ATP as a Stabilizing Ligand for High Valent Nickel Complexes

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Anionic, hard base ligands, e.g. SO_4^{2-}, HPO_4^{2-}, $P_2O_7^{4-}$, are know to stabilize, via axial coordination, the Ni(III) complexes with tetraazamacrocycle ligands, e.g. Ni(III)(cyclam), cyclam = 1,4,8,11–tetraazacyclotetradecane. $P_2O_7^{4-}$ seems to be an optimal ligand and surprisingly electrochemical and pulse radiolysis experiments even suggest that $Ni^{IV}L(P_2O_7)^{4-4n}$ (n = 1 or 2) can be formed but is short lived. These results suggest that ATP might also form the complex $Ni^{III}L(ATP)_2^{5-}$. Indeed the stability constant for the binding of ATP to $Ni^{III}L(H_2O)_2^{3+}$ is found to be $K_{eq} = 1.2\times10^{11}$ M^{-2} , $E_{1/2} = 0.41$ V for the $Ni^{III/II}L$ couple in solutions containing 0.016M ATP at pH 7.0. This complex is stable in aerated solutions. However the electrochemical oxidation of $Ni^{II}L^{2+}$ in aerated solutions containing ATP, results in an electrochemical irreversible process. This suggests that another plausible role of ATP in biological systems is the stabilization of high valent transition metal complexes.