



PHYSICO-CHEMICAL STUDIES OF TRANSITION METAL COMPLEXES DERIVED FROM 4-METHYL ISONITROSOACETOPHENONE (HIMAP)

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Abstract

Complexes derived from 4-methyl isonitrosoacetophenone HIMAP with Pd(II) and Pt(II) ions have been prepared. Structural investigation of the ligand and their complexes of formula Pd(IMAP)₂, Pt(IMAP)₂, have characterised on the basis of elemental analysis, molar conductance, magnetic susceptibility, infrared (FT-IR), ultraviolet and visible spectra (UV-Vis) and proton nuclear magnetic resonance (H NMR). The isolated complexes behave as non electrolyte in DMF solution. The diamagnetic and spectral features of the Pd(II) and Pt(II) complexes suggested square planar geometry.

Keywords: Transition metal complexes, non-electrolyte, susceptibility, palladium

Introduction

Metal complexes of bidentate oximes are capable of exhibiting a variety of structures owing to their potential ambidentate character. For many Ni(II) and Pd(II) complexes obtained from isomtroso β diketones asymmetrical ring structures have been reported^{1,2} Patel and co-workers³ have proposed a symmetrical five member ring structure. The ligand 4-methyl isonitrosoacetophenone (HIMAP) has been used for few analytical applications^{4,5}. However, structural studies of the Pd(II), Pt(II) complexes with HIMAP have not been reported as such. It was therefore considered worthwhile to prepare and characterize them and report their structural features on the basis of magnetic data, electronic, IR and NMR spectral studies.

Experimental

Chemicals: The chemicals used were of A.R. grade. The ligand 4-methyl isonitrosoacetophenone was prepared by the method described in the literature^{6,7}. The metal complexes are prepared as follows:-

Preparation of Pd(IMAP)₂ complex:- 0.625 g of HIMAP and 0.355g of PdCl₂ were dissolved in minimum quantity of alcohol and equal volume of water.

The palladium solution was added to the reagent solution drop wise with constant stirring. The pH of the resultant was adjusted to 3.5 - 4 with HCl / NH₄OH. A colored complex thus formed was digested on water bath for 20 minutes, it was filtered, washed with water, dried at 90°C for several hours. It was recrystallised from chloroform and analyzed for palladium, carbon, hydrogen and nitrogen.

Preparation of Pt(IMAP)₂ Complex:- 0.326g of HIMAP and 0.507g of chloroplatinic acid

was dissolved in minimum quantity of alcohol and equal volume of water. the, platinum solution was added to the reagent solution drop wise with constant stirring the pH, of the resultant solution was adjusted to 2.5 to 3. Then the solution was kept in a boiling water bath for 30 minutes, a colored complex was separated. It was filtered, washed with distilled water, dried at 100°C for 4 hours. It was recrystallised from chloroform and analyzed for platinum, carbon, hydrogen and nitrogen.

Physical Measurements: Magnetic measurements of solid complexes were carried out from room temperature to liquid nitrogen temperature with Govy balance using mercury tetra-thio-cyanato cobalt(II) as magnetic susceptibility standard.

Diamagnetic corrections were calculated by the method given in the literature. Visible and Ultraviolet spectra of the ligand and the complexes were recorded on a Shimadzu Zq Uv-2000 spectrophotometer. Infrared spectra of the ligand and the complexes were obtained on specord 75 ir in potassium bromide pellets. The conductance measurements were made in nitrobenzene solution.

Results and discussion

Analysis data and some properties of the complexes are reported in Table 1

On the basis of analytical data Pd(II) and Pt(II) complexes can be represented as M(IMAP)₂.

The complexes are colored and have good thermal stability. They are insoluble in water and dilute alkali solution. Suggesting absence of a free oxime group due to removal of oximino, proton during complexation this is supported the infrared spectral studies. The molar conductance values in nitrobenzene indicate their non-electrolytic nature⁸.

Magnetic Measurements: The result of magnetic susceptibility measurements in a variable temperature data suggest that the Pd(II) and Pt(II) complexes may be diamagnetic with square planer geometries^{9,10}. These suggestion are in agreement with spectral observation.

Electronic Spectra : The electronic spectral data for the complexes show a group of three or more bands in the 47.84 kK range which can be assigned as $\pi - \pi^*$ or ligand metal transitions.

The electronic spectral of HIMAP in methanol shows an intense band at 47.84 kK. It splits into two strong bands at 43.10 kK and 42.79 kK. these can be explained by presuming that the symmetric it electron system cloud of HIMAP. They may be assinged to $\pi - \pi^*$ transition. The electronic spectrum of Pt(II) complex resemble to those of tetrahedral or square planer Pt(II) complexes¹¹

Infrared Spectra : I.R. spectra (4000-400 cm^{-1}) of the complexes are practically identical. the frequencies of some significant band)of the free ligand and those of the metal complexes are reported in Table 4. The observed frequencies of different groups in the metal complexes have been assigned on the basis of literature data.

The $\nu_{\text{O-H}}$ of the oxime group observed at 3289 cm^{-1} in HIMAP is absent in the spectra of the complexes suggesting replacement of the oxime proton by the metal ion during complexation¹².

The peak observed near 1628, 1622, 1602 cm^{-1} in spectrum of Pd(IMAP)₂, Pt(IMAP)₂, respectively, may be assigned to the perturbed $\nu_{\text{C=O}}$ and /or $\nu_{\text{C=N}}$ stretching vibration involving bonding through oxygen, and nitrogen donor atoms. A bands appear in the range 1300-1200 cm^{-1} is reported that N-oxide

(N→O) stretching mode in aromatic ring compounds¹³. The bands at 1062, 1089, 1026 cm^{-1} in Pd(IMAP)₂, Pt(IMAP)₂, respectively are attributed to the N-O stretching in the ligand¹⁴.

It is significant to note that for metal complexes reported to have coordination only through the oxime oxygen or nitrogen atoms only. One medium to strong band at around 1050 or 1200-1250 cm^{-1} is found leading to a symmetrical six member ring structure¹⁶ or asymmetrical five member ring structure.

NMR Spectra : The nuclear magnetic resonance spectrum of HIMAP in DMSO solution reveals a peak around 8.64 δ (delta) due to the =NOH group. Two groups of bands corresponding to -CH and aromatic ring in HIMAP are observed at 2.72 δ and 7.62 δ respectively. The proton signal due to CH₃ proton appear at 2.09 (Table 3). It may be mentioned the dioxime solutions of ethyl - α -isonitrosoacetate (HEINA). Isonitrosoacetylacetone¹⁵ (HINAA) and Isonitrosoacetophenon (HINAP) show =NOH proton resonance at -9.27 δ , -8.65 δ and -8.6 δ respectively.

NMR spectra Pd(IMAP)₂, Pt(IMAP)₂, in DMSO solution exhibit peaks due to methyl methylene, and aromatic ring proton and do not show any proton signal due to the =NOH group. This suggests that there complexes have been formed by the replacement of the proton of the =NOH group by the metal ion. It is interesting to note that the peaks due to methyl proton Pd(IMAP)₂ appear at lower value compared to that of methyl proton in the reagent HIMAP. Further signals of the aromatic ring group in these complexes occur at higher field. Side with respect to that of aromatic ring signal in HIMAP.

TABLE NO.1 ANALYTICAL DATA, COLOUR MOLAR CONDUCTANCE IN NITROBENZENE AND μ_{eff} AT ROOM TEMPERATURE *

COMPLEX	COLOUR	%C	%H	%N	%M	M	μ_{eff}
Pd(IMAP) ₂	Yellowish	50.46 (50.19)	3.95 (3.74)	6.83 (6.50)	25.12 (24.72)	10.2	Diamagnetic
Pt(IMAP) ₂	Gray	41.26 (41.62)	3.79 (3.10)	5.38 (5.39)	38.86 (38.09)	9.5	Diamagnetic

Table No.2 Nuclear Magnetic Resonance Signals Observed in 4- methyl isonitrosoacetophenon (HIMAP) and its metal complexes.

HIMAP	Pd(IMAP) ₂	Pt(IAMP) ₂	Assignments
8.64 δ	-	-	= NOH
7.62 δ	7.57 δ	7.57 δ	Aromatic ring

2.72 δ	2.64 δ	2.71 δ	-CH group
2.17 δ	2.28 δ	2.01 δ	- CH ₃ group

Values in delta (δ) w.r. to TMS or reference standard.

Table 3 : Infrared Frequencies (4000 to 400 cm⁻¹) of ligand and metal complexes

Ligand	Pd(II)	Pt(II)	Assignment of group
3289	---	---	OH, Ar-H
---	3427	3415	Ar-H
1640	---	---	C=O
---	1628	1622	C=N, C=O
1448	1434	1419	CH ₃
---	1260	1195	N O
1079	1062	1089	N-Oxide
---	840	802	N-O
763	757	756	Para Sub.

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