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T16

Conformation of d(ATGG)–*cis*Pt(NH_3)$_2$ in Aqueous Solution by Proton Magnetic Resonance Spectroscopy

S. TRAN-DINH, J. M. NEUMANN

Service de Biophysique C.E.N. Saclay, 91191 Gif sur Yvette, Cédex, France

J. P. GIRAULT, J. C. CHOTTARD

Laboratoire de Chimie, Ecole Normale Supérieure, 75231 Paris Cédex 05, France

T. HUYNH-DINH and J. IGOLEN

Unité de Chimie Organique, Institut Pasteur, 75724 Paris Cédex 15, France

The conformation of an adduct d(ATGG)–*cis*Pt resulting from the interaction of the antitumor *cis*Pt(NH_3)$_2$$Cl_2$ with a short DNA fragment dApTpGpG has been investigated by ^{1}H NMR at 500 MHz and at various temperatures. The chemical shift and coupling constant measurements confirm the CD and UV results that divalent platinum binds covalently to the N-7 atoms of the two adjacent guanines in the same strand as in the case of diguanosine monophosphates [1, 2]. Analysis of the coupling constants between the deoxyribose protons (Fig. 1) shows that the sugar ring of the internal dG adopts the N conformation ($C_{3'}$-endo) (91% N) while the external dG and the other residues adopt the S conformation ($C_{2'}$-endo) (70–80% S). In the case of unplatinated oligomer, the S conformation is largely predominant (>70%) for all residues of d(ATGG).

The relaxation time and nuclear Overhauser measurements indicate that the orientation of the two guanines is *anti*, in agreement with the previous results obtained for the dimers r(GpG)–*cis*Pt, d(GpG)–*cis*Pt [1, 2]. Surprisingly, on decreasing temperature from 80 to 25 °C, the $H_{1'}$, resonance of the internal dG (Fig. 1) and the $H_{4'}$ resonance of the internal dT (not shown) shift and broaden substantially and finally disappear at $t < 40$ °C. These results suggest that d(ATGG)–*cis*Pt tends to associate with neighbouring molecules and the conformation of this adduct changes with temperature. It seems likely that at low temperature the base protons (H-6 and CH_3) of dT are situated 'inside' the adenine ring whereas the sugar protons of dT are very close to the guanine ring of the internal dG.

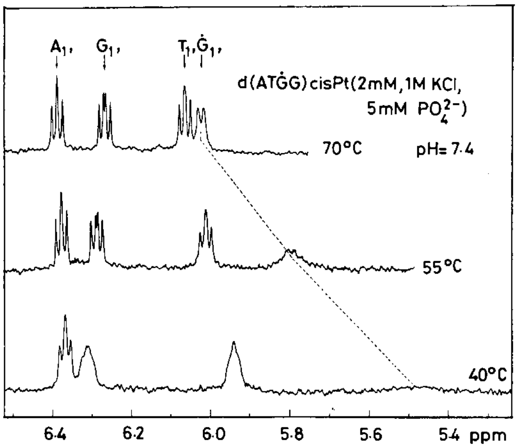

Fig. 1. 500 MHz ^{1}H NMR spectra of the H_1' protons of d(ATGG)–*cis*Pt in aqueous solution at various temperatures.

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T17

Structural Studies on Metal-ATP Complexes: X-Ray Structures of Mg(II), Ca(II), Mn(II) and Co(II) Ternary Complexes with ATP and Dipyridylamine

R. CINI

Istituto di Chimica Generale, Università di Siena, 53100 Siena, Italy

M. SABAT, M. SUNDARALINGAM

Department of Biochemistry, University of Wisconsin, Madison, Wis. 53706, U.S.A.

M. C. BURLA, A. NUNZI, G. POLIDORI and P. F. ZANAZZI

Istituto di Mineralogia, Università di Perugia, 06100 Perugia, Italy

The enzyme-catalyzed reactions of transferring simple and substituted phosphoryl groups, such as nucleotidyl groups, are among the most fundamental biochemical processes. Enzymes which utilize one of the nucleotides as a cofactor or substrate usually require a specific complex of the nucleotide with metal ion for activity. The metal ions are involved in a number of mono-, bi- and tri-dentate coordination geometries and some of the forms may be preferred by specific enzymes over the others as substrates. X-ray studies of several metal-polyphosphate