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Nuclear Magnetic Resonance Studies of Pt(II) and Pd(II) Complexes with 4-Amino-2,6-dimethyl Pyrimidine

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Interactions of Pt(II) and Pd(II) with 4-amino-2,6-dimethyl pyrimidine have been studied employing elemental analysis, infrared, proton and carbon-13 nuclear magnetic resonance techniques. The metal is bound to N-1' position of the ligand inspite of the two adjacent methyl groups coupled with the fact that N-1' position might have been protonated under our experimental condition (pH = 3.5). The amino protons are shifted and split into two due to hindered rotation about C-4' carbon.

Introduction

Inspite of the numerous investigations which have been undertaken on the interaction of thiamine with various metal ions, very few have resulted in direct metal-to-nitrogen bond. While some of these interactions are very strong [1], others are very weak [2, 3]. Early investigators [4, 5] have proved that the active part of thiamine is the pyrimidine ring. The multi coordination site nature of thiamine has apparently made it a weak ligand. The electron pairs which could have been effectively engaged in bonding with a metal are involved in the *pi* systems of the pyrimidine and thiazolium rings. In our opinion, the fact that the pyrimidine ring is coupled with thiazolium ring makes the lone pair of electrons at any of the possible coordination site relatively unavailable for complexation. If our assumption is correct, the electron pairs in the pyrimidine or substituted pyrimidines should be more easily available for complexation. In order to prove this hypothesis, we have studied the interactions of Pt(II) and Pd(II) with 4-amino-2,6-dimethyl pyrimidine. We hope to compare the chemical shifts in these complexes with the chemical shifts of Pt(II) and Pd(II) thiamine complexes reported earlier [1]. Aside from the fact that Pt(II) and Pd(II) complexes are widely used in the synthesis of *cis* and *trans* isomers of various complexes, they are also potential anticancer agents [1].

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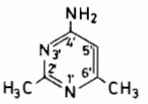


Fig. 1. Numbering scheme of 4-amino-2,6-dimethylpyrimidine (ADMPY).

Experimental

Deuterated dimethyl sulfoxide and 4-amino-2,6-dimethyl pyrimidine (ADMPY) were purchased from Aldrich Chemical Company. Palladium chloride, $PdCl_2$, was bought from Fisher Scientific Company while K_2PtCl_4 was donated by Dr. R. X. Williams of our department.

Proton and carbon-13 NMR spectra were recorded on Nicolet 200 MHz, while infrared spectra were recorded on Beckman IR-33 spectrometer. Deuterated dimethyl sulfoxide, DMSO-d_6, was used as the solvent with tetramethylsilane, TMS, as the internal reference standard. All ^1H and ^{13}C chemical shifts are expressed in parts per million (ppm) downfield from TMS. The melting points were determined in capillaries and were uncorrected. The complexes are prepared using the literature method [1]. Elemental analyses were performed by Galbraith Laboratories of Knoxville, Tennessee.

Anal. Calcd. for Pd(ADMPY)Cl_3, $PdC_6H_9N_3Cl_3$: C, 21.44; H, 2.70; N, 12.51; Cl, 32.87; Pd, 31.24%. Found: C, 22.06; H, 2.70; N, 12.89; Cl, 32.89; Pd, 32.80%.

Anal. Calcd. for Pt(ADMPY)Cl_3, $PtC_6H_9N_3Cl_3$: C, 16.96; H, 2.12; N, 9.90; Cl, 24.82; Pt, 45.96%. Found: C, 16.99; H, 2.18; N, 10.7; Cl, 25.06; Pt, 44.97%.

Results and Discussion

A tabulation of the major IR bands of the metal free ligand and its metal complexes is given in Table I.

TABLE I. Selected IR Data (cm^{-1}) for ADMPY, $Pt(ADMPY)Cl_3$ and $Pd(ADMPY)Cl_3$ in KBR Pellet.[a]

ADMPY	$Pt(ADMPY)Cl_3$	$Pd(ADMPY)Cl_3$
–	3560 s	3560 s
–	3410 s	3405 s
3360 bd	3285 s	3310 s
3160 bd	3208 sh	3220 sh
3000 sh	3060 w	3065 w
2940 sh	–	–
1664 s	1665 s	1665 s
1595 s	1615 s	1615 s
1485 w	1500 m	1500 m
1370 m	1435 m	1430 m
1250 m	1375 m	1390 m
1180 s	1190 m	1195 m
984 s	1040 s	1045 s
830 s	915 s	980 s
770 w	750 w	755 w

[a]Abbreviations: s, strong, m, medium; w, weak; sh, shoulder; bd, broad; sp, sharp.

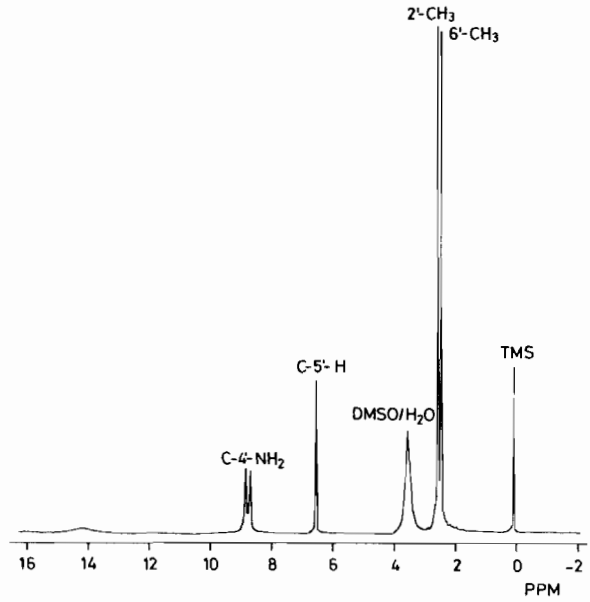
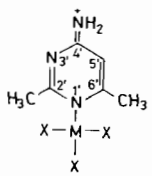


Fig. 2. ^1H NMR of $Pt(ADMPY)Cl_3$ or $Pd(ADMPY)Cl_3$.

This ligand, ADMPY (Fig. 1), has three possible coordination sites, namely N–1′, N–3′ and NH_2. The presence of NH_2 stretch (assym. and sym.) at 3360 and 3160 cm^{-1} for the ligand, 3285 and 3208 cm^{-1} for Pt(II) complex, 3310 and 3220 cm^{-1} for Pd(II) complex as well as the NH_2 band at 1665 cm^{-1} precludes the amino group as a site of metal coordination. The change in position of the NH_2 stretch in these complexes may be due to structural change upon complexation (see Structures I and II). Although ring nitrogen coordination is evident, our IR data do not distinguish between N–1′ and N–3′ coordination. However, this difficulty was resolved by the NMR techniques. Additional support for structural change upon complexation is reflected in the two new bands which occur at 3560 and 3410 cm^{-1} for the Pt(II) and Pd(II) complexes.

Table II shows the ^1H NMR chemical shifts of ADMPY and its metal complexes. The fact that 2′–CH_3 and 6′–CH_3 protons are shifted by approximately 0.1 ppm may suggest symmetry about the metal (Structure I), and also confirms our assumption that coordination is through N–1′ position of the ligand.

Where M = Pt(II) or Pd(II) and X = Cl



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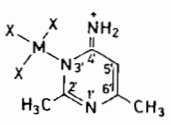

II

TABLE II. ^1H NMR Chemical Shifts of ADMPY, $Pt(ADMPY)Cl_3$ and $Pd(ADMPY)Cl_3$.[a]

Proton	ADMPY	$Pt(ADMPY)Cl_3$	$Pd(ADMPY)Cl_3$
6′–CH_3	2.28,s	2.38,s	2.38,s
2′–CH_3	2.40,s	2.49,s	2.49,s
C–5′–H	6.10,s	6.45,s	6.44,s
C–4′–NH_2	6.52,s	8.75–8.61,d	8.81–8.61,d

[a]Abbreviations: s, singlet; d, doublet; ADMPY = 4-amino-2,6-dimethyl pyrimidine.

TABLE III. ^{13}C NMR Chemical Shifts of ADMPY, $Pt(ADMPY)Cl_3$ and $Pd(ADMPY)Cl_3$.

Carbon	ADMPY	$Pt(ADMPY)Cl_3$	$Pd(ADMPY)Cl_3$
6′–CH_3	22.84	18.08	17.95
2′–CH_3	24.86	21.13	20.99
C–5′	99.54	101.08	101.98
C–6′	163.42	154.34	154.21
C–4′	163.50	161.69	161.64
C–2′	165.70	164.55	164.48

The fact that the amino protons are split and shifted by more than 2 ppm may be supportive of structures I and II. This observation may be ascribed to hindered rotation about C–4′ carbon, resulting in the amino protons being unequivalent. This observation is consistent with the findings of the

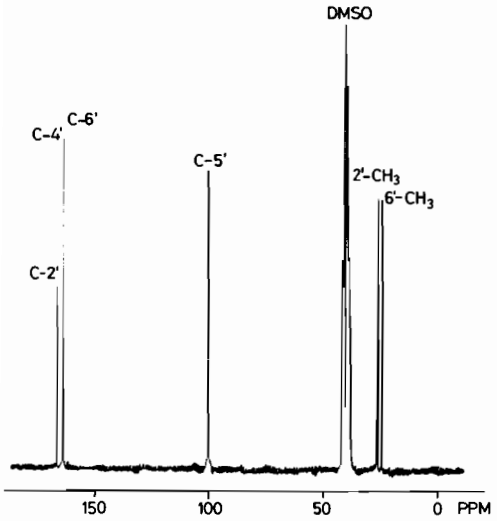

Fig. 3. ^{13}C NMR of 4-amino-2,6-dimethylpyrimidine, ADMPY.

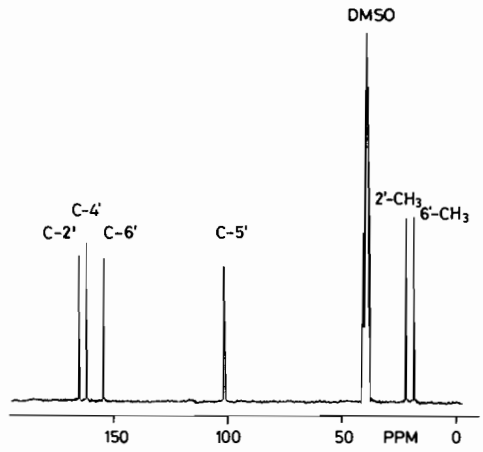

Fig. 4. ^{13}C NMR OF $Pt(ADMPY)Cl_3$.

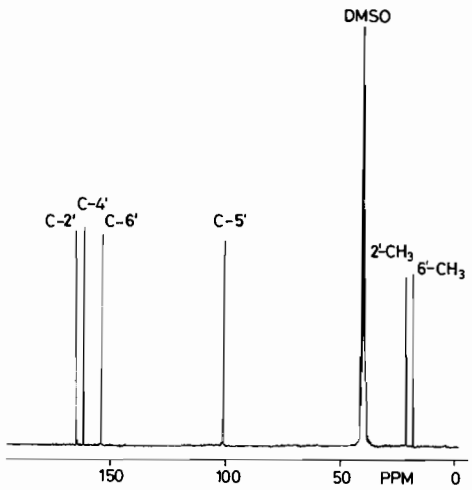

Fig. 5. ^{13}C NMR of $Pd(ADMPY)Cl_3$.

earlier investigators [6]. The fact that the metal is four coordinate may suggest square planar complexes. This is expected since most Pt(II) and Pd(II) complexes are square-planar.

Table III shows ^{13}C NMR chemical shifts of the ligand and its metal complexes. The most interesting observation here is C–6′ carbon which almost collapsed with C–4′ carbon in the ligand (Fig. 3). It was only through expansion that we were able to detect that C–6′ and C–4′ resonances show up almost at the same point. Although all the carbons are shifted upfield, 6′–CH_3, 2′–CH_3 and C–6′ carbons which are in the close proximity of the assumed coordination site experience more upfield shift than the others (Figs. 4 and 5). Thus ^{13}C NMR has provided additional support for coordination through N–1′ position of the ligand.

It is very interesting to observe that inspite of the steric hindrance from 6′–CH_3 and 2′–CH_3 methyl groups coupled with the fact that N–1′ position might have been protonated under our experimental condition (pH = 3.5), Pt(II) and Pd(II) could still bind through N–1′ position of the ligand. In the Pt(II)– and Pd(II)–thiamine complexes reported earlier [1] similar observation was made. Another interesting observation is that 2′–CH_3 protons shifted downfield by approximately 0.1 ppm in this work as well as in the earlier one [1]. In this work, C–6′, C–2′, C–4′ and 2′–CH_3 carbons shifted upfield by approximately 9, 1, 2 and 4 ppm, respectively. Whereas in the previous work [1], the corresponding carbons shifted by 12, 1,5 and 4 ppm, respectively. From these results one may conclude that the effect of the thiazolium portion may be kinetic since the chemical shifts with and without the thiazolium portion are essentially the same for these complexes (reference 1 and this work).

Although, structures I and II are possible, we believe that structure I is more reasonable on the basis of the large ^{13}C chemical shift experienced by C–6′ carbon (9 ppm). Coordination through N–3′ position is unlikely, since one would expect a greater chemical shift for 2′–CH_3 protons which are ortho to N–3′ position than 6′–CH_3 protons which are para to N–3′ position.

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