

Spectroscopic Investigations of Late Transition Metal Complexes by Methanobactin Chromophores

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Project Abstract: Methanotrophic bacteria catalyze the aerobic oxidation of methane to methanol using enzymes with copper (Cu)-based active sites. To facilitate the acquisition of Cu ions some methanotrophic bacteria secrete small peptides known as methanobactins which strongly bind Cu and function as an extracellular Cu recruitment relay analogous to siderophores and iron. In addition to copper, methanobactins are known to form complexes with other late transition metals, including mercury (Hg). Methanobactins have a rich photochemistry and are ideal candidates for spectroscopic study, but a detailed characterization of their spectroscopic features remains incomplete and the solution-phase interactions of methanobactins with late transition metals remains ambiguous.

We present the first combined computational and experimental spectroscopy investigation of characterizing methanobactin-metal (i.e., zinc [Zn], Cu, and Hg) complexes. We observe characteristic differences in absorption spectra of methanobactin complexes with the three late transition metals and compare our experimental data with electronic structure calculations based on the coordination geometry observed in crystal structure data. Apart from characteristic absorbance changes, the complexation of methanobactin with transition metals results in a fluorescence emission. Drawing on previous investigations of the active site of the wild-type green fluorescent protein, we propose a mechanism for the observed fluorescence enhancement. We note spectroscopic indications of slow dynamical changes in mixtures of methanobactin-SB2 and Hg(II) and propose an Hg(II)-concentration-dependent oligomerization process. Collectively, our results shed new light on the binding interactions which characterize the chelation of late transition metals by methanobactin peptides.