

## I.R. Study of synthesized mixed ligand complexes

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(Received: October 30, 2008; Accepted: December 05, 2008)

### ABSTRACT

Study of metal complexes has been of great importance. Versatile chelating ability of the biologically active neutral bases in the latest aspect in the development of the co-ordination chemistry. IR spectroscopic method is sensitive and convenient to deduce the structure of an unknown molecule with this view in this study some mixed ligand complexes of altered biological activity were prepared.

**Key words:** IR study, mixed ligand complexes.

### INTRODUCTION

Ligands containing N, S and O donor atoms are reported as anti cancerous, antiviral antibacterial and anti fungal. The metal chelates have vital importance in analytical, medicinal, and industrial field. It is observed its metal biological activity of a potentially active ligand is altered many times in terms of its metal chelate with suitable ion. Co-ordination compounds of metals are also present in plant and animal kingdom eg. Chlorophyll and vitamin B<sub>12</sub>. With this view using Ni (ii) Zn (ii) and some ligand eg. Npa, TCA, PIC, FA, HQ, some mixed ligand complexes were prepared.

Infra-red adsorption spectroscopy is used to confirm the structure of synthesised compounds. In the infra-red region, a molecule possesses different stretching and banding vibrations of a bond, because it requires certain amount of energy.

### MATERIAL AND METHODS

All the complex studies during the present course of investigations were prepared by the method of Musumeci given as follow.

Equimolecular (1:1) {alcoholic, 10ml

(0.05M)} solution of the two ligands were mixed together with constant shaking. To this mixture, an aqueous solution of Ni (II) acetate (10ml, 0.05M) was added slowly with vigorous solution of ammonia. It was again well-adjusted almost 6-7 by adding a dilute for some time. The resulting precipitate was filtered washed first with distilled water and then alcohol followed by ether. The resulting solid was dried under vacuum over P<sub>4</sub>O<sub>10</sub> in a desiccator. Infra-red spectra of the synthesised metal complexes were recorded on Perkin Elmer model 577 spectrophotometer in KBr matrix at RSIC, Delhi University, Delhi.

### Isolation of mixed ligand complexes

The following mixed-ligand complexes were prepared by above state method.

- (i) 1:1:1, M (II) - Npa - TCA
- (ii) 1:1:1, M (II) - Npa - PIC
- (iii) 1:1:1, M (II) - Npa - FA
- (iv) 1:1:1, M (II) - Npa - HQ

Where M = Ni (II), Zn (II)  
Npa - N-(2-pyridino)-anthranlic acid  
ODA - Oxydiacetic acid  
TDA - Thiodiacetic acid

TCA - Thiophene - 2- carboxylic acid

PIC - 2-picolinic acid

FA - Furan-2-carboxylic acid

HQ - 8-hydroxyquinoline

## RESULTS AND DISCUSSION

### M (II)-Npa-TCA Complexes

A moderate frequency at about - NH stretching 3400 in free ligand Npa is shifted to 3310  $\text{cm}^{-1}$  and 3320  $\text{cm}^{-1}$  Ni (II) - Npa - TCA and Zn (II) - Npa - TCA complexes, respectively. These observations suggest that metal-ligand bonding is taking place through 'N' of NH group with the metal ion. An appearance of a moderate band at 1585

$\text{cm}^{-1}$  in Npa is definitely due to -NH bonding which overlaps with the frequency caused by the aromatic ring. Lowering of this frequency in the case of related metal of Npa, further indicate the involvement of nitrogen in co-ordination. The free ligand TCA shows a spectral band at 610  $\text{cm}^{-1}$  which is shifted to 585  $\text{cm}^{-1}$  in metal complexes showing the co-ordination of thiophene moiety with metal. New spectral bands at 555  $\text{cm}^{-1}$ , 450  $\text{cm}^{-1}$ , 460  $\text{cm}^{-1}$ , 385  $\text{cm}^{-1}$  and 375  $\text{cm}^{-1}$ , 320  $\text{cm}^{-1}$ , 325  $\text{cm}^{-1}$  and 350  $\text{cm}^{-1}$  confirm the formation of metal complexes. Spectral band at 3400  $\text{cm}^{-1}$  and another spectral band at 850  $\text{cm}^{-1}$  and 840  $\text{cm}^{-1}$  and 840  $\text{cm}^{-1}$  indicate that water molecules are co-ordinated with in these complexes.

Table 1: Spectral data of 1:1:1 M (II) - Npa - L

S. No.	Table Assigned	Wave number ( $\text{cm}^{-1}$ )							
		M (II)-Npa - TCA		M(II) - Npa - PIC		M(II) - Npa-FA		M(II)-Npa-HQ	
		Zn (II)	Ni (II)	Zn (II)	Ni (II)	Zn (II)	Ni (II)	Zn (II)	Ni (II)
1.	Co-ordinated H <sub>2</sub> O molecule	3400	3420	3500	3450	3410	3450	3420	3400
2.	-NH Stretching	3310	3320	3350	3400	3360	3380	3300	3320
3.	Carbonyl Stretching of COOH-group	1660	1670	1650	1660	1620	1615	1590	1600
4.	Aromatic c-c multiple bonding	1590	1580	1575	1580	1615	1610	1560	1590
5.	-NH bending	1415	1420	1540	1535	1500	1520	1540	1540
6.	-CN Stretching	1310	1315	1290	1300	1300	1310	1310	1315
7.	-Pyridine Ring	1145	1125	1160	1150	1150	1145	1100	1120
8.	Benzene Ring	1110	1095	1085	1080	1070	1080	1090	1085
9.	Out of plane - CH bending	815	810	810	810	815	810	815	815
10.	Out of plane - CH deformation	715	710	660	650	675	660	640	645
11.	-MN bonding	385	375	440	425	420	360	450	430
12.	-MS bonding	320	325	370	325	380	305	360	330

Physical data of the isolated complex

S.No	Compound	Colour	Soluble in
1.	Ni(II)-Na-TCA	Light green	DMF, THF, CAN, NBZ, DCM, MeOG, EtOH
2.	Ni (II) - Npa - PIC	Green	DMF, THF, MeOH, EtOH
3.	Ni (II) - Npa - FA	Green	DMF, THF, ACN, MeOH, EtOH
4.	Ni (II) - Npa - HQ	Yellowish Green	DMF, THF, NBZ, MeOH, EtOH

**M(II) Npa-FA complex A**

Spectral band  $3400\text{cm}^{-1}$  in free ligand Npa is due to NH stretching vibration which is shifted to lower frequency region of  $3360\text{cm}^{-1}$  and  $3380\text{cm}^{-1}$  in Ni (II) - Npa - Fa and Zn (II) - Npa - FA complexes. A moderate band at  $1585\text{cm}^{-1}$  is due to NH bonding which is shifted to  $1500\text{cm}^{-1}$  and  $1520\text{cm}^{-1}$  in metal complexes. Lowering of these frequencies in the case of related metal chelates indicates the involvement of nitrogen in co-ordination. I.R. spectral data of ligand shows a band at the frequency of  $700\text{cm}^{-1}$  which is lowered to  $660\text{cm}^{-1}$  and  $670\text{cm}^{-1}$ . Indicating in repective metal complexes showing the attachment of furan with the metal ion. Some new spectral bands at  $420\text{cm}^{-1}$ ,  $360\text{cm}^{-1}$  and  $305\text{cm}^{-1}$  show the formation of MO and MN-bonding in metal complexes. Co-ordinated water molecule is also confirmed by the spectral bands

at different frequencies in Metal (II) - Npa - FA complexes.

**M (II) - Npa - PIC complex**

A moderate spectral band in lio and Npa at  $3400\text{cm}^{-1}$  is shifted to  $3350\text{cm}^{-1}$  and  $3400\text{cm}^{-1}$  which suggests that bonding in M (II) - Npa - PIC complexes is taking place through N of NH Ground to the metal ion. Another band at  $1585\text{cm}^{-1}$  which is due to  $1540\text{cm}^{-1}$  and  $1535\text{cm}^{-1}$  in two complexes which indicate the involvement of nitrogen the presence of pyridine ring of ligands which is lowered to  $1160\text{cm}^{-1}$  and  $1150$  showing the participation of pyridine ring in the formation of metal complexes. Water molecule is present in the complexes and new spectral bands at  $3500\text{cm}^{-1}$  and  $3450\text{cm}^{-1}$  of MO and MN shows the complex formation.

**Elemental analysis of isolated Mixed Ligand Complexed Analysis (%) (Calculated/found)**

S.No	Compound	C	H	N	Metal
1.	Ni(II)-Na-TCA	50.28/(49.72)	1.72/(1.67)	5.91/(6.20)	14.47/(14.02)
2.	Ni (II) - Npa - PIC	50.26/(48.86)	3.95/(3.69)	9.77/(10.00)	13.66/(14.44)
3.	Ni (II) - Npa - FA	40.67/(40.00)	5.84/(5.76)	6.81/6.48)	14.29/(13.88)
4.	Ni (II) - Npa - HQ	58.10/(57.20)	3.91/(3.69)	9.68/10.00)	13.53/(12.66)

**M(II) - Npa- HQ complex**

The IR frequency around  $3400\text{cm}^{-1}$  is due to -NH strethcing of Npa which is shifted by  $100\text{cm}^{-1}$  and  $80\text{cm}^{-1}$  in the metal complexes. Frequency of NH banding is also lowered in the I.R. spectrum indicating that bondingn between mental and ligand is taking place through 'N' of -NH group. Spectral band at  $1165\text{cm}^{-1}$  is lowered to  $1100\text{cm}^{-1}$  and  $1120$  in two complexes. Carbonyl stretching of COOH around  $1700\text{cm}^{-1}$  in Npa ligand is shifted to  $1590\text{cm}^{-1}$  and  $1600\text{cm}^{-1}$  indicating the participation of this

functional group in the formation of metal complex. Carbonyl stretching of -COOH is at the spectral band at  $1700\text{cm}^{-1}$  Npa ligand which shifted to  $1590\text{cm}^{-1}$  indicating the participation of this functional group in the formation of metal complex. Spectral bands around the region of  $3420\text{cm}^{-1}$  and  $3400\text{cm}^{-1}$  indicate the presence of coordinated water molecules. Apperance of new bands in far IR region in  $450\text{cm}^{-1}$   $430\text{cm}^{-1}$  and  $360\text{cm}^{-1}$ ,  $330\text{cm}^{-1}$  show MO and MN bonding in the metal complexes.

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