



## Synthesis and Structural Elucidation of Complexes of Some 3d-Series Divalent Transition Metals with 2-hydroxy-4-nitro acetophenone hydrazone, Schiff Base Ligand

PREM MOHAN MISHRA

Professor in Chemistry, M.L.S.M.College, Darbhanga, Bihar - 846 004, India.

(Received: April 18, 2013; Accepted: May 23, 2013)

### ABSTRACT

The ligand 2 – hydroxy – 4 - nitro acetophenone hydrazone was synthesized by the condensation reaction. Complexes of Co(II), Ni (II) and Cu(II) was prepared by refluxing metal salts with the ligands. Properties of complexes have been studied by elemental analysis, study of solubility, decomposition temperature, magnetic susceptibility, electrical conductivity, electronic and IR spectra of ligands and complexes. On the basis of the experimental results probable structures of all the metal complexes have been proposed.

**Key words:** Synthesis, structure, complex compound 2 – Hydroxy – 4 – nitroacetophenone hydrazone, Co (II), Ni(II), Cu(II), Schiff's base, Elemental analysis, Electronic spectra, IR spectra.

### INTRODUCTION

Schiff's bases are organic compounds having an azomethine group ( $>C=N$ ). Various studies<sup>1-2</sup> have shown that  $>C=N$  group has considerable biological importance<sup>3-5</sup>. A broad spectrum of biological potential is reported to be associated with a number of Schiff's bases<sup>6-8</sup>. Many evidences show that biological activity of a Schiff's base enhances many fold on its co-ordination with suitable metal ions<sup>9-17</sup>. Due to this interesting structural features and important applications we have undertaken the study of synthesis and characterization of complexes of Co(II), Ni(II) and Cu(II) with Schiff's base.

### EXPERIMENTAL

#### Preparation of ligand

3 gms of hydrazine hydrochloride was dissolved in dil. HCl and 6 gms of 2 – Hydroxy – 4 – nitroacetophenone was dissolved in methanol. Both the solution were mixed together and refluxed for an hour. Yellowish coloured precipitate appeared on cooling the solution. The crude product was recrystallised from alcohol and melting point was recorded (M.P = 480 K). The pure dried compound was chemically analysed (Table – 1). The compound is soluble in alcohol but insoluble in acetone and water.

**Preparation of complexes**

Aqueous solution of chlorides of divalent metals (cobalt, nickel and copper) was prepared. Ligand was dissolved in methanol. Aqueous solution of metal chloride was mixed with methanolic solution of ligand and the mixture was refluxed on water bath for about three hours. The cold mixture was again refluxed with 2N ammonium hydroxide for an hour. On cooling the mixture metal complex is

precipitated. The precipitate was washed, dried and analysed chemically (Table – 1).

**RESULTS****Solubility**

All the complexes of cobalt, nickel and copper are soluble in DMF but insoluble in water. Cu(II) complex dissolves slightly in ethanol whereas

**Table 1: Elemental analysis data of ligand and complexes**

Name of compound	Symbol of elements				
	C	H	N	O	M
Ligand (HNAPH)	49.32 (49.23)	4.48 (4.61)	21.46 (21.53)	(24.74 (24.61)	—
[Co(HNAPH) <sub>3</sub> ]	44.48 (44.51)	3.65 (3.71)	20.42 (20.40)	22.25 (22.26)	9.20 (9.12)
[Ni(HNAPH) <sub>3</sub> ]	44.83 (44.92)	3.65 (3.74)	19.38 (19.65)	22.94 (22.46)	9.20 (9.23)
[Cu(HNAPH) <sub>2</sub> ]	42.45 (42.52)	3.50 (3.54)	18.42 (18.60)	21.53 (21.25)	14.10 (14.06)

Theoretical value is given in parenthesis

**Table 2: Decomposition temperature, magnetic moment and electrical conductivity**

Complex	Decomposition temperature	Magnetic moment in (BM)	Molar electrical conductivity (Ohm <sup>-1</sup> )
[Co(HNAPH) <sub>3</sub> ]	573 K	4.9	17.4
[Ni(HNAPH) <sub>3</sub> ]	523 K	3.01	18.9
[Cu(HNAPH) <sub>2</sub> ]	513 K	1.82	13.8

**Table 3: Electronic spectral data of complexes**

Complex	Electronic spectra, d-d transition bands (in cm <sup>-1</sup> )	Assignment
[Co(HNAPH) <sub>3</sub> ]	9500	<sup>4</sup> T <sub>1g</sub> – <sup>4</sup> T <sub>2g</sub> (F)
	19495	<sup>4</sup> T <sub>1g</sub> – <sup>4</sup> A <sub>2g</sub> (F)
	22315	<sup>4</sup> T <sub>1g</sub> – <sup>4</sup> T <sub>1g</sub> (P)
[Ni(HNAPH) <sub>3</sub> ]	11240	<sup>3</sup> A <sub>2g</sub> (F) – <sup>3</sup> T <sub>2g</sub> (F)
	15995	<sup>3</sup> A <sub>2g</sub> (F) – <sup>3</sup> T <sub>1g</sub> (F)
	24685	<sup>3</sup> A <sub>2g</sub> (F) – <sup>3</sup> T <sub>1g</sub> (P)
	10750	Spin forbidden transition
[Cu(HNAPH) <sub>2</sub> ]	13845 - 14000	<sup>3</sup> E <sub>g</sub> – <sup>3</sup> T <sub>2g</sub>

Table 4:

Ligand(HNAPH)	Position of absorption bands (cm <sup>-1</sup> )			Assignment
	[Co(HNAPH) <sub>3</sub> ]	[Ni(HNAPH) <sub>3</sub> ]	[Cu(HNAPH) <sub>2</sub> ]	
3420	3390	3400	3400	NH <sub>2</sub> stretching
3195				O – H (Hydrogen bonded)
3140	3140	3140	3140	C – H stretching
3075	3080	3080	3080	> N – H stretching
2980		2980		C – H (Aromatic) stretching
2750				C – H stretching
2460	2460	2460	2460	Skeletal vibrations
2200	2200	2200	2200	
1910	1900	1900	1900	
16501620	16751630	16701625	16651635	NH <sub>2</sub> , > N – H bending
1590	1570	1565	1555	C = N stretching
1405	1395	1395	1395	C – N stretching
1260	1300	1290	1295	C – O (Phenolic)
920	920	920	920	Characteristic vibrations of 1,2,4 – tri – substituted benzene ring
840	840	840	810	
780	780	780	785	
-	580	510	510	M – N bond
	490	475	470	M – O bond

complexes of cobalt and nickel are insoluble in methanol, ethanol and acetone.

## DISCUSSION

### Structure of ligand

The interpretation of I. R. spectra is quite complicated due to the presence of various similar groups and hence many absorption bands. However, comparison of the spectral bands of the

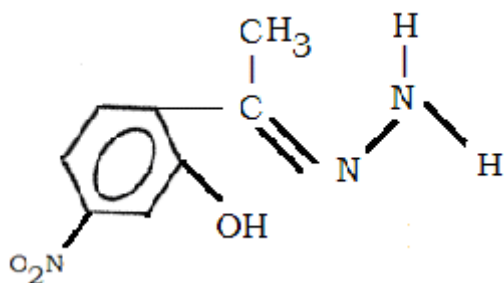


Fig. 1: 2-Hydroxy – 4 – nitroacetophenone

ligand (HNAPH), with those of its complexes (Table – 4), gives some important information regarding the nature of the ligand as well as the co-ordination sites through which metal ion co-ordinate with the ligand.

The broad band at 3195 cm<sup>-1</sup> in the ligand assignable to phenolic O – H (hydrogen bonded) stretching frequency disappears in the Ni (II), Co(II) complexes showing deprotonation of phenolic

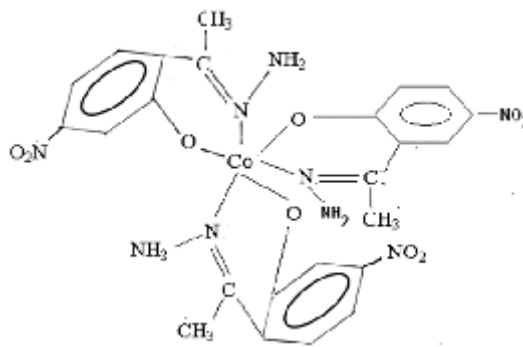
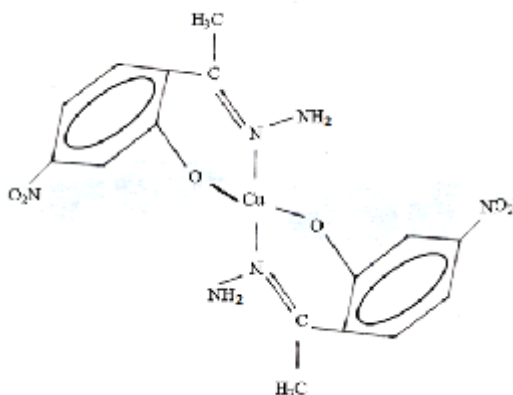


Fig. 2: Tris ( 2 – hydroxy – 4 – nitro acetophenone hydrazone) cobalt (II)

protons through complexation<sup>18</sup>. The ligand also shows strong bands near  $1260\text{ cm}^{-1}$  which may be attributed to the phenolic  $\nu_{C-O}$  vibration. A shift of this band to higher frequency ( $1300, 1290$  &  $1295\text{ cm}^{-1}$ ) in the complexes indicated chelation of the ligand to metal ion through phenolic oxygen.

The ligand exhibit a band near  $3420\text{ cm}^{-1}$  and  $3075\text{ cm}^{-1}$  which are assigned to  $\text{NH}_2$  and  $>N-H$  stretching<sup>19</sup> respectively, does not change appreciably in the complexes indicating non-involvement of  $>N-H$  and  $\text{NH}_2$  nitrogen atom in chelate formation. Bands at  $2460\text{ cm}^{-1}$ ,  $2200\text{ cm}^{-1}$ ,



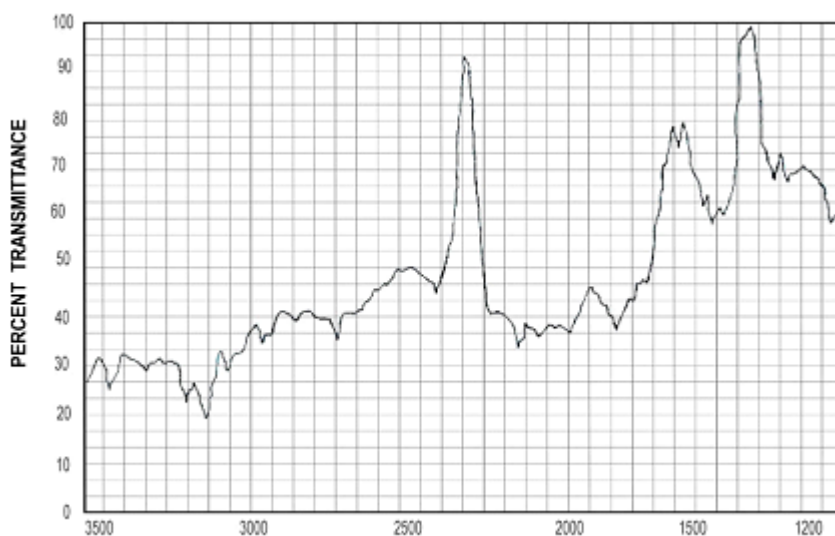
**Fig. 3 : Bis - ( 2 - hydroxy - 4 - nitro acetophenone hydrazone) Cu (II)**

$1900\text{ cm}^{-1}$ ,  $920\text{ cm}^{-1}$ ,  $840\text{ cm}^{-1}$  and  $780\text{ cm}^{-1}$  are the characteristic bands of the compound which remain unaffected in complex formation.

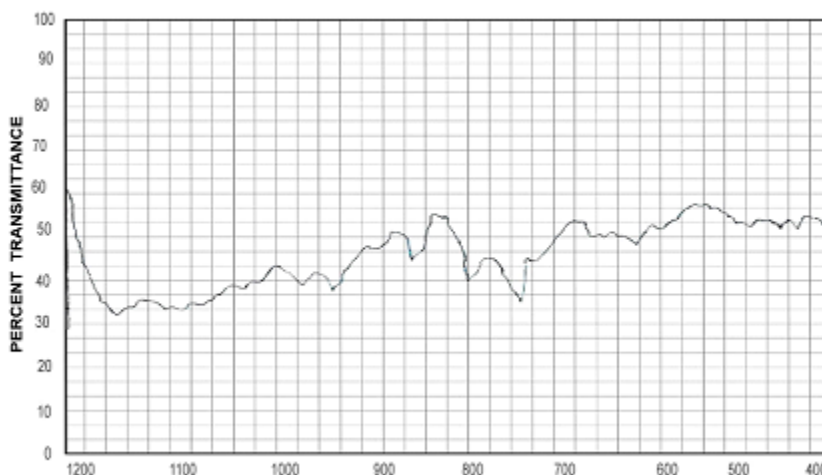
In these cases of metal complexes, the most interesting feature noted is about the doublet band<sup>20</sup> observed in the I. R. spectrum of the ligand near  $1620\text{ cm}^{-1}$ . The higher one goes upto  $1650\text{ cm}^{-1}$  to  $1675\text{ cm}^{-1}$  probably due to the bending mode of the  $\text{NH}_2$  group which remain practically unaffected and shows that the  $\text{NH}_2$  and  $>N-H$  mostly does not take part in the co-ordination. The other component which is due to  $C=N$  group stretching frequency shifts to the lower frequency about ( $\sim 1570\text{ cm}^{-1}$ ,  $1565$  &  $1555\text{ cm}^{-1}$ ) in complexes, indicating the co-ordination through  $C=N$  (imine) group. In the case of Ni (II) and Cu(II) it has been observed that as the reaction is carried out at higher  $p^H$ , co-ordination of Ni(II) and Cu(II) through  $C=N$  group, takes place by deprotonation. Martin and co-workers<sup>21</sup> have also reported the same results.

A sharp band at  $1590\text{ cm}^{-1}$  observable in the free ligand is assigned to  $C=N$  vibration of Schiff's base residue. This band shifts to the lower frequencies in the complexes, which indicates that azomethine nitrogen of  $C=N$  takes part in co-ordination.

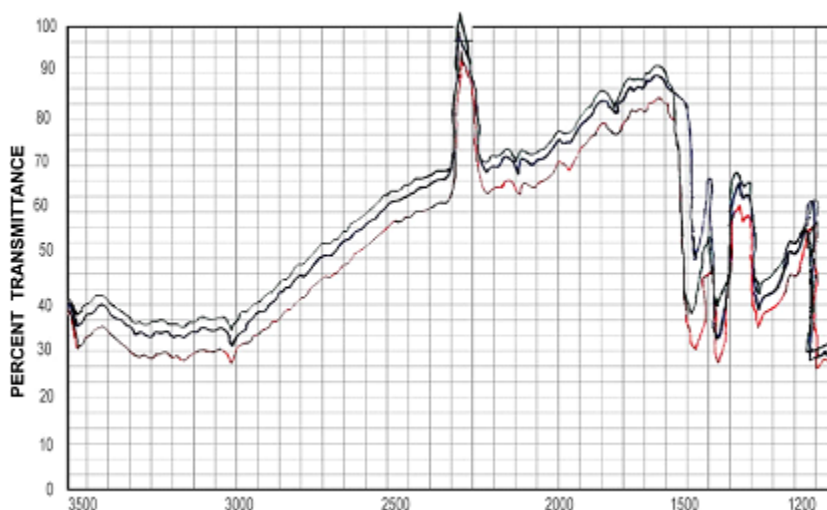
Graphs of IR spectral bands of ligand and complexes



**Graph 1: 2 - hydroxy - 4 - nitro acetophenone hydrazone ( HNAPH)**



Graph 2: 2-hydroxy-4-nitro acetophenone hydrazone (HNAPH)

Graph 3: (a) : [Co(HNAPH)<sub>3</sub>], (b) : [Ni(HNAPH)<sub>3</sub>], (c) : [Cu(HNAPH)<sub>2</sub>]

The  $\nu_{\text{C=N}}$  due to nitro group, appearing in the region  $1405 \text{ cm}^{-1}$  in the free ligand, remains unaltered in all the complexes, suggesting non-participation of nitro group in co-ordination.

Thus 2-Hydroxy-4-nitroacetophenone hydrazone (HNAPH) behaves as a bidentate ligand co-ordinating through phenolic oxygen (C-O), nitrogen atom of C=N, of azomethine group and nitrogen atom of C=N, of imine group. It is further confirmed with experimental report.

It is noteworthy that the ligand behaves as monoprotic for all the metal ions under investigation except for Ni (II) and Cu (II) when complexation is carried out at higher  $\text{pH}$  ( $\text{pH} = 9$ ). In the later cases ligand behaves like biprotic involving the deprotonation of C=NH (imine) proton. The structure of ligand may be represented as

#### Structure of complexes

The diffuse reflectance spectra of cobalt complex gives three d-d transition bands which have been assigned to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ ,  ${}^4\text{T}_{1g}(\text{F})$

$\rightarrow^4A_{2g}$  (F) and  $^4T_{1g}$  (F)  $\rightarrow^4T_{1g}$  (P) and suggest an octahedral geometry<sup>22</sup>. Linkage of metal ions with the ligand through oxygen and nitrogen is further confirmed by the presence of I.R. bands. The room temperature magnetic moments of these Co(II) complexes around 4.9 BM suggest presence of three unpaired electrons and outer orbital octahedral structure for its complex. Molar conductance value suggest non-electrolytic nature of the complex. Taking all these facts into account an octahedral structure has been given to this complex.

Ni(II) complex show four bands in their reflectance spectra favouring an octahedral stereochemistry. Out of these four bands, three can be assigned to spin allowed d-d transition eg  $^3A_{2g}$  (F) –  $^3T_{2g}$  (F),  $^3A_{2g}$  (F)  $\rightarrow^3T_{1g}$  (F) and  $^3A_{2g}$  (F) –  $^3T_{1g}$  (P).

The fourth band near 10750  $\text{cm}^{-1}$  is probably spin forbidden and may be assigned to  $^2B_{1g} \rightarrow ^2E_g$  transition.

The effective magnetic moment value (2.94 BM) are in good agreement with an octahedral geometry having two unpaired electrons.

#### Electrical conductivity data indicates non-electrolytic nature of nickel complex

Copper (II) has configuration which makes Cu (II) subject to John – Teller distortion, if placed in an environment of cubic like regular octahedral or tetrahedral symmetry and this has a profound effect on all its stereochemistry<sup>23-24</sup>.

The typical distortion is an elongation along one four fold axis, show that there is planar array of four short Cu-L bonds with two trans long ones. In the limit of course, the elongation leads to a situation indistinguishable from square co – ordination as found in many discrete complexes of Cu (II) . Thus the cases of tetragonally distorted “Octahedral” co – ordination and square co – ordination cannot be sharply differentiated.

Because of the relatively low symmetry of the environments in which the  $\text{Cu}^{2+}$  ion is characteristically found, detailed interpretation of spectra and magnetic properties are somewhat complicated even though one is dealing with the equivalent of a one – electron case<sup>25-28</sup>.

The complex  $[\text{Cu}(\text{HNAPH})_2]$ , show a band at 2000  $\text{cm}^{-1}$  in their electronic spectra, which suggest their square planar geometry, assigned to the overlap of  $^2B_{1g} \rightarrow ^2A_{1g}$ , and  $^2B_{2g} \rightarrow ^2E_g$  transitions<sup>29</sup>.

The magnetic moment of these complexes correspond well with the presence of one unpaired electron and gives a specific information about their stereochemistries.

The molar conductance values suggest non – electrolytic nature of these complexes. Taking all these facts into consideration, along with their elemental analysis the most probable structures of these complexes are given below. These results are in conformity with our observations reported earlier

#### REFERENCES

1. S. J. Gruber, C. M. Harris and E. Sinn : *J Inorg Nucl. Chem*, **30**: 1805 (1968)
2. M. Kato, K. Imai, Y. Muto, T. Tokki and H. B. Jonassen; *J. Inorg. Nucl. Chem.* **35**: 109 (1973)
3. M. Gulloli, L. Casello, A. Pasini and R. Ugo, *J. Chem. Soc. Dalton Trans*, 379 (1977)
4. L. Muslim, W. Roth and H. H. Erlenmeyer: *Acta Chem. Hev*, **36**: 36 (1983)
5. R. R. Vyas and R. N. Mehta: *J. Ind. Chem. Soc.* **68**: 294 (1991).
6. M. R. Manrao and V. K. Kaul, *Indian J. Agric. Chem.*, **32**: 33 (1990)
7. M. R. Manrao and Chander Kanta, V. K. Kaul, *Indian J. Nematol*, **27**: 208 (1997).
8. R. H. Ububi and P. Purushottamachar, *Indian J. Heterocyclic Chem.*, **9**: 189 (2000).
9. K. D. Rainsford, M. W. Whitehouse, J. Pharm Pharmacol, **28**: 83 (1976), *Chem. Abstract*, **85**: 15392 (1976)
10. K. D. Domag, R. Buchnisch, F. Mietzsch and H. Schmidt, *Naturewiss, Enschaften*, **33**: 315 (1946).
11. F. P. Dwyer, F. Maythew and A. Shulman, *Bril*,

- J. Cancer*, **19**: 195 (1965).
12. D. R. Williams, *Chem. Rev.* **72**: 203 (1972).
  13. A. Furst and R. T. Haro, *Progr. Exp. Tumor Res.*, **12**: 102 (1969).
  14. J. A. Gim and H. G. Patering, *Cancer Res.*, **27**: 1278 (1967).
  15. Z. Limermeister, B. *Naturforsch.*, **5**: 79 (1950).
  16. C. W. Johnson, J. W. Joyner and R. P. Perry, *Antibiotics Chemotherapy*, **2**: 636 (1952).
  17. N. E. Morrison and F. M. Collins, *Inst. J. Leprosy*, **49**: 180 (1981).
  18. D. L. Leusing and B.L. Leach: *J. Am. Chem. Soc.* **60**, 1098.
  19. R. H. Holm, G.W. Everett and A. Chakravorty : *Prog. Inorg. Chem.* **7**, 161,(1966).
  20. M. S. Patil & J. R. Sah: *J. Ind. Chem. Soc.* **16**, 944 (1981).
  21. R. B. Martin, M. Chamberlin and J. T. Chem. ; *J. Am. Chem. Soc.* **16**: 944 (1981) *Soc.* **82**: 495 (1960).
  22. M. S. Patil & J. R. Slah; *J. Ind. Chem. Soc.* **58**: 944 (1981)
  23. W. E. Hatfield and R. Whymon : *Transition Metal Chemistry* **5**: 47 (1969).
  24. B. J. Hathaway and D. E. Billing: *Coordination Chem. Rev.* **5**: 143 (1970).
  25. F. A. Cotton and G. Wilkinson; *Advanced Inorganic Chemistry*, Wiley Eastern Ltd. London Edn 7 (1984)
  26. J. R. Dyer: *Applications of Absorption spectroscopy of organic compounds*. Prentice Hall of India Pvt. Ltd. New Delhi (1974)
  27. R. S. Drago: *Physical methods in Inorganic Chemistry*. Affiliated East West Press Ltd. New Delhi, India (1978).
  28. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination compounds*; John Willey International, New York (1970).
  29. I. M. Procter, B. J. Hathaway and P. A. Necholls: *J. Chem. Soc. A*, 1968 (1978).
  30. B.K. Rai and Puja Anand, *Orient J. Chem.*, **28**(1): (2012).
  31. B.K. Rai, Rachana Kumar and Amrita Thakur., *Orient J. Chem.*, **28**(2): (2012).
  32. P. K. Jha, I. K. Jha and Prem Mohan Mishra: *Asian Journal of Chemistry*; **17**(4): 2239-2242 (2005)
  33. B.K. Rai and Puja Anand, *Orient J. Chem.*, **28** (2012).
  34. Prasad A. and B.K. Rai., *Orient J. Chem.*, **25** (2009).
  35. Mohir Kumar and Shamim Ahmad., *Orient J. Chem.*, **26**(4): (2012).
  36. B.K. Rai and Bimal Kumar., *Orient J. Chem.*, **26** (2010).
  37. P. M. Mishra, D. K. Choudhary, Shiv Shakti, J. J. R. Chy., *Journal of Ultra Chemistry*; **8**(3): 415-420 (2012).