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An FT-IR and ^{1}H NMR Spectral Study of Sugar Ring Conformations in Guanosine and in several Platinum(II) Complexes

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Studies with various oligonucleotides and DNAs have shown that intrastrand cross-linking of two adjacent guanines is a major coordination fate of the *cis*-$\mathrm{Pt(NH_3)^{2+}}$ moiety [1]. In addition, a study of *cis*-$\mathrm{[Pt(NH_3)_2(oligonucleotide)]^{2+}}$ complexes in aqueous solution by high field nuclear magnetic resonance [2] has shown interesting conformational changes in the sugar moiety as a result of coordination. The FT-IR spectra in the solid state of some metal complexes of 5′-GMP, 5′-IMP, RNA, and DNA have been reported, and the transition from a C2′-*endo*, *anti* to a C3′-*endo*, *anti* conformation was suggested by a few marker bands in the 1000–600 cm^{-1} region for the two puckered forms of the sugar moiety [3].

In the present work, the conformations of the sugar ring in platinum–guanosine complexes in the solid state were studied by FT-IR, and the results were compared with the data of ^{1}H NMR obtained in aqueous solution.

Experimental

The FT-IR spectra were taken in the 1000–600 cm^{-1} region and recorded on a DIGILAB FTS-15C/D Fourier Transform Infrared Interferometer equipped with HgCdTe detector (Infrared Associates, New Brunswick, N.J.), a KBr beam splitter and a Globar source. The spectra were obtained as KBr pellets with a resolution of 4 to 2 cm^{-1}. The platinum–guanosine complexes were prepared according to the methods described in the literature [4, 5].

Results and Discussion

X-ray structural analysis has shown that the sugar in guanosine [6] adopts C2′-*endo*, *anti*, *gg* as well as Cl′-*exo*, *anti*, *gg* puckering, while in *cis*-$\mathrm{[Pt(NH_3)_2(Guo)_2]^{2+}}$ [7] and $\mathrm{[Pt(en)(Guo)_2]^{2+}}$ [8] it has a C3′-*endo*, *anti*, *gg* conformation. As is shown in Fig. 1, the FT-IR spectrum of guanosine gives the marker band at 824 cm^{-1} assigned to a sugar-ring vibrational mode which is indicative of a C2′-*endo*, *anti* conformation. In the spectra of *cis*-$\mathrm{[Pt(NH_3)_2(Guo)_2]^{2+}}$ and $\mathrm{[Pt(en)(Guo)_2]^{2+}}$ the band at 824 cm^{-1} decreases in intensity or disappears, while a new band appears at 797 and 798 cm^{-1}, respectively when the conformation changes from a C2′-*endo*, *anti* to a C3′-*endo*, *anti*. Furthermore, bands at 799 cm^{-1}, 800 cm^{-1}, and 798 cm^{-1}, respectively were found in the spectra of guanosine complexes, $\mathrm{[Pt(diaminodiol)(Guo)_2]^{2+}}$, $\mathrm{[Pt(diaminotriol)(Guo)_2]^{2+}}$, and $\mathrm{[Pt(diaminotetrol)(Guo)_2]^{2+}}$ formed with the new optically pure diamino(polyol) platinum complexes **1**–**3**, respectively, shown in Fig. 2*. This suggests the presence of a C3′-*endo*, *anti* conformation for the sugar moiety.

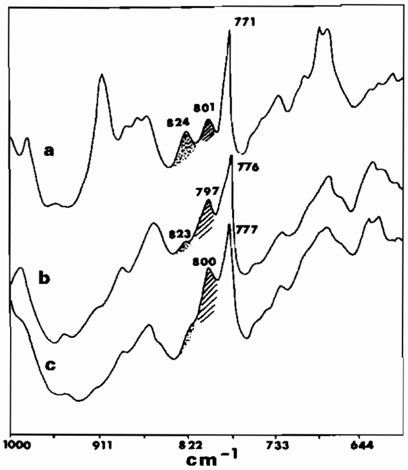

Fig. 1. FT-IR spectra of guanosine and its platinum complexes. (a) guanosine, (b) *cis*-$\mathrm{[Pt(NH_3)_2(Guo)_2]^{2+}}$, (c) $\mathrm{[Pt(diaminotriol)(Guo)_2]^{2+}}$.

Lee and Sarma [9], and Kim and Sarma [10] have proposed a method to estimate the population of C2′-*endo*, *anti* and C3′-*endo*, *anti* conformations of the ribose ring from the sum of $J_{1'2'}$ and $J_{3'4'}$ coupling constants. The chemical shifts, coupling constants, and conformational populations for guanosine and its platinum complexes are given in Table I. The results indicate that for the free guanosine molecule and its platinum complexes, except $\mathrm{[Pt(diaminotriol)(Guo)_2]^{2+}}$, the *gauche-gauche*(*gg*) conformation is predominant (69–76%). Moreover, this study also indicates that the proportion of C3′-*endo*, *anti* increases from 38% for free guanosine to 47% for *cis*-$\mathrm{[Pt(NH_3)_2(Guo)_2]^{2+}}$, in agreement with the other platinum–guanosine complexes (Table I).

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*For a synthesis and X-ray analysis of the *cis*-platinum complexes of diaminoalditols see ref. 5.

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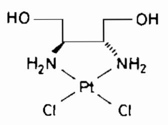
TABLE I. Chemical Shifts, Coupling Constants, and Conformational Population of Guanosine and its Platinum Complexes

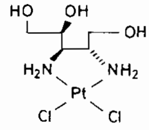
Compound	(ppm) H8	J (Hz) 1'2'	2'3'	3'4'	4'5'	4'5''	5'5''	C(4')–C(5') $gg \rightleftarrows g/t$		Ribose ^{3}E(%)
Guo^a		5.9	5.2	3.7	3.2	3.8	−12.5	69	31	38
m^{7}G^a		4.5	5.2	4.9	2.7	3.6	−13.1	76	24	51
$[Pt(NH_3)_3(Guo)]^{2+}$	8.55	5.3	5.2	4.3	2.9	4.1	−12.7	69	31	45
$[Pt(dien)(Guo)]^{2+}$	8.46	5.2	5.2	4.4	2.9	4.1	−12.8	69	31	46
cis-$[Pt(NH_3)_2(Guo)_2]^{2+}$	8.35	4.9	5.1	4.5	2.9	4.1	−12.8	69	31	47
$[Pt(en)(Guo)_2]^{2+}$	8.33	4.8	5.1	4.5	2.9	4.0	−12.8	70	30	47
$[Pt(diaminodiol)(Guo)_2]^{2+}$ from **1**	8.32	4.8	5.1	4.5	2.5	4.0	−12.8	74	26	47
$[Pt(diaminotriol)(Guo)_2]^{2+}$ from **2**	8.32	5.9	4.3	5.4	n.v.	4.0	n.v.	n.v.	n.v.	56
	8.25	5.3	4.7	4.9						51
$[Pt(diaminotetrol)(Guo)_2]^{2+}$ from **3**	8.27	4.8	5.1	4.6	2.7	3.8	−12.8	74	26	48

^{a}Ref. 10; n.v.: not visible. 400 MHz ^{1}H NMR were taken in D_2O, and DSS was used as external reference.



1

2,3-diamino-2,3-dideoxy-D-threitol dichloro platinum



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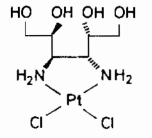
2,3-diamino-2,3-dideoxy-D-xylitol dichloro platinum



3

3,4-diamino-3,4-dideoxy-D-iditol dichloro platinum

Fig. 2. Structure of new optically pure diamino(polyol) platinum(II) complexes.

Based on the FT-IR and ^{1}H NMR spectroscopic data, it appears that there is a tendency to increase the C3′-*endo*, *anti*, *gg* sugar pucker in aqueous solution upon platination slightly, whereas in the solid state such a tendency is much stronger.

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