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Interactions of Pt(II) and Pd(II) with 2,4-Dimethyl-6-hydroxylpyrimidine

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Interactions of Pt(II) and Pd(II) with 2,4-dimethyl-6-hydroxylpyrimidine have been studied, employing elemental analysis, proton magnetic resonance and infrared spectroscopic techniques. The metal is bound to two ligand molecules through nitrogen and hydroxyl group. The complexes isolated have been formulated as $ML_2X_2 \cdot H_2O$, where M = Pt or Pd and X = Cl. The structures proposed for these complexes are based on the elemental analyses and physical measurements.

Recently, much attention has been paid to platinum and palladium containing complexes due to their potent anti-tumor activities [1–4]. Earlier studies [5–7] have also pointed to the fact that small variations in the ligands could produce remarkable differences in anti-tumor activity, most especially, of the *cis* isomers of these complexes. This letter reports the synthesis and characterization of Pt(II) and Pd(II) complexes with 2,4-dimethyl-6-hydroxylpyrimidine (DMHPY).

The chemicals (K_2PtCl_4, K_2PdCl_4 and D_2O) used in this work were purchased from Aldrich Chemical Company and were used without further purifications. The synthetic approach was described in earlier works [3, 8]. *Anal.* Calcd. for $Pt(DMHPY)Cl_2 \cdot H_2O$, $PtC_{12}H_{16}N_4O_2Cl_2 \cdot H_2O$: C, 27.07; H, 3.38; Pt, 36.67%. Found: C, 27.51; H, 3.40; Pt, 37.17%. *Anal.* Calcd. for $Pd(DMHPY) Cl_2 \cdot H_2O$, $PdC_{12}H_{16}N_4O_2Cl_2 \cdot H_2O$: C, 32.48; H, 4.06; Pd, 24.00%. Found: C, 32.66; H, 4.07; Pd, 23.51%. The elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

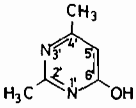

Fig. 1. Structure of 2,4-dimethyl-6-hydroxylpyrimidine.

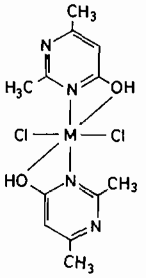

Fig. 2. Possible *trans* structure of Pt(II) and Pd(II) Complexes.

^1H NMR studies were performed in D_2O on HITACKI PERKIN ELMER R-600 High Resolution NMR Spectrometer. Table I shows the proton chemical shifts in parts per million of the ligand and its metal complexes. A modest 0.93 ppm downfield experienced by C–2′–CH_3 protons is indicative of complexation at N–1′ position of the ligand. The 6′–OH signal could not be observed, obviously, due to exchange with deuterium.

Infrared spectra in KBr were recorded on a Perkin Elmer model 621 spectrometer. The IR data clearly show very strong support for the structures proposed for these complexes. For example, the band at 315 cm^{-1} in both Pt(II) and Pd(II) complexes are assigned to metal–chloride based (4.9). Evidence for metal–nitrogen bond is reflected in the medium bands at 560 and 510 cm^{-1} in both complexes. This is in excellent agreement with the previous work [4]. Kurzak and Wajda also observed a medium band

TABLE I. ^1H NMR Data for the Complexes.

Proton	DMHPY	$Pt(DMHPY)Cl_2 \cdot H_2O^a$	$Pd(DMHPY)Cl_2 \cdot H_2O^b$
C–4′–CH_3	3.11	3.06	2.93
C–2′–CH_3	3.22	4.15	4.15
C–5′–H	7.01	6.89	6.71

[a] Sulfur–yellow crystals decomposed at 291 °C. [b] Orange–yellow crystals decomposed at 298 °C.

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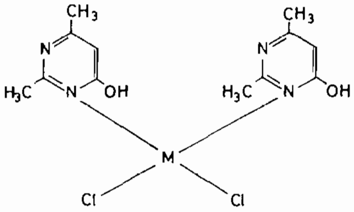

Fig. 3. Possible *cis* structure of Pt(II) and Pd(II) Complexes.

around 480 cm^{-1} for their molybdenum metal complexes [10]. The very weak band at 3420 and 3200 cm^{-1} are due to water molecule. Ligand bands at 1415, 1390 and 1360 cm^{-1}, involving contribution of deformation modes of the OH group have slightly moved to 1435, 1395 and 1365 cm^{-1}, respectively, in the complexes. This result implies possible coordination of the metal to the hydroxyl group of the ligand. The strong bands at 3000 and 2900 cm^{-1} are obviously due to ν(C–H) aromatic.

In view of the 0.93 ppm chemical shift experienced by C–2′–CH_3 protons, which are *ortho* to the assumed coordination site (Table I), and the strong evidence from IR data with respect to metal–nitrogen and metal–chloride bond, and the slight shift of the OH group, we proposed the possible *cis* and *trans* structures for these complexes (see Figs. 1–3).

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