



	Experiment title: Combined SAXS/EXAFS study of the intercalation of novel Cu and Zn complexes in DNA	Experiment number: SC-3581
Beamline: BM26A	Date of experiment: from: 17/04/2013 to: 22/04/2013	Date of report: 04/03/14
Shifts: 15	Local contact(s): Dipanjan Banerjee, Sergey Nikitenko	<i>Received at ESRF:</i>
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Report:

X-Ray Absorption Spectroscopy (XAS) experiments were carried out at the BM26A beamline of European Synchrotron Radiation Facility (ESRF), Grenoble. The spectra were recorded in fluorescence mode with a 9-elements Ge detector on the Ni (8333 eV), Cu (8979 eV) and Zn (9659 eV) respectively, on buffered aqueous solutions, in Tris-HCl 1 mM, of [1]=503 μ M, [2]=95 μ M and [3]=457 μ M, both with and without DNA at a molar concentration of 4:1 DNA/metal complex. The sample solutions were quenched in liquid nitrogen and the spectra recorded at 80K using a cryostat, averaging 10 spectra per sample for about 6 hours. XAS spectra were averaged and normalized with Athena.¹ EXAFS spectra were fitted with Viper.² FEFF8.4 was used to calculate theoretical amplitudes and phases for the EXAFS analysis, and full multiple scattering simulations on the XANES.³

The XANES spectrum of the zinc(II) complex **3** in aqueous solution, isolated (blue line) and in the presence of ct-DNA (green line) are reported in Fig. 1a. The corresponding Fourier transformed EXAFS (FT-EXAFS) spectra for the same samples are shown in Fig. 1b. By comparison with the literature,⁴ it can be concluded that the near-edge features in the XANES spectra of both **3** and of **3**/ct-DNA solutions are typical of Zn^{2+} ions in an octahedral coordination environment.

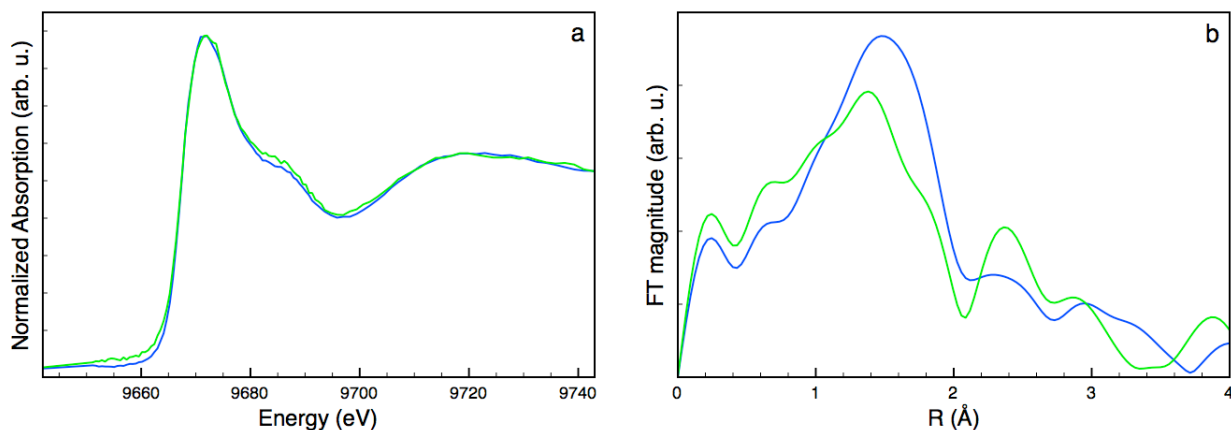


Figure 1. Zn K-edge XANES (a) and FT-EXAFS (b) of **3** 457 μM (blue) and in the presence of ct-DNA 1.692 mM (green) in Tris-HCl 1 mM aqueous solutions.

The FT-EXAFS spectrum of **3** (Fig. 1b, blue line) shows a broad first coordination peak, between 1.4-2.0 Å (uncorrected for phase shift), and several other contributions between 2 and 3 Å, arising from the multiple scattering paths of the C, O and N atoms of the chelating ligand.

The EXAFS spectrum of the isolated complex is significantly modified by the addition of an excess of DNA, at a $[\mathbf{3}]/[\text{DNA}_{\text{phosphate}}]$ molar ratio of about 0.27. In these conditions, the solution experiments reported above have shown the metal complex to be fully intercalated. Analogous aqueous solutions of the nickel(II) and copper(II) complexes **1** and **2** undergo photoreduction and/or photodegradation to some extent, both as isolated species and in the presence of DNA, when exposed to the synchrotron X-ray beam. The presence of metal-metal distances (either from the formation of metal nanoparticles or from polymerization of the complexes) was detected in the spectra, which were not analyzed further.

In the presence of DNA, an overall change in the local structure of Zn^{2+} is evident. Firstly, the first coordination shell loses one or two apical H_2O molecules, as witnessed by the decrease in the broad contribution around 1.5 Å (Fig 1b). Moreover, a sharp increase of the feature around 2.4 Å is visible.

These results were just published in A. Lauria, R. Bonsignore, A. Terenzi, A. Spinello, F. Giannici, A. Longo, A.M. Almerico, G. Barone, “Nickel(II), copper(II) and zinc(II) metallo-intercalators: structural details of the DNA-binding by a combined experimental and computational investigation”, *Dalton Transactions* DOI: 10.1039/C3DT53066C

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