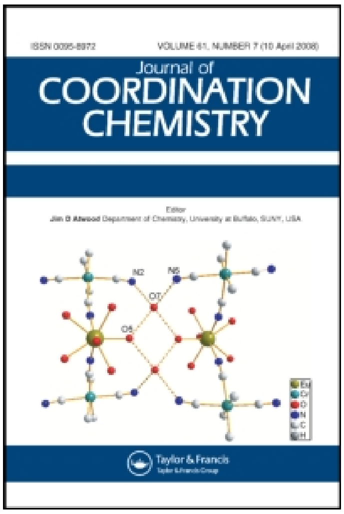

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization and antimicrobial activity of a new macrocycle and its transition metal complexes

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To cite this Article Nishat, Nahid , Rahis-Ud-Din and Dhyani, Swati(2009) 'Synthesis, characterization and antimicrobial activity of a new macrocycle and its transition metal complexes', Journal of Coordination Chemistry, 62: 6, 996 — 1004
To link to this Article: DOI: 10.1080/00958970802339651
URL: http://dx.doi.org/10.1080/00958970802339651

Journal of Coordination Chemistry
Vol. 62, No. 6, 20 March 2009, 996–1004

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Synthesis, characterization and antimicrobial activity of a new macrocycle and its transition metal complexes

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(*Received 1 March 2008; in final form 23 May 2008*)

The semicarbazone (L^1) has been prepared by reaction of semicarbazide and glutaraldehyde (2 : 1) in distilled water and methanol (1 : 1). The reaction of semicarbazide, glutaraldehyde and diethyl oxalate in distilled water and methanol gave Schiff-base L^2, 1,2,4,7,9,10-hexaazacyclo-pentadeca-10,15-dien-3,5,6,8-tetraone. Complexes of first row transition metal ions Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) have also been synthesized. The ligand and its complexes were characterized by elemental analysis, molar conductance, magnetic moment measurements, IR, ^{1}H NMR, UV–Visible spectra and thermogravimetric analysis (TGA). Molar conductance values show that the complexes of Ni(II), Cu(II), Zn(II), Mn(II) and Co(II) are 1 : 2 electrolytes. On the basis of electronic spectral studies and molar conductance measurements an octahedral structure has been proposed for Mn(II) and Co(II) complexes, tetrahedral for Zn(II) complex and square planar for Ni(II) and Cu(II). The thermal behavior of the compounds, studied by TGA in a nitrogen atmosphere up to 800°C, reveal that the complexes have higher thermal stability than the macrocycle. All the synthesized compounds and standard drugs kanamycin (antibacterial) and miconazole (antifungal) have been screened against bacterial strains *Staphylococcus areus*, *Escherichia coli* and fungal strains *Candida albicans*, *Aspergillus niger*. The metal complexes inhibit growth of bacteria to a greater extent than the ligand.

Keywords: Schiff-base macrocyclic ligand; Ni(II) and Cu(II) square planar complexes; Antibacterial and antifungal activities

1. Introduction

Macrocyclic complexes of transition metal ions are of great interest due to presence of several potential donor atoms and their ability to coordinate either in neutral and deprotonated form [1]. Curtis first reported the synthesis of some macrocycles [2], since then various macrocyclic ligands such as cyclam [3], cyclen [4], aminobenzaldehyde trimers and tetramers [5] have been reported. Macrocycles are important in understanding molecular process occurring in biochemistry [6], material science [7] and catalysis [8]. Transition metal complexes with macrocyclic ligands have received much attention as an active part of metalloenzymes [9] and as diagnostic agents in magnetic resonance imaging (MRI) [10]. Macrocyclic ligands are best for complex

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802339651

formation due to their greater kinetic and thermodynamic stability over open chain analogues. The discovery of cisplatin [(*cis*-diaminedichloridoplatinum(II)] by Rosenberg *et al.* provided an impetus to synthesize macrocyclic metal ion complexes having biological importance [11]. The industrially important phthalocyanine metal complexes [12] have a wide range of biological properties [13]. Since various Schiff bases have anticancer [14] and antimicrobial [15] properties, here we synthesize a macrocycle derived from semicarbazone, and a series of Schiff-base macrocyclic complexes with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) are presented. The antimicrobial activity of metal complexes are better than the ligand.

2. Experimental

2.1. *Materials*

Glutaraldehyde, transition metal chloride (S.D. Fine-Chem. Ltd.), semicarbazide (CDH) and diethyl oxalate (E. Merck) were used as received. Solvents were distilled before use. Microorganisms were isolated in suitable environments.

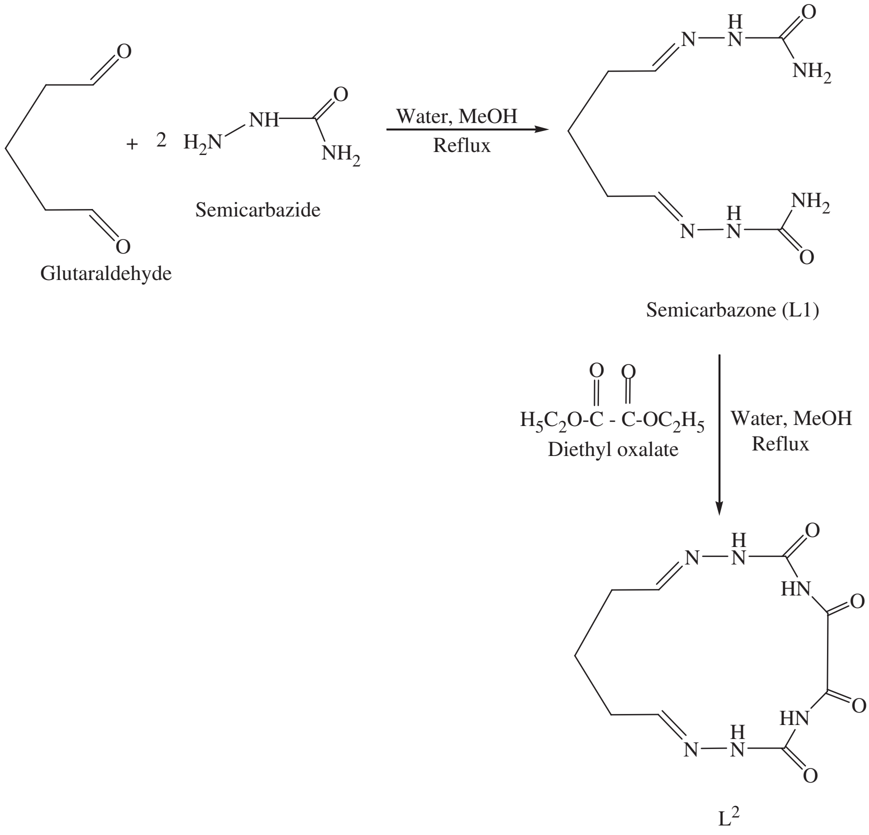
2.2. *Preparation of semicarbazone (L^1) and Schiff base macrocyclic ligand (L^2)*

2.2.1. Synthesis of the semicarbazone, (L^1). Semicarbazide (2.23 g, 40 mmol) was dissolved in distilled water and methanol (1 : 1, 100 cm^3) and added dropwise with constant stirring to a solution of glutaraldehyde (3.77 mL, 20 mmol) in methanol (50 cm^3). The resulting mixture was heated under reflux with constant stirring for 4 h. Half of the solvent was evaporated under reduced pressure. After refrigeration for 2 days, a brick red precipitate was filtered, washed with MeOH/ether and dried over fused calcium chloride (yield 60%).

2.2.2. Synthesis of the Schiff base (L^2), 1,2,4,7,9,10-hexaazacyclo-pentadeca-10,15-dien-3,5,6,8-tetraone. The semicarbazone (L^1) (2.14 g, 10 mmol) in distilled water and methanol (100 cm^3, 1 : 1) was added dropwise to the solution of diethyl oxalate (1.36 mL, 10 mmol) in methanol (25 cm^3). The reaction mixture was refluxed for 3 h and then reduced to half volume by evaporation on a rotary evaporator. After refrigeration for 2 days, an orange solid that collected was filtered, washed with MeOH/ether and dried over fused calcium chloride (yield: 58%). Scheme 1 presents the synthesis of semicarbazone (L^1) and Schiff base.

2.2.3. Synthesis of the complexes with L^2. Methanolic solution (50 mL) of copper(II) chloride (1.34 g, 10 mmol) was added to the solution of L^2 (2.68 g, 10 mmol) in 100 mL of distilled water and methanol (1 : 1) with constant stirring for 4 h. The dark brown precipitate that collected was filtered off, washed with ethanol and then dry diethyl ether, and dried over fused calcium chloride (yield 70%).

Mn(II), Co(II), Ni(II) and Zn(II) complexes of L^2 were synthesized by similar procedure. The colored precipitates were filtered, washed with ethanol and then dry diethyl ether, and dried over fused calcium chloride (yields 56–64%).



Scheme 1. Synthesis of semicarbazone (L^1) and Schiff base (L^2).

2.3. *Analytical and physical measurements*

IR spectra of the compounds were recorded on a Perkin–Elmer FTIR spectrometer, model 621, using KBr disks from 4000–400 cm^{-1}. The percentage of carbon, hydrogen and nitrogen of the ligands and the complexes were determined by Elemental Analyzer System GmBH varion, ELIII. Conductivity measurements were carried out on a CM-82T Elico conductivity bridge and magnetic measurements were done with a model 155 Allied Research vibration sample magnetometer at room temperature. UV-visible spectra of the complexes were done on a Lambda EZ201 Perkin–Elmer spectrometer in DMSO. The ^{1}H NMR spectra of the macrocyclic ligand and the complexes were run in DMSO-d_6 on a Bruker Spectrospin DPX-300 MHz spectrometer. Thermogravimetric analysis (TGA) was done on a TA Analyzer 2000 (TA Instrument). Chlorine was estimated gravimetrically [16] and metal ions were determined by EDTA complexometric titration following decomposition of their complexes with fuming nitric acid [17].

2.4. *Antimicrobial activity of microorganisms*

The antibacterial activities of the ligand and the complexes in DMSO were evaluated *in vitro* by disc diffusion technique [18]. The bacterial strains were nourished in nutrient broth at 37°C for 48 h. Whatman No. 4 filter article discs (6 mm diameter) were impregnated with stock solution of the compound (50 μg mL^{-1}) and dried under sterile conditions. The antifungal activities were evaluated by the spore germination technique [19]. The solution (0.1 mL) of the test compounds of 50 μg mL^{-1} concentrations in DMSO was placed on spores of the test fungi with the help of a sterilized inoculation needle. Finally the discs were incubated at 37°C for 48 h (for bacteria) and at 25°C for 72 h (for fungi), where inhibition zones were detected around each disc. At the end of incubation, the inhibition zones around the walls were measured in millimeters. DMSO was used as control and kanamycin and miconazole were also screened under similar conditions for comparison to a reference standard.

3. Results and discussion

Condensation of semicarbazide and glutaraldehyde (2 : 1 molar ratio) in water and methanol (1 : 1) yields brick red semicarbazone (L^1). It is soluble in water but insoluble in common organic solvents except DMSO. The semicarbazone refluxed and stirred with diethyl oxalate (1 : 1 molar ratio) gave orange Schiff base, L^2. The reaction of L^2 with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in water and methanol (1 : 1) yielded $[M'L^2(H_2O)_2]Cl_2$, where M′ = Mn(II), Co(II), $[ML^2]Cl_2$ and M = Ni(II), Cu(II), Zn(II). The analytical data, molar conductances, colors and m.p. are listed in table 1.

All are stable in air and soluble in DMSO. The molar conductivities of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of L^2 in 10^{-3} M DMSO indicated 1 : 2 electrolytic nature (118–140 Ω^{-1} cm^2 mol^{-1}) [20].

3.1. *Infrared spectra*

Relevant IR spectral bands of L^1 and L^2 and the complexes are given in table 2. The disappearance of characteristic bands of carbonyl groups (C=O) of glutaraldehyde and the appearance of bands corresponding to azomethine groups (C=N) indicate formation of semicarbazone. The strong band at 1655–1666 cm^{-1} may be assigned to ν(C=N) vibration [21]. In L^1 and L^2, bands at 2927–2935 cm^{-1} correspond to ν(C–H) stretches. The ligands (L^1 and L^2) exhibit ν(N–H) of primary amide (3426 cm^{-1}), ν(N–H) of secondary amide (3315 cm^{-1}), ν(C=O) (amide group) at 1680–1690 cm^{-1} region and ν(C=O) (oxalate group) at 1620 cm^{-1} [22]. In the complexes, ν(C=N), ν(C–H) and ν(N–H) (secondary amide) are shifted to lower frequency by 17–37 cm^{-1}, suggesting coordination of metal *via* nitrogen. The appearance of strong bands in the 415–460 cm^{-1} region in all the complexes corresponds to ν(M–N) [23]. Bands at 515–518 cm^{-1} are strong evidence for the participation of water molecule [24] in coordination.

3.2. *Electronic spectra and magnetic moment*

The observed electronic spectral bands of the macrocyclic complexes 10^{-3} M in DMSO, magnetic moment values, nephelauxetic parameter (β), Racha parameter (B) and 10 Dq are given in table 3. The UV–Visible spectra of Mn(II) complex of L^2 exhibit three

Table 1. Analytical data, color, m.p., percentage yield and molar conductance of L^1, L^2 and the complexes.

Compounds (Formula weight)	Color	M.p. (°C)	Yield (%)	Molar conductance (Ω^{-1} cm^2 mole^{-1})	Analysis% found (Calcd)				
					C	H	N	Cl	M
$C_7H_{14}N_6O_2$, (L^1) (214.22)	Brick red	170	60	–	39.17 (39.24)	6.55 (6.58)	39.25 (39.23)	–	–
$C_9H_{12}N_6O_4$, (L^2) (268.22)	Orange	220	58	–	39.98 (39.93)	4.50 (4.45)	31.33 (31.34)	–	–
$[MnL^2(H_2O)_2]Cl_2$ (430.97)	Deep yellow	260	64	138	25.23 (25.30)	2.80 (2.77)	19.46 (19.50)	16.41 (16.45)	12.67 (12.70)
$[CoL^2(H_2O)_2]Cl_2$ (434.96)	Light pink	270	62	128	25.00 (25.06)	2.73 (2.78)	19.25 (19.32)	16.26 (16.30)	13.44 (13.50)
$[NiL^2]Cl_2$ (397.81)	Light red	245	56	118	27.10 (27.15)	3.00 (3.04)	21.08 (21.11)	17.78 (17.82)	14.70 (14.75)
$[CuL^2]Cl_2$ (402.67)	Dark brown	268	70	132	26.85 (26.82)	2.96 (3.00)	20.81 (20.86)	17.56 (17.60)	15.72 (15.78)
$[ZnL^2]Cl_2$ (404.51)	White	250	64	140	26.66 (26.70)	3.02 (3.00)	20.70 (20.76)	17.55 (17.52)	16.18 (16.16)

Table 2. Characteristic IR bands (cm^{-1}) of the ligands and complexes.

Compounds	ν(N–H)	ν(C=O)	ν(C=O) (oxalate group)	ν(C–H)	ν(C=N)	ν(M–N)	ν(M–H$_2$O)
Ligand (L^1)	3426	1690 m	–	2927	1655 s	–	–
Ligand (L^2)	3315	1680 m	1620 m	2935	1660 s	–	–
[MnL^2(H$_2$O)$_2$]Cl$_2$	3290	1672 m	1616 m	2910	1642 s	415 s	515 s
[CoL^2(H$_2$O)$_2$]Cl$_2$	3292	1682 m	1618 m	2908	1640 s	425 s	518 s
[NiL^2]Cl$_2$	3278	1678 m	1624 m	2912	1625 s	420 s	–
[CuL^2]Cl$_2$	3285	1675 m	1620 m	2915	1638 s	460 s	–
[ZnL^2]Cl$_2$	3280	1670 m	1618 m	2918	1626 s	440 s	–

Table 3. Magnetic moments and electronic spectral bands of the complexes.

Compound	Magnetic moment (B.M.)	Electronic bands (cm^{-1})	Possible assignment	ε^a	10 Dq (cm^{-1})	(B) (cm^{-1})	β
[MnL^2(H$_2$O)$_2$]Cl$_2$	5.90	25095	$^4E_g(G) \leftarrow {}^6A_{1g}$	12	9315	7110	0.78
		20800	$^4T_{2g}(G) \leftarrow {}^6A_{1g}$	15			
		16805	$^4T_{1g}(G) \leftarrow {}^6A_{1g}$	10			
[CoL^2(H$_2$O)$_2$]Cl$_2$	4.38	19800	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	15	8236	6755	0.66
		14320	$^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$	11			
		11765	$^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$	13			
[NiL^2]Cl$_2$	Diamagnetic	24690	Charge Transfer	18	–	–	–
		21505	$^1B_{1g} \leftarrow {}^1A_{1g}$	14			
		19050	$^1A_{2g} \leftarrow {}^1A_{1g}$	15			
[CuL^2]Cl$_2$	1.70	25120	Charge Transfer	14	–	–	–
		15267	$^2A_{1g} \leftarrow {}^2B_{1g}$	12			
		12250	$^2E_g \leftarrow {}^2B_{1g}$	10			
[ZnL^2]Cl$_2$	Diamagnetic	–	–	–	–	–	–

$\varepsilon^a = \mathrm{dm^3\,mol^{-1}\,cm^{-1}}$.

bands at 25,095, 20,800 and 16,805 cm^{-1}, which correspond to $^4E_g(G) \leftarrow {}^6A_{1g}$, $^4T_{2g}(G) \leftarrow {}^6A_{1g}$ and $^4T_{1g}(G) \leftarrow {}^6A_{1g}$ transitions, respectively. On the basis of electronic spectral bands and observed magnetic moment value for five unpaired electrons (5.90 B.M. very close to the calculated value) suggest octahedral geometry for Mn(II).

The observed magnetic moment value (4.83 B.M.) of the cobalt(II) complex of L^2 is in the range expected for three unpaired electrons. The electronic spectra showed three bands appearing at 19,800, 14,320 and 11,765 cm^{-1}, which correspond to $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$, $^4A_{2g}(G) \leftarrow {}^4T_{1g}(F)$ and $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ transitions, respectively. The magnetic moment value and electronic spectra are consistent with octahedral geometry around cobalt(II) [25].

Three spectral bands for [NiL^2]Cl$_2$ at 24,690, 21,505 and 19,050 cm^{-1} may be assigned as the charge transfer (24,696 cm^{-1}), while the last two bands can be assigned to $^1B_{1g} \leftarrow {}^1A_{1g}$ and $^1A_{2g} \leftarrow {}^1A_{1g}$ transitions, respectively, for a square planar geometry around nickel(II). The diamagnetism of the complex further confirms square planar geometry [26].

The electronic absorption spectra of the Cu(II) complex exhibit a charge transfer band at 25,120 cm^{-1} and other bands at 15,267 cm^{-1} and 12,250 cm^{-1}, assigned as given in table 3. The magnetic moment value of the copper(II) complex is 1.70 B.M. suggesting square planar [27, 28] geometry around Cu(II). No transitions were observed in the visible region for zinc(II) complex of L^2 consistent with the d^{10} configuration of the Zn(II) ion.

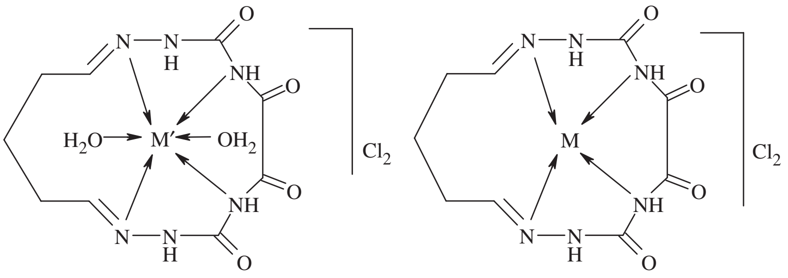
Suggested structures are shown in figure 1.

3.3. *^{1}H NMR spectra*

The ^{1}H NMR data (table 4, spectra in Supplemental Material) for L^1 and L^2 in DMSO-d_6 show triplets in the region 2.54–2.72 ppm, assigned to $–CH_2–$ protons [29], while multiplets in the region 3.22–3.45 ppm may be attributed to the middle methylene protons ($–CH_2–$, 2H). A doublet observed at 7.80–8.01 ppm was assigned to N=C–H (2H protons), and a singlet at 9.89–9.91 ppm corresponds to N–N–H (2H protons) [30]. The peak for L^1 for $–CONH_2$ appears at 6.30 ppm as a singlet, however, in the macrocyclic ligand (L^2) the peak for –CONH– was shifted to downfield at 8.52 ppm for secondary amide [31]. The Ni(II) and Zn(II) complexes of L^2 exhibit high δ values of N=C–H and –CONH– due to the low electron density upon complex formation.

3.4. *Antimicrobial activity*

The free ligand L^2 and metal complexes were tested against the bacterial species *Staphylococcus areus*, *Escherichia coli* and fungal species *Candida albicans*, *Aspergillus niger*. Some antibiotics were evaluated for their antimicrobial activities and the results compared with the free ligand and its transition metal complexes.



$[M'L^2(H_2O)_2]Cl_2$ $[ML^2]Cl_2$

Figure 1. Suggested structures of the metal complexes with ligand (L^2), M′ = Mn(II), Co(II), M = Ni(II), Cu(II), Zn(II).

Table 4. ^{1}H NMR spectra of the ligands (L^1 and L^2) and the Ni^{2+} and Zn^{2+} complexes δ (ppm).

Compound	$–(CH_2)_2–$(4 H)	$–(CH_2)–$(2 H)	$–CONH_2$(4 H)	–CONH– (sec amide)	N–NH(2H)	–N=CH–(2 H)
L^1	(2.15–2.70) t	(3.22–3.68) m	6.30 s	–	9.91 s	(8.06–8.16) d
L^2	(2.20–2.72) t	(3.22–3.68) m	–	8.52 b	9.89 s	(7.98–8.20) d
$[NiL^2]Cl_2$	(2.18–2.32) t	(3.32–3.60) m	–	8.85 b	10.01 b	(8.32–8.56) d
$[ZnL^2]Cl_2$	(2.20–2.46) t	(3.36–3.50) m	–	8.98 b	10.00 b	(8.46–8.70) d

Table 5. Antibacterial and antifungal activity of ligand and complexes (zone formation in mm). Zone of inhibition[a] (in mm) at 50 μg mL^{-1} concentration.

Compounds	*S. aureus*	*E. coli*	*C. albicans*	*A. niger*
Kanamycin (antibacterial)	27	29	–	–
*Miconazole (antifungal)	–	–	22	25
Ligand (L1)	6	7	6	8
Ligand (L^2)	7	8	6	9
$[MnL^2(H_2O)_2]Cl_2$	12	11	10	11
$[CoL^2(H_2O)_2]Cl_2$	15	17	13	18
$[NiL^2]Cl_2$	16	13	15	11
$[CuL^2]Cl_2$	15	13	17	13
$[ZnL^2]Cl_2$	20	19	12	15

*Antibiotics
[a]Including disc diameter.

The investigated ligand and the metal complexes as antimicrobial agents were screened in addition to known antibiotics using kanamycin as a standard antibacterial agent and miconazole as antifungal agent. The results are tabulated in table 5. A comparative study of the ligand and its complexes indicates the highest inhibition zone of all the metal complexes was found against *S. aureus* and *E. coli*.

The antifungal activities (table 5) indicate that $[CoL^2(H_2O)_2]Cl_2$ and $[NiL^2]Cl_2$ show moderate activity against *C. albicans* and $[CuL^2]Cl_2$ and $[ZnL^2]Cl_2$ complexes against *A. niger*. $[CuL^2]Cl_2$ shows good antifungal activity against *C. albicans*, while $[MnL^2(H_2O)_2]Cl_2$ and $[ZnL^2]Cl_2$ complexes show poor activity against *C. albicans* and $[MnL^2(H_2O)_2]Cl_2$ and $[NiL^2C]Cl_2$ complexes against *A. niger*. $[CoL^2(H_2O)_2]Cl_2$ exhibits excellent antifungal activity against *A. niger*.

3.5. *Thermogravimetric analysis (TGA)*

The thermograms in TGA of metal complexes can be subdivided into four regions. The first region extends to 180°C showing elimination of coordinated water with approximately 7% weight loss except for nickel(II) and copper(II) complexes showing only 1.5% weight loss, indicating absence of coordinated water in Ni(II) and Cu(II) complexes. The non–coordinated chlorides in all metal complexes were eliminated at 200–300°C with 16–17% weight loss; in the macrocycle there is 21% weight loss in this region. The third region started from 330°C while for L^2 it started from 300°C. The complexes are thus more thermally stable than the macrocycle. All the metal complexes decompose to metal oxide at 745°C while the macrocycle changes to residue at 700°C. The metal content as residue was calculated and found to be consistent with the elemental analysis of the complexes.

Acknowledgements

Financial support by Third World Academy of Sciences, Italy, through research grant No. 00-047 RG/CHE/AS is greatly acknowledged, and we also wish to thank Prof. Kishwar Saleem, Head, Department of Chemistry, Jamia Millia Islamia, New Delhi, for recording IR spectra.

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