

Synthesis and Spectroscopic Studies of Pt (II) and Ni (II) Complex Compounds with Hydantoin Derivatives

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Abstract: New Pt(II) Complex of 5-(Hydroxy-phenyl-methyl)-5-phenyl hydantoin (HPMPH) and Ni(II) complex of 5-Methyl-5-phenyl-hydantoin (MPH) were synthesized and characterized by elemental analysis, FT-IR and UV-VIS spectra. The spectral and elemental analysis indicated a square planar structure of Pt(II) complex and a tetrahedral structure of Ni(II) complex with ligands coordinated via the nitrogen atoms.

Key words: Pt(II) · Ni(II) complexes · Hydantoin · Cis-Diammineplatinum(II) dichloride

INTRODUCTION

The bonding of hydantoin with transition metal ions is interest because of presence of imidazole groups along protein chains which involve histidine residues [1, 2]. The complexation of transition metals with five-member heterocyclic ligands possessing more than one donor atom, are of great interest in the chemistry of coordination compounds [3, 4]. Biological activity of complexes with hydantoin derivatives has been widely studied as antitumoral and anti bacterial effects. [5-10] but little attention was paid to HMPMH and MPH with Ni(II) and Pt (II) ions. In this work we have prepared and characterized new Pt(II) and Ni(II) complexes of using these ligands.

The main motive of this work is to lower the side effect while maintaining similar or higher efficiency than the parent ligand [11, 12]. In this work the parent ligand is chlorine in both *cis*-platin and nickel tetrachloride complexes. The present study explains the platinum and nickel complex formation and determination of their structure.

Experimental

Characterization Technique: The elemental analysis of carbon, hydrogen and nitrogen was carried out using series II 2400 PERKINELMER model. FT-IR spectra were recorded on JASCO FT/IR model 410 instruments operating within the range 400-4000 cm^{-1} . The UV-Visible spectra of the samples were run on JASCO UV-Visible model V-530 spectrometer.

Reagents: All chemicals used were analytical grade. The *cis*-platin (*cis*-DDP) was obtained from Sigma-Aldrich.

Synthesis of Complex [Pt (HPMPH) (NH₃)₂] (NO₃)₂·H₂O: Cis-[Pt (NH₃) Cl₂] (0.1 g) were added to 0.07 M AgNO₃, as water solution (10mL). The mixture was heated to 60°C at constant stirring. The precipitate formed was filtered off anhydrous ethanol (4mL) solution of 5-(Hydroxy-phenyl-methyl)-5-phenyl (HPMPH) (0.094 g) was added to the filtrate and the mixture was evaporated to dryness at 60°C. The dark green substance was isolated [13]. Then washed with ethanol and dried at room temperature (Figure 1).

Elemental analysis:

Calculated for CHN: C, 30.23; H, 3.14; N, 13.11.
Found: C, 30.10; H, 3.25; N, 13.11.

Synthesis of Complex Ni (MPH) Cl₂: A solution of (1.47g) of 5-methyl-5-phenyl hydantoin in (20 mL) pure acetone was added while stirring to solution of (2.1g) tetrabutyl ammonium chloride plus (0.5g) nickel chloride in (20mL) pure acetone. The blue crystalline precipitate was filtered washed with acetone and dried (Figure 2)

Elemental Analysis:

Calculated for CHN: C, 41.89; H, 2.90; N, 8.14.
Found: C, 41.61; H, 3.10; N, 8.13.

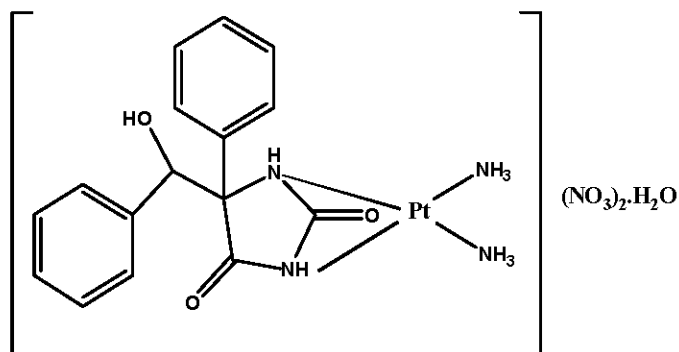


Fig. 1: Complex of [Pt (HPMPH) (NH₃)₂] (NO₃)₂.H₂O

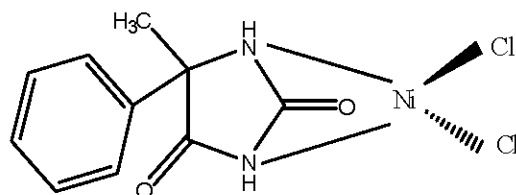


Fig. 2: Complex of Ni (MPH) Cl₂

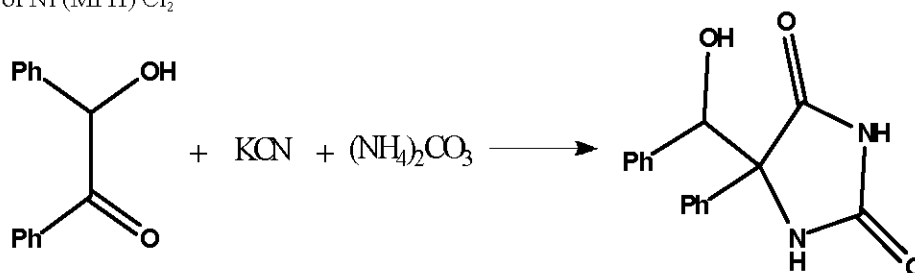


Fig. 3: Reaction of Preparation of HPMPH

Preparation of HPMPH: HPMPH prepared by Henze, H. R. and Speer reference [14].

0.02 mole of benzoin (α -Hydroxybenzyl-phenyl ketone) is dissolved in 50 cc of 50% alcohol and 9.1 g (0.08 mole) of ammonium carbonate and 2.6 g. (0.04 mole) of potassium cyanide added. This mixture is warmed under a condenser at a temperature of 58-60°C for two hours, the solution concentrated to approximately two-thirds of the initial volume and chilled in an ice-bath. If, however, no separation of hydantoin occurs, subsequent acidification with hydrochloric acid under hood and further chilling usually suffices to precipitate the yellow crystals of hydantoin (Figure 3).

IR (cm⁻¹): 3380 and 3415(-NH), 1678 and 1722(C=O)

Elemental Analysis

Calculated for CHN: C, 68.08; H, 4.96; N, 9.90.
Found: C, 67.90; H, 4.30; N, 9.81;

RESULTS AND DISCUSSION

Characterization of the complexes On the basis of elemental analysis the structure formula of complexes are [Pt (HPMPH) (NH₃)₂] (NO₃)₂, Ni (MPH) Cl₂. The platinum complex (green) was soluble in water and ethanol. The nickel complex (blue) soluble in water but its color changes to pale green. This change indicates that the water molecules replace ligands.

Infrared Spectra of Platinum Complex: In order to obtain information about the coordination mode of the ligand, the IR spectra of the complex and the free ligand were recorded (Figure 4, 5). The data obtained are shown in Table 1.

It is evident that the C=O group is not involved in the coordination as both of the two ν (C=O) bands present in spectrum of the complex are not affected.

On the other hand, the band of complex in the range of stretching NH- ν_s (NH) and ν_a (NH) at 3377 and 3413 cm⁻¹ indicate shifting of 3 and 2 cm⁻¹ respectively.

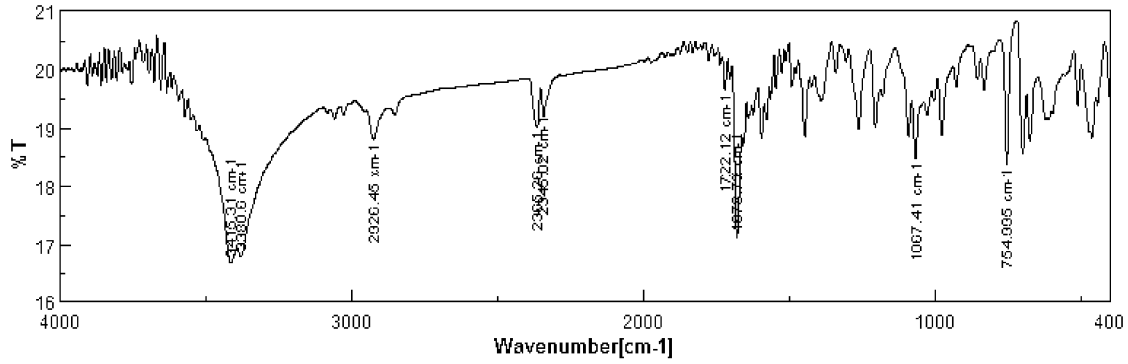


Fig. 4: The FTIR Spectrum of HPMPH Ligand

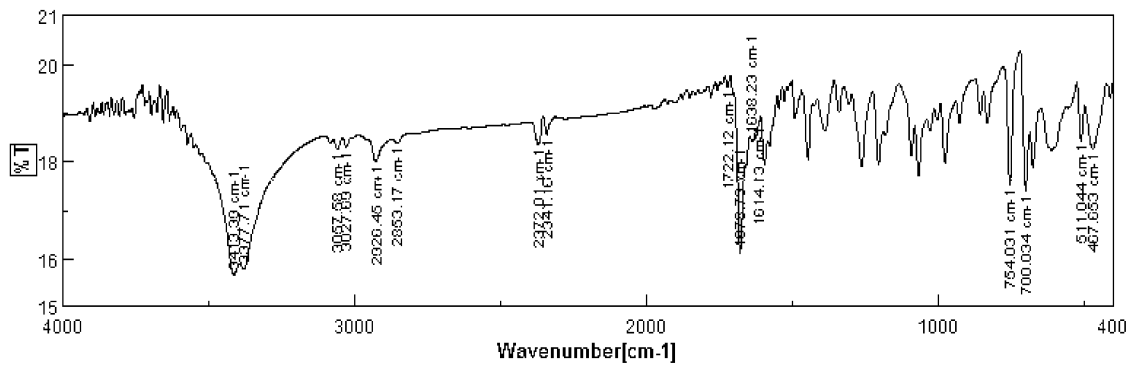


Fig. 5: The FTIR Spectrum of Pt(II) Complex

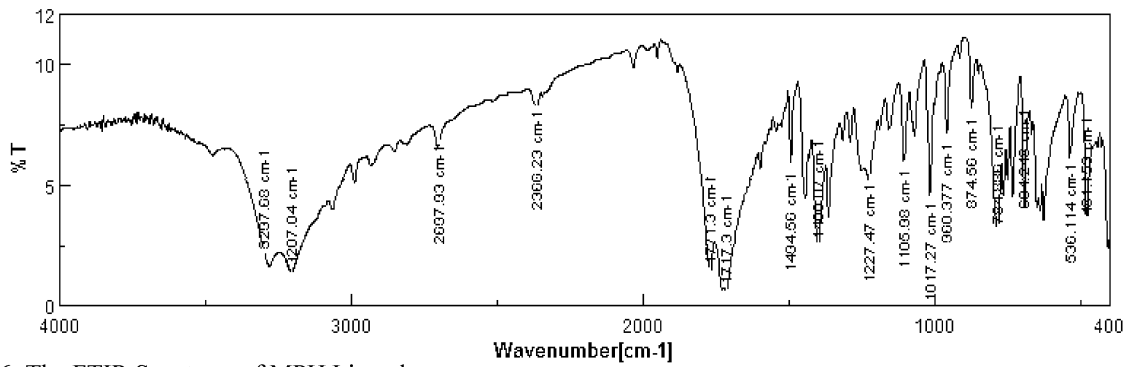


Fig. 6: The FTIR Spectrum of MPH Ligand

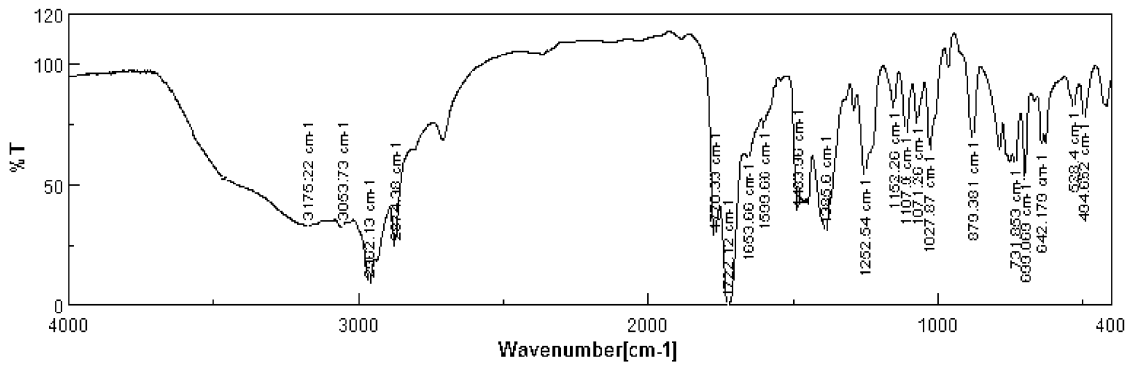


Fig. 7: The FTIR Spectrum of Ni(II) Complex

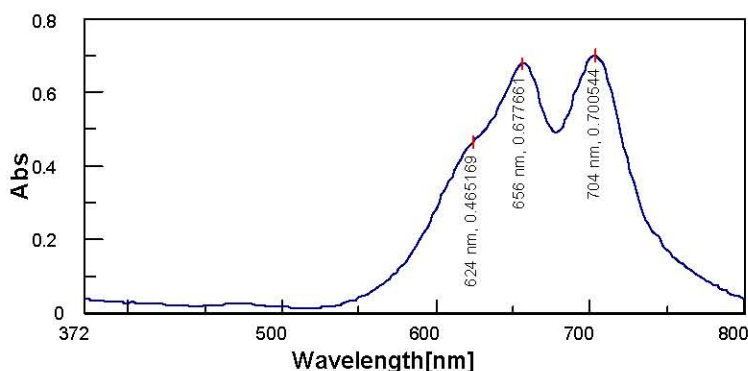


Fig. 8: The UV-VIS Spectrum of Nickel Complex.

Table 1: IR data for the free ligand [5-(Hydroxy-phenyl-methyl)-5-phenyl hydantoin] and for the complex [Pt (HPMPH) (NH₃)₂ (NO₃)₂] (cm⁻¹)

Compound	$\bar{\nu}(\text{NH})$	$\nu(\text{NH})$	$\nu(\text{Pt-N})$	$\nu(\text{C=O})$
Ligand	-	3415		1722
	-	3380		1678
Complex	1638	3413	511	1722
	1614	3377	467	1678

Table 2: IR data for free ligand [5-Methyl-5-phenyl-hydantoin] and for the complex [Ni (MPH) Cl₂] (cm⁻¹)

Compound	$\bar{\nu}(\text{NH})$	$\nu(\text{NH})$	$\nu(\text{Ni-N})$	$\nu(\text{C=O})$
Ligand	-	3297		1771
	-	3207		1717
Complex	1653	3175	528	1770
	1599	3053	494	1718

Bands in the range of deformation vibration characteristic for the coordination mode $\bar{\nu}(\text{NH})$ at 1638 and 1614 cm⁻¹ are observed. The $\nu(\text{Pt-N})$ bands at 511 and 467 confirm the *cis*-position of the ligands in the complex [15, 16].

Infrared Spectra of Nickel Complex: The IR spectral data of ligand and the complex are shown in Figure 6, 7 and Table 2.

The bands in the range of N-H stretching vibrations of the complex were shifted to lower frequency (3297, 3207) compared to those of the free ligand. This suggests coordination through the NH group. It is also evident that the C=O groups is not involved in the coordination as both the two $\nu(\text{C=O})$ bands present in spectrum of the complex are not affected. The bands in the 494-528 cm⁻¹ are characteristic to ligand-metal bonding.

UV-Vis Spectra: The d-d transition of [Pt (HPMPH) (NH₃)₂] (NO₃)₂ in H₂O could not be observed. The finely powdered sample of nickel complex is dissolved in ethanol and the spectrum is recorded from 372 to 800 nm (Figure 8).

Gives the optical spectrum of the nickel complex. Two strong peaks and one shoulder are observed at 704, 656 and 624 nm and the assignments are:

$${}^3T_1(F) ? {}^3T_2(F), 704 \text{ nm} = 14204.54 \text{ cm}^{-1}$$

$${}^3T_1(F) ? {}^3T_1(P), 656 \text{ nm} = 15243.90 \text{ cm}^{-1}$$

$${}^3T_1(F) ? {}^3A_2(F), 624 \text{ nm} = 16025.64 \text{ cm}^{-1}$$

CONCLUSION

According to the elemental analysis, only one molecule of ligands is coordinated to the metal ion. This result shows that the geometry of complexes are either square planar or tetrahedral. Basing on spectral studies, it can be concluded that the Nickel and Platinum complexes have respectively tetrahedral and square planar geometry. The plausible structures of the complexes are given in Figure 1,2. In the end complex Pt (II) and Ni (II) should be considered for antitumor activity studies.

REFERENCES

- Edsall, J.T., G. Felsenfeld, D.S. Goodman and F.R.N. Gurd, 1954. J. Amr. Chem. Soc., 76: 3054.
- Kotton, W.L., R.N. Dexter, R.E. Clark and F.R.N. Gurd, 1958. J. Amr. Chem. Soc., 80: 4188.
- Basson, W.D. and A.L. Du preez, 1974. J.Chem.Soc.Dalton Trans., 24: 1708.
- Larkworthy, L.F. and J.M. Tabatabaei, 1977. Inorganica Chimica Acta, 21: 265.
- Wernecke, E., 1916. Deut. Med. Wochschr, 42: 1193-1194.
- Lee, C.S. and L.Z. Benet Anal. Profiles, 1978. Drug. Subs., 7: 231.
- Cole, A., P. M. May and D. R. Williams, 1981. Agents Actions, 11: 296.
- Gupta, V.K., R. Prasad and A. Kumar; 2003. Talanta, 60: 149.

9. Bakalova, A., 2006. *J. of the Chemical Technology and Metallurgy*, 41: 119-124.
10. West, D.X., A.E., Liberta, S.B. Padhye, P.B. Chikate, A.S. Sonawane, O. Kumbhar and R.G. Yerande, 1993. *Coord. Chem. Rev.*, 123: 49.
11. Karaff, I.H., 1988. *Clinical Application of Platinum and Other Metal Coordination Compounds in Cancer Chemotherapy*, Nicolini.M(Ed), Martinus Nijhoff Publishing, Boston, pp: 351.
12. Jamiesson, E.R. and S.J. Lippard, 1999. *Chem. Rev.* 99(98): 2467-2474.
13. Bakalova, A., *et al.* 2005. *European J. Med. Chemistry*, 40: 590-596.
14. Henze, H.R. and R.J. Speer, 1942. *J. Am. Chem. Soc.*, 64: 522-523.
15. Larkworthy, L.F. and J.M. Tabatabaei, 1970. *J. Chem. Soc. Dalton*, pp: 814.
16. Kushev, D., *et al.* 2002. *J. Inorganic Biochemistry*, 89: 203.