



Composite Bio-Inorganic Material of P-Methoxy Isonitroso Acetophenone (P-MINAP) with Fe (II)

R. G. Gajbhiye, *R. D. Raut

Department of chemistry, Vidya Vikas Arts, Commerce & Science College, Samudrapur Dist- Wardha

*Department of chemistry, J. B. College Of Science, Wardha Dist- Wardha

rahul.gajbhiye433@gmail.com

ABSTRACT

Metal complexes of transition metal such as Fe (II) with p-methoxy isonitroso acetophenone (P-MINAP) have been synthesized and characterized on the basis of element analysis, Infrared spectroscopy and thermal studies. The spectra along with magnetic data suggest Octahedral geometry of Fe (II) Complex.

Keywords: - p-MINAP, Fe (II), Magnetic Susceptibility, Octahedral geometry.

Introduction: -

The literature survey of the past few years reveals the fact that a significant development in the field of biological activity of metal chelates plays a vital role in the cause and treatment of cancer¹⁻³. The ligand p-methoxy isonitrosoacetophenone (p-MINAP) have been used for few analytical applications⁴⁻⁵. The ligand p-bromoisonitrosoacetophenone (p-BrINAP) & p-chloroisonitrosoacetophenone (P-CIINAP) have also been studied for few transition metals⁶⁻⁷. The structural studies of ligand p-methoxy isonitroso acetophenone (P-MINAP) have already been studied with transition metals for possible complex formation⁴. However, structural studies of the complexes of Transition metals with p-methoxy isonitroso acetophenone have not been reported so far. The present paper describes the isolation and characterization of complexes of Transition metals such as Fe (II) with p-methoxy isonitroso acetophenone on the basis of elemental analysis & spectroscopic study.

EXPERIMENTAL SECTION

All the chemicals used were of A.R. grade. The ligand p-Methoxy isonitroso acetophenone (P-MINAP) is commercially available in the market. The basic principle underlying this preparation is that of Claisen rearrangement⁵. It was synthesized by dissolving 11.5 g of sodium in 230 ml of absolute alcohol and to these solution small portions of 58 ml amyl nitrate and 65 ml of p-Methoxy 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-methoxy 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 299 °C.





Preparation of Fe (p-MINAP)₂ complex :-1:2 stoichiometric ratios of Ferrous Sulphate and (p-MINAP) were dissolved in minimum quantity of absolute alcohol and equal volume of distilled water. The Ferrous Sulphate solution was added to the reagent solution drop wise with constant stirring. The pH of the resultant solution was adjusted to 3.5 - 4 with HCl / NH₄OH. A yellowish green colored complex thus formed was digested on water bath for 20 minutes; it was filtered, washed with distilled water, dried at 90°C for several hours. It was recrystallized from chloroform and finally analyzed for copper, carbon, hydrogen and nitrogen.

RESULTS AND DISCUSSION

Analysis data and some properties of the complexes are reported in Table 1. On the basis of analytical data Fe (II) complex can be represented as M(p-MINAP)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.

Electronic Spectra: The electronic spectrum of Fe (II) complex (Table 1) was consistent with a very broad intense band in the 52.33 kK region and band in the 40.89 kK range. A shoulder also appears in the 50.74 kK region. This region screened by the intense charge transfer band exhibited the broad maxima at 52.13 kK.⁹ The spectrum data of Fe (II) Complex indicates that the octahedral geometry of the complex.¹⁰

Table 1: Electronic Spectral data of complexes

Complex	Absorption spectra in methanol (nm)	Wave No kK
Fe (p-MINAP) ₂	194	52.13
	196	50.74
	241	40.89

Table -2 Analytical Data, Color and μ eff. at room temperature

COMPLEX	COLOUR	% C	% H	% N	% M	μ eff.
Fe (4-MINAP) ₂	Yellowish green	57.57 (57.64)	5.27 (5.29)	6.60 (6.67)	15.19 (15.22)	Diamagnetic

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 3. The observed frequencies of different groups in the metal complexes have been assigned on the basis of literature data.





The ν_{O-H} of the oxime group observed at 3289 cm^{-1} in (p-MINAP) is absent in the spectra of the complexes suggesting replacement of the oxime proton by the metal ion during complexation ¹¹. The peak observed near $1628, 1622, 1602\text{ cm}^{-1}$ in spectrum of Fe (p-MINAP)₂ may be assigned to the perturbed $\nu_{C=O}$ and /or $\nu_{C=N}$ stretching vibration involving bonding through oxygen, and nitrogen donor atoms. A band appears in the range $1300-1200\text{ cm}^{-1}$ is reported that N-oxide (N→O) stretching mode in aromatic ring compounds ¹². The bands at $1062, 1089$, in Fe (p-MINAP)₂ are attributed to the N-O stretching in the ligand ¹³.

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 $1200-1250\text{ cm}^{-1}$ is found leading to a symmetrical six member ring structure ¹⁴ or asymmetrical five member ring structure.

Table 3: Infrared Spectral Frequencies (4000 to 400 cm^{-1}) of ligand and metal complexes

p-MINAP	Fe (II)	Assignment of group
3290	---	OH, Ar-H
---	3430	Ar-H
1640	---	C=O
---	1630	C=N, C=O
---	1260	N O
1080	1060	N-Oxide
---	840	N-O
763	757	Para Sub.
693	695	

CONCLUSION

On the basis of analytical, IR and spectral data, the metal ligand composition was found to be 1 : 2 and octahedral geometry has been assigned to Fe (II) complex.

REFERENCES

1. Rosenberg B., *Nature*, 222, 385 (1969).
2. Canali L. and Sherrington D. C., *Chem. Soc. Rev.*, 28, 85 (1999).
3. Tejam A. B. and Thakkar N. V., *Indian J. Chem*, 36 (A), 1008 (1997).
4. Barhate V. D., Patil M. R., *Curr Sci (India)*, 1989,58, 291
5. Patel N. J. , Halder B. C., *J. Inorg Nucl Chem*, 1967,29,1037
6. Bhole N. N., Raut R. D., Choudhari M. D., *Int.J.Emer.Tech.Sci.*2011,4(2),72-78
7. Bagade P. N., Raut R. D., Jadhav S. Z., *J. chem. Pharm. Res.*, 2013, 5(5):365-368





8. Geary W J, *Coord. Chem. Rev.*, **1971**, 7, 81-85.
 9. Lewis G N, **J. Am. Chem. Soc.** **1962**, 38, 762-765.
 10. Mishra A P, Jain R K, *J. Chem. Pharm. Res.* **2010**.2(6)51-61
 11. Deshmukh R G and Thakkar NY, *Indian J. Chem.* **1985** , 23A, 1066-1070.
 12. Taylor TWJ and Ewbank EK, *J. Chem. Soc.* **1926**, 2811-2815.
 13. Talwar U B and Haldar BC, *J. Inorg. Nucl. Chem.* **1970**, 32, 213-217.
 14. Thakkar N V and Deshmukh RG, *Indian J. Chem.* **1994**, 33A, 224-230.
-

