$$2[NiCp_2]_0 = n = [NA]_0 = [NA] + [NA^*] \quad (A5)$$

$$\text{total lithium} = m = [MA] + [MA^*] + 2[M_2A_2] + 2[M_2AA^*] + 2[M_2(A^*)_2] \quad (A6)$$

$$\text{total label} = a = [MA^*]_0 + 2[M_2(A^*)_2]_0 + [M_2AA^*]_0 \quad (A7)$$

$$\text{total [LiCp]} = v = [MA] + [MA^*] \quad (A8)$$

$$\text{total [(LiCp)}_2] = \mu = [M_2A_2] + [M_2AA^*] + [M_2(A^*)_2] \quad (A9)$$

In terms of these parameters, the amount of label on lithium species at any time is

$$a - x = [MA^*] + 2[M_2(A^*)_2] + [M_2AA^*] \quad (A10)$$

Using a purely statistical analysis, the rate of approach to equilibrium is given by

$$\frac{dx}{dt} = R_1\left\{\frac{[MA^*]}{v}\frac{[NA]}{n} - \frac{[MA]}{v}\frac{[NA^*]}{n}\right\} + R_2\left\{\frac{[M_2(A^*)_2]}{\mu}\frac{[NA]}{n} + \frac{1}{2}\frac{[M_2AA^*]}{\mu}\frac{[NA]}{n} - \frac{1}{2}\frac{[M_2AA^*]}{\mu}\frac{[NA^*]}{n} - \frac{[M_2A_2]}{\mu}\frac{[NA^*]}{n}\right\} \quad (A11)$$

We now make the following substitutions in eq A11

$$[NA] = n - x$$

$$[NA^*] = x$$

$$[MA^*]/v = (a - x)/m$$

$$[M_2(A^*)_2]/\mu = (a - x)^2/m^2$$

$$[M_2AA^*]/\mu = 2(a - x)(m - a + x)/m^2$$

$$[M_2AA]/\mu = (m - a + x)^2/m^2$$

This leads to

$$\frac{dx}{dt} = R_1\left\{\frac{a-x}{m} - \frac{x}{n}\right\} + R_2\left\{\frac{(a-x)^2}{m^2} + \frac{(a-x)(m-a+x)}{m^2} - \frac{x}{n}\right\} \quad (A12)$$

Since R_1 and R_2 are independent, the two bracketed terms in eq A12 must vanish at t_∞. In either case, one finds

$$n = mx_\infty/(a - x_\infty) \quad (A13)$$

The substitution $mx_\infty/(a - x_\infty)$ for n in eq A12 gives

$$\frac{dx}{dt} = \{R_1 + R_2\}\left(\frac{a}{m}\right)\left(1 - \frac{x}{x_\infty}\right) \quad (A14)$$

Equation A14 may be integrated to yield eq A15 in terms of $t_{1/2}$

$$R_1 + R_2 = 0.6931mx_\infty/at_{1/2} \quad (A15)$$

Since $x_\infty = na/(m + n)$, eq A15 may be written

$$R_1 + R_2 = 0.6931mn/(m + n)t_{1/2} \quad (A16)$$

Substituting $[LiCp]_{tot}$ for m and $2[NiCp_2]_{tot}$ for n, we finally get

$$R_1 + R_2 = \frac{0.6931}{t_{1/2}}\frac{2[NiCp_2]_{tot}[LiCp]_{tot}}{2[NiCp_2]_{tot} + [LiCp]_{tot}} \quad (A17)$$

Equation A17 is the same as eq 3, showing that eq 3 is appropriate for the present example of exchange by two paths. We found experimentally that R_1 and R_2 may be further expressed as

$$R_1 = k_0[LiCp]_{tot}[NiCp_2]_{tot} \quad (A18)$$

$$R_2 = k_1[LiCp]_{tot}^2[NiCp_2]_{tot} \quad (A19)$$

Registry No. $Ni(C_5H_5)_2$, 1271-28-9; LiC_5D_5, 37013-18-6; LiC_5D_5·(TMEDA), 51464-50-7; $Ni(C_5D_5)_2$, 51510-35-1; $Mn(C_5H_5)_2$, 1271-27-8.

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Binding Sites between Platinum(II) and Purine or Pyrimidine Ribosides

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Proton magnetic resonance spectra are reported for the interactions between [Pt(dien)Cl]Cl (dien = $NH_2CH_2CH_2NHCH_2CH_2NH_2$) and purine or pyrimidine ribosides in aqueous and D_2O solutions. The binding sites were located by deuteration of the aromatic protons. Both N_1 and N_7 of adenosine and purine riboside are coordinated simultaneously to two different platinum atoms upon mixing the base and [Pt(dien)Cl]Cl in 1:1 ratio. In the case of 6-methylaminopurine riboside, N_7 is significantly favored as a binding site, but N_1 also becomes a binding site when the ratio of [Pt(dien)Cl]Cl to ligand is greater than unity. In cytidine, N_3 is the binding site, whereas uridine does not interact at all with platinum under these conditions.

Introduction

Recently, our work has been centered around platinum nucleoside complexes[1,2] because of their antitumor activity. In an earlier work,[2] we found that guanosine (G), inosine (I), and xanthosine (X) act as monodentate ligands using N_7 as a binding site. Adenosine (A), however, behaves as a bidentate ligand with both N_1 and N_7 coordinated to two platinum atoms. This result led us to consider N_1 of adenosine as a

(1) (a) P. C. Kong and T. Theophanides, "Second International Symposium on Platinum Coordination Complexes in Cancer Chemotherapy," Wadham College, Oxford, England, April 16–18, 1973; (b) N. Hadjiliadis, P. Kourounakis, and T. Theophanides, *Inorg. Chim. Acta*, 7, 226 (1973).

(2) P. C. Kong and T. Theophanides, *Inorg. Chem.*, 13, 1167 (1974).

pyridine-type site and N_1 of G, I, and X as pyrrole-type sites. Therefore, pyridine-type nitrogens are stronger bases[3] than pyrrole-type nitrogen and should be better binding sites for platinum. In this paper, we report nmr data on other purine bases with pyridine-type atoms N_1. Our purpose was to see if they act as bidentate ligands with platinum. Since N_3 of cytidine and uridine can be classified as pyridine- and pyrrole-type bases, respectively, their interactions with platinum were also examined.

Results and Discussion

Adenosine. The preparation of adenosine complexes with $[Pt(en)Cl_2]$ (en = ethylenediamine) is similar to that of inosine complexes.[2] The analytical data are consistent with the empirical formula, $[Pt(en)A_2]Cl_2 \cdot 4H_2O$. The protons H_2, H_8, and H_1' of adenosine complexes gave a very complicate nmr spectrum in D_2O solutions and assignment of the bands was difficult. In order to simplify matters the diethylenetriamine (dien) complex of the formula, [Pt(dien)Cl]Cl, was used instead of $[Pt(en)Cl_2]$. In [Pt(dien)Cl]Cl only one chlorine atom is available to be displaced by adenosine and the possibility of chelation of adenosine no longer exists. However, the nmr spectra of its complex with adenosine are still just as complicated as those of $[Pt(en)A_2]Cl_2$, as shown in Figure 1 (top). The dien complex [Pt(dien)Cl]Cl is very soluble in water and it is possible to change the ratio of platinum to adenosine. Upon increasing the ratio of Pt/A, the intensities of the peaks in the downfield region increased and those upfield decreased sharply. At a ratio of $Pt/A \geq 3$, the spectrum simplified to that shown in Figure 1 (bottom). The spectrum consists of two main peaks with two platinum-195 satellites on both sides, and the peaks of H_1' are reduced into a doublet. This behavior is interpreted to indicate that the two protons on the purine ring are coupled with ^{195}Pt and give two triplets in which each main peak overlaps with one satellite. When 8-deuterioadenosine was used the main signal at 9.06 ppm and one satellite disappeared leaving a triplet with intensities 1:4:1 due to 34% abundance of ^{195}Pt. The assignment of the peaks is now straightforward. The peak at 8.85 ppm is the H_2 resonance and at 9.06 ppm the H_8. This order is the same as that of free adenosine.[4] The space between the two peaks has only slightly changed compared to that of free adenosine[4] and it is because H_2 and H_8 shift downfield to the same extent. The three bond coupling constants are about 26 Hz, *i.e.*, the same as those of $^3J_{Pt-H_8}$ of I, G, and X complexes.[2] Since the peaks are shifting downfield to the same extent and have the same coupling constants, the two protons are affected equally by platinum.

In the nmr spectrum of inosine complexes the two peaks were separated by 30 Hz (0.5 ppm) compared to those of free inosine[2] of 8 Hz (0.13 ppm). This indicates that one platinum atom on the purine ring cannot affect the two protons equally and thus adenosine must act as a bidentate ligand linked to two platinum atoms through N_1 and N_7. This can also explain why this complex becomes predominant with increasing concentration of platinum.

Adenosine has been reported to bind to Zn(II), Co(II), and Hg(II) with chelation at N_7 and at the amino group.[5-7]

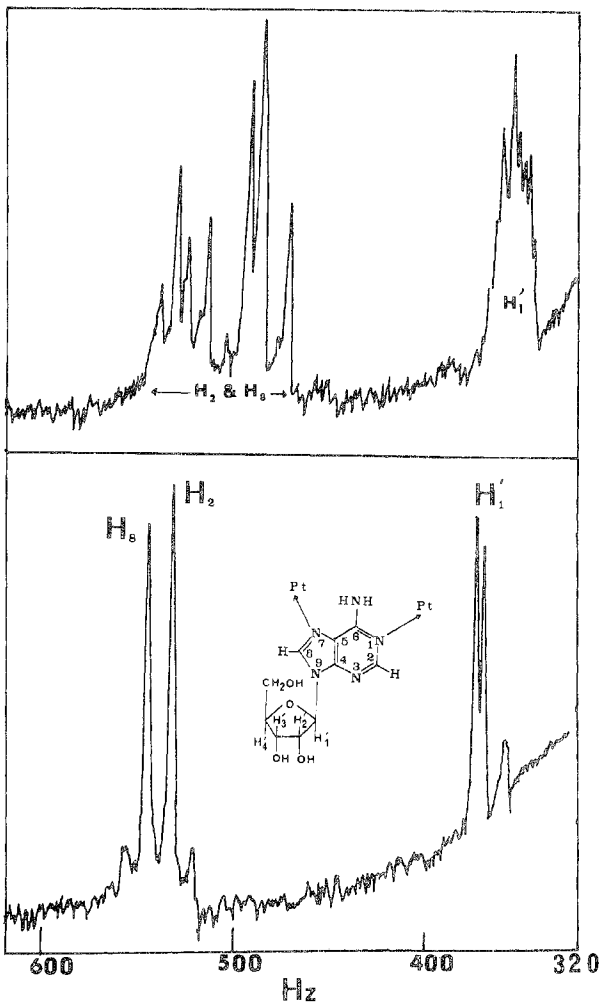

Figure 1. The proton nmr spectra in D_2O: (a) top, [Pt(dien)Cl]Cl: adenosine, 1:1; (b) bottom, [Pt(dien)Cl]Cl in large excess.

Shimokawa, *et al.*,[8] have suggested that the amino group of adenosine is the preferred binding site for Zn(II), Cd(II), and Hg(II) while the N_7 site is preferred for Mg(II), Ca(II), Hg(II), and Sr(II). Although we cannot see the nmr signal of the amino group in D_2O, we can discuss this group from the point of view of coupling constants and stereochemical considerations. The fact that $^3J_{Pt-H_2}$ is equal to $^3J_{Pt-H_8}$ indicates that one platinum atom is linked to N_1 and one to N_7. If the amino group was the binding site, the coupling ($^4J_{Pt-H_2}$) should be much smaller than $^3J_{Pt-H_8}$ because the spin-coupling constant decreases with increasing number of bonds between platinum and proton.[9] For example, the coupling in pyridine complexes is $J_{Pt-H_o} = 33$ Hz and $J_{Pt-H_m} = 10$ Hz for ortho and meta protons, respectively.[10] Furthermore, it is difficult to arrange the two planes of [Pt(dien)] to form bonds with N_7 and the amino group of the purine ring simultaneously. It is of interest to note that Eichhorn, *et al.*,[11,12] found that amino groups do not bind

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(12) N. A. Berger and G. L. Eichhorn, *Biochemistry*, 10, 1847 (1971).

Table I. Chemical Shifts of Aromatic Protons and H_1' of Purine Ribosides, Cytidine, and Their Complexes with Platinum (ppm)

Ligand (L)	[Pt(dien)Cl]Cl/L	H_5	H_2	H_8	H_6	H_1'
Adenosine	0		7.90	8.05		6.02
	Large excess		8.85	9.06		6.18
8-Deuterioadenosine	0		7.90			6.02
	Large excess		8.90			6.20
Purine riboside	0		8.83	8.66	9.00	6.16
	3		9.46	9.44	10.22	6.30
6-Methylaminopurine riboside	0		8.00	8.23		5.81
	1		8.27	8.83		6.05
Adenosine N_1-oxide	0		8.47	8.62		6.06
	2		8.77	9.11		6.16
Cytidine	0	5.96			7.75	5.71
	1	6.08			7.86	5.86

to Cu(II) and that multiple-base binding is taking place with the sites of 3′- and 5′-AMP with an equilibrium favoring the species with Cu(II) bound to N_7.

8-Deuterioadenosine. In order to find how many species exist in solution when the ratio of Pt/L = 1, the 8-deuterioadenosine was used and the peaks due to H_8 were removed. The basic spectrum consists of four peaks still well separated as shown in Figure 2 (top) and the assignment of these peaks becomes now straightforward.[2] The first signal at 7.90 ppm is the H_2 resonance of the free adenosine; the second one at 8.25 ppm is due to H_2 of the PtN_7 (adenosine N_7 coordinated to platinum). This latter signal does not show coupling and shifts slightly downfield.[2] The third peak is due to the PtN_1 (adenosine N_1 coordinated to platinum). The H_2 shows a coupling constant now and shifts downfield. The fourth peak is $PtN_{1,7}Pt$, (adenosine N_1,N_7 bridging to two platinum atoms). The H_2 shifts downfield further and the coupling is unchanged. As the concentration of platinum is increased the fourth peak increases and the others decrease. Finally, when a large excess of Pt was used a triplet was observed and H_1' gives a doublet as shown in Figure 2 (bottom), proving the presence of the linkage PtN_1 in addition to PtN_7. Therefore, there are four species in solution when Pt/L = 1, *i.e.*, free adenosine and complexes PtN_7, PtN_1, and PtN_7,N_1Pt.

Purine Riboside. The downfield spectrum of purine riboside in D_2O solutions is shown in Figure 3 (top). It consists of three resonance peaks which were assigned to H_8, H_2, and H_6, from right to left,[4] respectively. Li, *et al.*,[13] found that N_7 of purine is the preferred site for Zn(II) and Cu(II). On mixing the ligand and platinum in a 1:1 ratio the D_2O solution gave complicated spectra showing several species in solution. Upon changing the ratio to Pt/L ≥ 3, the spectrum simplified to that shown in Figure 3 (bottom). The two upfield peaks almost coalesce into one (0.03 ppm apart) with a coupling constant of 26 Hz and the downfield peak of H_6 with a value of $^3J_{Pt-H_6}$ of 44 Hz. The separation between the upfield and downfield peaks H_6 and H_2 or H_8 is 0.73 ppm. We assign the two upfield peaks to H_2 and H_8 resonances which are affected equally by the platinum atom closest to them. The downfield peak with the large coupling constant of 44 Hz is due to H_6 because it is affected by both platinum atoms linked to N_1 and N_7 in the bridging complex $PtN_{1,7}Pt$. This behavior is analogous to adenosine. The positions of the peaks are shown in Table I.

6-Methylaminopurine Ribosides. The methyl substitution on the amino group ($NHCH_3$) increases the steric hindrance around N_1 and it would be difficult for the platinum to approach N_1. Upon mixing the ligand with platinum in 1:1 ratio, the reaction is nearly complete because only small amounts of free ligand can be observed in the nmr spectrum shown in Figure 4. The spectrum consists of two peaks, an upfield singlet at 494 Hz and a downfield triplet at 530 Hz, $^3J_{Pt-H_8}$ = 26 Hz. Its D_8 derivative did not show the triplet at 530 Hz and this proved that N_7 is the binding site. The methyl group protons shifted from 2.93 to 3.27 ppm on complexation. Upon increasing the Pt/L ratio to 2 or more, a new peak appeared at 548 Hz which is due to the bridging species, $PtN_{1,7}Pt$. However, even with a saturated solution of platinum the coordination of N_1 is not yet complete. It is interesting to compare the spectra of adenosine and purine riboside in the ratio 1:1 with 6-methylaminopurine riboside. The bridging species, $PtN_{1,7}Pt$, in adenosine already exists in a 1:1 ratio, while in the case of 6-methylaminopurine riboside N_1 becomes a binding site after the completion of N_7. This is due to the steric hindrance of the methyl group making N_1 unable to compete with N_7 efficiently in coordination with platinum. It should be remembered that $[Pt(dien)Cl]^+$ is a bulky cation as well.

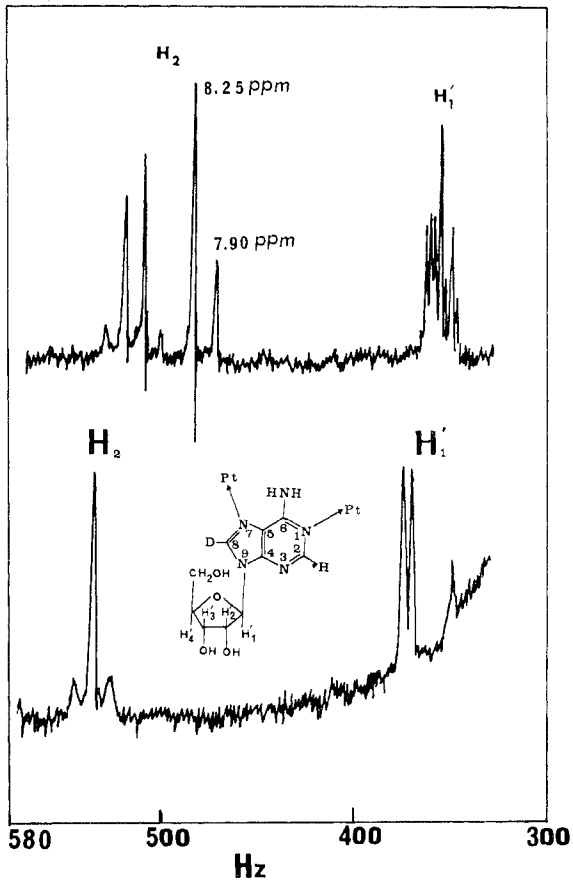

Figure 2. The proton nmr spectra in D_2O: (a) top, [Pt(dien)Cl]Cl: 8-deuterioadenosine, 1:1; (b) bottom, [Pt(dien)Cl]Cl in large excess.

(13) S. M. Wang and N. C. Li, *J. Amer. Chem. Soc.*, 88, 4592 (1966).

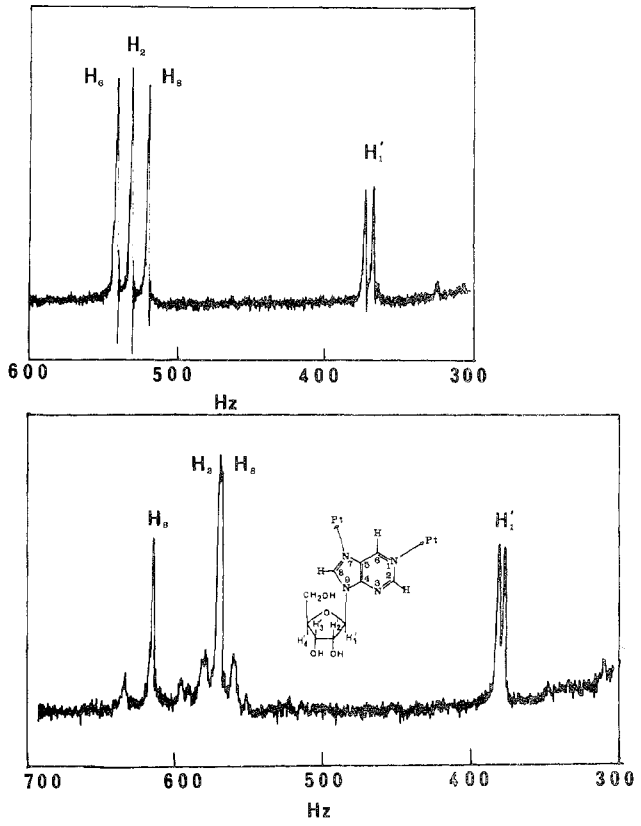

Figure 3. The proton nmr spectra in D_2O: (a) top, purine riboside; (b) bottom, [Pt(dien)Cl]Cl:purine riboside, 3:1.

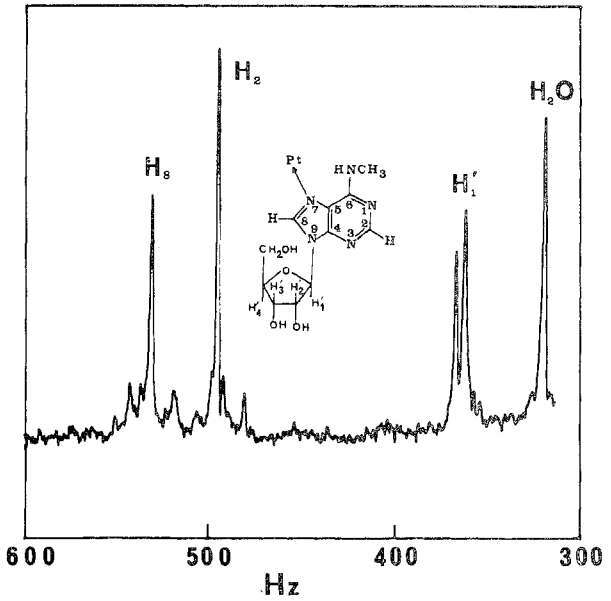

Figure 4. The proton nmr spectrum of [Pt(dien)Cl]Cl in D_2O: platinum complex:*N*-6-methylaminopurine riboside, 1:1.

Adenosine N_1-Oxide. The N_1 position of adenosine is blocked by an oxygen atom and N_1 can no longer be a binding site. Upon mixing with [Pt(dien)Cl]Cl in a 1:1 ratio, the reaction was not complete. The aromatic protons of the free ligand at 506 and 516 Hz assigned to H_2 and H_8, respectively, were present in the spectrum. Upon increasing the ratio of Pt/L to 2, a small amount of free ligand was still left as shown in Figure 5, but there are two strong peaks, an upfield singlet and a downfield triplet $^3J_{Pt-H_8} = 24$ Hz which is the same with the $^3J_{Pt-H_8}$ of the inosine, guanosine,

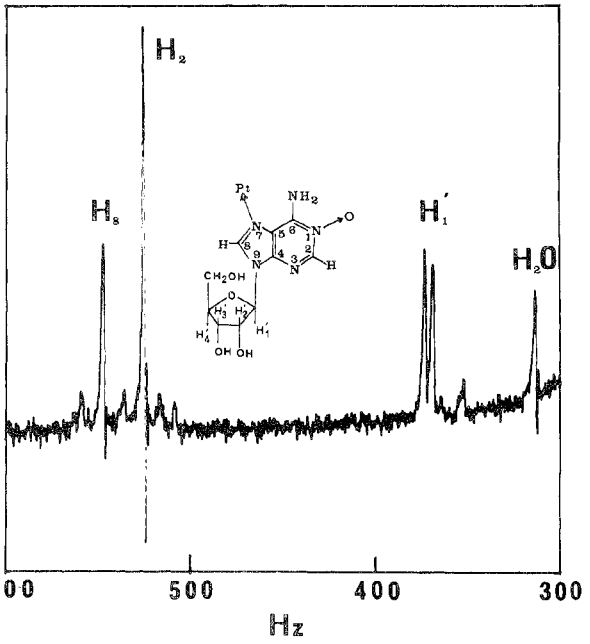

Figure 5. The proton nmr spectrum of [Pt(dien)Cl]Cl in D_2O: platinum complex:adenosine N_1-oxide, 2:1.

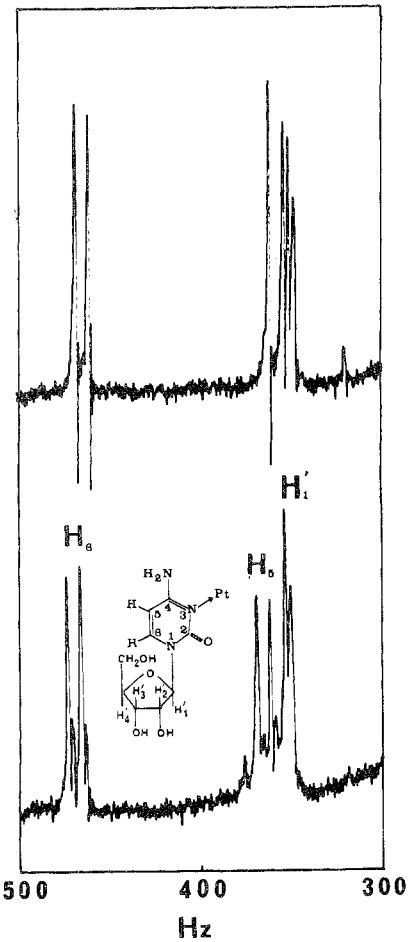

Figure 6. The proton nmr spectra in D_2O: (a) top, cytidine; (b) bottom, [Pt(dien)Cl]Cl:cytidine, 1:1.

and xanthosine complexes.[2] The binding site in this ligand is the position N_7. Although pyridine *N*-oxide complexes of platinum have been reported,[14] the $^4J_{Pt-H_o}$ of ortho protons

(14) M. Orchin and P. J. Schmidt, *Coord. Chem. Rev.*, 3, 345 (1968).

was not detectable. If the oxygen atom of adenosine N_1-oxide was the binding site, the value of $^4J_{PtON_1C_2H_2}$ should be smaller than $^3J_{PtN_1C_2H_2}$ (22 Hz for adenosine) or not detectable at all. We found a coupling constant of 24 Hz in this complex and the possibility of assigning this large coupling constant to $^4J_{PtON_1C_2H_2}$ must be ruled out.

To our knowledge, no purine ribosides studied to date have been found to coordinate through N_3. If we consider N_3 as a binding site, in addition to N_1 and N_7, then the coupling constant of H_2 should be of the order of 45 Hz, as it was found in the case of purine riboside for H_6. The chemical shift also should be significantly changed due to the presence of the platinum atoms at N_1 and N_3. This was not observed. Furthermore, molecular models show that if N_3 was coordinated to platinum, H_1' of the sugar group comes close to it and should, therefore, show coupling.[9] In this conformation, the H_1' is directed toward the square plane of the platinum complex and should have a significant coupling with ^{195}Pt. It is shown in Figures 1-3 (bottom) that H_1' gives a doublet as a result of coupling with H_2', which is the same as in the free ligand. No platinum-195 satellites were observed. Therefore, the possibility of N_3 coordination is ruled out.

Cytidine. The nmr spectra of cytidine in D_2O have been reported.[15] The H_6 is a downfield doublet and the H_5 an upfield doublet close to the doublet of H_1'. On complexation, both H_5 and H_6 moved downfield slightly and the H_5 peaks were well separated from those of H_1', as shown in Figure 6. The spectrum consists of platinum-195 satellites at the left side of H_5. This weak signal is not the spinning peak of H_2O. It is assigned to $^4J_{Pt-H_5} = 8$ Hz, which is close to $^4J_{Pt-H_m}$ of pyridine complexes (H_m meta proton of pyridine).[10] The value of $^5J_{Pt-H_6}$ is too small to measure. The above results show that the platinum atom is closer to H_5 than to H_6. Both cytidine and cytosine bind to Zn(II) and Cu(II) at N_3.[5,11,13] These findings led us to conclude that N_3 of cytidine is the binding site for platinum.

Uridine. On mixing [Pt(dien)Cl]Cl with uridine, the H_5, H_6, and H_1' resonances remained unchanged. It is evident that uridine does not coordinate to platinum under these conditions. It has been reported that uridine did not bind to Zn(II)[5] and Hg(II),[7] and also thymidine did not bind to Cu(II).[11] Platinum seems to follow the trend.

Experimental Section

The nuclear magnetic resonance spectra were obtained on a Varian 60 spectrometer in D_2O solutions using DSS as an internal reference. The nucleosides were purchased from Raylo Chem. Ltd., and the ethylenetriamine complexes, [Pt(dien)Cl]Cl, were prepared following the method of Mann.[16]

Preparation of Deuterio Derivatives. For the 8-deuterioadenosine and 8-deuterio-6-methylaminepurine riboside, 0.3–0.5 g of nucleoside was dissolved in 15 ml of D_2O at 60–70° and was left for 2 days (if the temperature was higher, the standing time was shorter[17]). The solution was then evaporated to dryness under reduced pressure at 0°. 100% deuteration of H_8 was indicated from the nmr spectra.

Preparation of Solutions. In general the ligand and the platinum complex solutions were 0.1 *M* in D_2O (pH 7.50). In those cases where a large excess of the platinum complex [Pt(dien)Cl]Cl was used, this was added directly into an nmr tube which contained 0.1 *M* solution of both ligand and [Pt(dien)Cl]Cl; no correction was made for the small change in volume. In those cases where the ligand was not very soluble in D_2O, the suspension was heated at 50–60° until all of the ligand had dissolved.

Registry No. Pt, 7440-06-4; adenosine, 58-61-7; purine riboside, 550-33-4; 6-methylaminopurine riboside, 1867-73-8; adenosine N_1-oxide, 146-92-9; cytidine, 65-46-3.

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(16) F. G. Mann, *J. Chem. Soc., London*, 466 (1934).

(17) M. P. Schweizer, S. I. Chan, G. K. Helmkamp, and P. O. P. Ts'o, *J. Amer. Chem. Soc.*, 86, 696 (1964).

Contribution from the Instituto di Chimica Generale e Inorganica, Universita, Laboratorio CNR, Florence, Italy

Synthesis and Characterization of 1,8-Naphthyridine Complexes of 1.5-Valent Nickel

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The bidentate ligand 1,8-naphthyridine (napy) reacts with nickel(II) salts to form not only nickel(II) complexes but also to form a series of dimeric complexes of the general formula $[Ni_2(napy)_4X_2]Y$ (X = halogen, NCS, NO_3; Y = PF_6, $B(C_6H_5)_4$) in which the nickel has a formal oxidation number of +1.5. A single-crystal X-ray structural analysis of the complex $[Ni_2(napy)_4Br_2]B(C_6H_5)_4$ was performed on the basis of 2402 independent reflections collected by a PW 1100 diffractometer. The compound crystallizes with four formula units in a monoclinic cell of symmetry $P2_1/c$ and dimensions $a = 9.931$ Å, $b = 32.311$ Å, $c = 16.535$ Å, and $\beta = 101.5°$. The structure was solved by a combination of Patterson and direct methods and refined by the full-matrix least-squares method to $R(F) = 0.077$ and $R_w(F) = 0.085$. The structure consists of binuclear cations $[Ni_2(napy)_4Br_2]^+$ and tetraphenylborate anions $B(C_6H_5)_4^-$. The coordination polyhedron consists of a distorted bicapped prism in which each nickel atom is bound to four nitrogen atoms of four napy molecules. The four nitrogen atoms lie in a plane about the nickel and the bromine at the apex. Each napy molecule acts as a bridge linking together two nickel atoms, the nickel atoms in each unit being 2.41 Å apart. The magnetic and spectral electronic properties of the compounds are discussed. The electronic spectrum of the $[Ni_2(napy)_4Br_2]B(C_6H_5)_4$ complex is discussed on the basis of single-crystal polarized data.

In recent years the coordinating properties of the ligand 1,8-naphthyridine (napy) have been the subject of many investigations.[1] A range of complexes of napy with both transition and nontransition metals have been characterized.

Generally napy has been found to function as a bidentate ligand toward single metal atoms forming complexes with coordination numbers of 6 and 8.[1a] Recently a case has been reported for napy acting as monodentate.[1b]

We have studied the complexing properties of napy and of its 4-methyl derivative (menapy) toward nickel salts in solvents of low dissociating power (*e.g.*, ethanol, butanol) and have isolated bivalent nickel complexes of the general for-