

Synthesis and Characterization of Cobalt(II), Nickel(II) and Copper(II) Complexes of 14-Membered Macrocyclic Ligand

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This paper deals with the synthesis and characterization of a macrocyclic ligand (L) and its metal complex compounds with the general formula $[M-L(CH_3COO)_2]$ for M= Co(II), Ni(II) and Cu(II) where L is a 14-membered macrocyclic ligand resulted through the condensation reaction of *o*-phenylene diamine and ethyl acetoacetate. The ligand and its coordination compounds were formulated according to the chemical analysis, electronic, infrared, 1H NMR and mass spectra, magnetic susceptibility as well as thermogravimetric analysis.

Key Words: Cobalt(II), Nickel(II), Copper(II) Complexes, Macrocyclic ligand.

INTRODUCTION

There has been considerable interest in the synthesis of transition metal complexes of macrocyclic ligand systems because they play vital roles in biological systems¹. Also, interest in these species stems largely from the enhanced kinetic and thermodynamic stability of their complexes relative to those of related open chain ligands. Generally, macrocyclic complexes are also of interest because of the synthetic flexibility involved in their preparation, which allows for systematic variation in parameters such as ring size, the nature of the donor atoms and the steric and electronic effects associated with the groups located on the periphery of the macrocyclic ring².

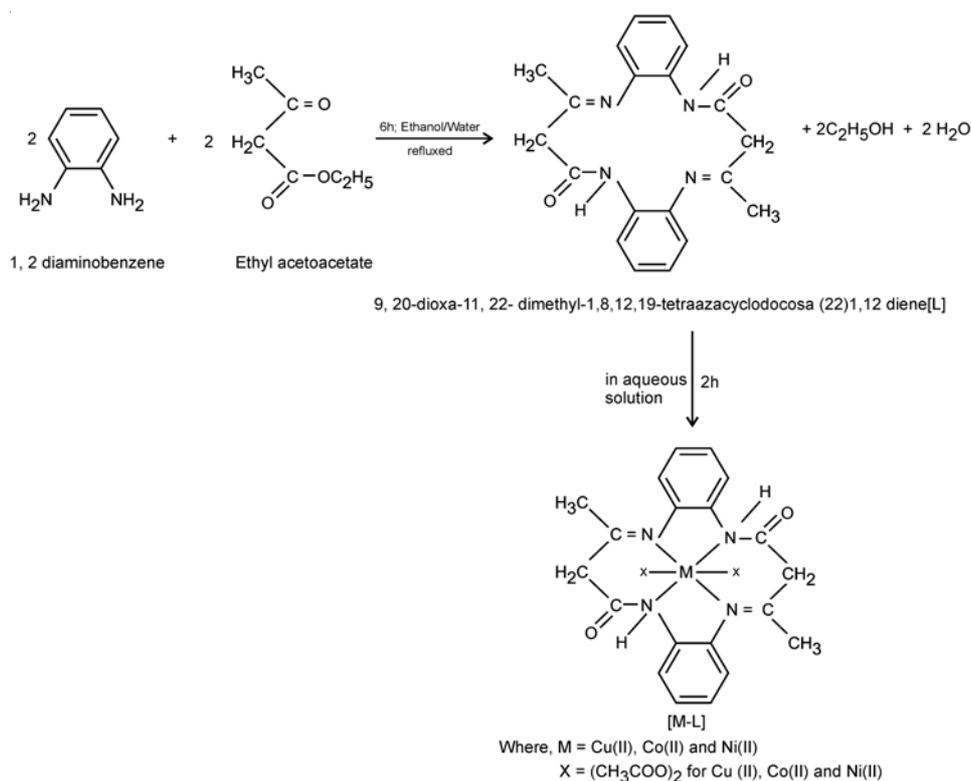
The aim of this work was the production of novel macrocyclic ligand and its cobalt(II), nickel(II) and copper(II) complexes by using environmentally benign methods (**Scheme-I**). Thus, macrocyclic ligand and its complexes were synthesized and characterized by using different techniques.

EXPERIMENTAL

All chemicals and solvents were reagent grade and used as received. C, H, N and M analyses were determined at the Analytical Unit of RSIC Chandigarh University, Chandigarh. IR spectra (as KBr pellets) were recorded ($4600-400\text{ cm}^{-1}$) on a Perkin-Elmer 681 spectrophotometer. Electronic spectra in the 200-900 nm region were recorded on a Perkin-Elmer 550 spectrophotometer. Mass spectra were recorded on Jeol SX-102(FAB), 1H NMR spectra were obtained with a Perkin-Elmer R32-90

MHz spectrometer using TMS as internal standard and DMSO- d_6 as solvent from CDRI, Lucknow. Magnetic susceptibilities were measured at 25 °C by the Gouy method using mercuric tetrathiocyanato-cobaltate(II) as the magnetic standard and thermogravimetric analyses were carried out on TGA/DTA-851, METTLER TOLEDO at RSIC, RTM, Nagpur University, Nagpur.

Preparation of macrocyclic ligand 9,20-dioxa-11,22-dimethyl-1,8,12,19-tetraazatricyclodocosa-(22)-1,12-diene (L): 1,2-Diaminobenzene (0.01 mol, 1.0 g) in ethanol/water (25 mL) and ethyl acetoacetate (0.01 mol, 1.2 mL) dissolved in ethanol/water (25 mL), mixture of both the reactants have been refluxed for 6 h. Then volume concentrated on the steam bath until yellow coloured crystals begin to form. The product has been purified by crystallization from hot water and 1 g of activated charcoal (to remove coloured impurities). Thus, white crystalline pure macrocyclic ligand has been collected. (**Scheme-I**) (Yield: 2.7 g; 78 %) The purity of the crystalline ligand has been checked by TLC.



Scheme-I

Preparation of {M(II)-(L)-(CH₃-COO)₂}: To the hot aqueous solution of ligand (L) (0.01 mmol, 3.4 g), hot aqueous solution of metal acetates (M-(CH₃COO)₂·xH₂O; 0.01 mmol) with few drops of acetic acid was added. The solution mixture

was then refluxed for 2 h. On cooling, coloured precipitate formed, was then filtered and washed with cold water and dried in vacuum (**Scheme-I**). The analytical data are given in Table-1.

TABLE-1
ANALYTICAL DATA OF TETRAAZA MACROCYCLIC
LIGAND (L) AND ITS COMPLEXES

Compd.	Half decomposition temp. (°C)	Colour	Elemental analysis (%): Calcd. (Found)				m.w.
			M	C	H	N	
[L]	220	White	–	69.01 (68.96)	6.10 (5.74)	15.99 (16.09)	348
[Co-L]	340	Violet	11.06 (10.96)	54.96 (54.44)	4.77 (4.50)	10.68 (11.99)	524
[Ni-L]	350	Light Green	10.03 (10.01)	49.82 (48.50)	4.49 (4.85)	9.68 (10.76)	578
[Cu-L]	395	Pale blue	11.99 (11.50)	45.36 (45.09)	3.78 (3.98)	10.58 (11.65)	529

RESULTS AND DISCUSSION

The introductory recognition of the macrocyclic ligand has been obtained from its IR spectrum which shows the absence of uncondensed functional groups (NH_2 , $\text{O-C}_2\text{H}_5$) stretching mode of starting materials *i.e.*, *o*-phenylene diamine and ethyl acetoacetate. The IR spectrum of macrocyclic ligand [L] exhibits sharp bands probably due to its crystalline nature (Fig. 1). $\nu(\text{N-H})$ stretching frequency^{3,4} shows bands at $3300\text{-}3290\text{ cm}^{-1}$. For $\nu(>\text{C}=\text{N})$ stretching vibrations⁵ medium bands have been observed at $1600\text{-}1700\text{ cm}^{-1}$. The bands observed in the region. 1590 , 1575 , 1490 and 1450 cm^{-1} clearly indicates the presence of aromatic ring. The subsistence of *o*-disubstituted aromatic ring⁶ ($\text{C}_6\text{H}_4\text{N}_2$) has also been confirmed by observing a sharp band at 745 cm^{-1} . In addition, the existence of aromatic C-N group⁷ has been proved as a result of sharp peak observed at 1390 cm^{-1} (Table-2).

The main shifts have been noticed in the IR spectra of the corresponding macrocyclic complexes such as appearance of new bands and sharp peaks between regions $445\text{-}440\text{ cm}^{-1}$ indicate $\nu(\text{M-N})$ stretching vibrations⁸ suggesting that imide nitrogen is coordinated with metal ions. Besides this, there is no identification of M-O bond, as no band is attributed to $\nu(\text{M-O})$ ($600\text{-}500\text{ cm}^{-1}$) vibrations⁹ that mean amide oxygen is none coordinating and the position of imide band in the ligand does not undergo any change in complexes. The sharp peaks observed in the region $1580\text{-}1400\text{ cm}^{-1}$ indicate the retention of aromatic ring in ligand [L] as well as in metal complexes (Table-2). Also, a new broad peak is observed in the region $3489\text{-}3350\text{ cm}^{-1}$ which may be attributed to crystal water¹⁰ in case of Ni(II) macrocyclic complex. (IR spectra of macrocyclic ligand and its coordination compounds Co(II), Ni(II) and Cu(II) are given in Fig. 1).

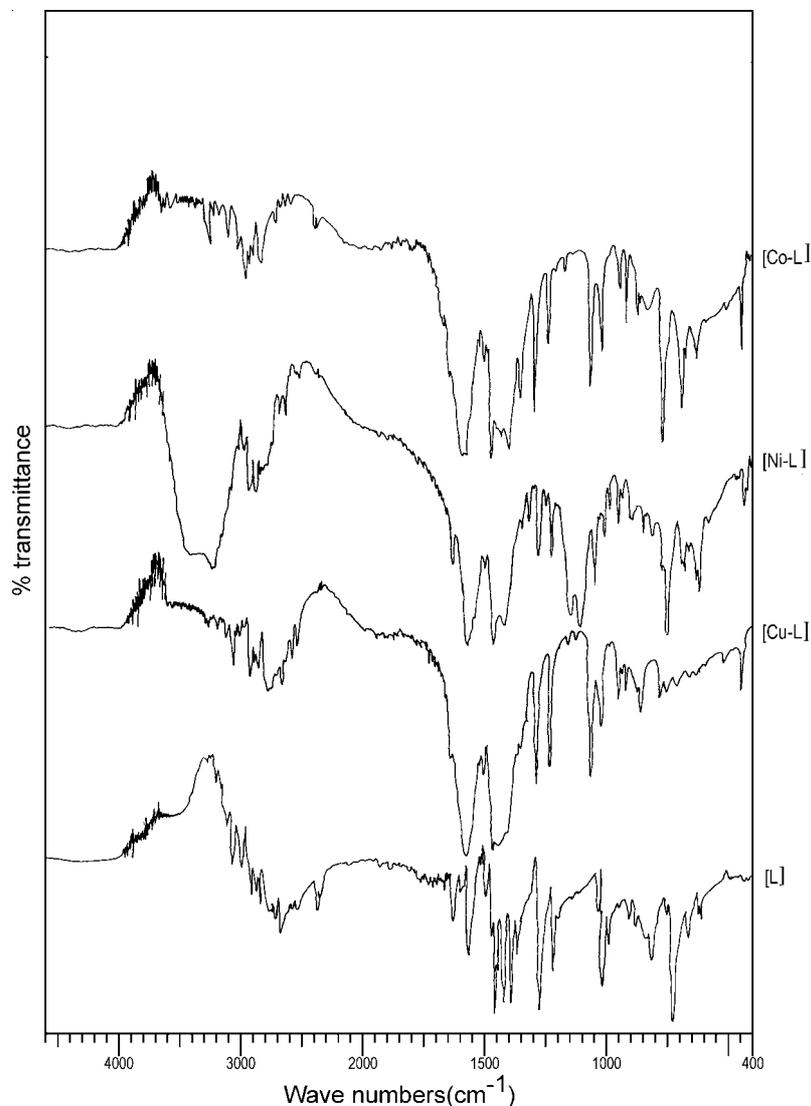


Fig. 1. Infrared spectra of macrocyclic ligand and its complexes

The ¹H NMR spectrum of the macrocyclic ligand does not show any signal, which is attributable to primary amino protons, *i.e.* starting materials such as *o*-phenylene diamine and ethyl acetoacetate, suggesting that the proposed macrocyclic skeleton has been formed by condensation reaction. The ¹H NMR spectrum of the ligand shows singlet at δ 2.52 corresponding to $>\text{CH}_2$ (4H) protons of ethyl acetoacetate¹¹. The ¹H NMR spectrum of macrocyclic ligand [L] shows a broad signal in the region δ 7.11-7.13, which indicates the existence of benzene ring¹² in the macrocyclic skeleton. In addition, the spectrum shows distinguish singlet at δ 7.46 that may be assigned to amide protons (2H)¹³.

TABLE-2
IR SPECTRAL DATA FOR GIVEN TETRAAZA MACROCYCLIC
LIGAND (L) AND ITS COMPLEXES

Groups	IR frequencies of the macrocylic ligand (cm ⁻¹)	IR frequencies of the macrocylic complexes (cm ⁻¹)		
		Co	Ni	Cu
v(N-H)	3290 m	3200 m	3145 m	3150 m
v(>C=N)	1600 m	1550 m	1499	1560
Aromatic ring	1590, 1575, 1490, 450 m	1580, 1570, 1490 m	1567, 1550, 1453 m	1500, 1460, 1400 m
<i>o</i> -Disubstituted aromatic ring	745 v	750 v	734 v	750 v
Aromatic (C-N)	1390 s	1300 s	1345 s	1290 s
(M-N)	–	445 m	440 m	440 m
Crystal water	–	–	3489-3350 m	–

¹H NMR spectra of Co(II), Ni(II) and Cu(II) macrocylic complexes show multiplets in the region δ 2.43-3.3 attributed to methylene (CH₂) protons (4H) of acetoacetate moiety¹². Again the ¹H NMR spectra of macrocylic complexes show singlets in the region 7.09-7.10 ppm corresponding to phenyl ring protons¹² (C₆H₄; 8H). However, no band could be identified, which may correspond to primary amino protons. Thus, ¹H NMR spectra further support the formation of macrocylic framework. Moreover, a broad signal in the region δ 7.8- δ 8.30 that is attributed to amide protons (Table-3). The shift of signals towards lower field is an identification of coordination of the macrocycle. (¹H NMR spectrum of the macrocylic ligand [L] is given in Fig. 2 and representative ¹H NMR spectrum of Cu(II) macrocylic complex is given in Fig. 3).

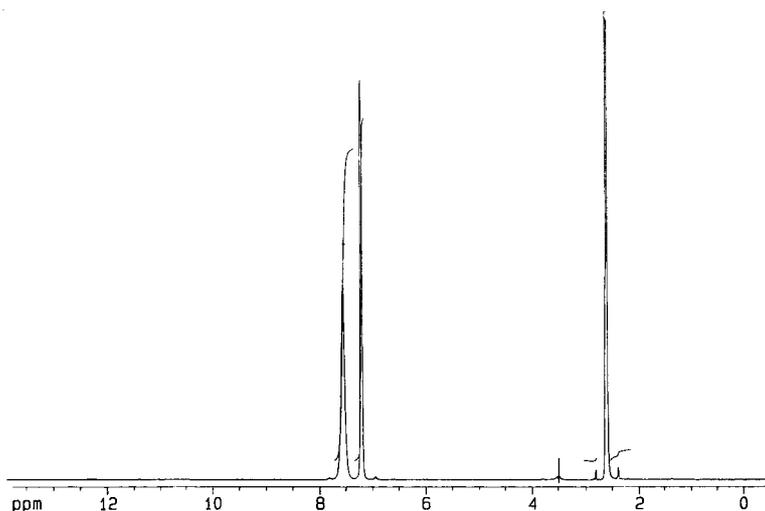


Fig. 2. Proton NMR Spectrum of macrocylic ligand [L]

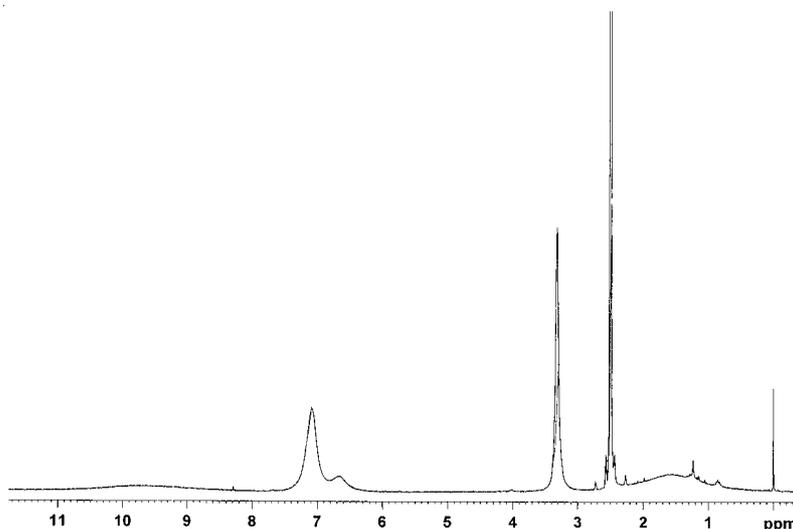


Fig. 3. Representative proton NMR spectrum of macrocyclic complex [Cu-L]

TABLE-3
¹H NMR SPECTRAL DATA OF MACROCYCLIC LIGAND [L] AND
 ITS TRANSITION METAL COMPLEXES

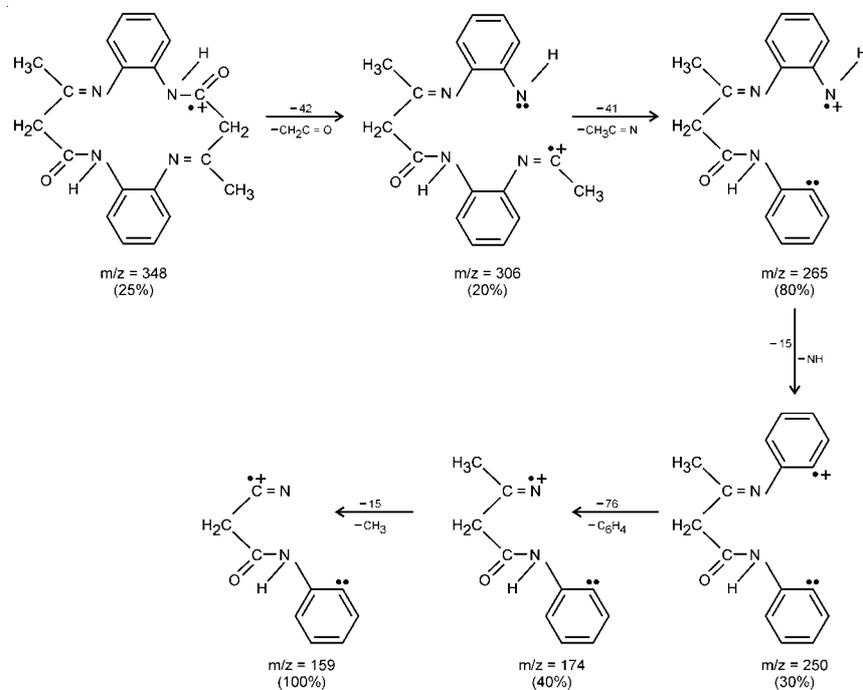
Nature of proton	Chemical shifts of macrocyclic ligand (δ ppm)	Representative chemical shifts of macrocyclic complexes (δ ppm)	
		Cu	Ni
Aromatic (Ar-H)	7.11-7.13 d	7.09 s	7.1 s
-NH (secondary amide)	7.46 s	8.30 s	7.8 s
>CH ₂ (methylene group)	2.52 s	2.43-2.56 q	3.3 s

d = doublet, s = singlet, q = quartet, m = multiplet

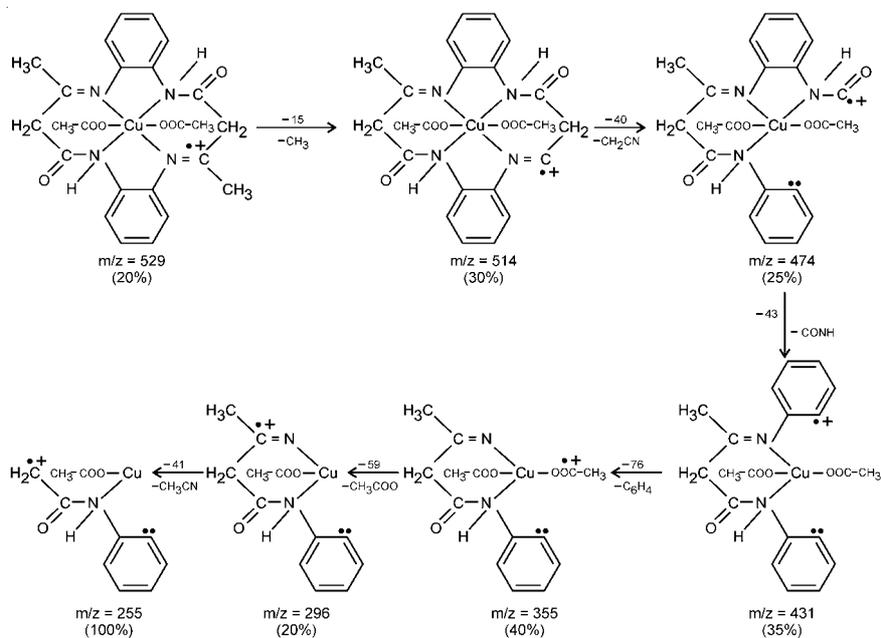
Determination of molecular weight of macrocyclic ligand (L) and its transition metal complexes by mass spectra has been very useful in completing its characterization. The representative fragmentation pattern of the ligand and its representative complex are shown in the Figs. 4 and 5 and in Schemes II and III, respectively.

The details of magnetic moments, tentative geometries and electronic spectral bands¹⁴ of macrocyclic complexes observed in the graphs are given in the Table-4.

In the present thermal study of the three-macrocyclic complexes, no sharp changes in weight loss have been observed. Thus, TG curves indicated their macrocyclic coordinating nature, whereas in case of simple coordinating compounds weight loss is sharp¹⁵. The Freeman-Carroll¹⁶ method is generally used to evaluate the order of reaction and other thermodynamic parameters, whereas, Sharp-Wentworth method¹⁷ is used to evaluate the activation energy. Kinetic parameters of macrocyclic complexes of (L) are given in Table-5.



Scheme-II: Fragmentation pattern of macrocyclic ligand [L]



Scheme-III: Representative fragmentation pattern of macrocyclic complex [Cu-L]

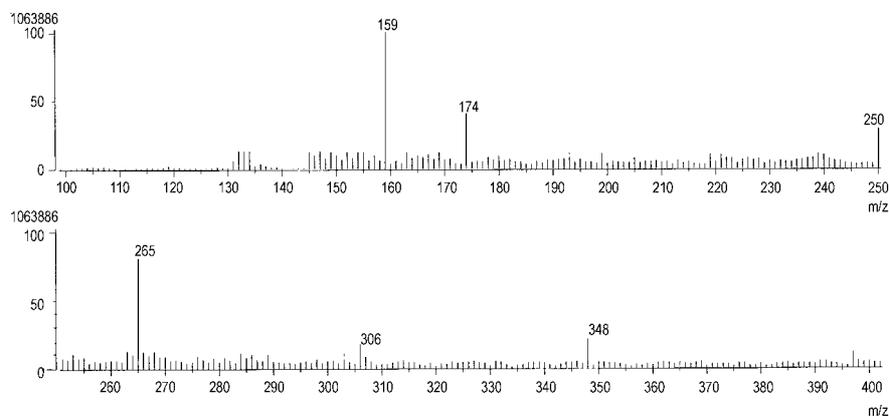


Fig. 4. Mass spectrum of macrocyclic ligand (L)

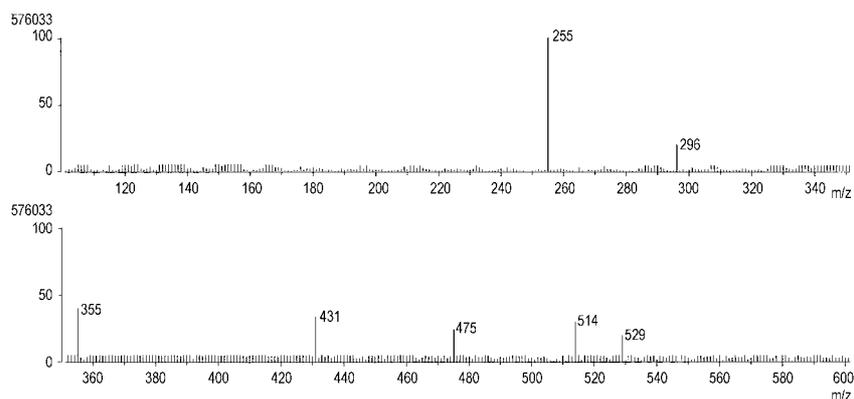


Fig. 5. Representative mass spectrum of macrocyclic complex (Cu-L)

TABLE-4
MAGNETIC AND ELECTRONIC SPECTRAL DATA OF MACROCYCLIC COMPLEXES

Compounds	Magnetic property and geometry at room temperature (BM)	Electronic spectra (cm ⁻¹)
[Co-L]	2.10 (Octahedral)	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ 16,750-16,761
		${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ 23,376-23,392
[Ni-L]	2.10 (Octahedral)	${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ 16,400-16,434
		${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ 27,701-27,708
[Cu-L]	1.313 (Distorted octahedral)	${}^2B_{1(g)} \rightarrow {}^2B_{2(g)}$ 16,370-16,381
		${}^1B_{1(g)} \rightarrow {}^2E_{(g)}$ 19,511-19,523

[Co(II)-L-(OAc)₂]: Thermo gram of [Co(II)-L-(OAc)₂] is shown in Fig. 6. The read-through of the TG reveals that there is no mass loss up to 320 °C. In the first step, after 320 °C there is a rapid mass loss is observed up to 560 °C which may be due to elimination of functional groups CONH + CH₂ + CH₃CN and 2 acetate groups

TABLE-5
KINETIC PARAMETERS OF MACROCYCLIC COMPLEXES OF (L)

Macrocyclic complexes	Activation energy* (KJ/mol)		ΔS (KJ)	ΔF (KJ)	Z (S ⁻¹)	S* (KJ)	n (found)
	FC	*SW					
[Co(II)-L]	17.870	18,98	-165.93	128.760	150.330	220.98	1(0.8)
[Ni(II)-L]	82.207	82.57	-293.87	192.117	608.817	191.20	1(0.7)
[Cu(II)-L]	33.980	35.01	-167.03	90.870	432.870	412.32	1(0.8)

FC* = Freeman Carroll method, SW* = Sharp-Wentworth method; DS = Entropy change, DF= Free energy change, Z = Frequency factor, S* = Apparent entropy change.

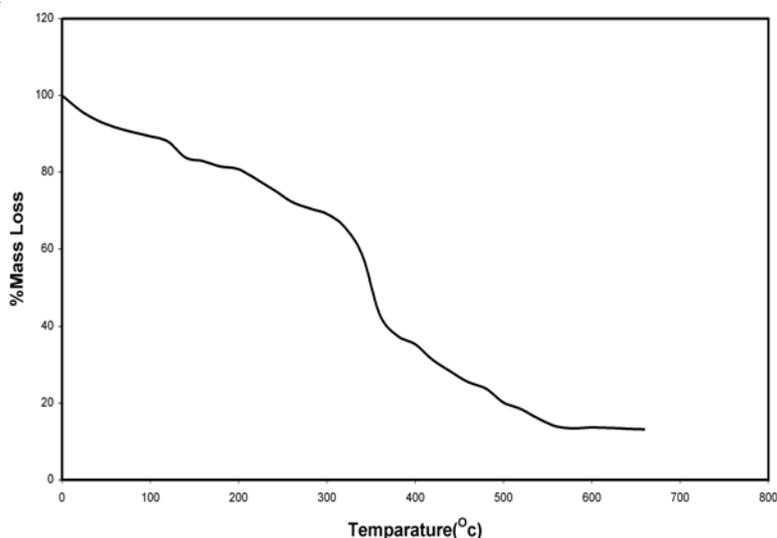
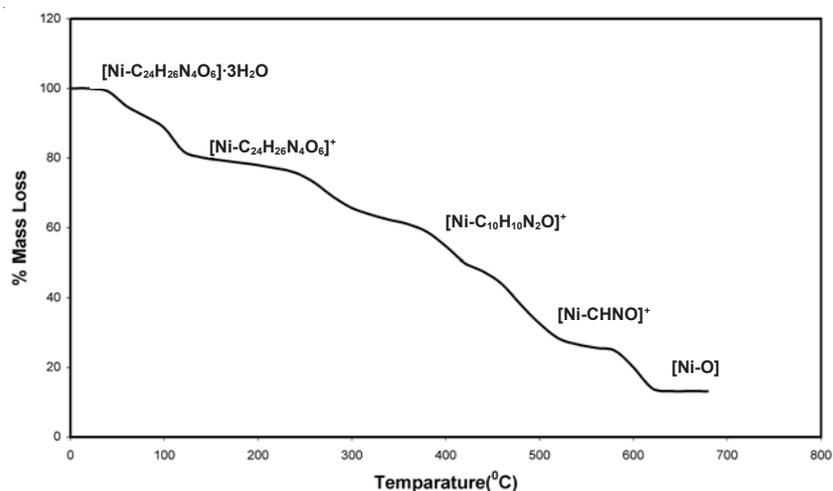


Fig. 6. Thermogram of [Co(II)-L]

(found: 41.22, calcd.: 42.84 %). After 560 °C, the residue obtained may be of stable oxide of cobalt *i.e.* Co₃O₄ as a result of oxidation-reduction reactions. (found: 45.41, calcd.: 44.10 %).

[Ni(II)-L-(OAc)₂·3H₂O]: Thermogram of [Ni(II)-L-(OAc)₂·3H₂O is shown in Fig. 7. The perusal of the TG reveals that it consists of three steps. It can be seen that there is no mass loss up to 40 °C. In the first step, after 40 °C there is a mass loss upto 120 °C, which may be due to elimination of three water molecules (found: 10.30, calcd.: 9.0 %). In second step, the loss of mass is like a slope from 260 °C to 520 °C, due to elimination of one-phenyl groups, functional groups like 2 acetate groups + CONH + CH₂ + CH₃-CN (obsd: 50.51 %, calcd.: 50.03 %). In the third step, the rapid loss is observed from 580-620 °C due to elimination of CH₃-CN + CH₂ + phenyl ring (found: 22.66, calcd.: 23.56 %). After this there is a gradual decrease in mass loss observed up to 640 °C, the residue obtained may be of stable NiO (found: 13.20, calcd.: 12.90 %).

Fig. 7. Thermogram of [Ni(II)-L]·3H₂O

[Cu(II)-L-(OAc)₂]: Thermogram of [Cu(II)-L-(OAc)₂] is shown in Fig. 8. The perusal of the TG reveals that it consists of two steps. It can be seen that there is no mass loss upto 200 °C. In the first step, after 200 °C there is a rapid mass loss up to 300 °C, which may be due to elimination of CONH + CH₂ + CH₃CN + 2 acetate groups (found: 42.78, calcd.: 40.79 %). In second step, the loss of mass is very slow from 460 °C up to 520 °C, due to elimination of phenyl group + CH₂ + CH₃CN (found: 25.48, calcd.: 24.73 %). After this, there is a gradual decrease in mass loss observed up to 600 °C, the residue obtained may be of CuO (found: 15.90, calcd.: 14.20 %).

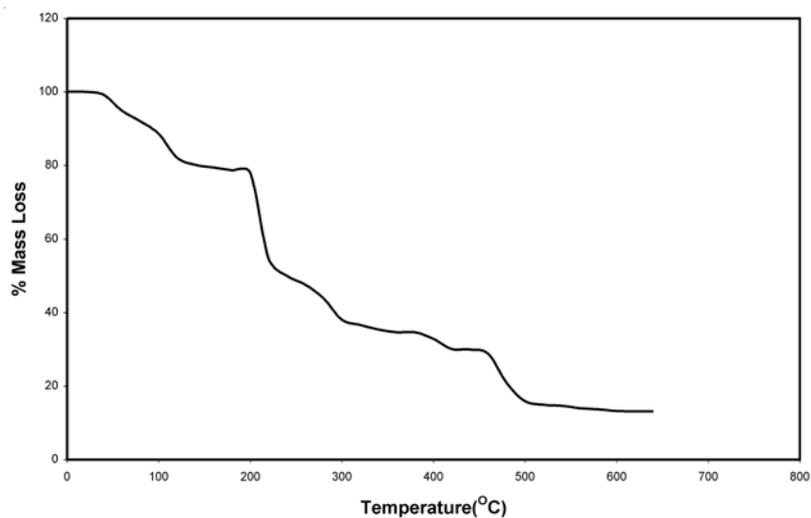


Fig. 8. Thermogram of [Cu(II)-L]

Conclusion

The present investigation deals with the synthesis and characterization of tetraaza macrocyclic ligand and its transition metal complexes. On the basis of various physicochemical studies, the nature as well as to some extent structure and stereochemistries of macrocyclic ligand and its complexes have been suggested.

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