

## Synthesis and Characterization of Co II, Ni II and Cu II Complexes with a Macro Cyclic ligand 5,7,12,14-Tetramethyldibenzeno (b,i)-1,4,8,11-Tetraaza Cyclotetra dec-2,4,6,9,11,13 Hexaene

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### ABSTRACT:

A series of complexes of the type  $MLB_2$  {M=Co(II), Ni(II) & Cu (II), B=H<sub>2</sub>O, pyridine & different picolines} have been synthesized with the macro cyclic ligand, H<sub>2</sub>L (FIG.1). Characterization of the ligand as well as complexes have been done on the basis of elemental analysis, spectral studies conductivity & magnetic susceptibility measurements. Ligand has been found to co-ordinate through all the four nitrogen atoms. The complexes are found to be octahedral. The remaining two coordination sites are satisfied by oxygen of H<sub>2</sub>O or nitrogen donor molecules such as pyridine & different pico lines.

**KEY WORDS :** Pico lines, macro cyclic species, micro cyclic ligand, macro cyclic complexes.

### INTRODUCTION:

Much works have been done on metal complexes with tetra-aza macrocyclic ligands followed by extensive work on the metal –controlled template & metal –free non-template synthesis of macrocyclic species<sup>1-7</sup>. Therefore, in the present investigation, we report a series of complexes of Co (II), Ni (II) & Cu (II) of the type  $MLB_2$  with macro cyclic ligand, H<sub>2</sub>L, Me<sub>4</sub> (14)-tetraene N<sub>4</sub>.

### EXPERIMENTAL:

All the chemical used in the present work were from BDH of the reagent grade. Acetyl acetone & o-phenylene diamine obtained from Aldrich (USA) were used without further purification. For the preparation of the ligand, the procedure as reported in literature was followed<sup>1-6</sup>. o-phenylene diamine was dissolved in dry & cold methanol & allowed to react with methanolic solution of acetylacetone in equimolar proportion under reflux on a water bath for several hours at room temperature. The solution thus obtained on crystallization produced a yellowish coloured solid which was then filtered, washed & finally dried over KOH in a dessicator. The compound was further analysed & found to contain C=76.64%, H=6.97% and N=16.28% which corresponds with the formula C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>. The solution of ligand in methanol was allowed to react with the ethanolic solution of metal acetate in equimolar proportion under reflux on water bath for several hours at room temperature. The resulting solution on crystallization gave solids of different colour for different metals. The solid was then filtered, washed & dried over KOH in a dessicator. Acetates of Co (II), Ni (II) and Cu (II) was used separately and the complexes with each metal were prepared with the microcyclic ligand H<sub>2</sub>L in the presence of bases like H<sub>2</sub>O, pyridine & different picolines. On the basis of the analytical data (Table-1), the complexes were found to possess the molecular formula (Fig.2) of the type  $MLB_2$  where M=Co (II), Ni (II) & Cu (II) & B=H<sub>2</sub>O, pyridine & α-picoline, β-picoline and γ-picoline. Copper was estimated iodometrically. Nickel and Cobalt were estimated gravimetrically as bis-dimethyl glyoximate Ni (II) & CuSo<sub>4</sub> respectively. C, H & N were estimated by semi micro combustion method.

**CONDUCTIVITY MEASUREMENTS:**

Electrical conductivity of solutions of complexes were measured by conductivity meter bridge manufactured by wiss-Techen Werch Stathen type –LBR at room temperature in DMF (solvent). The cell constant was measured at (room temperature) 30 ° using N/10 and K/100 KCl solution.

**UV –VISIBLE SPECTRO PHOTOMETRIC MEASUREMENT:**

The electronic absorption spectra of the complexes were recorded with hitachi -320 spectro photometer at CDRI, Lucknow.

**IR SPECTRA:**

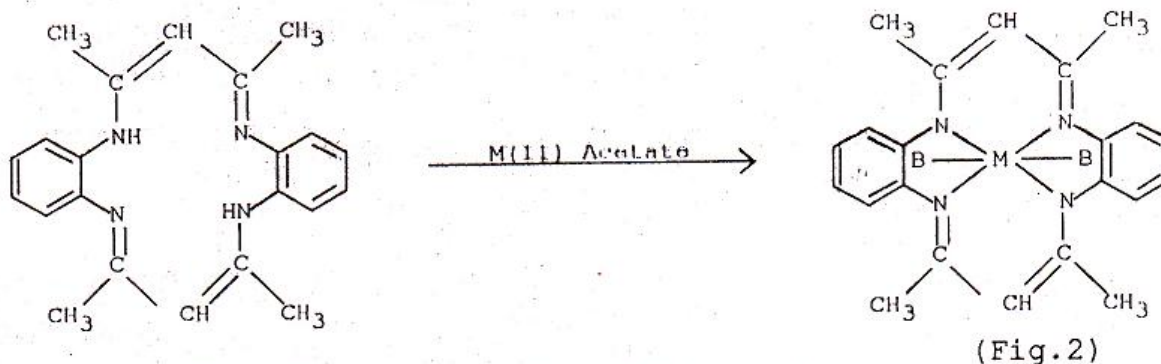
The infra –red spectra were recorded on perkin Elemer 577 spectro photometer using KBr pellets in the range of 4000-400 cm<sup>-1</sup> at CDRI, Lucknow.

**MAGNETIC SUSCEPTIBILITY:**

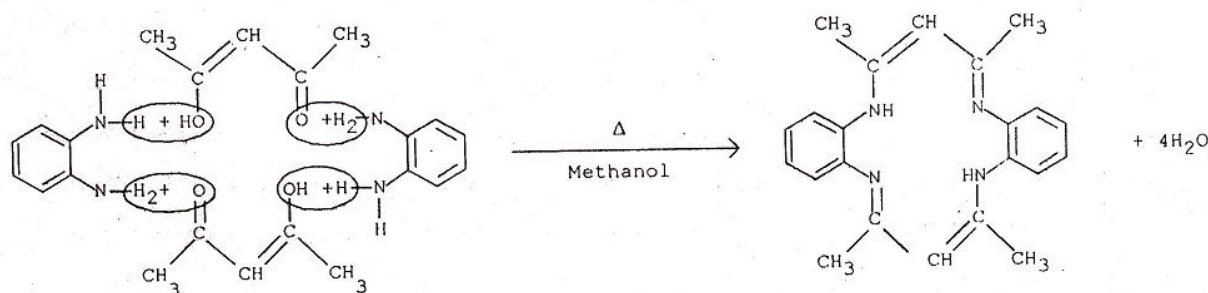
Magnetic susceptibility of the complexes were determined by Gouy's method {by using Hg[Co(NCS)<sub>4</sub>] as a calibrant.

**RESULTS & DISCUSSION:**

The reaction taking place in the preparation of the ligand & of its metal complexes involving acetylacetonone (enolic), o-phenylene diamine and M (II) acetals can be represented as follows:-



(Fig.1)



(Fig.2)

All the coloured complexes are stable at room temperature. The molar conductance values in the range of 25 to 40 for the complexes using  $10^{-3}$  molar solution in DMF (Table-1) indicate their non electrolytic as well as covalent nature. The analytical data (Table-1) shows that these macrocyclic complexes can be represented as  $M[(C_{22}H_{22}N_4)(B_2)]$  where  $M=Co, Ni, Cu$  and  $B=H_2O, \text{pyridine} \ \& \ \text{different picolines}$ . Molecular weight of these complexes indicates the monomeric nature of the complexes.

Analytical, Magnetic Moment and  
Electrical Conductance Data of the Complexes

Compound	$\mu_{eff}$ (BM)	$\Lambda_m$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )	Analysis & found(cal)		
			M	C	H
$[Co(C_{22}H_{22}N_4)(H_2O)_2]$	4.90	25	13.40 (13.48)	60.35 (60.42)	6.00 (5.95)
$[Co(C_{22}H_{22}N_4)(\text{pyridine})_2]$	4.88	30	10.48 (10.53)	68.65 (68.70)	6.80 (5.72)
$[Co(C_{22}H_{22}N_4)(\alpha\text{-picoline})_2]$	4.95	35	9.95 (10.03)	69.45 (69.51)	6.20 (6.13)
$[Co(C_{22}H_{22}N_4)(\beta\text{-picoline})_2]$	4.92	20	9.90 (10.03)	69.40 (69.51)	6.18 (6.13)
$[Co(C_{22}H_{22}N_4)(\gamma\text{-picoline})_2]$	4.90	30	9.90 (10.03)	69.40 (69.51)	6.22 (6.13)
$[Ni(C_{22}H_{22}N_4)(H_2O)_2]$	3.00	25	13.35 (13.44)	60.35 (60.45)	6.05 (5.95)
$[Ni(C_{22}H_{22}N_4)(\text{pyridine})_2]$	2.98	35	10.40 (10.50)	68.65 (68.73)	5.80 (5.72)
$[Ni(C_{22}H_{22}N_4)(\alpha\text{-picoline})_2]$	2.95	30	9.85 (10.00)	69.40 (69.50)	6.15 (6.13)
$[Ni(C_{22}H_{22}N_4)(\beta\text{-picoline})_2]$	3.00	35	9.95 (10.00)	69.42 (69.50)	6.18 (6.13)
$[Ni(C_{22}H_{22}N_4)(\gamma\text{-picoline})_2]$	2.98	20	9.90 (10.00)	69.38 (69.50)	6.20 (6.13)
$[Cu(C_{22}H_{22}N_4)(H_2O)_2]$	1.90	30	14.30 (14.38)	59.70 (59.79)	6.00 (5.88)
$[Cu(C_{22}H_{22}N_4)(\text{pyridine})_2]$	1.92	25	11.20 (11.26)	68.05 (68.14)	5.75 (5.67)
$[Cu(C_{22}H_{22}N_4)(\alpha\text{-picoline})_2]$	1.95	35	10.50 (10.65)	68.10 (68.97)	6.15 (6.08)
$[Cu(C_{22}H_{22}N_4)(\beta\text{-picoline})_2]$	1.90	40	10.55 (10.65)	68.80 (68.97)	6.12 (6.08)
$[Cu(C_{22}H_{22}N_4)(\gamma\text{-picoline})_2]$	1.94	30	10.60 (10.65)	68.82 (68.97)	6.14 (6.08)

Table -1



**Table -2****Electronic and IR Spectral Data of the Complexes**

Compound	Colour	IR Spectral data (cm <sup>-1</sup> )		Electronic Spectral data (cm <sup>-1</sup> )	
		$\nu(\text{C=N})$	$\nu(\text{M-N})$		
[Co(C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> )(H <sub>2</sub> O) <sub>2</sub> ]	pinkish brown	1630	445	17100	22200
[Co(C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> )(Pyridine) <sub>2</sub> ]	golden brown	1625	440	16800	21800
[Co(C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> )( $\alpha$ -picoline) <sub>2</sub> ]	"	1620	420	16700	21500
[Co(C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> )( $\beta$ -picoline) <sub>2</sub> ]	"	1620	425	16750	21400
[Co(C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> )( $\gamma$ -picoline) <sub>2</sub> ]	"	1625	425	16800	21500
[Ni(C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> )(H <sub>2</sub> O) <sub>2</sub> ]	greenish brown	1645	440	8600	18800
[Ni(C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> )(Pyridine) <sub>2</sub> ]	faint brown	1640	445	8500	18900
[Ni(C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> )( $\alpha$ -picoline) <sub>2</sub> ]	brown	1635	435	8400	18500
[Ni(C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> )( $\gamma$ -picoline) <sub>2</sub> ]	"	1645	440	9000	19500
[Cu(C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> )(H <sub>2</sub> O) <sub>2</sub> ]	green	1635	445	10000	14000
[Cu(C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> )(Pyridine) <sub>2</sub> ]	"	1626	440	9600	13600
[Cu(C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> )( $\alpha$ -picoline) <sub>2</sub> ]	"	1635	435	9500	13500
[Cu(C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> )( $\beta$ -picoline) <sub>2</sub> ]	"	1645	440	9000	13400
[Cu(C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> )( $\gamma$ -picoline) <sub>2</sub> ]	"	1640	445	9500	13500

**I.R SPECTRA:**

The I R spectrum (Table 2) of the micro cyclic ligand shows a weak band at 3260 cm<sup>-1</sup> and strong band at 2930 cm<sup>-1</sup> which are associated with  $\nu(\text{N-H})$  and  $\nu(\text{C-H})$  respectively. The -C-CH<sub>3</sub> and -CH<sub>2</sub>- groups present in the ligand are indicated by bands at 1830cm<sup>-1</sup> and 1430 cm<sup>-1</sup> respectively. Specific bands indicate the presence of phenyl ring in the ligand molecule. The characteristic bands due to chelated acetylacetonate ligand appear at 1565-1500 cm<sup>-1</sup> indicating the presence of  $\nu(\text{C-C})$  vibration in the ligand. All the complexes show a band around 1620 cm<sup>-1</sup> due to  $\nu(\text{C-N})$ . In the spectrum of the ligand this band appears at 1650 cm<sup>-1</sup>. Lowering of this band in complexes suggests participation of emine nitrogen atom in coordination. At the same time, no band is obtained around 1750-1650 cm<sup>-1</sup> which indicates the condensation of the amine and ketone groups. The bands around 450 cm<sup>-1</sup> in all the complexes indicate  $\nu(\text{M-N})$  vibration which further confirms the co-ordination of nitrogen atoms of these groups with the metals.

**ELECTRONIC SPECTRA & MAGNETIC MOMENT STUDIES:**

The values of magnetic moment of Co (II) complexes (Table 1) at room temperature in the range of 4.85-4.95 BM are higher than the spin only value due to high orbital contribution resulting from  ${}^4T_{1g}$  ground state. Thus the magnetic character of the complexes suggests that  $CoL(B_2)$  should be octahedral in nature. The Co (II) complexes (Table 2) show a weak band at  $8200\text{ cm}^{-1}$  due to  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$  and in the region of  $17000\text{--}22,000\text{ cm}^{-1}$ . The latter shows signs of splitting into two components, one at  $19500\text{ cm}^{-1}$  due to  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$  and the other at  $21,500\text{ cm}^{-1}$  due to  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ . Finally electronic spectra of Co (II) complexes indicates the octahedral arrangement of the ligands around Co (II) ion. The values of magnetic moments for Ni (II) complexes have been found to be in the range of 2.90 to 3.10 BM indicating octahedral nature of the complexes. The complexes of Ni (II) show three bands associated with the spin – allowed transitions from the  ${}^3A_{2g}$  ground to the three excited triplets terms  $\{ {}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F) = 8,600\text{ cm}^{-1}$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F) = 15,000\text{ cm}^{-1}$ , and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P) = 18,600\text{ cm}^{-1}$  indicating the octahedral geometry of the complexes. The value of the magnetic moment of Cu (II) complexes have been found to be in the range of 1.90 –1.95 BM suggesting octahedral nature of the complexes. In case of Cu (II) complexes, a broad band is located in the range of  $10,000\text{ cm}^{-1}$  to  $14,000\text{ cm}^{-1}$  supporting the octahedral or tetragonal field for the complexes<sup>7</sup>. The  ${}^1H$  NMR spectrum of the ligand shows five kinds of protons namely  $---CH_3$ , ArH (two kinds) &  $>N---H$  protons. The signal due to  $>N---H$  proton disappears in the spectra of the complexes and the signal due to proton shifted towards down-field suggesting the co-ordination of the adjacent N---atoms to the metal ions. The results obtained are in good agreement with the literature<sup>8</sup>.

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