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# Synthesis of New Macrocyclic Complexes of Transition Metals: Structural Characterization and Biological Activity[1]

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**Abstract**—Condensation reaction between benzildihydrazone and pyridine 2,3-dicarboxylic acid, pyridine 3,4-dicarboxylic acid or pyridine 2,4-dicarboxylic acid in methanol led to novel Schiff base macrocyclic ligands $L_1$, $L_2$, and $L_3$ respectively. Metal complexes of the type $[MLCl_2]$, [M = Co(II), Ni(II)], were synthesized by the reaction of a free macrocyclic ligand (L) with the corresponding metal salts in a 1 : 1 molar ratio. The complexes were characterized on the basis of analytical data, molar conductivity and magnetic susceptibility measurements, IR, $^1H$, and $^{13}C$ NMR, and electronic spectral data. Those demonstrated that all the complexes had octahedral arrangement around the metal ions. The ligand and its complexes were screened for their antibacterial, antifungal and DNA cleavage activities. The studies demonstrate that the complexes possessed antimicrobial and DNA cleavage activities.

**Keywords:** Ni(II) and Co(II), macrocyclic complexes, spectral analysis, antibacterial activity, antifungal activity, DNA cleavage activity

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## INTRODUCTION

Importance of macrocyclic complexes in biological processes [1, 2], catalysis [3], radio therapeutic and medical imaging [4] has been demonstrated. Macrocyclic ligands can be used in systematic alteration of kinetic and thermodynamic factors that indicate the patterns of transition metals reactivity [5–7].

Aza-macrocyclic ligands were tested in recognition of DNA, RNA and related biomolecules [8–10]. Macrocyclic Schiff base ligands are characterized by their mixed hard-soft donor character and versatile coordination behavior [11, 12], enantioselective catalytic reactions [13] and various biological activities [14]. Polyamide macrocycles have been used in construction of the corresponding polyazamacrocyclic complexes [15, 16].

Herein, we report a new series of three novel Schiff base macrocyclic ligands and their transition metal complexes of the type, $[MLCl_2]$ (M = Co(II), Ni(II)) and their biological properties.

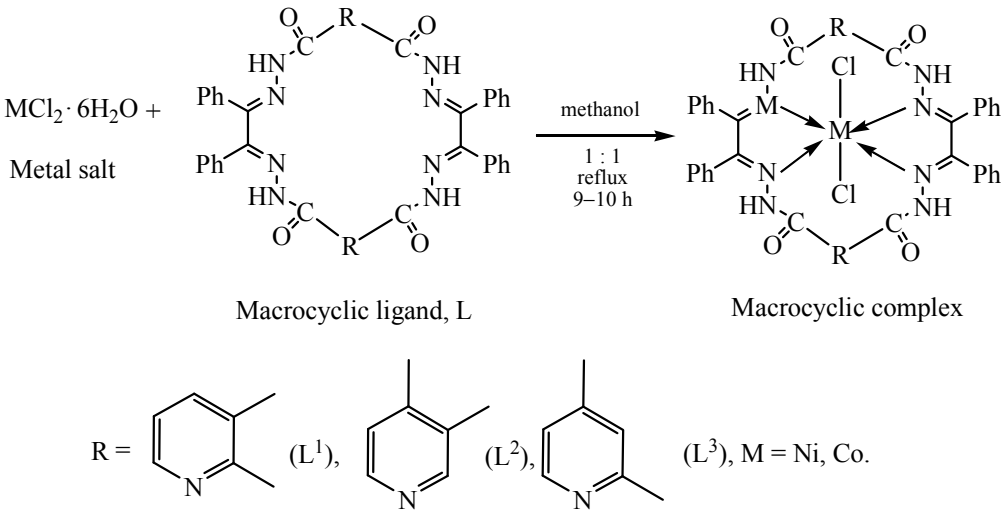
[1] The text was submitted by the authors in English.

## RESULTS AND DISCUSSION

A [2+2] condensation reaction between benzildihydrazone and pyridine dicarboxylic acid in methanol resulted in formation of novel Schiff base macrocyclic ligands (L), that upon subsequent treatment with appropriate metal salts in a 1 : 1 molar ratio in methanol yielded macrocyclic complexes of the type, $[MLCl_2]$ [M = Co(II), Ni(II)] (Scheme 1). The ligands and their complexes were stable at room temperature and soluble in dimethylformamide and dimethyl sulfoxide. Formation of ligands and their complexes was ascertained by elemental analyses (Table 1), FT-IR (Table 2), and $^1H$ and $^{13}C$ NMR spectra (Table 3). Overall geometry of the complexes was inferred from the values of magnetic moments and electronic spectra [17]. Low values of molar conductances of $10^{-3}$ molar solutions of the complexes in dry DMF (12–21 $\Omega^{-1}$ cm$^2$ mol$^{-1}$) indicated their non-electrolytic nature.

**IR spectra.** In the spectra of ligands the sharp band in the region of 3230–3275 cm$^{-1}$ was attributable to the non-coordinated amide nitrogen [18] due to cyclization. Strong absorption bands (1580–1605 cm$^{-1}$) indicated condensation of the OH group of diacids and the $NH_2$ group of benzildihydrazone and formation of

**Scheme 1.** Synthesis of macrocyclic complexes.




macrocyclic Schiff bases. The low value of ν(C=N) stretching vibrations at 1580–1605 $cm^{-1}$ indicated a drift of the lone pair of azomethine nitrogen towards the metal atom [19]. Accordingly, coordination took place via nitrogen of the C=N groups. Four recorded amide bands were similar to those reported for other macrocyclic complexes [20]. The bands of the C=O group (1690–1708 $cm^{-1}$) indicated that oxygen of the carbonyl group was not coordinated to the metal atom. The band in the region of 425-472 $cm^{-1}$ could be assigned to ν(M–N) and indicated that the complexation took place via the nitrogen atom [21].

**NMR spectra.** Absence of characteristic peaks of protons of the amino group in $^1H$ NMR spectra confirmed the process of cyclization [22] (Table 3).

**Electronic spectra.** Geometry of metal ions in the complexes was determined from the position and

T**able 1.** Analytical data and physical properties for the ligands and their complexes

| Compounds | mp, °C | Color | Found, % | | | | Calculated, % | | | | $M_W$ | | Molar conductivity |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | M | C | H | N | M | found | calculated | |
| $L^1$ | 147 | Yellow | 71.70 | 4.78 | 18.95 | – | 71.79 | 4.82 | 18.96 | – | 738.70 | 738.75 | – |
| $L^2$ | 145 | Yellow | 71.70 | 4.80 | 18.94 | – | 71.79 | 4.82 | 18.96 | – | 738.72 | 739.75 | – |
| $L^3$ | 142 | Yellow | 71.70 | 4.80 | 18.94 | – | 71.79 | 4.82 | 18.96 | – | 738.72 | 738.75 | – |
| $[Ni(L^1)Cl_2]$ | 212 | Light green | 58.0 | 3.46 | 16.10 | 6.72 | 58.09 | 3.48 | 16.13 | 6.76 | 867.12 | 868.35 | 20.0 |
| $[Ni(L^2)Cl_2]$ | 213 | Light green | 58.05 | 3.45 | 16.10 | 6.72 | 58.09 | 3.48 | 16.13 | 6.76 | 867.96 | 868.35 | 17.0 |
| $[Ni(L^3)Cl_2]$ | 215 | Light green | 58.05 | 3.44 | 16.10 | 6.72 | 58.09 | 3.48 | 16.13 | 6.76 | 867.95 | 868.35 | 21.2 |
| $[Co(L^1)Cl_2]$ | 220 | Light yellow | 57.95 | 3.43 | 16.05 | 6.73 | 58.08 | 3.48 | 16.13 | 6.78 | 867.11 1 | 868.59 | 20.1 |
| $[Co(L^2)Cl_2]$ | 225 | Light yellow | 57.02 | 3.45 | 16.05 | 6.73 | 58.08 | 3.48 | 16.13 | 6.78 | 867.11 | 868.59 | 18.0 |
| $[Co(L^3)Cl_2]$ | 222 | Light yellow | 58.01 | 3.40 | 16.09 | 6.74 | 58.08 | 3.48 | 16.13 | 6.78 | 867.12 | 868.59 | 19.0 |

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

| Compound | ν(N–H) | ν(amide) | | | | ν(M–N) | ν(C=N) |
|---|---|---|---|---|---|---|---|
| $L^1$ | 3230 | 1670 | 1530 | 1230 | 640 | – | 1622 |
| $L^2$ | 3248 | 1685 | 1520 | 1230 | 638 | – | 1621 |
| $L^3$ | 3230 | 1695 | 1525 | 1230 | 642 | – | 1622 |
| $[Ni(L^1)Cl_2]$ | 3242 | 1700 | 1550 | 1240 | 670 | 435 | 1605 |
| $[Ni(L^2)Cl_2$ | 3240 | 1715 | 1545 | 1242 | 655 | 435 | 1602 |
| $[Ni(L^3)Cl_2$ | 3245 | 1710 | 1550 | 1250 | 665 | 435 | 1585 |
| $[Co(L^1)Cl_2$ | 3245 | 1700 | 1560 | 1235 | 645 | 470 | 1590 |
| $[Co(L^2)Cl_2$ | 3275 | 1695 | 1555 | 1240 | 635 | 471 | 1592 |
| $[Co(L^3)Cl_2$ | 3255 | 1695 | 1552 | 1243 | 640 | 472 | 1580 |

**Table 3.** $^1H$ and $^{13}C$ NMR spectral data for the ligands

| Ligand | NMR spectra, δ, ppm | | | | | |
|---|---|---|---|---|---|---|
| | $^1H$ | | $^{13}C$ | | | |
| | –NH, s | Ar-H, m | phenyl-C | pyridine-C | C=N | CONH |
| $L^1$ | 8.74–8.99 | 7.2312–7.9373 | 125.54, 126.08, 126.52, 127.50,127.70, 128.92, 129.00, 129.15, 129.62, 129.67,130.80,139.42, 141.24 | 147.17,147.25, 147.82, 149.76 | 166.50, 167.67 | 191.51, 195.21 |
| $L^2$ | 8.74–8.99 | 7.3097–7.9258 | 125.50, 126.52, 127.51, 128.36, 128.83, 129.25, 129.57,131.35 136.49, 137.77, 139.42, 141.33 | 147.15, 147.45, 147.98, 151.48, 152.40 | 166.45, 167.89 | 191.55, 195.2 |
| $L^3$ | 8.74–8.99 | 7.2312–7.9373 | 125.51, 126.26, 127.67, 128.29, 128.90, 129.10, 129.36, 129.69, 131.88,139.40, 139.59, 141.34 | 147.65, 148.53, 148.69, 150.76, 152.60 | 166.48, 167.77 | 191.45, 195.23 |

number of the *d–d* transition peaks in the electron absorption spectra (Table 4). The spectra of Co(II) and Ni(II) complexes were recorded at room temperature. The accumulated data were in good agreement with the literature data on the high spin six-coordinated octahedral complexes, according to which the high spin octahedral Co(II) complex is characterized by three electron transitions: $^4T_{1g}(F) \rightarrow {}^4T_2g(P)$ ($\nu_1$), $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ($\nu_2$), and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)$ ($\nu_3$). Spectra of the Co(II) complexes contained three absorption bands in the regions 9110–9130, 18400–18455, 21700–22850 $cm^{-1}$ of high spin octahedral complexes, transition energy ratio of the second to the first was 2.0–2.1. The ligand field parameters ($\Delta q$, $B$, β, and β%) were calculated for the Co(II) complexes. The Racah parameter ($B$) was found to be 846–917 $cm^{-1}$ (< 971 $cm^{-1}$), which indicated that the ligand and the metal orbits overlapped. The nephelauxetic ratio (β) for the cobalt complexes was less than the unit due to the metal bonding to the ligand having a partially covalent character. Electronic spectra of Ni(II) complex $[NiLCl_2]$, exhibited three bands in the regions 9925–9980, 15095–15480, and 24814–25740$cm^{-1}$ assigned to the $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ($\nu_1$), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ($\nu_2$), and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ ($\nu_3$) transitions respectively in an octahedral environment. The value of Racah parameter B'(756.33) was less than the free ion value (1040) indicating a considerable covalent character of the metal-ligand bond. The $\nu_2/\nu_1$ ratio (1.51–1.55) confirmed octahedral coordination of Ni(II) ion. The ligand field parameters ($\Delta q$, $B$, β, and β%) demonstrated that contribution of the covalent bond in the metal-ligand bonding was significant [23].

**Mass spectrum.** The mass spectrum of $[NiL^2Cl_2]$ complex was studied as the representative case. Its

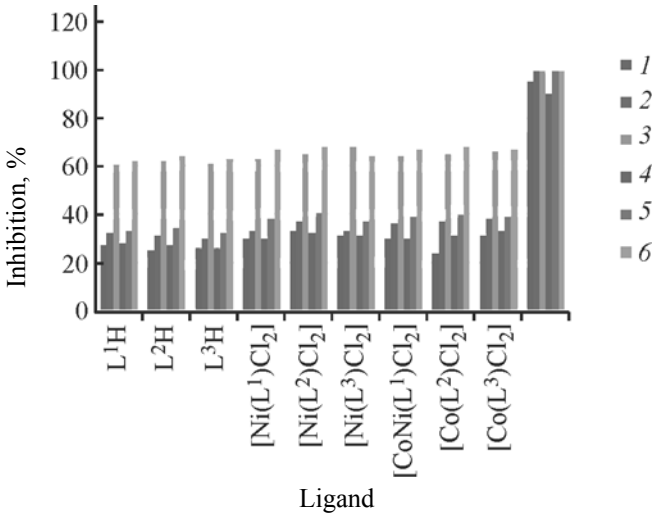



**Fig. 1.** Fungicidal screening data for the ligands and their Ni(II) and Co(II) [Inhibition after 96 h (%) (concentration in ppm)]: (*1*) *Aspergillus flavus* 50 ppm, (*2*) *Aspergillus flavus* 100 ppm, (*3*) *Aspergillus flavus* 200 ppm, (*4*) *Fusarium semitectum* 50 ppm, (*5*) *Fusarium semitectum* 100 ppm, (*6*) *Fusarium semitectum* 200 ppm,

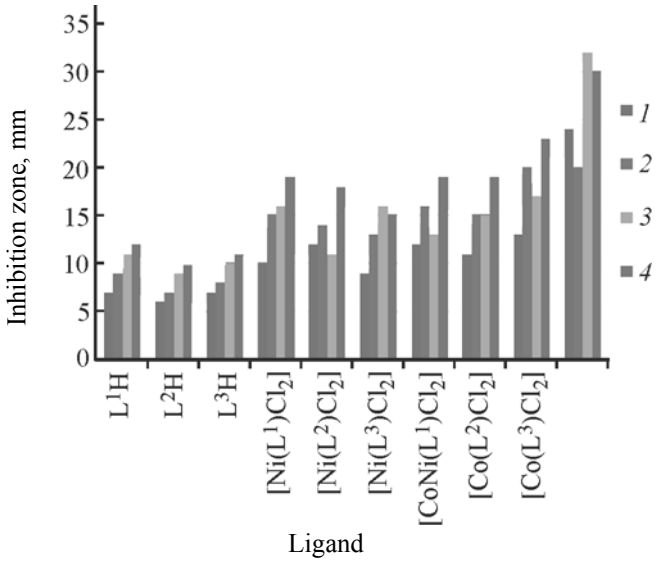



**Fig. 2.** Antibacterial screening data of the ligands and their Ni(II), Co(II) complexes [diameter of inhibition zone (mm) (concentration in ppm), after 24 h]: (*1*) *Escherichia coli*, (+) 500, (*2*) *Escherichia coli*, (+) 1000, (*3*) *Staphylococcus aureus*, (–) 500, (*4*) *Staphylococcus aureus*, (–) 1000.

molecular ion peak was observed at *m/z* 867.04 being in good agreement with its molecular weight and the monomeric nature of the complex.

**Biological screening.** *Antimicrobial assay.* The ligands and their complexes were evaluated for their antimicrobial activity against two bacteria (*Staphylococcus aureus* and *Escherichia coli*) and two fungi (*Fusarium semitectum* and *Aspergillus flavus*) (Figs. 1 and 2). The results were compared with those of the standard drug streptomycin for bacteria and itraconozole for fungi. All the ligands and their respective complexes were determined to be sensitive against all fungal and bacterial strains tested. There was recorded a considerable increase in toxicity of the complexes as compared to the free ligands. Evidently, the concentration plaid a vital role in enhancing the degree of inhibition. The enhanced activity of the synthesized complexes, as compared to the activity of the ligands, could be explained in terms of the Overtone's concept and Tweedy's chelation theory [24, 25]. According to the Overtone's concept, a lipid membrane surrounding the cell facilitates the passage of substances that dissolve in lipids making liposolubility to be an important factor of antimicrobial activity. Upon chelation, polarity of the metal ion was reduced to a larger extent owing to overlapping of the ligand orbitals and partial sharing of the positive charge of the metal ion with the charge of the donor groups. Delocalization of π-electrons over the entire chelate ring enhances lipophilicity of the complexes. Due to increased lipophilicity, the complexes can easily penetrate into a lipid membrane and block the metal binding sites of enzymes of microorganisms. Such complexes also disturb cellular respiration, thus blocking proteins synthesis, making further growth of an organism impossible. In general, metal complexes are more active than the ligands as they may serve as principal cytotoxic species.

*DNA cleavage activity.* Agarose gel electrophoresis was used to study DNA cleavage activity of the synthesized ligands and their Ni(II) and Co(II) complexes of the type $[NiLCl_2]$ and $[CoLCl_2]$ (where L = $L^1$, $L^2$ and $L^3$) against *Escherichia coli* (ATCC 25922) [26, 27]. Under experimental conditions, the ligands and their metal complexes demonstrated DNA cleavage activity. Untreated DNA was not cleaved (Fig. 3, band 1). The ligands (Fig. 3, bands 3–5) and Ni(II) and Co(II) complexes (Fig. 3, bands 6–11) generated different bands as compared with control *E. coli* DNA (Fig. 3, band 2) due to the conversion of supercoiled DNA into open circular forms by cleavage of the plasmid DNA at a concentration of 5 μg/mL. Ligands exhibited partial cleavage of DNA. Ni(II) and Co(II) complexes demonstrated higher DNA cleavage activity than the ligands. Difference in DNA cleavage efficiency could be due to different binding affinities

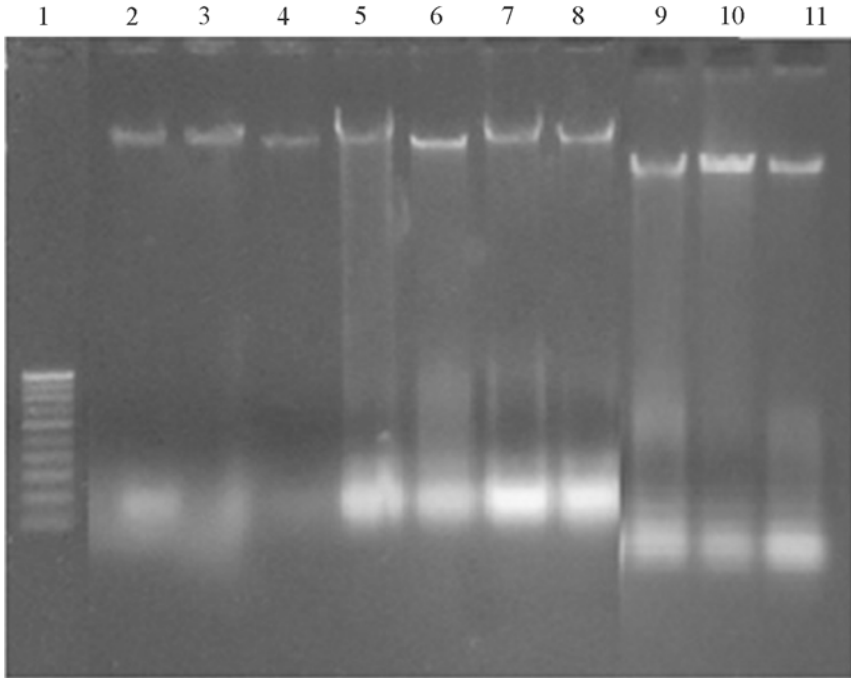



**Fig. 3.** DNA cleavage gel diagram of synthesized compounds: (1) standard molecular weight marker; (2) control DNA of *E. Coli*; (3–5) *E. Coli* DNA treated with the ligands $L^1$, $L^2$ and $L^3$ respectively; (6–11)1 *E. Coli* DNA treated with (Ni $L^1Cl_2$), (Ni $L^2Cl_2$), (Ni $L^3Cl_2$), (Co $L^1Cl_2$), ($CoL^2Cl_2$), ($CoL^3Cl_2$) complexes, respectively.

of the ligands and their respective metal complexes to DNA.

## EXPERIMENTAL

The chemicals benzil (Merck), hydrazinehydrate (Merck) and pyridine dicarboxylic acids (Fluka) were used as received. Metal salts (Merck) were commercially available pure samples. Benzildihydrazone was prepared by the reaction of benzil and hydrazine hydrate in methanol in a 1 : 2 molar ratio.

Molecular weights were determined by the Rast Camphor method [28]. The metals content was determined gravimetrically. Nitrogen was determined by the Kjeldahl's method [29]. Carbon and hydrogen analysis was performed on a CDRI, Lucknow. IR spectra (KBr pellets) were recorded on a Nicolet Magna FTIR-550 spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were measured on a JEOL GSX 400MHz FX-1000 spectrometer in DMSO-$d_6$ using TMS as an internal standard. Mass spectra were measured at USIC, University of Rajasthan, Jaipur. Electronic spectra were recorded on a Shimadzu-1800 UV spectrophotometer.

**Synthesis of macrocyclic ligands ($L_1$, $L_2$ and $L_3$).** To a solution of benzildihydrazone (2 mmol, 0.446 g) in methanol (25 $cm^3$) a methanolic solution (25 $cm^3$) of pyridine 2,3-dicarboxylic acid, pyridine 3,4-dicarboxylic acid or pyridine 2,4-dicarboxylic acid (0.334 g) was slowly added upon constant stirring. Refluxing of the mixture lasted for 6–7 h. The volatiles were evaporated leaving a light yellow solid product, which was filtered off, washed repeatedly with methanol and dried in vacuum.

**Synthesis of macrocyclic complexes.** Solution of a ligand and either $CoCl_2$ or $NiCl_2$ in a 1 : 1 ratio were stirred upon heating for 9–10 h. The corresponding solid product was filtered off, washed with cyclohexane and recrystallized from methanol (Table 1). Purity of the compounds was tested by TLC using silica gel-G as a stationary phase.

**Biological activity.** *Antibacterial studies.* The newly synthesized ligands ($L^1$–$L^3$) and the complexes were screened for the antibacterial activity against two bacteria including *Staphylococcus aureus* (ATCC 29213), *Escherichia coli* (ATCC 25922) in accordance to Kirby–Bauer disc diffusion method using Müeller-Hinton agar (B Lal, Laboratories, Rajasthan, India). The Müeller–Hinton agar medium containing beef infusion 300 g, casamino acid 17.5 g, starch 1.5 g, agar-agar 17.0 g, and sterilized water 1000 $cm^3$ was pipetted

into a petri dish and allowed to solidify. pH of the agar was adjusted to be 7.2–7.4 at room temperature. The compounds were dissolved in DMSO in 500 and 1000 ppm concentrations [30, 31]. Paper discs (Whatman no. 1 filter paper, diameter 6 mm) were soaked in the solutions of varied concentrations, dried and placed on the medium previously seeded with organisms in petri dishes at a suitable distance. The petri dishes were stored in an incubator at 35°C for 24 h. *Streptomycin* was used as standard (+ve control). DMSO was used as the negative control. Antibacterial activity of standard antibiotic *Streptomycin* was recorded using the same method.

*Antifungal activity.* Antifungal activity of the ligands and synthesized complexes were tested *in vitro* against two pathogenic fungi, *Fusarium semitectum* (ATCC 200360) and *Aspergillus flavus* (ATCC 204304) by the well diffusion method [32]. Each tested culture was streaked on to a non-inhibitory agar medium to obtain isolated colonies. After incubation at 35°C overnight, 4 or 5 well-isolated colonies were selected with an inoculum's needle and transferred to a tube of sterile saline or nonselective broth. Inoculum was prepared using the yeasts from a 24 h culture on sabouraud dextrose agar, which was prepared by dissolving sabouraud dextrose (65 g in 1000 $cm^3$ of distilled water). Petri dishes (8 cm diameter) containing 20 $cm^3$ of sabouraud dextrose agar as a solid media for preparing wells were used for analysis. The compounds were introduced in the well (6 mm) after diluting in a definite amount of DMSO for reaching concentrations of 50, 100, and 200 ppm. These petri dishes were wrapped in polythene bags containing a few drops of alcohol and placed in an incubator at 35°C for 24–48 h. The controls were also run and three replicates were used in each case. After incubation, the diameter of the zones of complete inhibition (including the diameter of the well) was measured and recorded in ppm. The linear growth of the fungus was obtained by measuring the diameter of the fungal colony after four days and the percentage inhibition was calculated as:

$$\text{Inhibition \%} = \frac{C - T}{C} \times 100\%.$$

Here $C$ is a diameter of the fungus colony in the control plate after 96 h and $T$ is a diameter of the fungal colony in the test plates after the same period.

The antifungal screening data of compounds were compared with the standard (Itraconazole) (Figs. 1 and 2).

*DNA cleavage analysis.* **Preparation of culture media.** The primary culture of *E. coli* (ATCC25922) was inoculated on nutrient broth (peptone 5 g, beef extract 3 g, sodium chloride 5 g, and distilled water 1000 mL at pH 7.0), which was autoclaved at 121°C under 15 psi pressure for 15 min. The seeded media was incubated at 37°C for 24 h on a shaker (180 rpm). The secondary culture was obtained by transferring this primary culture to the fresh nutrient broth by adding an equal amount (25 mL each) of primary culture and fresh medium. After 48 h of incubation of secondary culture, DNA was isolated and the bands were visualized on an UV transilluminator.

**Isolation of DNA.** A 1000-μL fresh bacterial culture was centrifuged for 10 min to obtain a pellet. To this pellet, 250 μL of cell lysis buffer (100 mmol/L Tris, pH 8.0, 50 mmol/L EDTA, 50 mmol/L lysozyme) was added and further centrifuged to obtain the supernatant at 10 000 rpm (g value 11 410) for 10 min and incubated for 1 h at –20°C. To the supernatant 250 μL of saturated phenol, chloroform and isoamyl alcohol were added in the ratio of 25 : 24 : 1, respectively, and the whole mixture was again centrifuged to collect the upper aqueous layer. To the collected aqueous layer, a double amount of chilled ethanol and 50 μL of sodium acetate were added and upon centrifugation precipitated DNA was separated. The pellet was dried and dissolved in TAE buffer (100 mmol/L Tris pH 8.0 adjusted with glacial acetic acid, 10 mmol/L EDTA) and refrigerated.

**Treatment of DNA with the samples.** The compounds (5 μg/mL) were added separately to the DNA sample and mixtures were kept in an incubator at 37°C for 2 h.

**Agarose gel electrophoresis.** The agarose gel electrophoresis method was used for analysis of cleaved products. One percent agarose gel was prepared by mixing 0.5 g of agarose and 50 mL of TAE buffer (4.84 g Tris base, pH 8.0, 0.5 mol/EDTA/1 L) by boiling until agarose dissolved completely. The agarose solution was poured into the gel tank and the temperature fixed at ca 60°C. Thickness of the gel was around 0.5 to 0.9 cm. The gel was left undisturbed and allowed to solidify at room temperature. The combs were gently lifted after pouring the TAE buffer at level of 0.5 to 0.8 cm above the gel surface, ensuring that wells remained intact. Loading of the 100-μL DNA samples (mixed with bromophenol blue dye in 1 : 1 ratio) was done carefully into the wells along with the

control and a constant voltage of 50 V was maintained for ca. 30 min. The gel was removed and stained with 10.0 μg/mL ethidium bromide for 10–15 min and the bands were visualized under a UV transilluminator to determine the extent of DNA cleavage. The results were compared with the standard DNA marker.

## CONCLUSIONS

New Ni(II) and Co(II) macrocyclic complexes of three ligands have been synthesized. Analytical and spectroscopic data indicated that the complexes possessed an octahedral geometry and the ligands were coordinated to the metal atoms in a tetradentate manner. Screening of antimicrobial activity and DNA cleavage activity revealed that the complexes were more potent than the free ligands.

## ACKNOWLEDGMENTS

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