(N7)-Platination and Its Effect on (N1) H-Acidification in Nucleoside Phosphate Derivates

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Pt(II) coordination, like of cis -(NH 3) 2 Pt(II), affects the acid-base properties of guanosine derivatives. The acidity constants of such complexes are calculated by curve-fitting procedures using published 1 H NMR shift data measured in aqueous solution (D 2 O) in dependence on pH (pD). Comparison of the p K a values of the ligands with those of the Pt(II) complexes reveals the expected behavior for (N7)-platination, i.e., (N1)H sites are acidified due to charge repulsion. These effects of Pt(II) are compared with those of Ni 2+ and Cd 2+ , allowing predictions for the acidification of Zn 2+ . Studied are the cis -(NH 3) 2 Pt(II) complexes of inosylyl(3′ăă5′)inosine, guanylyl(3′ăă5′)guanine (GpG) − , its 2′-deoxy relative d(GpG) − , and its phosphorylated derivative d(pGpG) 3− . The Pt(II) effect is mostly rather symmetrical, like with d(CpGpG) 2− , but it can also be quite asymmetrical, like with d(CpCpGpG) 3− or in the cyclohexylamine-substituted Cisplatin complex of d(GpG) − . Potential consequences for base pairing between the platinated guanine and the complementary cytosine are discussed. It is proposed that partial deprotonation of dG under the influence of Pt(II) at physiological pH leads in water to a marked reduction in pairs with intact Watson–Crick hydrogen bonds, thereby adding to the well established thermal destabilization of double-stranded DNA by G,G intrastrand cross-links of Cisplatin.

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