

# Insertion of a Bulky Rhodium Complex into a DNA Cytosine-Cytosine Mismatch: An NMR Solution Study

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## Abstract:

The bulky octahedral complex  $\text{Rh}(\text{bpy})_2\text{chrysi}^{3+}$  (chrysi = 5,6-chrysenequinonediimine) binds single-base mismatches in a DNA duplex with micromolar binding affinities and high selectivity. Here we present an NMR solution study to characterize the binding mode of this bulky metal complex with its target CC mismatch in the oligonucleotide duplex  $(5'\text{-CGGACTCCG-3}')_2$ . Both NOESY and COSY studies indicate that  $\text{Rh}(\text{bpy})_2\text{chrysi}^{3+}$  inserts deeply in the DNA at the mismatch site via the minor groove and with ejection of both destabilized cytosines into the opposite major groove. The insertion only minimally distorts the conformation of the oligonucleotide local to the binding site. Both flanking, well-matched base pairs remain tightly hydrogen-bonded to each other, and 2D DQF-COSY experiments indicate that all sugars maintain their original  $C_2\text{-endo}$  conformation. Remarkably,  $^{31}\text{P}$  NMR reveals that opening of the phosphate angles from a  $B_I$  to a  $B_{II}$  conformation is sufficient for insertion of the bulky metal complex. These results corroborate those obtained crystallographically and, importantly, provide structural evidence for this specific insertion mode in solution.

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