

Synthesis and Characterisation of Co(II), Ni(II) and Cu(II) Complexes with a Macrocyclic Ligand 5,7,12,14-Tetramethyldibenzo (b, i)-1,4,8,11-Tetraaza Cyclotetra Dec-2,4,6,9,11,13-Hexaene

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A series of complexes of the type MLB_2 ($M = Co(II), Ni(II)$ and $Cu(II)$, $B = H_2O$, pyridine and α, β or γ -picolines) have been synthesised with the macrocyclic ligand, H_2L . Characterisation of the ligand as well as complexes has been done on the basis of elemental analysis, spectral studies, conductivity and magnetic susceptibility measurements. The ligand has been found to coordinate through all the four nitrogen atoms. The complexes are found to be octahedral. The remaining two coordination sites are satisfied by oxygen of H_2O or nitrogen of nitrogen donor molecules such as pyridine and different picolines.

INTRODUCTION

Much work has been done on metal complexes with tetra-aza macrocyclic ligands followed by extensive work on the metal-controlled template and metal-free non-template synthesis of macrocyclic species¹⁻⁷. Therefore, in the present investigation, we report a series of complexes of Co(II), Ni(II) and Cu(II) of the type MLB_2 with a macrocyclic ligand, H_2L , $Me_4(14)$ -tetraene N_4 .

EXPERIMENTAL

All the chemicals used in the present work were from BDH of reagent grade. Acetylacetone and *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 followed¹⁻⁶. *o*-Phenylene diamine was dissolved in dry and cold methanol and allowed to react with the methanolic solution of acetylacetone in equimolar proportion under reflux on a water bath for several hours at room temperature. The solution thus obtained on crystallisation produced a yellowish coloured solid which was then filtered, washed and finally dried over KOH in a desiccator. The compound was further analysed and found to contain C = 76.64, H = 6.97 and N = 16.28% which corresponds with the formula $C_{22}H_{24}N_2$.

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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 crystallisation gave solids of different colour for different metals. The solid was then filtered, washed and dried over KOH in a desiccator. Acetates of Co(II), Ni(II) and Cu(II) were used separately and the complexes with each metal were prepared with the microcyclic ligand H_2L in the presence of bases like H_2O , pyridine and 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 $M = Co(II)$, $Ni(II)$ and $Cu(II)$ and $B = H_2O$, pyridine and α -picoline, β -picoline or γ -picoline.

Copper was estimated iodometrically. Nickel and cobalt were estimated gravimetrically as bis-dimethyl glyoximate Ni(II) and $CoSO_4$ respectively. C, H and N were estimated by semimicro combustion method.

Electrical conductivities 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 $30^\circ C$ using $N/10$ and $N/100$ KCl solutions. The electronic absorption spectra of the complexes were recorded with Hitachi-320 spectrophotometer at CDRI, Lucknow. The infrared spectra were recorded on Perkin-Elmer 577 spectrophotometer using KBr pellets in the range of $4000-400\text{ cm}^{-1}$ at CDRI, Lucknow. Magnetic susceptibilities of the complexes were determined by Gouy's method using $Hg[Co(NCS)_4]$ as a calibrant.

RESULTS AND DISCUSSION

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

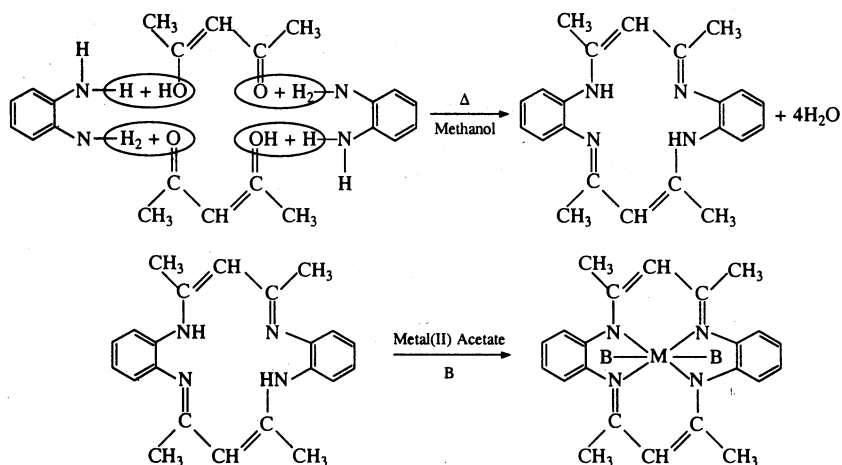


Fig. 1 and 2

$M = Co(II)$, $Ni(II)$ and $Cu(II)$ and $B = H_2O$, pyridine or different picolines

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) show that these macrocyclic complexes can be represented as $M[(C_{22}H_{22}N_4)(B_2)]$ where $M = Co, Ni, Cu$ and $B = H_2O, pyridine$ or different picolines. Molecular weights of these complexes indicate the monomeric nature of the complexes.

TABLE-1
ANALYTICAL, MAGNETIC MOMENT AND
ELECTRICAL CONDUCTANCE DATA OF THE COMPLEXES

Compound	μ_{eff} (BM)	Λ_m ($\Omega^{-1} \text{ cm}^2$ mol^{-1})	Analysis %, found (calcd.)			
			M	C	H	N
$[Co(C_{22}H_{22}N_4)(H_2O)_2]$	4.90	25	13.40 (13.48)	60.35 (60.42)	6.00 (5.95)	12.85 (12.81)
$[Co(C_{22}H_{22}N_4)(Py)_2]$	4.88	30	10.48 (10.53)	68.65 (68.70)	6.80 (5.72)	15.10 (15.02)
$[Co(C_{22}H_{22}N_4)(\alpha\text{-pic})_2]$	4.95	35	9.95 (10.03)	69.45 (69.51)	6.20 (6.13)	14.40 (14.31)
$[Co(C_{22}H_{22}N_4)(\beta\text{-pic})_2]$	4.92	20	9.90 (10.03)	69.40 (69.51)	6.18 (6.13)	14.35 (14.31)
$[Co(C_{22}H_{22}N_4)(\gamma\text{-pic})_2]$	4.90	30	9.90 (10.03)	69.40 (69.51)	6.22 (6.13)	14.34 (14.31)
$[Ni(C_{22}H_{22}N_4)(H_2O)_2]$	3.00	25	13.35 (13.44)	60.35 (60.45)	6.05 (5.95)	12.90 (12.82)
$[Ni(C_{22}H_{22}N_4)(Py)_2]$	2.98	35	10.40 (10.50)	68.65 (68.73)	5.80 (5.72)	15.10 (15.03)
$[Ni(C_{22}H_{22}N_4)(\alpha\text{-pic})_2]$	2.95	30	9.85 (10.00)	69.40 (69.50)	6.15 (6.13)	14.38 (14.31)
$[Ni(C_{22}H_{22}N_4)(\beta\text{-pic})_2]$	3.00	35	9.95 (10.00)	69.42 (69.50)	6.18 (6.13)	14.40 (14.31)
$[Ni(C_{22}H_{22}N_4)(\gamma\text{-pic})_2]$	2.98	20	9.90 (10.00)	69.38 (69.50)	6.20 (6.13)	14.35 (14.31)
$[Cu(C_{22}H_{22}N_4)(H_2O)_2]$	1.90	30	14.30 (14.38)	59.70 (59.79)	6.00 (5.88)	12.70 (12.68)
$[Cu(C_{22}H_{22}N_4)(Py)_2]$	1.92	25	11.20 (11.26)	68.05 (68.14)	5.75 (5.67)	14.95 (14.90)
$[Cu(C_{22}H_{22}N_4)(\alpha\text{-pic})_2]$	1.95	35	10.50 (10.65)	68.10 (68.97)	6.15 (6.08)	14.28 (14.20)
$[Cu(C_{22}H_{22}N_4)(\beta\text{-pic})_2]$	1.90	40	10.55 (10.65)	68.80 (68.97)	6.12 (6.08)	14.26 (14.20)
$[Cu(C_{22}H_{22}N_4)(\gamma\text{-pic})_2]$	1.94	30	10.60 (10.65)	68.82 (68.97)	6.14 (6.08)	14.25 (14.20)

Py = Pyridine, $\alpha, \beta, \gamma\text{-pic}$ = $\alpha, \beta, \gamma\text{-picoline}$.

TABLE-2
ELECTRONIC AND IR SPECTRAL DATA (cm^{-1}) OF THE COMPLEXES

Compound	Colour	IR spectral bands		Electronic spectral bands	
		$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{N})$		
$[\text{Co}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\text{H}_2\text{O})_2]$	Pinkish brown	1630	445	17100	22200
$[\text{Co}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\text{py})_2]$	Golden brown	1625	440	16800	21800
$[\text{Co}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\alpha\text{-pic})_2]$	Golden brown	1620	420	16700	21500
$[\text{Co}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\beta\text{-pic})_2]$	Golden brown	1620	425	16750	21400
$[\text{Co}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\gamma\text{-pic})_2]$	Golden brown	1625	425	16800	21500
$[\text{Ni}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\text{H}_2\text{O})_2]$	Greenish borwn	1645	440	8600	18800
$[\text{Ni}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\text{Py})_2]$	Faint brown	1640	445	8500	18900
$[\text{Ni}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\alpha\text{-pic})_2]$	Brown	1635	435	8400	18500
$[\text{Ni}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\beta\text{-pic})_2]$	Brown	1640	445	8500	19000
$[\text{Ni}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\gamma\text{-pic})_2]$	Brown	1645	440	9000	19500
$[\text{Cu}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\text{H}_2\text{O})_2]$	Green	1635	445	10000	14000
$[\text{Cu}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\text{Py})_2]$	Green	1626	440	9600	13600
$[\text{Cu}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\alpha\text{-pic})_2]$	Green	1635	435	9500	13500
$[\text{Cu}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\beta\text{-pic})_2]$	Green	1645	440	9000	13400
$[\text{Cu}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\gamma\text{-pic})_2]$	Green	1640	445	9500	13500

The IR spectrum (Table-2) of the macrocyclic ligand shows a weak band at 3260 cm^{-1} and a strong band at 2930 cm^{-1} which are associated with $\nu_{(\text{N}-\text{H})}$ and $\nu_{(\text{C}-\text{H})}$ respectively. The $-\text{C}-\text{CH}_3$ and $-\text{CH}_2-$ groups present in the ligand are indicated by bands at 1830 cm^{-1} and 1430 cm^{-1} respectively. Specific bands indicate the presence of phenyl ring in the ligand molecule. The characteristic bands due to chelated acetylacetonate ligand appear at $1565-1500 \text{ cm}^{-1}$ indicating the presence of $\nu_{(\text{C}=\text{C})}$ vibration in the ligand. All the complexes show a band around 1620 cm^{-1} due to $\nu_{(\text{C}=\text{N})}$. In the spectrum of the ligand this band appears at 1650 cm^{-1} . Lowering of this band in complexes suggests participation of amine nitrogen atom in coordination. At the same time, no band is obtained around $1750-1650 \text{ cm}^{-1}$ which indicates the condensation of the amine and ketone groups. The bands around 450 cm^{-1} in all the complexes indicate $\nu(\text{M}-\text{N})$ vibration which further confirms the coordination of nitrogen atoms of these groups with the metals.

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 cm^{-1} due to ${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$ and in the region of $22,000\text{--}17,000\text{ cm}^{-1}$. The latter shows signs of splitting into two components, one at $19,500\text{ cm}^{-1}$ due to ${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$ and the other at $21,500\text{ cm}^{-1}$ due to ${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$. Finally, electronic spectra of Co(II) complexes indicate 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 triplet terms ${}^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F) = 8,600\text{ cm}^{-1}$, ${}^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F) = 15,000\text{ cm}^{-1}$ and ${}^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P) = 18,600\text{ cm}^{-1}$ indicating the octahedral geometry of the complexes.

The values of 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 complexes⁷.

The 1H NMR spectrum of the ligand shows five kinds of protons namely $-CH_3$, >CH , ArH (two kinds) and >N-H protons. The signal due to >N-H proton disappears in the spectra of the complexes and the signal due to >CH proton shifted towards downfield suggesting the coordination of the adjacent N-atoms to the metal ions. The results obtained are in good agreement with the literature⁸.

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