ABSTRACT OF THE DISSERTATION

SYNTHESIS OF DIOXOPENTAAZAMACROCYCLES, FORMATION OF NICKEL COMPLEXES, AND CHEMISTRY OF DNA CLEAVAGE WITH MOLECULAR OXYGEN

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Dioxopentaazamacrocycles are pentadentate ligands with three amine nitrogens and two amide nitrogens in the cyclic ring. Their nickel(II) complexes were found to possess oxygen binding ability. Various new dioxopentaaza-macrocycles with a fluorine atom substituted in the C15 position were prepared efficiently in good yields. The X-ray structure of the green $NiHFN_5O_2$ (**85**)

complex, a precursor for oxygenation, exhibited the unique property of a perpendicular interaction between the carbonyl group and the nickel ion. The macrocyclic dioxopentaaza nickel(II) complexes display a similar structure around nickel except at the sixth coordination site but their O_2 reactivity was sensitive to the substituent group at the C15 position of coordinating ligands. Two X-ray structures of dioxopentaazamacrocyclic nickel complexes were obtained, giving some insight to the controlling factors for O_2 uptake. Oxygen binding studies were performed by UV spectroscopy and by oxygen electrode measurements using the $NiHFN_5O_2$ complex. The initial step for O_2 uptake is suggested to occur at the nickel center which is established by buffer effects and on the basis of a *trans* influence at the N7 position of the coordinating ligand. Based on the results of redox potential measurements, UV, oxygen electrode measurements, and X-ray structures, the cavity size of the coordinating ligand plane was proposed to control O_2 uptake at the nickel center. The change of the cavity size is believed to be due to a ligand conformational change.

For DNA strand scission, either with plasmid DNA or γ-^{32}P-labeled oligonucleotides, the macrocyclic dioxopentaaza nickel(II) complexes successfully demonstrated cleavage ability using ambient molecular oxygen without the need for additional oxidants or photochemistry. Deoxyguanosine model studies using the $NiHFN_5O_2$ complex indicated binding between the nickel complex and the N7 site of guanine.