711 eV, respectively. Samples were collected in fluorescence mode using a 30-element Canberra Ge array detector. The total incoming count rates from fluorescent photons were less than $100\,000 \text{ s}^{-1}$ per element, which is within the linear response range of the detector. Spectra were collected over a certain range using a step size of 0.35 eV through the edge. Individual scans typically took approximately 25 min for completion. All spectra were averaged, background subtracted, and normalized using SIXPACK.²⁵ Phase and amplitude files for the EXAFS fitting using SIXPACK were created with FEFF7.^{26,27} Because the metal binding sites with respect to M_E can be inferred from the chemical structure, the coordination numbers during EXAFS fitting were held constant at integral values given the geometry of either the carboxylate or hydroxamate binding sites for Cd/Zn or Fe, respectively. This procedure helps to reduce the errors in the fitted Debye–Waller factors of each ligand shell because they are strongly correlated with the coordination number.

Results and Discussion

Dynamic Light Scattering

The addition of Cd(II) or Zn(II) (3.5 mM) to a micellar solution²⁸ of Fe(III)– M_E (1.4 mM, pD 6.0, 37°C ; see Materials and Methods for sample preparation) produces a turbid solution that is a result of multilamellar vesicle formation.¹⁹ Dynamic light scattering (DLS) measurements on the vesicles prepared for this study reveal monodisperse Cd(II)- and Zn(II)-induced vesicles of Fe(III)– M_E (polydispersity < 0.2) that are $\sim 282 \pm 7 \text{ nm}$ in diameter for the Cd(II)-induced vesicles and $\sim 110 \pm 7 \text{ nm}$ in diameter for the Zn(II)-induced vesicles.²⁹ After equilibration for 72 h at 37°C , each vesicle suspension was centrifuged to sediment and concentrate the vesicles for X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) measurements.

X-ray Diffraction

XRD profiles of the sedimented Cd(II)- and Zn(II)-induced vesicles (Figure 2) reveal a Bragg peak at $Q_B^{\text{Cd,Zn}} \approx 1.20 \text{ nm}^{-1}$, which suggests that the sedimented vesicles have an interlamellar repeat distance of $2\pi/Q_B \approx 5.2 \text{ nm}$ that is consistent with our previously reported small-angle neutron scattering (SANS) data.¹⁹ The position of the Bragg peak ($Q_B^{\text{Cd,Zn}} \approx 1.20 - 1.26 \text{ nm}^{-1}$) is at approximately the same Q value as the Bragg peak observed in the SANS profiles of the dispersed (i.e., nonsedimented) Cd(II)- and Zn(II)-induced vesicles ($Q \approx 1.1 \text{ nm}^{-1}$).¹⁹ The shift in peak position of the Bragg peak in XRD profiles compared to that in SANS profiles suggests that the interlamellar repeat distance decreases slightly when the vesicles are sedimented.³⁰

X-ray Absorption Spectroscopy

The XANES spectra of cadmium in the sedimented Cd(II)-induced vesicles display an edge energy reflective of Cd(II) at $\sim 26\,700 \text{ eV}$. Similarly, XANES spectra of zinc in the sedimented Zn(II)-induced vesicles exhibit an edge energy at $\sim 9660 \text{ eV}$ that is consistent with Zn(II). EXAFS of the Zn and Cd K-edge absorption data shows oscillations that contain information on the distances between the metal cation and neighboring atoms. EXAFS spectra of the Cd(II) and Zn(II) sites were k^3 weighted (Figure 3) and plotted as pseudoradial distribution functions (Fourier transforms not corrected for phase shifts) to allow a comparison of the distances between the metal cation and the neighboring atoms. The most intense peak at $\sim 1.8 \text{ \AA}$ (uncorrected for phase) in the Cd(II) EXAFS spectrum is shifted to a slightly larger radius relative to the most intense peak in the Zn(II) EXAFS spectrum (Figure 3). This shift in peak position suggests that the nearest neighbors to Cd(II) reside further from the metal center than do the nearest neighbors to Zn(II), which is likely a result of the larger ionic radius of Cd(II) compared to that of Zn(II). Each Cd(II) and Zn(II) EXAFS spectrum fits to a model with six oxygen atoms in the first shell and two carbon atoms each in the second and third shells (Table 1). Such a model could be consistent with either bidentate coordination of two carboxylate ligands and two water molecules to Cd(II) and Zn(II) or with monodentate coordination of two carboxylates and four water ligands. However, the second-shell Zn–C distances in the EXAFS fits of the hexadentate Zn(II) (formate)₂(H₂O)₄ complex at $2.8\text{--}3.05 \text{ \AA}$ for monodentate coordination of formate versus Zn(II)(acetate)₂-(H₂O)₂ at $\sim 2.6 \text{ \AA}$ for bidentate coordination of acetate suggest that the coordination environment of the Zn(II)-induced vesicles is more consistent with monodentate carboxylate coordination (i.e., Zn–C at $2.88 \text{ \AA}$, Table 1).³¹

Each XANES spectrum of the Fe(III) site in the sedimented Cd(II)- and Zn(II)-induced vesicles displays an edge energy of $\sim 7122.7 \text{ eV}$ that is consistent with Fe(III). Each EXAFS spectrum of the Fe(III) site in the sedimented Cd(II)- and Zn(II)-induced vesicles displays a prominent peak at $\sim 1.6 \text{ \AA}$ (uncorrected for phase, Figure 4). The coordination number and bond distance estimates are six O atoms at $\sim 1.99\text{--}2.00 \text{ \AA}$ for the first shell and six C/N/O at $\sim 2.76\text{--}2.89 \text{ \AA}$ for the second shell, respectively (Table 2). Although additional shells can be fit at distances of up to $\sim 4.7 \text{ \AA}$, it is difficult to obtain precise values for the properties of those shells without making assumptions due to the large number of fitting variables required and the noise level in the data. Nonetheless, the fitted coordination numbers and distances are consistent with Fe(III) coordination by the two hydroxamate functionalities and the α -hydroxyamide moiety of the marinobactin headgroup (Figure 1).

Conclusions

The EXAFS spectra of Cd(II) and Zn(II) in the Cd(II)- and Zn(II)-induced vesicles of Fe(III)–marinobactin E are consistent with hexacoordinate Cd(II) and Zn(II) sites ligated by

six oxygen atoms of which two come from monodentate carboxylate ligands. The estimated metal–oxygen bond lengths to Zn(II) and Cd(II) (Table 1) are similar to those obtained from EXAFS spectra of model carboxylate compounds Zn(II)(acetate)₂³¹ and Cd(II)-(acetate)₂³² (i.e., ~2.1 and 2.28 Å, respectively). The longer metal–carbon distance for both Zn(II) and Cd(II) in the vesicles (2.88 and 3.10 Å, respectively, in Table 1 vs ~2.6 Å for bidentate coordination of acetate to Zn(II)³¹ and 2.70 Å for bidentate coordination of acetate to Cd(II)³²) is thus more consistent with monodentate coordination of carboxylate from the terminal carboxylate of marinobactin E than with bidentate coordination.

The EXAFS spectra of Fe(III) in the sedimented Cd(II)- and Zn(II)-induced vesicles corroborate the coordination of Fe(III) by the two hydroxamate groups and the α -hydroxy amide functionality of the marinobactin headgroup (Figure 1). The estimated Fe(III)–oxygen bond length of ~2.00 Å (Table 2) matches the Fe(III)–oxygen bond length obtained from EXAFS spectra of other ferric siderophore complexes such as Fe(III)–desferrioxamine B³³ and Fe(III)–enterobactin.³⁴ Similarly, the estimated Fe(III)–carbon/nitrogen distance obtained for Fe(III)–M_E (Table 2) matches the corresponding values of Fe(III)–desferrioxamine B and Fe(III)–enterobactin to within ~0.1 Å.^{33,34} Thus, Fe(III) EXAFS suggests that the coordination of Cd(II) or Zn(II) does not alter the Fe(III) coordination by the marinobactin headgroup.

XRD patterns obtained from sedimented Cd(II)- and Zn(II)-induced vesicles displayed a Bragg peak (Figure 2) at a similar Q value to the Bragg peak observed in SANS profiles of dispersed Cd(II)- and Zn(II)-induced vesicles.¹⁹ The preservation of the Bragg peak upon sedimentation indicates that the semicrystalline microstructure (i.e., interlamellar repeat distance) of the multilamellar vesicles is not significantly disturbed upon centrifugation.

Thus XAS and XRD results support biscarboxylate coordination from the peptide carboxylate to Cd(II) and Zn(II) as a mechanism to bridge the Fe(III)–M_E headgroups and thus drive the phase change from micelles to multilamellar vesicles. Future experiments using freeze–fracture transmission electron microscopy (FF-TEM) to image the metal-induced vesicles may lend additional insight into the structure of these self-assembled aggregates. Additional experiments are in progress to investigate the metal-induced phase behavior of other amphiphilic ligands, particularly with regard to developing strategies to tune metal-induced self-assembly reactions.

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28. The diameter and polydispersity of the Fe(III)–M_E micelles are 3.5 nm and 0.29, respectively, as determined from small-angle neutron scattering (SANS) measurements.¹⁹
29. The diameter of the Cd(II)-induced and Zn(II)-induced vesicles varies between preparations. Although the polydispersity is low for each vesicle sample, the average vesicle diameter obtained from at least 10 sample preparations of the same composition (i.e., 1.4 mM Fe(III)–M_E, 3.5 mM Zn(II), pD 6.0, 37 °C) varied from 90 to 170 nm for the Zn(II)-induced vesicles and from 80 to 282 nm for the Cd(II)-induced vesicles. The factors that affect vesicle size and nuclearity are under investigation.
30. Also evident in XRD profiles of the Cd(II)- and Zn(II)-induced vesicles is a second peak at $Q \approx 1.9\text{--}2.0 \text{ nm}^{-1}$. The position of this second peak in reciprocal space does not correspond to the expected peak position of secondary Bragg peaks for common aggregate morphologies such as lamellar, hexagonal, or cubic phases. The origin of the second Bragg peak will be the subject of future studies.
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Figure 1.
Structure of Fe(III)–marinobactins A–E. The headgroup contains a carboxylic acid moiety that is anionic at neutral pH.

Figure 2. XRD profiles of the sedimented Cd(II)- and Zn(II)-induced vesicles. The Bragg peak at Q_1 is located on each XRD profile. XRD profiles are offset on the y axis for clarity.

Figure 3. EXAFS spectra and Fourier transforms of Cd(II) and Zn(II) sites in sedimented Cd(II)- and Zn(II)-induced vesicles of Fe(III)–M_E, respectively. EXAFS spectra and Fourier transforms are offset on the y axis for clarity. Solid line (data); dotted lines (fits).

Figure 4. EXAFS spectra and Fourier transforms of Fe(III) sites in sedimented Cd(II)- and Zn(II)-induced vesicles. EXAFS spectra and Fourier transforms are offset on the y axis for clarity. Solid line (data); dotted lines (fits).

Scheme 1. Proposed Cation-Induced Carboxylate Cross-Linking of Fe(III)-M_E Headgroups as a Mechanism to Promote the Micelle-to-Vesicle Transition^a

^a The resulting “composite surfactant” would have a lower headgroup-area/tail-volume ratio that may favor vesicle formation.²²

Table 1

Cd(II) and Zn(II) EXAFS Fit Results for the First-Shell, Second-Shell, and Third-Shell Atoms

sample	shell	CN	distance (Å)	σ^2
Cd(II)-induced vesicles of Fe(III)-M _E	Cd/O	5.9	2.282 ± 0.007	0.011 ± 0.001
	Cd/C	2.0	3.10 ± 0.03	0.010 ± 0.003
	Cd/C	2.0	3.895 ± 0.008	0.008 ± 0.003
Zn(II)-induced vesicles of Fe(III)-M _E	Zn/O	5.9	2.047 ± 0.007	0.010 ± 0.001
	Zn/C	2.0	2.88 ± 0.02	0.008 ± 0.003
	Zn/C	2.0	3.88 ± 0.09	0.011 ± 0.016

Table 2

Fe(III) EXAFS Fit Results for the First-Shell and Second-Shell Atoms

sample	shell	CN	distance (Å)	σ^2
Cd(II)-induced vesicles of Fe(III)-M _E	Fe/O	6.0	1.999 ± 0.005	0.006 ± 0.001
	Fe/C	4.0	2.86 ± 0.08	0.006 ± 0.006
	Fe/N	2.0	2.79 ± 0.15	0.006
Zn(II)-induced vesicles of Fe(III)-M _E	Fe/O	6.4	1.992 ± 0.004	0.006 ± 0.001
	Fe/C	4.0	2.88 ± 0.01	0.003 ± 0.002
	Fe/N	2.0	2.76 ± 0.02	0.003