DNA modification and cleavage by a planar dinuclear nickel(II) Schiff-base complex with cationic substituents.

Yoshiteru Kakinuma, Hidekazu Arii, Makoto Chikira

Department of Applied Chemistry, Chuo University

It has been reported that cationic salen-type Schiff base metal complexes bind to DNA and the affinity and cleaving reactivity for DNA are affected by the bridging group in the quadridentate Schiff bases\textsuperscript{1).} In this study, we have synthesized a novel dinuclear nickel(II) Schiff-base complex \([\text{Ni}_2(\text{MS}_2\text{dp})(\text{pz})]^{2+}\) (I) and investigated the DNA binding mode, evaluating the binding affinity and oxidative cleavage reactivity.

The hypochromism observed in the UV-vis spectra of I on addition of calf-thymus DNA indicated that the complex binds specifically (binding constant \(K_b^s = 3.1 \times 10^6 \text{ M}^{-1}\) and sites size number \(n_1 = 26\)) and non-specifically (\(K_b^{ns} = 3.1 \times 10^4 \text{ M}^{-1}\), \(n_2 = 6\)). In the case of mononuclear nickel(II) complex \([\text{Ni(MSen)}]^{2+}\) (2), the hypochromic effect was too small for the estimation of the binding constant. Furthermore, a positive induced CD band was observed weakly for I at around 350 nm whereas negative induced CD bands were observed for 2 in the range 400 – 450 nm. The \(K\) and \(n\) values for 2 have been estimated from the induced CD bands for specific binding (\(K_b^s = 1.1 \times 10^6 \text{ M}^{-1}\), \(n_1 = 20\)) and for non-specific binding (\(K_b^{ns} = 6.0 \times 10^4 \text{ M}^{-1}\), \(n_2 = 6\)), respectively \textsuperscript{1).}

I cleaved plasmid DNA with OXONE in 100mM cacodylic acid buffer (pH 7.4) at 37 °C more mildly than 2. Above results suggest that the di-nikel center of I is involved more deeply in the ds-DNA from the pyrazole side.

![Figure 1](image)

Figure 1 Structure of \([\text{Ni}_2(\text{MS}_2\text{dp})(\text{pz})]^{2+}\) (left) and \([\text{Ni(MSen)}]^{2+}\) (right)

1) K. Fukiura et al., Abstract of ICBIC12, 2005.