DNA Binding Constants Of Ruthenium Oligopyridine Complexes.

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The complexes (1)-(3) of the general formulae [Ru(terpy)(dcbpy)X]n (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine; X = Cl, n = +1; X = NO, n = +3; X = NO2, n = -1) have been synthesized and characterized. The DNA binding properties of structurally similar complexes [Ru(terpy)(dcbpy)NO]n (3), [Ru(terpy)(4-CO2H-4'-Mebpy)NO2] (4) and [Ru(terpy)(bpy)NO2]+ (5) were studied and their DNA affinities (Kb) were calculated. Complexes (1) and (2) were isolated from acidic solutions as [PF6]- salts, with both carboxylic groups of dcbpy protonated. Since the formation conditions of (3) were in basic solution, both carboxylic groups of dcbpy were deprotonated and the anionic complex was isolated as sodium salt.

In order to investigate the role of the total complex charge to the DNA-binding affinity, the intrinsic binding constants Kb of (3), (4) and (5) were calculated according to the following equations:

\[
\frac{(\varepsilon_a - \varepsilon_f)}{(\varepsilon_b - \varepsilon_f)} = \frac{(b^2 - 2K_bC_t[DNA]/s)^{1/2}/2K_bC_t}{(2)}
\]

\[
b = 1 + K_bC_t + K_b[DNA]/2s
\]

\(\varepsilon_a\) is the extinction coefficient for the MLCT absorption band at every DNA concentration, \(\varepsilon_f\) is the extinction coefficient for the MLCT absorption band for the free complex, \(\varepsilon_b\) is the extinction coefficient for the MLCT absorption band at the DNA concentration when the complex is fully bound, \(K_b\) is the binding constant in M$^{-1}$, \(C_t\) is the initial (total) complex concentration in M, \([DNA]\) is the concentration of DNA (phosphate nucleotide) in M and \(s\) is the average number of DNA bases interacting with the complex.

From the plot \((\varepsilon_a - \varepsilon_f)/(\varepsilon_b - \varepsilon_f)\) vs. [DNA] and the non-linear fitting of the titration curve, the \(K_b\) and \(s\) values for the complexes (3), (4) and (5) were calculated as 6 x 10^4 M$^{-1}$ (s = 0.1); 8 x 10^4 M$^{-1}$ (s = 0.2); 9.7 x 10^6 M$^{-1}$ (s = 2.3) respectively. Obviously, the \(K_b\) and \(s\) values of the negatively charged complex (3) and the neutral one (4) are similar, while the value of the positive charged complex (5) is two orders of magnitude higher, indicating that the electrostatic forces between the phosphates of DNA and the complex enhance the binding strength. In addition, in cases of (3) and (4) the extremely low \(s\) values are consistent with a non-specific binding. Since all studied complexes do not intercalate between the DNA bases, the relatively high \(K_b\) values observed may reflect an additional interaction between the ligand -NO2 and the DNA.