

XAFS analysis of the characterization of metalloporphyrin complexes in solution at various pH values

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Introduction

Metalloporphyrins with electron-withdrawing substitutes, such as carboxyl groups, at the meso-positions and that are immobilized on inorganic supports act as efficient and selective catalysts for oxidation of hydrocarbons [1,2]. Porphyrin ligands, with electron-withdrawing substitutes (PPEW) are currently of interest as precursors to stable metalloporphyrin catalysts for a variety of hydrocarbon-oxygenation reactions that are important for future energy development [3]. X-ray absorption near edge structure (XANES) is an effective probe for acquiring the structure and electronic information around the specific atom. Such information can be useful for investigating the electronic structure of metalloporphyrin complexes. In this study, we measured XAFS spectra for a variety of metalloporphyrin complexes.

Experimental

Metal complexes of tetraphenylporphyrin (TPP) were purchased from Sigma-Aldrich Corp. (USA). Figure 1 shows a structure of the metal complexes of TPP.

Measurements of Co, Cu and Zn K-edge XAFS spectra were performed at the photon Factory, KEK, Tsukuba, Japan, using the beam line 12C under dedicated conditions, 2.5 GeV and 280-350 mA. Monochromatic radiation was obtained using a Si(111) monochromator. Two ion chambers with flowing nitrogen and 25-50% argon in nitrogen for I_0 and I , respectively, were used to determine the radiation intensity in the transmission mode.

Result

The Fourier transforms of the measured EXAFS function at various metal complexes of TPP are shown in Figure 2. Average Co-N, Cu-N, and Zn-N distances in the first shell are observed at 1.87, 1.88, and 1.97 Å, respectively. These curves have the same form. This result suggests that the local structure around metal ions is the same in three metal complexes of TPP. Further analysis is now in progress.

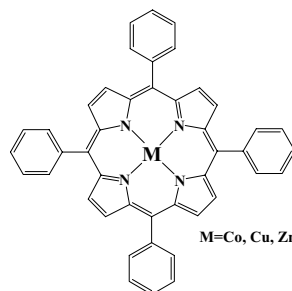


Figure 1 Structure of metal complexes of TPP

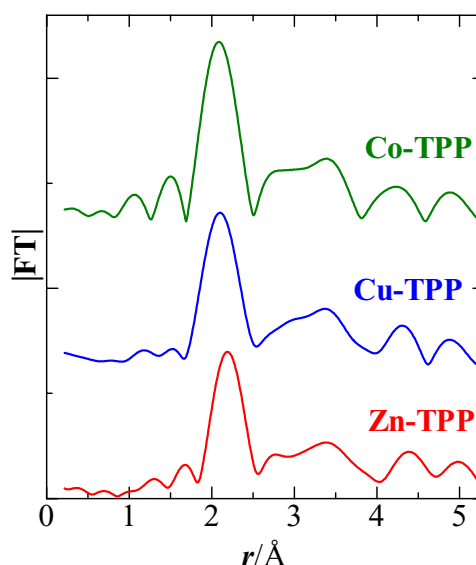


Figure 2 Fourier-transformed EXAFS function (not corrected for phase shift) for metal complexes of TPP

References

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