

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

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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 bases¹⁾. In this study, we have synthesized a novel dinuclear nickel(II) Schiff-base complex $[\text{Ni}_2(\text{MS}_2\text{dp})(\text{pz})]^{2+}$ (**1**) and investigated the DNA binding mode, evaluating the binding affinity and oxidative cleavage reactivity.

The hypochromism observed in the UV-vis spectra of **1** 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 $n_l = 26$) 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 $[\text{Ni}(\text{MSen})]^{2+}$ (**2**), the hypochromic effect was too small for the estimation of the binding constant. Furthermore, a positive induced CD band was observed weakly for **1** 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 ($K_b^s = 1.1 \times 10^6 \text{ M}^{-1}$, $n_l = 20$) and for non-specific binding ($K_b^{ns} = 6.0 \times 10^4 \text{ M}^{-1}$, $n_2 = 6$), respectively¹⁾.

1 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-nickel center of **1** is involved more deeply in the ds-DNA from the pyrazole side.

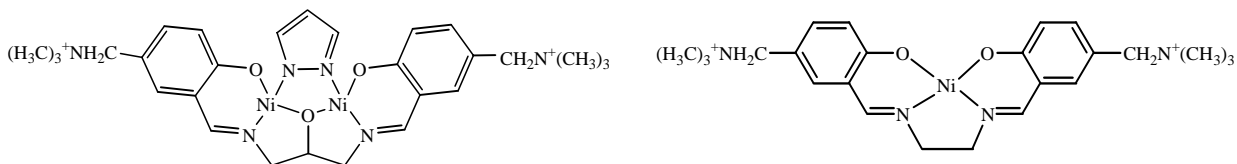


Figure.1 Structure of $[\text{Ni}_2(\text{MS}_2\text{dp})(\text{pz})]^{2+}$ (**1**) (left) and $[\text{Ni}(\text{MSen})]^{2+}$ (**2**) (right)

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