

Synthesis, Characterization & Antimicrobial Studies of Platinum (II), Palladium (II) And Fe (II) Complexes with Newly Synthesised Ligand p- Phenyl Isonitroso Acetophenone

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ABSTRACT:

The Pt(II) , Pd(II) and Fe(II) complexes of newly synthesised ligand p-Phenyl isonitrosoacetophenone (p-PhINAP) have been synthesized . The complexes of formula $Pt(p-PhINAP)_2$, $Pd(p-PhINAP)_2$ & $Fe(p-PhINAP)_2$ were investigated by element microanalysis for C,N,H,M. Infrared Spectra (IR), Proton Nuclear Magnetic Resonance Spectra (HNMR) and Magnetic properties. Based on spectral data, complexes appear octahedral geometry. The antimicrobial activity of the complexes against the microbes were higher than that of ligand p-Phenyl isonitrosoacetophenone .

Key word: $Pt(p-PhINAP)_2$, $Pd(p-PhINAP)_2$, $Fe(p-PhINAP)_2$, octahedral geometry, HNMR and antimicrobial activity.

Introduction :

Coordination chemistry is undoubtedly the most active research area in inorganic chemistry. Several coordination complexes have been synthesized and investigated during the past few decades. Ever since the importance of coordination phenomenon in biological processes was realized, lot of metal containing macromolecules have been synthesized and studied to realize the role of these ligands in biological systems, and they also contribute to the development of new metal-based chemotherapeutic agents. Transition metal complexes of oxime have been the most widely studied co-ordination compound in the past few years due to their unusual magnetic properties, novel structural feature and relevance to biological system[1-3]. With significant development in the field of biological activity of metal chelates plays vital role in the causes and treatment of Cancer[4,5]. The ligand p-bromoisoinitrosoacetophenone (p-BrINAP) and p-chloroisoinitrosoacetophenone (P-ClINAP) have also been studied for few transition metals[6,7].

However, structural studies of the complexes of transition metals with p-phenyl isonitroso acetophenone have not been reported so far. The present paper describes the synthesis and characterization of complexes of transition metals Pt(II), Pd(II) & Fe (II) with p-phenyl isonitroso acetophenone on the basis of elemental analysis, IR Spectra, NMR Spectra, Magnetic properties and Antimicrobial activity.

EXPERIMENTAL SECTION

All solvents, reagents, chemicals of A.R. grade and were commercially available and used as received without purification. The ligand isonitroso p-phenyl acetophenone was prepared by the method described in the literature.

The metal complexes were prepared as follows:-

Preparation of Pt (p-PhINAP)₂ complex :- A 0.409 g of chloroplatinic acid was dissolved in a minimum quantity of distilled water and equal volume of alcohol. Similarly 0.450g of p-PINAP was dissolved in a minimum quantity of alcohol and equal volume of distilled water.

The platonic solution was added to the reagent solution drop wise with constant stirring. The pH was adjusted to 2.0 to 3.0. Then the solution was kept in a boiling oilbath for 45 minutes, a colored complex was separated. It was filtered, washed with distilled water, dried at 100^oC for 4 hours. It was recrystallised from chloroform and analyzed for platinum, carbon, hydrogen and nitrogen.

Preparation of Pd (P-PhINAP)₂ Complex:-

Palladium chloride (0.177g) was dissolved in a minimum quantity of alcohol and equal volume of distilled water. Similarly 0.450g of p-PINAP was dissolved in a minimum quantity of alcohol and equal volume of water.

The palladium solution was added to the reagent solution drop by drop with constant stirring. The pH was adjusted to 3 – 4 with HCl / NH₄OH. This solution was refluxed on sand bath at 100^oC for 4-6 hrs and then kept in vacuum desicator for 24 hrs. A colored complex formed was digested on water bath for 30 minutes. It was filtered, washed with water and dried at 100^oC for several hours. It was recrystallized from chloroform and analyzed for palladium, carbon, hydrogen and nitrogen.

Preparation of Fe(p-PhINAP)₂ complex :-

0.450g. of p-PINAP was dissolved in a minimum volume of alcohol and equal volume of water was added. Similarly 0.392 g. of ferrous ammonium sulphate was dissolved in water. The FAS solution was added to reagent solution drop by drop with constant stirring. The pH was adjusted between 5.0 – 6.0 with buffer tablets. This solution was refluxed on oil bath at 100^oC for 2 hrs& then kept in vacuum desiccator for overnight. A blue colored solid complex was formed. It was filtered and dried under vacuum. The blue solid was dissolved in minimum amount of chloroform and solution was filtered, chloroform was removed at room temperature under reduced pressure. The blue colored complex was dried under vacuum and analyzed for iron, carbon, hydrogen and nitrogen.

Physical Measurements:

^1H NMR spectra were registered by using Ultra Shield. Infrared spectra were obtained on FTIR Bruker in potassium bromide pellets. Digital was used to measure the molar conductivity at 25 C for 10^{-3}M solution of DMSO Micro elemental analysis(C.H.N.) were performed using elemental analyzer..Magnetic measurements of complexes were carried out from room temperature to liquid nitrogen temperature with Gouy's balance using mercury tetra-thiocyanatocobalt (II) as magnetic susceptibility standard. Diamagnetic corrections were calculated by the method given in the literature.

RESULTS AND DISCUSSION

Quantitative analysis and some properties of the complexes are reported in Table 1. On the basis of analytical data Pt(II), Pd(II) and Fe(II) complexes can be represented as $\text{Pt}(\text{p-PhINAP})_2$, $\text{Pd}(\text{p-PhINAP})_2$ & $\text{Fe}(\text{p-PhINAP})_2$. By studying the prepared complexes, it was found to be thermally stable and dissolve in some solvents such as DMF,DMSO. From the data listed in the table (1), each the prepared complexes have the non-electrolytic nature of DMSO solvent in 10^{-3}M at 25°C [8].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 nature[9]

Table –1 Quantitative analysis , Color At room temperature

COMPLEX	COLOUR	% C	% H	% N	% M
$\text{Pt}(\text{p-PINAP})_2$	Gray	52.00 (52.25)	4.00 (3.14)	4.25 (4.35)	9.94
$\text{Pd}(\text{p-PINAP})_2$	Yellowish green	60.02 (60.59)	3.50 (3.64)	5.00 (5.05)	11.53
$\text{Fe}(\text{p-PINAP})_2$	Blue	66.44 (66.68)	4.00 (4.01)	5.32 (5.55)	12.69

Infrared Spectra:

I.R. spectra ($3900-400\text{ cm}^{-1}$) of the complexes are practically same. The frequencies of some significant band of the ligand and those with the metal complexes are reported in Table 2. On the basis of literature data, the observed frequencies of different groups in the metal complexes have been assigned.

The $\nu_{\text{O-H}}$ of the oxime group observed at 3280 cm^{-1} in (p-PhINAP) is absent in the spectra in complexes suggesting replacement of H- of OH group of oxime by the metal ion during complex formation with metal ion[10]. A band appears in the range $1200-1150\text{ cm}^{-1}$ is reported that N-oxide (N \rightarrow O) stretching mode in aromatic ring compounds[11]. The peak observed near $1608, 1612, 1600\text{ cm}^{-1}$ in spectrum of M (p-PhINAP)₂ 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 The bands at $1062, 1089$, in M(p-PhINAP)₂ are attributed to the N-O stretching in the ligand[12].

It is important to note that for metal complexes reported have coordination only through the oxime oxygen or nitrogen atoms only. One medium to strong band at around 1050 or $1200-1250\text{ cm}^{-1}$ is found leading to a symmetrical six member ring structure[13] or asymmetrical five member ring structure.

Table 2: Infrared Spectral Frequencies (4000 to 400 cm^{-1}) of ligand and metal complexes

p-PhINAP	Pt (II)	Pd (II)	Fe(II)	Assignment of group
3290	---	---	---	
---	3430	3405	3450	OH, Ar-H
1640	---	---	---	Ar-H
---	1630	1610	1625	C=O
---	1260	1184	1260	C=N, C=O
1080	1060	1081	1055	N O
---	840	795	839	N-Oxide
763	757	756	759	N-O
693	690	600	700	Para Sub.

NMR Spectra

NMR Spectra of Pt(p-PINAP)₂, Pd(p-PINAP)₂ and Fe(p-PINAP)₃ in DMSO solution exhibit peaks due to –CH group, CH₂ group & aromatic ring protons & does not show any proton signal due to =NOH group. This suggest that their 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 –CH₂ protons in M(p-PINAP)₂ appear at lower value compared to that of –CH₂ proton in the Ligand p-PINAP. Further signals of aromatic ring protons in these

complexes occur at lower field side with respect to that of aromatic ring signal in p-PINAP. The donor atom is closest to the metal ion which involved in the formation of metal ligand bond[14,15].

Proton magnetic resonance signals observed in p-Phenyl isonitroso acetophenone (p-PINAP) and its metal complexes are shown in Table 3

Table 3: Assignments of the ¹H NMR Signals in Ligand & Metal Complexes

Complex	=NOH Group	Aromatic Ring	-CH Group	Phenyl group
p-PhINAP	8.9	7.29 & 7.25	6.70	7.26
Pt(p-PhINAP) ₂	---	7.30 & 7.53	6.30	7.23
Pd(p-PhINAP) ₂	---	7.32 & 7.54	6.25	7.23
Fe(p-PhINAP) ₂	---	7.35 & 7.56	6.27	7.24

All Values in δ scale

Antimicrobial activity:

All the synthesized complexes are effective at concentration of 500 $\mu\text{g/mL}$. Antifungal activity of the same compounds were evaluated against *Klebsiella planticola*, *Candidaalbicans* and *Fusarium oxysporium*. Antibacterial activity of the synthetic metal complexes of p-Phenylisonitros Acetophenone was examined against eg *E.coli*, *S.aureus*, *P.aeruginosa*, *B.subtilis*, *B. cereus* and *K. pneumoniae*. [16,20].

Assays were performed in agar media with final concentration of 500 $\mu\text{g/mL}$

The results showed that the ligand and complexes of p-PhINAP exhibited poor to good antimicrobial activities against all the tested strains. Complexes of Mn, Zn, and Zr were shown maximum zone of inhibition and hence were found to control the growth of all strains of bacteria and fungi examined. It may be due to the more penetrating power of metal complexes to the cell wall of bacteria, which prevents the synthesis of peptidoglycan or may find better fit at the receptor site as compared to other compounds. Though the ligand exhibited antibacterial and antifungal activity against all the tested strains, but metal complexes are found more active and hence suggested its unsuitability against all the strains.

Table.4: Antibacterial Results of p-PhINAP & Synthesized Complex

Test complexes	Bacteria along with zone of inhibition(mm)					
	<i>Micrococcus luteus</i>	<i>Staphylococcus aureus</i>	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>	<i>Escherichia coli</i>	<i>Micrococcus luteus</i>
P-PhINAP	9	12	11	10	13	12
Pt(p-PhMINAP) ₂	15	16	15	14	16	14
Pdp-PhINAP) ₂	14	16	14	14	16	15
Fe (p-PhINAP) ₂	12	13	14	13	12	14
Gentamycin	17	20	18	18	20	19

Table 5: Antifungal Activity Data of P-MINAP & Synthesized complex

Compound	Fungi along with zone of inhibition(mm)		
	<i>Klebsiella planticola</i>	<i>Candida albicans</i>	<i>Fusarium oxysporium</i>
p-PhINAP	13	12	11
Pt(p-PhMINAP) ₂	19	18	17
Pd (p-PhINAP) ₂	17	16	15
Fe (p-PhINAP) ₂	18	17	16
Miconazole	22	21	22

CONCLUSION

the metal ligand composition was found to be 1: 2. by analytical, IR, NMR spectral data and magnetic properties. The geometry of complex octahedral geometry has been assigned to Pt(II), Pd(II), and Fe(II) Complex. *In vitro*, Antibacterial and Antifungal screening of these revealed that most of the compounds exhibited potent inhibited potential activity.

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