

Interactions of Flexible Diamine Bridged Dinuclear Ruthenium(II)-2,2'-Bipyridine Complexes with DNA

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There has been considerable interest recently in the DNA-binding of dinuclear ruthenium(II) complexes with polypyridine ligands. Selective coordination to nucleobases is influenced by structural and electronic factors arising from the nucleobase and the complex itself. In this study, we have investigated the syntheses of flexible diamine bridged dinuclear ruthenium(II)-2,2'-bipyridine complexes, $[\{\text{RuCl}(\text{bpy})_2\}_2(\mu\text{-BL})]^{2+}$ (bpy = 2,2'-bipyridine; BL = $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ ($n = 4$ (bn), 8 (on), 12 (don))) and the recognition of DNA by $[\{\text{RuCl}(\text{bpy})_2\}_2(\mu\text{-BL})]^{2+}$ using spectroscopic (UV-vis, ^1H -NMR, and CD) methods.

For reactions of $[\{\text{RuCl}(\text{bpy})_2\}_2(\mu\text{-BL})]^{2+}$ (40 μM) with mononucleotides (0.4 mM), changes in UV-vis spectra in the case of GMP (guanosine 5'-monophosphate) and TMP were monitored for 3 h. For example, the MLCT absorption bands of $[\{\text{RuCl}(\text{bpy})_2\}_2(\mu\text{-don})]^{2+}$ initially centered at 344 and 488 nm shifted to shorter wavelength with hyperchromism (for GMP) and hypochromism (for TMP) with time. The reactions of GMP or TMP with $[\{\text{RuCl}(\text{bpy})_2\}_2(\mu\text{-BL})]^{2+}$ were monitored by ^1H -NMR, suggesting that these dinuclear ruthenium(II) complexes bind to N7 and O4 positions of GMP and TMP, respectively. On the other hand, no change in UV-vis spectra in the case of AMP and CMP was observed. In competitive binding experiments for $[\{\text{RuCl}(\text{bpy})_2\}_2(\mu\text{-BL})]^{2+}$ with GMP versus TMP, the only GMP selectively coordinated to these ruthenium(II) complexes, resulting from substitution of Cl^- ligands by GMP. In addition, in the presence of CT-DNA the absorption peaks of the dinuclear ruthenium(II) complexes at shorter wavelength increased with time, indicating that $[\{\text{RuCl}(\text{bpy})_2\}_2(\mu\text{-BL})]^{2+}$ selectively bind to guanine N7 in DNA. The CD spectra of $[\{\text{RuCl}(\text{bpy})_2\}_2(\mu\text{-BL})]^{2+}$ (BL = on, don) in the presence of CT-DNA under standing for 3 h gave the same single positive peak in the 320 – 380 nm region, while in the case of $[\{\text{RuCl}(\text{bpy})_2\}_2(\mu\text{-bn})]^{2+}$ two positive peaks were observed in the 320 – 380 nm and 400 – 500 nm regions. The latter CD spectrum was the same as that of mononuclear ruthenium(II) complex $[\text{RuCl}(\text{ba})(\text{bpy})_2]^+$ (ba = *n*-butylamine).

In conclusion, we have shown here that $[\{\text{RuCl}(\text{bpy})_2\}_2(\mu\text{-BL})]^{2+}$ selectively bind to two guanine molecules in DNA and the flexible diamine bridged dinuclear ruthenium(II) complexes affect the ability to DNA-binding.