XAFS and Crystallographic Studies of Ni(II) Porphyrins in Single Crystals and in Solution

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Abstract. Nickel porphyrins serve as models for the active sites of several biological processes. Crystallographic and EXAFS results for a Ni meso-tetrapropyl porphyrin (NiTPrP) yield different Ni-N distances in solution and in the solid state. The Ni-N distances determined by single crystal polarized XAS and X-ray diffraction agree well. Polarized XANES experiments further establish that the pre-edge feature observed in square planar Ni(II) complexes is a 1s-4pz transition. The single crystal and solution EXAFS results demonstrate that conformational variations of the porphyrin macrocycle can readily be imposed by environmental and/or packing forces and can thereby modulate the chemical and physical properties of porphyrinic chromophores and prosthetic groups.

1. INTRODUCTION

The plane polarized nature of synchrotron radiation permits the measurement of polarized X-ray absorption near-edge spectra (p-XANES) and polarized extended X-ray absorption fine structure spectra (p-EXAFS) on oriented single crystals. The spectral features in the p-XANES and p-EXAFS regions depend on the orientation of the X-ray beam relative to the molecular principal axes, and thus, can be assigned to molecular orbitals and structure along a particular direction. From p-XANES studies of single crystal square-planar copper(II) complexes, it was previously possible to unambiguously assign a prominent near-edge peak as arising from a 1s-4pz transition by measuring the angular dependence of the peak amplitude.[1,2] Similar pre-edge peaks have been observed in other transition metals, such as Co and Ni, and it has been postulated that these are analogous 1s-4pz transitions. The pre-edge features are of interest because they serve as markers for the presence or absence of axial ligands in complexes of biological importance.

Crystallographic studies of Ni porphyrins have revealed a variety of macrocycle conformations ranging from planar to severely ruffled.[3] These conformational changes can significantly alter the porphyrin chemical and physical properties. The relative role of crystal packing versus internal forces in governing the molecular structure can be probed by comparing Ni-N bond lengths determined with EXAFS in solution and single crystals. Previous work has demonstrated that long Ni-N distances are typically found in planar porphyrins whereas short distances signal nonplanar conformations.[4] We present here a crystallographic and XAS studies for a low spin Ni(II)porphyrin which exhibits different conformations in solution and in the solid.

2. TECHNIQUES

Crystals suitable for x-ray diffraction and polarized XANES and EXAFS measurements were obtained by slow diffusion of n-hexane into a concentrated CH_2Cl_2 solution of NiTPrP (Ni(II) 5,10,15,20-tetra-*n*-propyl porphyrin). X-ray absorption measurements were carried out at beamlines X-19A and X-11A at the Brookhaven National Synchrotron Light Source. Data were collected with Si 111 (X-11A) and Si 220 or Si 311 (X-19A) monochromator crystals with slits adjusted to give ~1-2 eV resolutions. The samples were measured as fine powder or as ~2 mM solution in fluorescence mode with either a Canberra 13-element solid state detector or a Lytle ionization detector. For the single crystal measurement, a 0.3 x 0.1 x 0.08 mm crystal affixed to the end of a glass capillary was mounted on a two axis goniometer. The molecular orientations relative to the crystal axes are known from a crystallographic structure determination with the xy plane defined by the four nitrogens of the porphyrin macrocycle. The EXAFS data were analyzed quantitatively with the MacXAFS package using experimental standards.[5]

3. RESULTS and DISCUSSION

The crystal structure of NiTPrP was determined at 200 K, see Figure 1a. The molecule is planar with average Ni-N distances of 1.957 (3)Å. The molecules are coplanar in the unit cell, with distances of 5.01 and 3.60 Å between adjacent nickel atoms and porphyrin planes, respectively. For the polarized experiments, initial orientation of the crystal relative to the X-ray beam

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was accomplished by optimization of the pre-edge peak intensity as a function of the two angular motions. Subsequent rotation by 90° resulted in the nearly complete attenuation of the pre-edge peak amplitude as evident in Figure 1b. The XANES spectra for solutions and solids are a superposition of all edge transitions, see Figure 1c.

Figure 1. (a) Crystal packing diagram and an edge-on-view of the planar molecules of NiTPrP. (b) Angular dependence of the p-XANES spectra of the single crystal and (c) of a tetrahydrofuran solution.

The amplitudes for the EXAFS oscillations are attenuated for $\vec{e} \parallel \vec{z}$, but similar for $\vec{e} \perp \vec{z}$ and in solution. Also, the Fourier transforms of the solution and p-EXAFS data show similar first shell amplitude dependence's. These observations are consistent with the assignment of the pre-edge peak to a $1s-4p_z$ transition.

The p-EXAFS for the crystal yield average Ni-N distance of 1.96(2) Å in good agreement with the crystallographic results. However, in solution, shorter Ni-N distances of 1.90 Å are found which are diagnostic of a nonplanar macrocycle conformation. Multiple crystalline conformations have been observed for nickel porphyrins,[6] indicating low energy barriers to conformational changes. Our EXAFS results yield different Ni-N distances in solution and in single crystal, and thus provide direct evidence for the existence of more than one conformer.

4. CONCLUSION

The strong pre-edge XANES peak in square planar nickel(II) complexes is unambiguously assigned to a $1s - 4p_z$ transition. Solution and single crystal EXAFS as well as the crystallographic data for NiTPrP confirm the existence of multiple macrocycle conformations as evident by the varying Ni-N distances. These results demonstrate that environmental and/or packing forces can impose conformational variations on porphyrin derivatives, which in turn can modulate the physical and chemical properties of the metalloporphyrins.

Acknowledgments

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