XAFS Study of Ni M-DNA

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Introduction

M-DNA is a conductor [1] that is formed at pHs greater than 8.5 by replacing the imino protons of the bases in normal DNA (B-DNA) with Zn^{2+}, Ni^{2+}, or Co^{2+} ions[2]. An understanding of the electronic structure of M-DNA and its origin is of great interest when M-DNA is used as molecular wires for the development of biosensors and nanoelectronic devices. X-ray absorption fine structure (XAFS) measurements at the metal K edges have been carried out to investigate the local atomic structure surrounding the metal ions. N K-edge x-ray absorption near-edge structure (XANES) measurements have also been made to probe the electronic structure, and these results will be reported on elsewhere.

Methods and Materials

Two types of samples were prepared from sheared calf thymus DNA: (1) a control of B-DNA at pH 7 with Ni^{2+} (metal-B-DNA), in which the metal ions are bound to the outside of the helix, and (2) Ni-M-DNA. The complex with Ni^{2+} ions was prepared according the procedures described in Reference 1 and was dried *in vacuo*. $NiCl_2$ was used as the reference for Ni valence calibration, and a Ni-phthalocynine (NiPC) sample was used as the reference for the Ni-nitrogen bond in the Ni-M-DNA and metal-B-DNA samples. The sample powder was spread onto the adhesive side of Scotch® tape and then folded to obtain the desired sample thickness.

XAFS experiments were conducted on beamline 20-BM of the Pacific Northwest Consortium Collaborative Access Team (PNC-CAT) at the APS. A Si(111) double-crystal monochromator was used, and the beam was further conditioned by a Rh-coated flat glass mirror at glancing angle to reject the harmonic contents of the monochromatized beam. A further 10-20% second monochromator crystal detuning was applied to suppress the harmonic content more. Data were recorded in transmission mode by using N_2-gas-filled ionization chambers.

Results and Discussion

Figure 1 shows a comparison of the Ni K edge XANES) of Ni-M-DNA, Ni-B-DNA, $NiCl_2$, and NiPC. It is interesting to note that the pre-edge features in Ni-M-DNA and Ni-B-DNA are the same, indicating that a similar local symmetry of Ni in the two cases. However, the XANES of NiPC is quite different from that of the DNA samples. The energy thresholds determined by the peaks of the first derivatives of XANES indicate that the nickel in both Ni-M-DNA and Ni-B-DNA is in the 2+ oxidation state, as it is in $NiCL_2$. The structural difference between the conductor Ni-M-DNA and the control sample Ni-B-DNA is shown more clearly in XAFS. Figure 2 shows the magnitudes of the Fourier transformation of XAFS of Ni-M-DNA, Ni-B-DNA, and the control sample NiPC. The transformation k-space range is 2 to 12 $Å^{-1}$ and it is k^3-weighted. As shown in Fig. 2, the first coordination shells (Ni-N and O) in both Ni-M-DNA and Ni-B-DNA have similar bond lengths and comparable intensity (i.e., coordination is comparable if the bond strengths can be assumed to be the same); however, the shells immediately outside the nearest neighbor are quite different for these two samples. The conducting Ni-M-DNA has two distant shells at apparent distances of 2.1 Å and 2.7 Å (Fig. 2). At the latter distance, the model compound Ni-PC has its second nearest neighbor shell. On the other hand, the control sample Ni-B-DNA (nonconducting) shows a void around that distance. Detail modeling and curve-fitting analysis are underway to correlate the structural features of Ni-M-DNA and its transport properties.

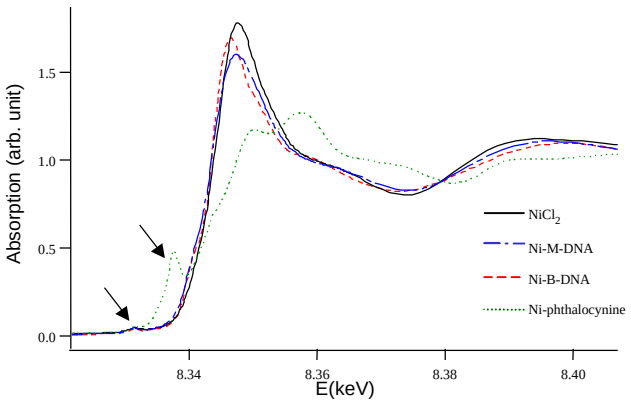

FIG. 1. A comparison of XANES. The arrows mark the pre-edge features of interest. The derivatives of these spectra indicate that the main thresholds of all four samples are the same (i.e., all the Ni in these samples is in a 2+ oxidation state, as is that in $NiCl_2$).

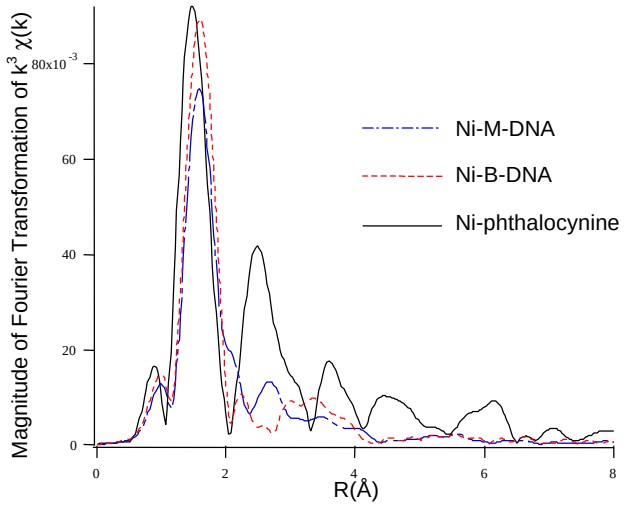

FIG. 2. Comparison of Fourier transforms of Ni-PC (solid line), Ni-M-DNA (dotted and dashed), and Ni-B-DNA (dashed).

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References

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