

## Synthesis and Characterisation of bivalent transition metal complexes with Schiff's base ligands

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### Abstract

Complexes of Co(II), Ni(II) & Cu(II) with 2-hydroxy – 4 – nitro acetophenone semi carbazone have been synthesized complexes were characterized by elemental analysis, magnetic and conductivity measurements electronic and IR spectral studies and thermal analysis. The ligand was found to be tridentate. The complexes of Cobalt (II) and Ni(II) was found to be hexa co-ordinated with octahedral structure where as complexes of Cu(II) was tetra co-ordinated with square planar structure.

*Key words* : Transition metal, complex compound, Schiff's base ligand, Co(II), Ni(II), Cu(II), Semicarbazone.

### Introduction

Schiff's bases are organic compounds containing azomethine group ( $>C=N$ ). Schiff's bases has drawn a lot of attention in the last few years because of their biocidal properties<sup>1-9</sup>. Schiff's base metal chelates have played a central role in the development of coordination chemistry<sup>10-14</sup>.

Literature survey reveals that biological activity of a ligand can be enhanced by chelation with suitable metal ions<sup>15-16</sup>.

In continuation of our previous work in the present communication we report preparation and characterization of Co(II),

Ni(II) and Cu(II) complexes with 2 – hydroxyl – 4 – nitro acetophenone semicarbazone.

### Experimental

#### *Preparation of ligand*

Nearly 5 gm of 2 – Hydroxy – 4 – nitro acetophenone was dissolved in methanol and treated with a solution containing 3.7 gm semi carbazide hydrochloride in water. The mixture was stirred well and it was refluxed for half an hour on a water bath and cooled. White crystals was separated. The crude white precipitate was recrystallized from alcohol as colourless needles. The melting point of the product was determined by Kjeedah's method and found to be 485 K. The pure compound is

slightly soluble in methanol and ethanol however, it is highly soluble in dimethyl formamide (DMF) but insoluble in water and acetone.

### *Preparation of complexes*

0.403 g Cobalt chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) and Metal salt solution was prepared by dissolving calculated amount of chloride of cobalt and nickel in water. 0.585 g nickel chloride was dissolved in water. While solution of copper chloride was prepared in ammonical solution of pH=9 in water. Ligand (HNAPS) was dissolved in DMF.

The two solutions were mixed in 1:1 ratio and refluxed for about 2 – 3 hours and left over night.

The grey precipitate of cobalt complex red precipitate of nickel and copper complex was obtained. The precipitates were separated and digested on the water bath for two hours and then left to stand for one hour.

The precipitate was filtered washed with water and recrystallised from water. The crystals were again washed and dried. The pure complexes were analysed chemically for the elements.

## **Results and Discussion**

Table 1. Elemental analysis data

Compound	% of elements observed (calculated)					
	C	H	N	O	Metal	
HNAPS	45.2 (45.38)	4.12 (4.20)	23.72 (23.53)	26.96 (26.89)		
$[\text{Co}(\text{HNAPS})_2]$	39.73 (40.54)	4.22 (3.38)	20.60 (21.02)	25.10 (24.03)	10.35 (11.03)	Co
$[\text{Ni}(\text{HNAPS})_2]$	40.06 (40.52)	3.98 (3.38)	20.85 (21.01)	24.16 (24.01)	10.95 (11.06)	Ni
$[\text{Cu}(\text{HNAPS})\text{NH}_3]$	34.06 (34.02)	3.85 (3.78)	21.78 (22.05)	21.07 (20.15)	19.14 (20.0)	Cu

Table 2. Decomposition temperature, electrical conductivity and magnetic moment data of complexes

Complexes	Decomposition Temperature (K)	Electrical conductivity ( $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ )	Magnetic moment (BM)
$[\text{Co}(\text{HNAPS})_2]$	463	11.2	4.2
$[\text{Ni}(\text{HNAPS})_2]$	513	10.4	2.92
$[\text{Cu}(\text{HNAPS})\text{NH}_2]$	513	10.4	2.92

Table 3. Electronic spectral data of complexes and their assignment

Complexes	$\bar{\nu}$ (in $\text{cm}^{-1}$ )	Assignment
[Co(HNAPS) <sub>2</sub> ]	9803	$^4T_{1g} \rightarrow ^4T_{2g}(\text{F})$
	19607	$^4T_{1g} \rightarrow ^4A_{2g}(\text{F})$
	22727	$^4T_{1g}(\text{F}) \rightarrow ^4T_{1g}(\text{P})$
[Ni(HNAPS) <sub>2</sub> ]	11240	$^3A_{2g}(\text{F}) \rightarrow ^3T_{2g}(\text{F})$
	16000	$^3A_{2g}(\text{F}) \rightarrow ^3T_{1g}(\text{F})$
	24690	$^3A_{2g}(\text{F}) \rightarrow ^3T_{2g}(\text{P})$
	10752	Spin forbidden transition
[Ni(HNAPS) NH <sub>3</sub> ]	20,000	$^2B_{1g} \rightarrow ^2A_{1g}, ^2E_g$

Table 3. IR Spectral bands ( $\text{cm}^{-1}$ ) of ligand and complexes

Ligand	Complexes			
HNAPS	[Co(HNAPS) <sub>2</sub> ]	[Ni(HNAPS) <sub>2</sub> ]	[Cu(HNAPS)NH <sub>3</sub> ]	Assignment
3460	3465	3460	3458	N – H stretching
3190	---	---	---	O – H (H- bonded)
2990	3000	2995	2992	C – H stretching
1660	---	1640	---	C=O stretching
1595	1585	1580	1590	C = N stretching
1435	1440	1445		N – H bending
1390	1395	1390	1385	C – N stretching
1230	---	---	1220	Skeletal in plane vibrations
1190			1190	
		1290	1295	C – O (phenolic)
1160	1155	1150	1150	Characteristic vibrations of 1,2,4 – trisubstituted benzene ring
1085	1095	1090	1090	
1070	1065	1060	1060	
920 – 935	925 – 935	920 – 930	920 – 930	C – N bending
	475	490	560	M – N bond
	515	520	510	M – O bond



## Discussion

### Structure of ligand :

#### 2 - Hydroxy-4 - Nitro Acetophenone Semicarbazone (HNAPS):

Co-ordination behaviour of the ligand (HNAPS) has been established by comparing its I. R. spectral data with those of its complexes.

The band at  $3200\text{ cm}^{-1}$  in the ligand assignable to phenolic O-H (hydrogen bonded) stretching frequency disappears in the Ni (II), Co(II), complexes, showing deprotonation of phenolic proton. The ligand also shows strong band at  $1270\text{ cm}^{-1}$  which may be attributed to the phenolic C - O vibration. A shift of this band to higher frequency ( $\sim 1305$ ) in the complexes indicates chelation of the ligand to metal ion through phenolic oxygen.

The sharp band at  $1585\text{ cm}^{-1}$  in the free ligand due to  $\nu_{\text{C}=\text{N}}$  of Schiff's base residue shifts to the lower frequency at ( $\sim 1575\text{ cm}^{-1}$ ) in the complexes showing co-ordination through the nitrogen atom. The lowering may be very small in some cases. The ligand band at  $\sim 1660\text{ cm}^{-1}$  may be assigned to  $\nu_{\text{C}=\text{O}}$  group which shows downward shifting in metal complexes, indicating participation of this group in co-ordination.

The absorption band at  $3460\text{ cm}^{-1}$  due to  $\nu_{\text{N}-\text{H}}$  group in the free ligand remains

unaltered in the complexes, indicating non-participation of this group in co-ordination.

A band present at  $1390\text{ cm}^{-1}$  in the I.R. spectra of the ligand is assigned to  $\nu_{\text{C}-\text{N}}$  due to nitro group. This band remains unchanged in all the complexes, suggesting non-participation of nitro group in co-ordination.

Thus, we come to a conclusion that the ligand, 2-Hydroxy-4-nitro acetophenone semicarbazone (HNAPS) behaves as a tridentate ligand for the metal ions, co-ordinating through (i) phenolic oxygen (C - O), (ii) nitrogen atom of C = N of azomethine group and (iii) ketonic oxygen C = O of enolic group.

This ligand is monoprotonic in all the cases except Ni(II) and Cu(II), at higher pH (pH = 9). It has been observed that in these cases a band present at  $1595\text{ cm}^{-1}$  in the free ligand disappears, perhaps due to deprotonation of the C=O (enolic) proton. These observations correspond to our previous results.<sup>17-23</sup>

It is worth mentioning at this stage that nitro group does not take part in co-ordination. Many workers have prepared complexes with Schiff's bases derived from substituted salicylaldehyde and reported non-participation of the substituents in the co-ordination. However, stability of the complex is certainly influenced by the presence of the substituents<sup>5, 6</sup>. The two tautomeric form of ligand may be represented as given below:

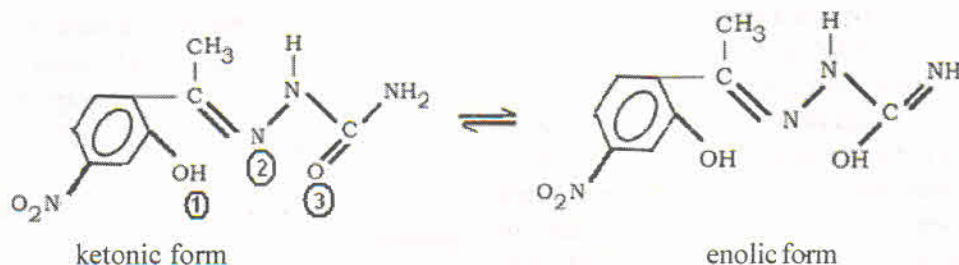


Fig 1. 2-Hydroxy - 4 - nitro acetophenone semi carbazone

### Structure of complexes :

The diffuse reflectance spectra of Co(II) complexes gives three d - d transition bands which have been assigned to  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  and suggest an octahedral geometry<sup>24</sup>. Linkage of metal ion with the ligand through sulphur, oxygen and nitrogen atoms of the ligand is further confirmed by the presence of I.R. bands near  $350\text{ cm}^{-1}$ ,  $500\text{ cm}^{-1}$  and  $550\text{ cm}^{-1}$  in the complexes<sup>24</sup>.

The room temperature magnetic moments of the Co (II) complex around 4.9 BM suggest presence of three unpaired electrons and outer orbital octahedral structure for these complexes. The molar conductance values suggest non-electrolytic nature of the complex  $[\text{Co}(\text{HNAPS})_2]$ .

Ni (II) complex show four bands in their reflectance spectra favouring an octahedral stereochemistry.<sup>25</sup> Out of these four bands, three can be assigned to spin allowed d - d transition, eg.  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ . The fourth band near  $10750\text{ cm}^{-1}$  is probably spin

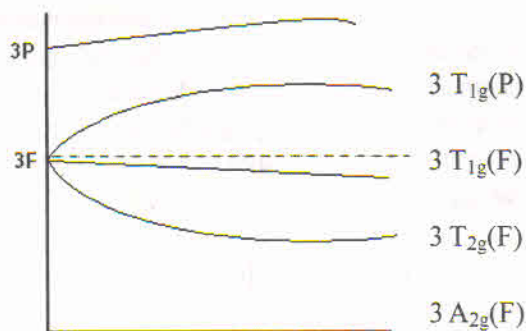


Fig. 2. Orgel diagram of Ni (II) complex.

forbidden<sup>26</sup> and may be assigned to  ${}^2B_{1g} \rightarrow {}^2E_g$  transition.

The  $\mu_{\text{eff}}$  values of the complexes (2.94 BM) are in good agreement with an octahedral geometry having two unpaired electrons. The complex  $[\text{Ni}(\text{HNAPS})_2]$  is found to be of non-electrolytic in nature. Now it is clear that these Ni (II) complexes have octahedral structures

Copper (II) has  $d^9$  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>27-28</sup>.

The typical distortion is an elongation along one four fold axis, so 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>29</sup>.

The complex  $[\text{Cu}(\text{HNAPS})\text{NH}_3]$ ,

show a band at  $2000\text{ cm}^{-1}$  in their electronic spectra, which suggest their square planar geometry, assigned to the overlap of  $^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$ , and  $^2\text{B}_{2g} \rightarrow ^2\text{E}_g$  transitions<sup>30</sup>.

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

The molar conductance values suggest non-electrolytic nature of these complexes while I.R. band near  $655\text{ cm}^{-1}$  suggests M-NH<sub>3</sub> bonding.

Taking all these facts into consideration, along with their elemental analysis the most probable structures of these complexes are given in 3, 4 and 5.

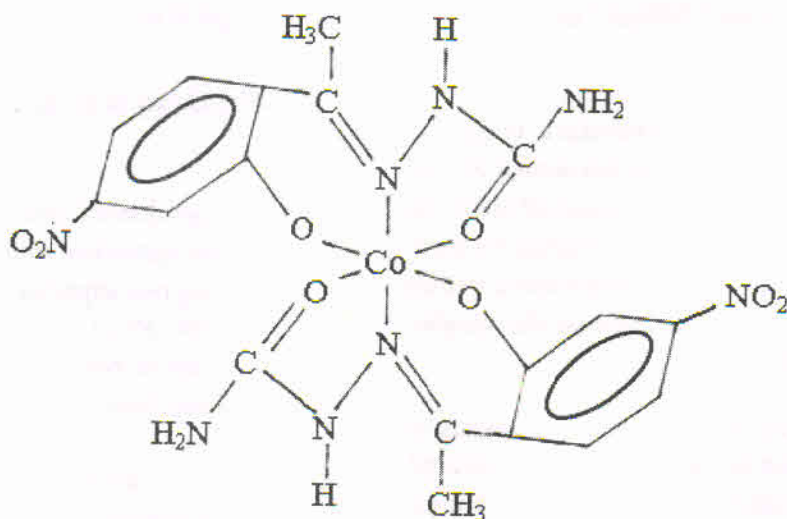


Fig. 3. Bis (2-hydroxy-4-nitro acetophenone semi carbazone) cobalt (II)



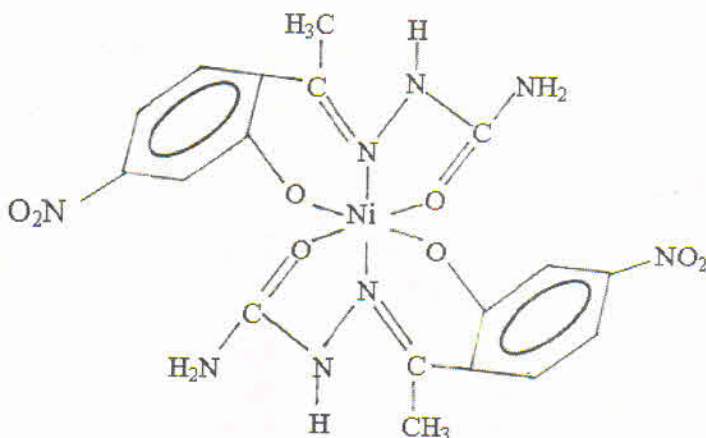


Fig. 4. Bis (2-hydroxy - 4 - nitro acetophenone semi carbazone) Nickel (II)

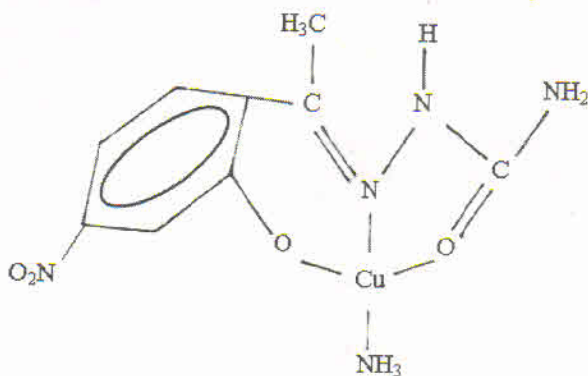


Fig. 5. Mono ammine 2 - hydroxy - 4 - nitro acetophenone semicarbazone Cu (II)

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