



Environmentally Microwave Assisted Synthesis and Characterization of Bio-Inorganic Material with Co(II)

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Abstract:

In the present investigation we synthesized and characterized the bio-inorganic material complex Co(II) of p- Iodo Isonitroso Acetophenone (p-IINAP) were synthesized from p-Iodo Acetophenone and characterized by on the basis of elemental analysis, molecular weight determination and molar conductance data. The bio-inorganic material of Schiff bases are widely studied because of the increasing recognition of their role in biological systems. Schiff bases and their complexes were recently found to have significant antitumor and biological activity. The isolated bio-inorganic materials of Schiff base behave as non-electrolyte in DMF solution. The electronic spectral data for ligand p-IINAP and complexes of Schiff base shows a group of three or more bands in the range 220 - 320 nm, which can be attributed to π - π^* transition and charge transfer transition. Infrared spectra (4000 - 400cm^{-1}) of the bio-inorganic materials are practically identical. The frequencies of some significant bands of the free ligand around 3320 - 3340cm^{-1} due to hydrogen bonded $-\text{OH}$ of $=\text{N}-\text{OH}$ stretching. The absence of $-\text{OH}$ stretching frequencies in the Co(II) complex indicates that the hydrogen of oxime group is replaced by transition metal ions on complex formation. The ^1H - NMR spectrum of bio-inorganic material in DMSO solution observed a peak due to different types of protons. The Magnetic measurements indicate that the complexes are Paramagnetic. The results indicate that the transition metal complex of Co(II) is hexa- coordinated and Octahedral Geometry.

Keywords: Bio-inorganic material, p-Iodo Isonitroso Acetophenone (p-IINAP), Elemental analysis, Magnetic measurements, Octahedral Geometry, ^1H -NMR, Infrared.

INTRODUCTION:

The Co-ordination chemistry of metal complexes with bio-inorganic material and their application have aroused considerable attention, mainly because of preparative accessibility, diversity and structural variability.[1] In co-ordination chemistry the first row of transition metals developed great interest due to metal ions play an important role in a number of biological processes such as biomolecules stabilizations, and

metalloenzyme[2,3]. Isonitrosoketones are expected to behave as versatile potential ambidentate ligands as they have three donor atoms of which only two can co-ordinate at a time to the same metal ion. They form stable chelates with transition metal ions showing a variety of structural feature [4-6]. It is, therefore, interesting to synthesize the different Isonitrosoketones as a bio-inorganic material with transition metal ions and investigating them by different methods. The bio-inorganic material of Schiff bases are widely studied because of the increasing recognition of their role in biological systems. Schiff bases and their complexes were recently found to have significant antitumor and biological activity [7]

As the biological activity of the complex strongly depends on the nature of the bio-inorganic material and on the transition metal coordination pattern, we have been interested by the study of the transition metal complexes which provides information about how biological systems achieve their specificity and stability and which display exceptionally higher stability.

The present investigation describe the synthesis of Co(II) complex of p-Iodo Isonitroso Acetophenone and their structural studies using elemental analysis and spectral study.

EXPERIMENTAL

Materials and Measurements

Apparatus and instruments employed are described elsewhere [8]. Chemicals used were of A. R. grade. The bio-inorganic material p-Iodo Isonitroso Acetophenone (p-IINAP) is commercially not available in the market. It was synthesized [9] by dissolving sodium metal in absolute alcohol and to these solution small portions of amyl nitrite and p-Iodo Acetophenone was added with constant stirring and cooling in the freezing mixture containing ice and sodium chloride at about 0°C. The mixture was kept for three days in a well Stoppard bottle in a refrigerator. At the end of this time, the yellowish green color mixture of sodium salt was obtained. It was filtered and dried in air. The dried sodium salt was dissolved in minimum quantity of ice cooled water and treated with equal volume of water-ethanol mixture. Precipitated p-Iodo Isonitroso Acetophenone was then filtered through suction and dried in vacuum .The crude product was recrystallized from benzene .Its melting point was found to be 302 °C.

Preparation of complexes

The 100 ml of 0.1 M solution of p-Iodo Isonitroso Acetophenone was taken in a round bottom flask. To this solution, 50 ml of 0.1 M solutions of metal salts of Cobalt acetate were added dropwise. This mixture was stirred using magnetic stirrer for 30 minutes and then refluxed on a water bath for three and half hours. The product was then filtered and washed with distilled water and dried.

Result and Discussion

The synthesized bioinorganic material with transition metal complex were colored, crystalline, stable in air, non-hygroscopic, and insoluble in water but soluble in polar solvent like DMF and DMSO. The ease of synthesis and high yield in single step reaction from commercially inexpensive reagents make these extremely attractive in coordination compounds. These metal complexes are insoluble in water. The metal complexes

decompose only at high temperatures suggesting that these are thermally stable complex. Composition and identity of the bio-inorganic material and its metal complex were carried out by elemental analysis and molar conductance are listed in Table-1 shows metal complexes have non electrolyte nature [10]. The structure of the synthesized bio-inorganic material p-IINAP and its transition metal complex were established with the help of spectral techniques. The spectroscopic data for the newly synthesized bio-inorganic material p-IINAP and transition metal complex are in good agreement with proposed formulation.

Table 1: Analytical and Physical data of the Bio-inorganic material and metal complex.

Compound	Mol. Formula	Colour	Mol. Wt.	C% Found (Calc)	H% Found (Calc)	N% Found (Calc)	I% Found (Calc)	Metal %	Molar Condu. $\text{Sm}^2\text{mol}^{-1}$
p-IINAP	$\text{C}_8\text{H}_6\text{O}_2\text{NI}$	Yellowish brown	275	34.94 (34.99)	02.19 (2.20)	5.09 (5.11)	46.14 (46.17)	----	----
Co(p-IINAP)_2	$\text{Co}(\text{C}_{16}\text{H}_{12}\text{O}_4\text{N}_2\text{I}_2)$	Light Green	609	31.55 (31.60)	1.98 (2.00)	4.59 (4.60)	41.67 (41.70)	09.67 (09.70)	6.89

Infrared Spectra: -

Infrared spectra ($4000\text{-}400\text{ cm}^{-1}$) of the bio-inorganic material and with transition metal complex are practically identical with each other. The frequencies of some significant band of the free bio-inorganic material and those of the transition metal complex are reported in Table 2. The observed frequencies of different groups in the bio-inorganic material and transition metal complexes have been assigned on the basis of literature data.

The -OH stretching vibration of the oxime group observed at 3327 cm^{-1} in (p-IINAP) is absent in the spectra of the complex suggesting replacement of the oxime proton by the transition metal ion during complexation[11]. The peak observed near 1740 cm^{-1} , 1608 cm^{-1} in spectrum of CO (p-IINAP)_2 may be assigned to the perturbed C=O and C=N stretching vibration involving bonding through oxygen, and nitrogen donor atoms respectively.

A band appears in the range $1200\text{-}1100\text{ cm}^{-1}$ is reported that N-oxide ($\text{N}\rightarrow\text{O}$) stretching mode in aromatic ring compounds [12]. It is significant to note that for metal complex reported to have coordination only through the oxime oxygen or nitrogen atoms only.

This suggests asymmetrical five member ring structure. In Co(II) complex two bands in the region cited earlier on asymmetrical structure with five member rings involving bonding through oximes nitrogen atom must be expected, such symmetrical structures.

Table 2: Infrared Spectral Frequencies (4000 to 400 cm⁻¹) of Bio-Inorganic Material and metal complex

Assignment	p-IINAP	Co(p-IINAP) ₂
Aromatic C-H	3024cm ⁻¹	3036 cm ⁻¹
OH of =N-OH	3327 cm ⁻¹	-----
-C=O	1740 cm ⁻¹	-----
-C=N	1608 cm ⁻¹	1549 cm ⁻¹
=C-H	1452 cm ⁻¹	1457 cm ⁻¹
=N→O	-----	1198 cm ⁻¹
Para Substituent	765 cm ⁻¹	795 cm ⁻¹
M-N	-----	656 cm ⁻¹

¹H NMR Spectra

¹H NMR Spectra of p-Iodo Isonitroso Acetophenone and its metal complexes such as Co(p-IINAP)₂ in DMSO solution exhibit peaks due to =CH group & C_a and C_b of aromatic ring protons H_a and H_b while does not show any proton signal due to =N-OH group. This suggest that their transition metal complex have been formed by the replacement of the proton of the =N-OH group by the metal ion.

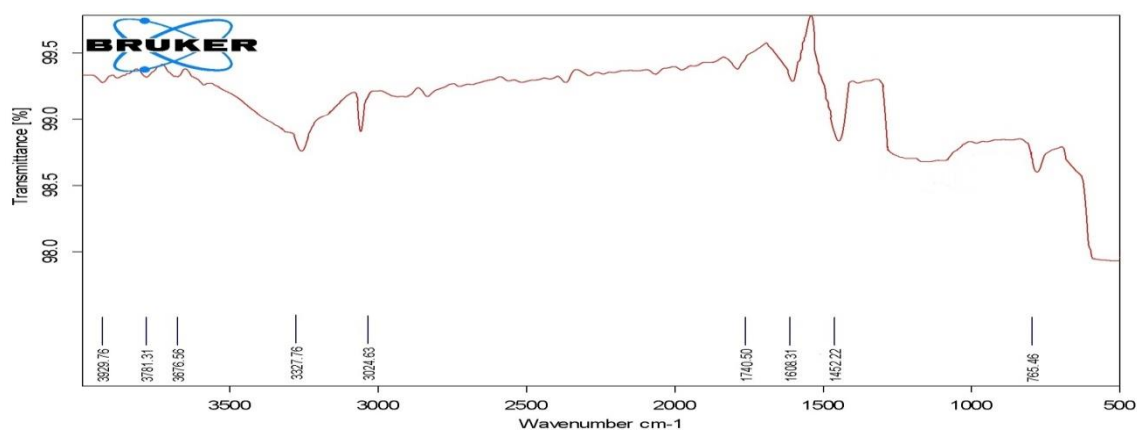
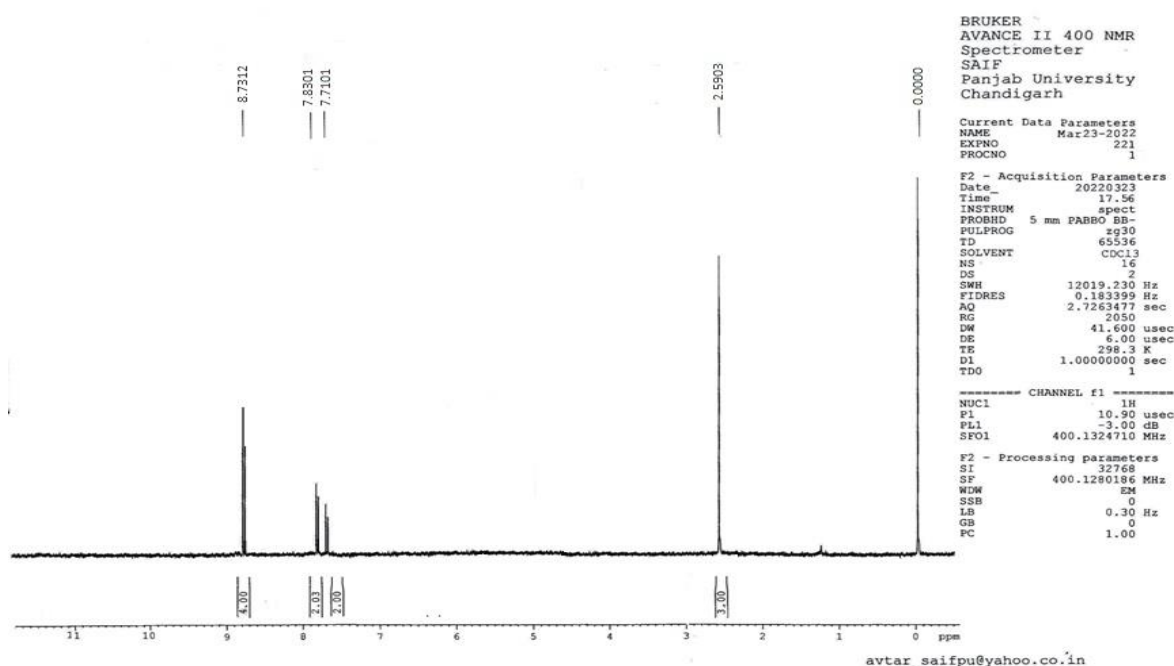
It is interesting to note that the peaks due to -CH protons in transition metal complexes appear at similar value compared to that of -CH proton in the reagent p-IINAP. Further ¹H NMR signals of aromatic ring protons in transition metal complex occur at higher field side with respect to that of aromatic ring signal in the bio-inorganic material P-Iodo Isonitroso Acetophenone (p-IINAP). The donor atom of the bio-inorganic material is closest to the transition metal ion which involved in the formation of metal bio-inorganic material bond.

¹H Nuclear magnetic resonance signals observed for bio-inorganic material p-Iodo Isonitroso Acetophenone (p-IINAP) and its transition metal complex are shown in Table 3 which is given below.

Table 3: Assignments of ¹H NMR Signals in p-IINAP & Metal Complexes

All Values in δ scale

Compounds	=N-OH group	Aromatic Ring -CH _a group	Aromatic Ring -CH _b group	-CH Group
p-IINAP	8.73	7.83	7.71	2.59
Co(p-IINAP) ₂	----	7.86	7.75	2.64

Figure.1. Infrared Spectra of Bio-Inorganic Material p-Iodo Isonitroso Acetophenone**Figure. 2. ¹H NMR Spectra of Bio-Inorganic Material P-Iodo Isonitroso Acetophenone**

CONCLUSION

On the basis of analytical, IR, ¹H NMR spectral data and magnetic properties, the metal ligand composition was found to be 1: 2. The geometry of complex octahedral geometry has been assigned to Co (II) Complex.

ACKNOWLEDGEMENT

The authors would like to thank all the teaching staff of the Department of Chemistry, Government Science College, Gadchiroli for all the support rendered during this study.

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