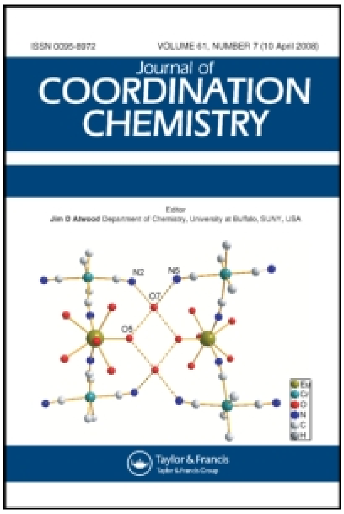

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# Synthesis, spectral and antimicrobial studies of transition metal complexes with novel macrocyclic ligand containing C=N and CO-NH group

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# Synthesis, spectral and antimicrobial studies of transition metal complexes with novel macrocyclic ligand containing C=N and CO–NH group

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This article reports synthesis of Co(II), Ni(II), Mn(II), Cu(II), and Zn(II) complexes with a new macrocyclic ligand 1,4,11,14-tetraazacyclonanodeca-5,10-dioxo-1,14-diene ($H_2L$). The ligand ($L_1$) was prepared by reaction of adipic acid and ethylenediamine in 1 : 2 ratio while the macrocycle was derived from 1,4-bis-(2′-amino-ethanamide)butane and glutaraldehyde. The synthesized complexes were characterized by elemental analysis, molar conductance, spectral analyses ($^1$H NMR spectra, FT-IR spectra, electronic spectra, and mass spectra), magnetic susceptibility measurements, and thermogravimetric studies. On the basis of electronic spectral studies and molar conductance measurements, octahedral geometry was confirmed for Ni(II), Mn(II), and Co(II) while tetrahedral for Zn(II) and square planar for Cu(II) complexes. The TGA results revealed that the complexes exhibited higher thermal stability than the macrocycle. All the complexes were screened against bacterial and fungal strains and preliminary antimicrobial results showed that these complexes inhibited bacterial/fungal growth to a greater extent than the ligand.

*Keywords*: Adipic acid; Macrocyclic ligand; Antibacterial and antifungal activity

## 1. Introduction

The chemistry of macrocyclic ligands is of immense scientific and technological significance [1, 2]. Macrocyclic complexes are more thermodynamically stable and selective metal ion binders than their open chain analogs. Tetraazamacrocyclic ligands and their metal complexes have attracted much interest for metal controlled template as well as metal free non-template synthesis of macrocyclic ligands [3]. Macrocycles having –CH=N, –CONH, and –NH groups impact enzyme mimicking studies, catalysis, radio pharmaceuticals, magnetic resonance imaging reagents, and antimicrobials [4–7]. Activity depends on the nature of the substituent, the number of heteroatoms, and the ring size of the macrocycle [8]. Amides are important as pharmaceutics [9], antimicrobials [10], and agrochemicals [11].

In the present study we have synthesized a macrocycle containing both –C=N (azomethine) and –CONH (amide) groups. A series of transition metal complexes containing macrocyclic ligand with both azomethine and amide was developed.

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## 2. Experimental

### 2.1. *Materials*

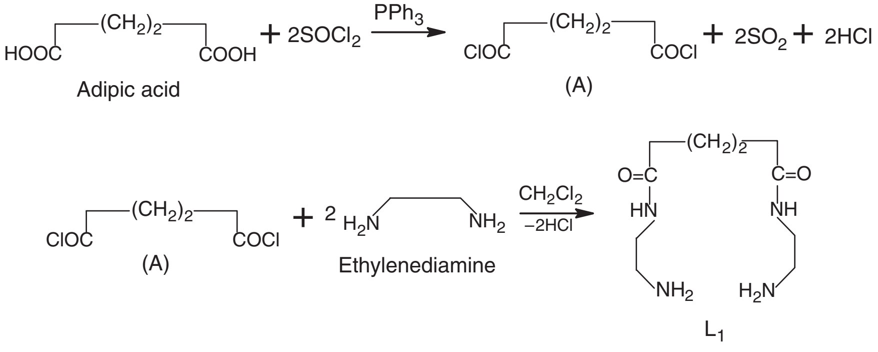
Glutaraldehyde, transition metal chloride (S.D. Fine-Chemicals, India), ethylenediamine (BDH) and adipic acid (Merck) were used as received. Solvents were distilled before use. Microorganisms were isolated in a suitable environment.

### 2.2. *Preparation of amide derivative ($L_1$) and macrocyclic ligand ($H_2L$)*

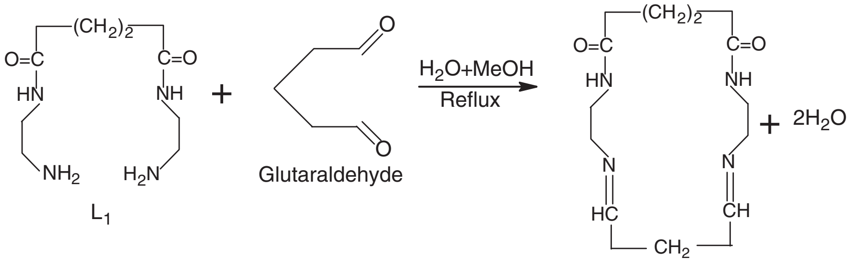
**2.2.1. Synthesis of $L_1$.** Adipic (1.46 g) acid and thionyl chloride (2 mL) were placed in a three-necked round bottom flask containing a catalytic amount of triphenylphosphine [12]. The mixture was refluxed until a clear yellow solution was obtained. An air condenser was then used to heat the reaction mixture for half an hour at 70–80°C for complete evolution of HCl gas. The yellow residue obtained was dissolved in $CH_2Cl_2$. A solution of ethylenediamine (1.32 mL) in $CH_2Cl_2$ (25 mL) was added to the above solution and the mixture was again refluxed for 7 h, which resulted in the formation of a white precipitate. The white precipitate obtained was washed several times with methanol, followed by diethyl ether and then dried over fused $CaCl_2$ (scheme 1).

**2.2.2. Synthesis of $H_2L$.** $L_1$ (2.31 g) in distilled water and methanol (50 mL) in 1 : 1 ratio were added dropwise to a solution of glutaraldehyde (3.77 mL) in methanol (25 mL). The reaction mixture was refluxed for 10 h at 40°C and then reduced to half its volume by evaporation on a rotatory evaporator. Upon cooling the reaction mixture at 4°C for 48 h, brown crystals were obtained. The crystals were purified with acetone, followed by diethyl ether and dried over $CaCl_2$ (scheme 2).

**2.2.3. Synthesis of metal complexes of type [M′(L)•2H₂O] and [M″L)].** An ethanolic solution of $H_2L$ (10 mmol, 2.95 g) was added to the ethanolic solution of Ni(II) chloride (10 mmol, 2.37 g) in 1 : 1 ratio with constant stirring at 50°C. The green precipitate of nickel complex obtained was washed by using acetone and diethyl ether and dried in a vacuum over $CaCl_2$. The complexes of Mn(II), Co(II), Cu(II), and Zn(II) were



Scheme 1. Synthesis of $L_1$.



Scheme 2. Synthesis of $H_2L$.

prepared by a similar procedure. The colors of the different metal complexes are given in table 1.

### 2.3. *Physical measurements*

The percentage of carbon, hydrogen, and nitrogen of the ligands and the complexes were determined by Elemental Analyzer System GmBH varion, ELIII (Roorkee IIT). The FTIR spectra were recorded on Perkin-Elmer FTIR spectrometer, model 621, using KBr discs from 400–4000 $cm^{-1}$. The conductivity measurements were carried out in DMSO on a CM-82T Elico conductivity bridge and magnetic measurements were done with a Model 155 Allied Research vibration sample magnetometer at room temperature. The $^1H$ NMR spectra of $L_1$, macrocyclic ligand, and the complexes were run in deuterated DMSO on a Bruker Spectrospin DPX-300 MHz spectrometer. UV-Visible spectra of the complexes were performed on a Lambda EZ201 Perkin-Elmer spectrometer in DMSO. Mass spectra of the complexes were carried out by FAB on a Jeol JMS DX-300. The X-ray diffraction was carried out on X-ray Powder diffractometer Model No. 1830. The thermogravimetric analysis (TGA) of the compounds was done using a Perkin-Elmer (IIT Roorkee) at 200 mL $min^{-1}$ flowing nitrogen. Chlorine was estimated gravimetrically and metals were determined by EDTA complexometric titration following decomposition of their complexes with fuming nitric acid. The antibacterial and antifungal activities were performed by the agar disk diffusion method [13]. The bacterial strains were nourished in nutrient broth at 37°C for 48 h. Whatman No. 4 filter paper discs (6 mm diameter) were impregnated with stock solution of the compound (50 g $mL^{-1}$) and dried under sterile conditions. The antifungal activities of the ligand and soluble complexes were evaluated by the spore germination technique [14]. The solution (0.1 mL) of the test compounds of 50 µg $mL^{-1}$ in DMSO was placed on spores of the test fungi with 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 observed.

## 3. Results and discussion

The reaction of dichloride derivative of adipic acid and ethylenediamine (1 : 2 molar ratio) in $CH_2Cl_2$ yielded white diamide ($L_1$). The diamide was refluxed and stirred

Table 1. Analytical data, color, melting point, percentage yield, and molar conductance of ligands and metal complexes.

| Compounds (formula weight) | Color | m.p. (°C) | Yield (%) | Molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$) | Analysis % found (Calcd) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | M | C | H | N |
| $C_{10}H_{22}N_4O_2$, ($L_1$) (231.302) | White | 190 | 68 | – | – | 52.34 (52.35) | 9.57 (9.58) | 24.23 (24.22) |
| $C_{15}H_{26}N_4O_2$, ($H_2L$) (295.884) | Dark brown | 250 | 55 | – | – | 61.40 (61.39) | 8.83 (8.85) | 18.93 (18.93) |
| $[Mn(L)\cdot 2H_2O]$ (384.806) | Yellow | 318 | 70 | 12 | 14.25 (14.27) | 47.20 (47.20) | 7.30 (7.33) | 14.57 (14.56) |
| $[Co(L)\cdot 2H_2O]$ (388.80) | Pink | 313 | 68 | 10 | 15.15 (15.16) | 46.70 (46.72) | 7.21 (7.25) | 14.40 (14.41) |
| $[Ni(L)\cdot 2H_2O]$ (388.561) | Light green | 328 | 72 | 25 | 15.11 (15.10) | 46.76 (46.75) | 7.23 (7.26) | 14.42 (14.41) |
| $[Cu(L)]$ (357.414) | Brown | 305 | 67 | 15 | 17.76 (17.78) | 50.83 (50.82) | 6.75 (6.77) | 15.67 (15.67) |
| $[Zn(L)]$ (359.258) | White | 308 | 64 | 28 | 18.21 (18.20) | 50.54 (50.56) | 6.70 (6.73) | 15.57 (15.59) |

with glutaraldehyde (1 : 1 molar ratio) forming a brown macrocyclic ligand ($H_2L$). The reaction of $H_2L$ with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) in ethanol yielded $[M'(L) \cdot 2H_2O]$, where $M' =$ Mn(II), Co(II), Ni(II), and $[M''(L)]$, where $M'' =$ Cu(II), Zn(II). The analytical data of the complexes are summarized in table 1. $L_1$ was soluble in distilled water while $H_2L$ was soluble in ethanol and DMSO. The molar conductance of Mn(II), Co(II), and Cu(II) complexes were lower than Zn(II) and Ni(II) complexes (table 1). All the synthesized metal complexes were insoluble in common organic solvents and stable in air. The complexes were characterized by spectral studies.

### 3.1. *Infrared spectra*

The characteristic FTIR bands of the ligands and mononuclear metal complexes are listed in table 2. $L_1$ showed a broad medium intensity band in the region 3235–3430 $cm^{-1}$ due to $\nu_{(N-H)}$ of amine and amide [15]. This band was absent in $H_2L$ while two new sharp bands were observed at 3229 and 1629 $cm^{-1}$ due to $\nu_{(N-H)}$ of amide and C=N, respectively [16], confirming condensation of $-NH_2$ in $L_1$. In the FT-IR spectra of metal complexes, the C=O band of amide group and the C=N band shift to lower wave numbers by 10–20 $cm^{-1}$ revealing participation of amide and azomethine nitrogens in coordination to metal. The spectra of $L_1$ and $H_2L$ have a strong band at 1675 and 1668 $cm^{-1}$, respectively, which can be correlated to the C=O stretch [17]. This band occurs in all the metal complexes at lower frequency (1650–1655 $cm^{-1}$) compared to the pristine ligand. A strong band at 2920–2930 $cm^{-1}$ was assigned to C–H stretching of $-CH_2$ in all the compounds. Bands in the regions 1538–1600 $cm^{-1}$ and 662–675 $cm^{-1}$ were attributed to the $\delta_{HOH}$ deformation and rocking modes of coordinated water, respectively, confirming the presence of coordinated water in Mn(II), Co(II) and Ni(II) complexes [18]. Participation of nitrogen in the coordination was confirmed by the band in the region 410–425 $cm^{-1}$ in all the metal complexes [19].

### 3.2. *$^1$H NMR spectra*

The $^1$H NMR spectra of $L_1$ and $H_2L$ showed a peak at 7.23 and 7.26 ppm, respectively, due to –NH protons of amide [20]. The spectrum of $L_1$ displayed a broad peak at 3.11 ppm attributed to $-NH_2$ protons [16], absent in $H_2L$ and Zn complex. The signal observed at 8.16 and 8.29 ppm in $H_2L$ and Zn complex, respectively, was assigned to –CH=N– protons [21]. The absence of $NH_2$ protons and the presence of

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

| Compounds | $\nu(NH_2/NH)$ | $\nu$(C–H) | $\nu$(C=O) (amide group) | $\nu$(C–N) | $\nu$(C=N) | $\nu$(M–N) |
|---|---|---|---|---|---|---|
| Ligand ($L_1$) | 3430–3235 | 2930 s | 1675 | 1390 s | – | – |
| Macrocycle ($H_2L$) | 3229 m | 2928 s | 1668 | 1385 s | 1629 s | – |
| $[Mn(L) \cdot 2H_2O]$ | – | 2925 s | 1652 | 1370 s | 1612 s | 415 s |
| $[Co(L) \cdot 2H_2O]$ | – | 2925 s | 1650 | 1365 s | 1615 s | 410 s |
| $[Ni(L) \cdot 2H_2O]$ | – | 2920 s | 1650 | 1370 s | 1610 s | 425 s |
| [Cu(L)] | – | 2922 s | 1655 | 1367 s | 1611 s | 419 s |
| [Zn(L)] | – | 2924 s | 1653 | 1366 s | 1613 s | 418 s |

–CH=N– protons confirmed formation of macrocycle from $L_1$ and glutaraldehyde. In spectra of $L_1$, $H_2L$ and Zn complex, peaks at 2.54–2.56 ppm –$(CH_2)_n$– and 3.32–3.37 ppm ($CH_2$–CO) were correlated to methylene protons [22]. For $L_1$, methylene protons of ethylenediamine were at 3.60 ppm (–$CH_2$–$NH_2$) and 2.97 ppm (–$CH_2$–NH) while in $H_2L$ and Zn complex, the former peak was absent. A triplet at 3.54–3.56 ppm due to the presence of ($CH_2$–N) confirmed the disappearance of the –$NH_2$ group [21, 23]. In the Zn complex, the peak at 3.55 ppm ($CH_2$–N) attributed to methylene protons of ethylenediamine shows the same environment due to deprotonation of the amide group.

### 3.3. *UV-spectra*

The magnetic moments and electronic absorption bands with various ligand field parameters for Co, Ni, Mn, Zn, and Cu complexes are given in table 3. The magnetic moment value for the Co(II) complex (4.56 B.M.) is within the range of octahedral complexes. The cobalt complex displayed three bands at 7270, 13,971, and 19,600 $cm^{-1}$, assigned to $^4T_{1g}$ $(\nu_1) \rightarrow {}^4T_{2g}$ (F), $^4T_{1g} \rightarrow {}^4A_{2g}$ $(\nu_2)$, and $^4T_{1g}$ $(\nu_3) \rightarrow {}^4T_{1g}$ (P), corresponding to octahedral geometry [24]. Electronic spectra of Ni complex have bands at 10,026 and 18,740 $cm^{-1}$ and a charge transfer band at 24,500 $cm^{-1}$, indicating octahedral geometry [25]. The magnetic moment of nickel complex was 2.95 B.M., showing two unpaired electrons. The copper (II) complex exhibited bands at 11,130, 17,555, and 23,958 $cm^{-1}$ corresponding to square planar geometry [26]. The first two bands were assigned to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions, but the third band was probably enveloped into a strong charge transfer band. The band at 22,220–26,040 $cm^{-1}$ in the spectra of complexes was observed due to ligand metal charge transfer (LMCT) [27].

The Mn(II) complex revealed a magnetic moment corresponding to five unpaired electrons (5.86 B.M.). The electronic spectral bands of complexes possessed weak absorption bands at 16,582, 20,448, and 25,400 $cm^{-1}$. These bands were assigned to $^6A_{1g} \rightarrow {}^4T_{1g}$ (4G), $^6A_{1g} \rightarrow {}^4T_{2g}$ (4G), and $^6A_{1g} \rightarrow {}^4A_{1g}$ (4D), respectively [28], for

Table 3. Electronic spectral bands of the macrocyclic complexes.

| Compound | Magnetic moment (B.M.) | Electronic bands ($cm^{-1}$) | Possible assignment | $\varepsilon^a$ | 10 $D_q$ ($cm^{-1}$) | ($B$) ($cm^{-1}$) | $\beta$ |
|---|---|---|---|---|---|---|---|
| [Mn(L) · $2H_2O$] | 5.86 | 25,400 | $^6A_{1g} \rightarrow {}^4A_{1g}$ (4D) | 12 | 5198 | 866 | 0.90 |
| | | 20,448 | $^6A_{1g} \rightarrow {}^4T_{2g}$ (4G) | 15 | | | |
| | | 16,582 | $^6A_{1g} \rightarrow {}^4T_{1g}$ (4G) | 10 | | | |
| [Co(L) · $2H_2O$] | 4.56 | 19,600 | $^4T_{1g}$ (F) $\rightarrow {}^4T_{1g}$ (P) | 15 | 8515 | 886 | 0.91 |
| | | 13,971 | $^4T_{1g}$ (F) $\rightarrow {}^4A_{2g}$ (F) | 11 | | | |
| | | 7,270 | $^4T_{1g}$ (F) $\rightarrow {}^4T_{2g}$ (F) | 13 | | | |
| [Ni(L) · $2H_2O$] | 2.95 | 24,500 | $^3A_{2g}$ (F) $\rightarrow {}^3T_{1g}$ (P) | 18 | 10,026 | 877 | 0.81 |
| | | 18,740 | $^3A_{2g}$ (F) $\rightarrow {}^3T_{1g}$ (F) | 14 | | | |
| | | 10,026 | $^3A_{2g}$ (F) $\rightarrow {}^3T_{2g}$ (F) | 15 | | | |
| [Cu(L)] | 1.70 | 23,958 | Charge transfer | 14 | – | – | – |
| | | 17,555 | $^2B_{1g} \rightarrow {}^2A_{1g}$ | 12 | | | |
| | | 11,130 | $^2B_{1g} \rightarrow {}^2E_g$ | 10 | | | |
| [Zn(L)] | Diamagnetic | – | – | – | – | – | – |

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

octahedral Mn(II). The diamagnetic Zn(II) complex was assigned tetrahedral geometry by elemental analysis and spectral data.

### 3.4. *Mass-spectra*

As Co, Ni, and Mn complexes have almost similar weights, the mass spectrum of Ni complex only is reported (Supplementary material). A peak at 389.8 amu corresponds to the molecular ion ($M^+ + 1$) and a peak at 293.1 amu corresponds to $H_2L$. Both the tetrahedral and square planar geometries of Zn and Cu complexes, respectively, exhibited no bonding with water. The mass spectrum of the Cu complex serves as a sample for the Zn complex with a peak at 358.4 amu, confirming the molecular ion ($M^+ + 1$). The peak at 293.8 amu can be correlated to $H_2L$.

### 3.5. *X-ray diffraction*

The X-ray diffraction profile of Cu (Supplementary material) shows Cu (111) and Cu (200) peaks at $2\theta = 43^\circ$ and $50^\circ$, respectively [29]. The peaks at $2\theta = 15^\circ$ and $20^\circ$ in the plane (100) were attributed to the ligand.

### 3.6. *TGA analysis*

The TGA thermograms of $L_1$, $H_2L$, nickel complex, and copper complex (Supplementary material) show 2–3% loss in weight in the temperature range 100–175°C for the metal complexes, correlated to removal of lattice water. The coordinated water molecules in Co, Mn, and Ni complexes were eliminated between 175 and 235°C with 10–12% weight loss while the Zn and Cu complexes did not show weight loss in this temperature range. The onset of decomposition of all the metal complexes occurs in the temperature range 350–355°C. Above 650°C, the thermal decomposition releases metal oxides. The metal content in the residue was consistent with elemental analysis. The onset of decompositions of $L_1$ and $H_2L$ were observed from 280°C to 300°C. Hence, the metal complexes were more thermally stable than $L_1$ and $H_2L$.

### 3.7. *Antimicrobial activity*

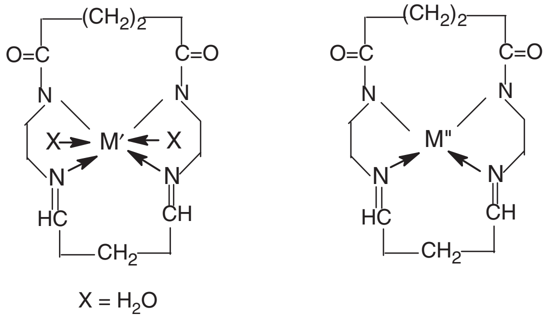
The macrocyclic ligand and its transition metal complexes were screened against four bacteria and two fungi with respect to *kanamycin* (antibacterial) and *miconazole* (antifungal) as standard drugs. The results shown in table 4 reveal that the metal complexes have higher activity compared to the macrocyclic ligand. Chelation, stability constant, molar conductivity, solubility, and magnetic moment are responsible for increasing the antimicrobial activity of metal complexes [30–32]. The maximum bacterial growth inhibition was shown by Zn(II) and Cu(II) complexes while in the case of fungi the maximum growth inhibition was shown by Ni(II) complex.

## 4. Conclusion

Transition metal complexes of Co(II), Ni(II), Mn(II), Cu(II), and Zn(II) were synthesized with a macrocyclic ligand and geometries established by elemental and

Table 4. Antibacterial and antifungal activity of ligand and complexes as zone of inhibitions (in mm) at 50 μg mL$^{-1}$ concentration.

| Compounds | *Staphylococcus aureus* | *Escherichia coli* | *Bacillus subtillis* | *Solmonella typhimurium* | *Fusarium oryzae* | *Candida albicans* |
|---|---|---|---|---|---|---|
| Ligand ($H_2L$) | 9 ± 2 | – | 9 ± 3 | 11 ± 2 | – | 10 ± 3 |
| $[Mn(L) \cdot 2H_2O]$ | 12 ± 2 | 15 ± 2 | 19 ± 2 | 14 ± 2 | 16 ± 2 | 19 ± 2 |
| $[Co(L) \cdot 2H_2O]$ | 18 ± 2 | 20 ± 3 | 16 ± 2 | 16 ± 3 | 12 ± 3 | 13 ± 2 |
| $[Ni(L) \cdot 2H_2O]$ | 16 ± 2 | 19 ± 2 | 20 ± 3 | 17 ± 2 | 25 ± 2 | 14 ± 2 |
| [Cu(L)] | 19 ± 2 | 15 ± 2 | 24 ± 1 | 20 ± 2 | 15 ± 2 | 19 ± 2 |
| [Zn(L)] | 10 ± 2 | 14 ± 2 | 24 ± 2 | 13 ± 2 | 20 ± 2 | 15 ± 3 |
| Kanamycin | 29 | 32 | 31 | 31 | – | – |
| Miconazole | – | – | – | – | 31 | 28 |



M′ = Co(II), Ni(II), Mn(II) M″ = Cu(II), Zn(II)

Figure 1. Suggested structures of metal complexes with ligand $H_2L$.

spectral analyses (figure 1). The metal complexes were thermally more stable than $L_1$ and $H_2L$. Some metal complexes showed good antimicrobial activity against bacteria and fungi, indicating possible pharmaceutical applications. Further testing of the antimicrobial activity of the complexes is being undertaken in our laboratory.

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