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Dihalobis(2,4-dimethyl-6-hydroxypyrimidine) Platinum(II) and Palladium(II) Complexes: Nuclear Magnetic Resonance Study

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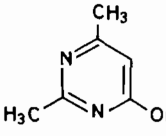
Abstract

Proton and carbon-13 nuclear magnetic resonance techniques have been used diagnostically to establish the binding site of 2,4-dimethyl-6-hydroxypyrimidine in Pt(II) and Pd(II) complexes. All the complexes formed are 1:2 (metal:ligand) complexes and have been proven to be *cis* isomers by employing the Kurnakov test. The ^{13}C NMR resonances of both the ligand and its complexes have been assigned for the first time.

Introduction

In a preliminary communication on this system [1] we reported the synthesis and proton nuclear magnetic resonance of the chloro analogues of Pt(II) and Pd(II) complexes. Both *trans* and *cis* structures were proposed. In the present report the work has been extended to the bromo and iodo analogues and we wish to present detailed proton and carbon-13 NMR spectral data of the six complexes. The impetus for this work arose partly from the need to establish whether these complexes are in the *trans* or *cis* form and partly to compare the chemical shifts in these complexes with those recently reported [2] since the ligands (structures I and II) in both sets of complexes contain identical functional groups.



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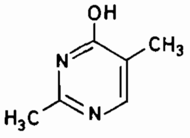

II

Experimental

Potassium tetrachloroplatinate(II), potassium tetrachloropalladate(II), deuterated and regular dimethyl sulphoxide, deuterium oxide, dioxane, lithum iodide, lithium bromide and 2,4-dimethyl-6-hydroxypyrimidine were purchased from Aldrich Chemical Company and were used without any further purification. Proton and carbon-13 NMR spectra were recorded on a High Resolution 200 MHz Spectrophotometer. Proton NMR spectra were run in D_2O as solvent with dioxane as internal reference standard while the carbon-13 NMR spectra were run in DMSO/DMSO-d_6 (4:1).

Preparation of the Complexes

The chloro analogues were prepared as earlier described [1] while the bromo and the iodo complexes were prepared employing a method similar to that already reported by Theophanides *et al.* [3] and Adeyemo *et al.* [4]. The elemental analysis confirmed the chemical formula to be $ML_2X_2 \cdot H_2O$ [M = Pt or Pd and X = Cl, Br or I].

Results and Discussion

The numbering scheme of the ligand is given in Fig. 1.

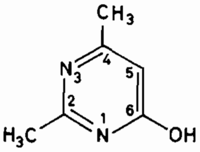

Fig. 1. Numbering scheme of the ligand.

^{1}H NMR Spectra

The proton NMR chemical shifts of the ligands and the complexes are given in Table 1. The assignments of the resonances are based on previous studies including off-resonance techniques [3,5,6]. Four resonances are expected but three were observed for the free ligand and they were assigned as follows: a singlet at 3.11 ppm is due to C_4-CH_3 while the singlet at 3.22 ppm is due to the C_2-CH_3 signal. The signal at 7.01 ppm is ascribed to the C_5-H resonance. The C_6-OH signal could not be observed due to the exchange with deuterium.

In all six complexes, the C_4-CH_3 resonances hardly shifted while the C_2-CH_3 resonance is deshieded

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TABLE 1. ^{1}N NMR Data for the Ligand and its Complexes

Compound	Proton		
	C_4-CH_3	C_2-CH_3	C_5-H
Ligand	3.11	3.22	7.01
$PtL_2Cl_2 \cdot H_2O$	3.06	4.15	6.86
$PtL_2Br_2 \cdot H_2O$	3.01	4.12	6.82
$PtL_2I_2 \cdot H_2O$	3.08	4.15	6.79
$PdL_2Cl_2 \cdot H_2O$	2.93	4.15	6.71
$PdL_2Br_2 \cdot H_2O$	3.00	4.13	6.84
$PdL_2I_2 \cdot H_2O$	3.03	4.14	6.80

(~0.92 ppm) and C_5-H is shielded (~0.2 ppm). This positive shift observed for the C_2-CH_3 resonance in the Pt(II) and Pd(II) complexes compared to the free ligand is a strong indication for a N-1 metal covalent bond. This positive chemical shift which is comparable to those observed by Adeyemo *et al.* [1, 2] is also consistent with that observed by a host of other investigators [3, 5–9].

Since 2,4-dimethyl-6-hydroxypyrimidine has three coordination sites (N-1, N-3, OH) it is only reasonable to advance a sound argument for establishing the most likely coordination site. Assuming that coordination is via N-3 of the ligand, one would expect similar changes for C_4-CH_3 and C_2-CH_3 proton resonances upon complexation at N-3. Since our observation is not in agreement with this hypothesis, it could be concluded that N-3 is not coordinated. Considering N-1 as the coordination site, one would expect C_2-CH_3 and C_6-OH resonances which are *ortho* to this assumed coordination site to be deshielded by about twice as much as C_4-CH_3 and C_5-H protons which are *para* and *meta*, respectively to the N-1 of the ligand. Although the C_6-OH signal could not be observed due to exchange with deuterium, a significant positive shift (~0.92 ppm) observed for the C_2-CH_3 protons compared to the shift observed for C_4-CH_3 and C_5-H protons is in support of N-1 as being coordinated.

^{13}C NMR Spectra

The ^{13}C NMR spectrum of 2,4-dimethyl-6-hydroxypyrimidine is given in Fig. 2. A representative ^{13}C NMR spectrum of the Pt(II) and Pd(II) complexes is shown in Fig. 3.

The ^{13}C NMR chemical shifts of the ligand and its Pt(II) and Pd(II) complexes are given in Table 2. The assignments for the free ligand and its complexes are reported for the first time. The free ligand shows six carbon resonances as expected which are assigned as follows: two resonances at 22.03 and 24.36 ppm are due to C_4-CH_3 and C_2-CH_3 carbons, respectively, while the signals at 110.64 and 159.40 ppm are ascribed to C_5 and C_4 carbons, respectively. The most downfield resonances, 163.38 and 165.32 ppm are due to C_2 and C_6 carbons respectively. It must be admitted that the assignment of C_2 and C_4 carbon resonances, employing the conventional method, is impossible since neither of these two closely spaced carbon resonances is protonated. Consequently the assignment was based on inspection. It is believed that the C_2 carbon which is connected to two ring nitrogens should occur at a slightly lower field than the C_4 carbon which is connected to one ring nitrogen and one carbon. In all six complexes, all the carbon resonances are deshielded except C_5 carbon which experienced an upfield shift of ~3 ppm. The C_2, C_6 and C_2-CH_3 carbons which are adjacent to the assumed coordination site (N-1) are deshielded by about 5, 6 and 4 ppm, respectively. The C_4-CH_3 and C_4 carbons are slightly deshielded by about 1 and 1.5 ppm, respectively. It is quite clear from these

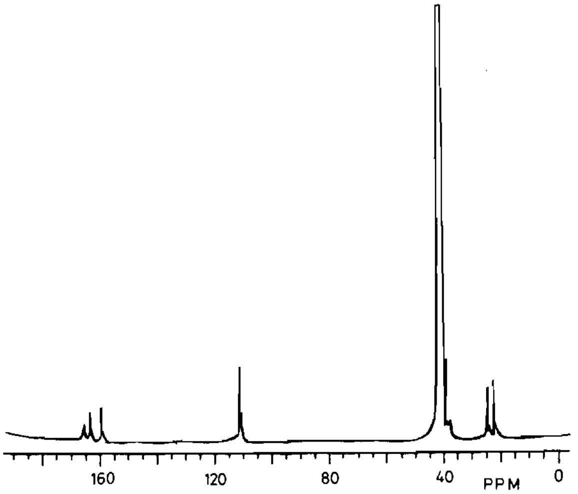

Fig. 2. ^{13}C NMR spectrum of 2,4-dimethyl-6-hydroxypyrimidine.

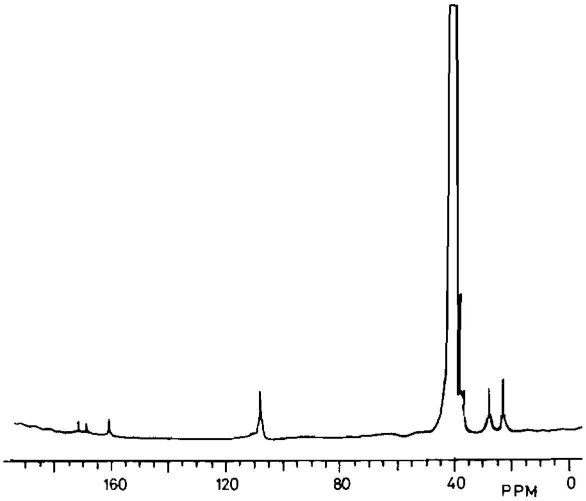

Fig. 3. Representative ^{13}C NMR spectrum of the Pt(II) and Pd(II) complexes.

TABLE 2. ^{13}C NMR Data of the Ligand and its Complexes

Compound	Carbon					
	C_4-CH_3	C_2-CH_3	C_5	C_4	C_2	C_6
Ligand	22.03	24.36	110.64	159.40	163.38	165.32
$PtL_2Cl_2 \cdot H_2O$	23.24	28.14	107.72	160.86	168.58	171.49
$PtL_2Br_2 \cdot H_2O$	23.19	28.10	107.81	160.73	168.52	171.43
$PtL_2I_2 \cdot H_2O$	23.20	28.17	107.76	160.78	168.49	171.50
$PdL_2Cl_2 \cdot H_2O$	23.21	28.20	107.69	160.81	168.50	171.47
$PdL_2Br_2 \cdot H_2O$	23.28	28.18	107.78	160.84	168.51	171.42
$PdL_2I_2 \cdot H_2O$	23.25	28.19	107.70	160.72	168.52	171.51

chemical shifts that N-1 of the ligand is coordinated since the carbon resonances in the immediate environment of the assumed coordination site are the most downfield shifted.

It is interesting to compare the chemical shifts observed in these new complexes with those of the Pt(II) and Pd(II) complexes of 2,5-dimethyl-4-hydroxypyrimidine reported recently [2] since the ligands in both set of complexes contain identical functional groups.

In the new complexes, the C_2-CH_3 resonance experienced a downfield chemical shift of ~0.92 ppm whereas the same protons shifted downfield by ~0.80 in the 2,5-dimethyl-4-hydroxypyrimidine Pt(II) and Pd(II) complexes [2] compared to the free ligands. Also in the new complexes, C_2, C_6 and C_2-CH_3 resonances which are adjacent to the assumed coordination site (N-1) shifted downfield by about 5, 6 and 4 ppm, respectively whereas in the previous complexes [2] the same carbon resonances shifted downfield by about 3.41, 0.98 and 2.26 ppm, respectively.

In summary, the absence of complex proton and carbon-13 NMR spectra confirms the non-polymeric nature of these new complexes [10]. A positive chemical shift of ~0.92 ppm observed for C_2-CH_3 protons which are adjacent to the assumed coordination site (N-1) is a strong indication for metal ligand covalent bonding [1, 2, 9]. The significant downfield chemical shifts experienced by C_2 (5 ppm), C_6 (6 ppm) and C_2-CH_3 (4 ppm) carbon resonances which are adjacent to the assumed coordination site also lend support to our assumption that N-1 of the ligand is coordinated. This observation is in good agreement with earlier reports [2, 9]. The Kurnakov test [11] proved that all the new complexes were *cis* isomers.

Acknowledgements

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