

Synthesis Characterization and Biological Studies of Novel Isonitroso Phenyl 2 Propanone and its complexes with Cu(II), Ni(II) and Co(II)

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Abstract- Ligation properties of Isonitroso Phenyl 2 Propanone with Pt(II) & Pd(II) have been investigated. The synthesized complexes are characterized on the basis of elemental analysis, magnetic, electronic & spectral studies. The complexes confirm 1:2 stoichiometries and are non electrolyte in nature. The ligand has been found to coordinate to metal ion through two oximino nitrogen atoms. Further two coordination sites of metal ion are satisfied by oxygen atoms.

Index Terms- Magnetic susceptibility, Isonitroso Phenyl 2-Propanone, I.R. studies, Metal Complexes

I. INTRODUCTION

The coordination chemistry of Isonitroso ketones is an intensive area of study and numerous transition metal complexes of these ligands have been investigated¹. The development of the field of bioinorganic chemistry has increased the interest in Isonitroso based complexes, since it has been recognized that many of these complexes may serve as models for biologically important species^{2,4}. Coordination compounds derived from numerous Isonitroso ketones have been reported because of their anti-tuberculosis, antimicrobial and corrosion inhibitors⁵⁻⁷. Further legating behavior of Isonitroso ketones is of great interest since it has the ability to chelate metal ion through nitrogen and or oxygen donor centers. Keeping the above facts in mind and in continuation of our research work^{8,9} on transition metal complexes with Isonitrosoketones, in the present paper we report the synthesis characterization and biological studies of transition metal complexes of Cu(II), Ni(II) and Co(II) with Isonitroso Phenyl 2 Propanone.

II. MATERIALS & METHOD

The reaction was carried out with analytical reagent grade chemicals. The glasswares used were made of pyrex glass. The organic solvents were redistilled before use. However melting point apparatus was used with open capillary tubes for the determination of melting points, which were uncorrected. Elemental analysis was done on Perkin Elemer elemental auto analyzer & CHNS thermoquest auto analyzer. I.R. spectra were recorded on Perkin Elemer RX1 Spectrophotometer in Nujolmull/KBr pellets. ¹HNMR spectra were recorded on Bruker FT 300 at 300 MHz Nmr spectrophotometer at CDRI Lucknow. The chemical shifts were reported in δ units relative

to TMS used as an internal standard. The antifungal and antibacterial activity of ligand INP2P is determined by disk diffusion method using various biological strains according to the method described elsewhere¹⁰.

III. EXPERIMENTAL

The ligand isonitroso Phenyl 2 Propanone was prepared in three steps as described in the literature. The metal complexes are prepared in 1:2 ratios as follows

Preparation of Metal complexes

1. Preparation of Cu(INP2P)₂: 0.199gms of copper acetate was dissolved in minimum quantity of alcohol and equal volume of water was added. Similarly 0.326gms of HINP2P was dissolved in minimum quantity of alcohol was added. The copper solution was added to reagent solution drop wise with constant stirring in a beaker. The solid complex formed was digested on water bath for 2 Hrs. On cooling it was filtered through filter paper and washed with 50% alcohol.

2. Preparation of Ni(INP2P)₂: 0.326gms of HINP2P was dissolved in minimum volume of alcohol and equal volume of water was added. Similarly 0.237gms Nickel acetate was dissolved in alcohol and water (1:1). The nickel solution was added to reagent solution drop wise with constant stirring. The pH was adjusted to 5-5.6 with HCl/NH₄OH. A green colour solid complex was formed, separated, recrystallised from chloroform.

3. Preparation of Co(INP2P)₂: Aqueous solution of Cobalt nitrate and HINP2P was mixed in the molar ration of 1:2 and pH of solution was maintained 6-6.5 by HCl/NH₄OH. On refluxing for an hour yellow colour complex was formed, filtered and recrystallised from chloroform.

IV. RESULTS AND DISCUSSION

Magnetic measurements of solid complexes were carried out from room temperature to liquid nitrogen temperature with Gouy's balance. Dimagnetic corrections were calculated by the method given in the literature. The physical and analytical data in Table-1 indicate that Cu (II), Ni (II) and Co (II) can be reported as M (INP2P)₂. The complexes are colored and have good thermal stability. They are insoluble in water and dilute alkali solutions suggesting absence of free oxime group. Due to removal of free oximino proton during complexation supported

by I.R. studies. The molar conductance value in nitro benzene indicates their non electrolytic nature.

Magnetic Measurements: The results of magnetic susceptibility measurements in a variable temperature data suggest that the Cu (II), Ni (II) complexes may be diamagnetic with square planer geometries. And Co (II) complexes are diamagnetic which suggest a low spin octahedral coordination. The magnetic moment of Cu(II), Ni(II), Co (II) complexes are in the range of 1.49-2.05 B.M, 2-3.0 -3.67 B.M. and 3.90- 5.23 B.M. respectively. These suggestions are in agreement with spectral data¹¹⁻¹².

Electronic Spectra: The electronic spectra of INP2P in DMSO show as intense band at 211nm. It splits into two strong bands 241nm and 250nm. This can be explained by presuming that the symmetric π electron system cloud of INP2P becomes asymmetric by the dissociations of a proton.

The absorption spectrum of Cu(INP2P)₂ could be examined in chloroform solution because it is insoluble in other solvents. In chloroform solution it exhibits bands at 216 nm, 345 nm and 348 nm. The band at 216 nm shows $\pi - \pi^*$ transition and the band at 345 nm may be assigned to a charge transfer transition on the basis of its position and intensity. The colored Copper (II) complexes usually show an absorption band into range 210-340 nm and it is made up of at least two or three overlapping symmetrical bands. The charge transfer band in the solid occurs at 345 nm suggests a distorted octahedral geometry.

The spectra of Co (INP2P)₂ discloser $\pi - \pi^*$ transitions at 224 nm and 227 nm. The appearance of $\pi - \pi^*$ bands in the metal complex at different positions compared to those of $\pi - \pi^*$ bands of INP2P, indicates that the energy states of π electron system of iron INP2P suffer substantial alteration on complex formation Co(INP2P)₂ which reveals a charge transfer band at 298 nm in DMSO and chloroform solutions. The d-d transition bands are not observed because they are probably masked by high intensity charge transfer transitions. The spectrum of Co (INP2P)₂ exhibits a broad maximum at 359 nm and a shoulder at 298 nm which appear to be due to charge transfer transitions.

The nickel complex of HINP2P in chloroform solution shows a band at 223 nm & 237 nm which is attributed to $\pi - \pi^*$ transition and a shoulder at 348 nm which may be attributed to the charge transfer transitions. $^3A_{2g} \rightarrow ^3T_{1g}$ and $^3A_{2g} \rightarrow ^3T_{2g}$ Gray and Balhausen¹³ have discussed charge transfer transition in square planer cyanides of Ni(II), Pd(II) and Pt(II) on the basis of the molecular orbital theory and have demonstrated that three bands corresponding to the metal ligand transitions.

Infrared Spectra:

They have been examined in the region 4000-400 cm⁻¹. The infrared spectrum of free ligand HINP2P shows a broad band around 3190.17 cm⁻¹ is known to be lowered due to the hydrogen bonding^{106, 107}. Therefore the absorption near 3190.17 cm⁻¹ in HINP2P is assigned to the hydrogen bonded OH stretching. This assignment is further confirmed by the presence of new band at 2925.18 cm⁻¹ in the spectrum of the HINP2P. HINP2P shows two picks at 1640.40 cm⁻¹ and 1602.44 cm⁻¹ which may be attributed to the $\nu C=O$ and $\nu C=N$ respectively.

In the infrared spectrum of the free ligand INP2P in KBr pellet a broad band is observed in the range 3190.17 cm⁻¹ to 2925.18 cm⁻¹ due to hydrogen bonded OH of =NOH. One of the important features of the infrared spectra of the metal complexes Co (INP2P)₂, Ni (INP2P)₂ and Cu (INP2P)₂ in KBr pellets is that they do not show the OH stretching frequency in the region. The absence of OH stretching frequency in the above metal complexes indicates that the hydrogen of the oxime group is replaced by the metal atom on complex formation.

¹HNMR: NMR Spectrum of Cu(INP2P)₂, Ni(INP2P)₂ & Co(INP2P)₂ in DMSO solution exhibit peak due to -CH, methylene and aromatic ring protons & do not show any proton signal due to =N-OH. This suggest that these complexes have been formed by replacement of =N-OH group by the metal ion. It is interesting to note that the peaks Due to methylene proton in Cu(INP2P)₂ appear at lower value compared to that of methylene proton in the reagent INP2P.

Antimicrobial activity: Antibacterial activity of the synthetic metal complexes of isonitroso phenyl 2 propanone was examined against *E. coli*, *S. aureus*, *P. aeruginosa*, *B. subtilis*, *B. cereus* and *K. pneumoniae*. Antifungal activity of the same compounds was evaluated against *C. albicans*, *A. niger* and *F. oxysporium*. Assays were performed in agar media with final concentration of 500 μ g/mL. Complexes Co(INP2P)₂, Ni(INP2P)₂, Cu(INP2P)₂ were found to show moderate to good activity against all the tested strains of bacteria and fungi. Though the ligand exhibited antibacterial and antifungal activity against all the tested strains, its activity is less when compared with its metal complexes and hence suggested its unsuitability against all the strains. None of the synthesized complex showed more activity as compared to the standard drug.

Table-1: Elemental Analysis and Magnetic Moment of the Complexes

Compound	% C	% H	% N	%Methyl	μ
INP2P	66.4 (66.25)	5.70 (5.52)	8.31 (8.53)	-----	----- -
Cu(INP2P) ₂	55.65 (55.74)	4.05 (4.13)	7.11 (7.22)	16.32 (16.40)	1.72
Ni(INP2P) ₂	56.35 (56.45)	4.15 (4.18)	7.29 (7.31)	15.22 (15.33)	2.86
Co(INP2P) ₂	56.15 (56.40)	4.09 (4.17)	7.26 (7.31)	15.19 (15.39)	4.66

* Theoretical calculated value in parenthesis

Table-2: Infra Red Spectra of INP2P and Complexes.

Assignments	INP2P	Cu(INP2P) ₂	Ni(INP2P) ₂	Co(INP2P) ₂
OH, Ar-H	3190.17	-----	-----	----
Ar-H	----	3474.22	3475.62	3475.62
C=O	1640.40	----	----	----
C=N	1602.44	1607.96	1608.48	1608.48
N-Oxide	1047.75	1052.42	1052.21	1052.21
N-O	924.19	937.96	937.88	937.88

Table-3: NMR Spectra of INP2P and Complexes

Assignments	INP2P	Cu(INP2P) ₂	Ni(INP2P) ₂	Co(INP2P) ₂
=N-OH	8.30 δ	-----	-----	-----
-CH group	6.74 δ	6.17 δ	6.21 δ	6.74 δ
-CH ₂ group	3.38 δ	3.40 δ	3.40 δ	3.38 δ
Aromatic Ring	7.18 δ	7.18 δ	7.18 δ	7.18 δ

Table-4: Antibacterial Activity Data of INP2P & Synthesized Complexes

Compound	Bacteria along with zone of inhibition (mm)					
	<i>E. coli</i>	<i>S. aureus</i>	<i>P. aeruginosa</i>	<i>B. Subtilis</i>	<i>B. Cerus</i>	<i>K. Pneumoniae</i>
L	10	12	11	11	12	10
IIIa	14	16	15	14	17	16
IIIb	14	15	16	13	17	16
IIIc	13	16	14	14	16	17

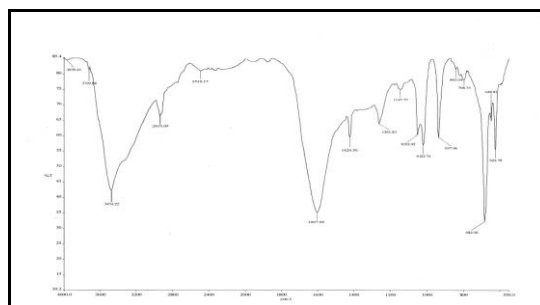
L = INP2P, IIIa = Cu(INP2P)₂, IIIb = Ni(INP2P)₂, IIIc = Co(INP2P)₂,

Table-5: Antifungal Activity Data of INP2P & Synthesized Complexes

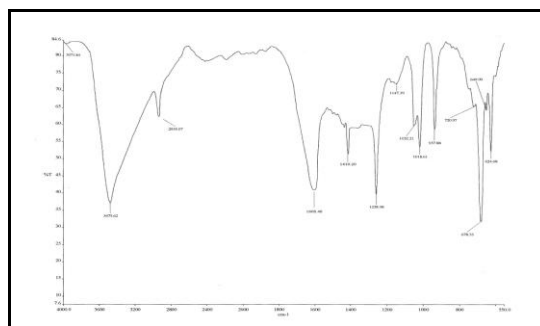
Compound	Fungi along with zone of inhibition (mm)		
	<i>C. albicans</i>	<i>A. niger</i>	<i>Fusarium Oxysporium</i>
L	13	11	12
IIIa	19	18	19
IIIb	18	16	19
IIIc	19	17	18

L = INP2P, IIIa = Cu(INP2P)₂, IIIb = Ni(INP2P)₂, IIIc = Co(INP2P)₂,

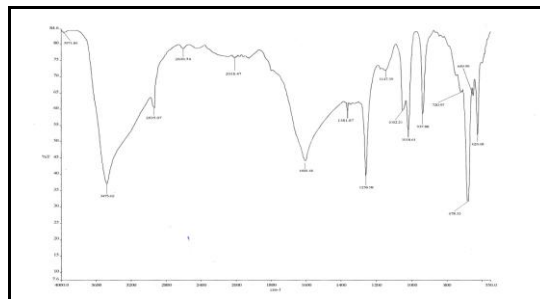
INFRARED SPECTRA OF Ni(INP2P)₂



INFRARED SPECTRA OF Co(INP2P)₂



INFRARED SPECTRA OF Cu(INP2P)₂



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