



Synthesis, characterization and antimicrobial studies of novel Schiff bases and their complexes

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Received 12 December 2019; revised and accepted 02 February 2021

Novel Schiff bases, Furan-2-carboxylic acid pyridin-4-ylmethyleneamide, and Thiophene-2-carboxylic acid 1H-indol-2-ylmethyleneamide and their mononuclear Ni(II) and Cu(II) complexes have been synthesized and characterized by elemental analysis, molar conductance, UV-visible, FT-IR, ^1H NMR and EPR spectroscopy. The complexes are non-electrolytes as evidenced from the molar conductance values. The ligands and their complexes have been tested for their antimicrobial activity against one gram positive bacteria, *Bacillus subtilis*, gram negative bacteria, *Escherichia coli* and fungi *Candida albicans*. It is found that metal complexes exhibited more activity than the free ligand.

Keywords: Schiff base, Copper complex, Nickel complex, Antimicrobial activity

The coordination chemistry of transition metals and their derivatives has got much attention in recent years¹ because many of the biological processes which are fundamental to life are controlled by transition metals². Many of these coordination compounds possess remarkable biological properties such as antibacterial^{3,4}, analgesic², antifungal^{3,4}, antimalarial^{5,6}, antiviral^{7,8}, anticancer^{9,10}, antidiabetic^{11,12}, anti-HIV^{13,14} activities and plant growth regulating activity¹⁵. Nitrogen, oxygen and sulphur donor ligands possess a range of biological applications like antitumor, antibacterial, antifungal, antimalarial and antiviral activities¹⁶ and they can bind the biomolecules at their active sites¹⁷. Due to the excellent donor properties of azo group, the complexes containing azo groups exhibit excellent antimicrobial activity¹⁸. The presence of azomethine linkage (C=N) present in certain compounds is also a basic structural necessity for biological activity¹⁹. Remarkable enhanced antibacterial²⁰, antifungal²⁰ and anticancer activities^{21,22} have been observed for complexes containing azomethine linkage.

Hydrazones which belong to Schiff base family has the functional group ($>\text{N}=\text{N}=\text{C}<$) in which the azomethine group is adjacent to another nitrogen atom^{23,24}. The biological activities of hydrazones are due to the presence of lone pair electrons of sp^2 hybridized orbitals of azomethine nitrogen²⁴⁻²⁶. Hydrazones which contain an azomethine proton ($-\text{NHN}=\text{CH}-$) is therapeutically important for new

drug development²⁷. The additional donor site, $>\text{C}=\text{O}$ of aroyl, acyl and heteroaroyl hydrazone Schiff base compounds makes the hydrazones more flexible and versatile. This additional donor site makes hydrazones as good polydentate chelating ligand and can coordinate with various transition and inner transition metals in numerous ways²³. Hydrazones and their metal complexes show varied applications in the fields such as antifungal, antibacterial, antioxidative and cytotoxic studies²⁸. They have been found to be potential chemotherapeutic agents.

The characteristic properties of coordination compounds depends on the nature of donor atom, steric factors, nature of the metal ion, structure of the coordinating ligand, the metal-ligand interaction and the nature of the solvent employed²⁹. Schiff bases show excellent biological activities against many pathogenic bacteria, fungi and against certain cancerous cells^{18,30}. Schiff bases having chelative donor sites like nitrogen, oxygen and sulphur when coordinated to metal ions an enhanced biological activity is observed^{7,31}.

Generally metal chelates have enhanced activity than the free ligand³². As chelation increases biological activity also increases^{7,31} because chelation increases the cell permeability. On chelation the polarity of the metal ion reduces and the lipophilic nature of the metal ion enhances²¹.

This enhanced lipophilic nature favours cell permeability. Thus metal atoms can permeate more effectively through the lipid layer of microbes

destroying them or blocking their active sites^{15,31}. Thus one of the ways to improve the biological activity is to increase the number of chelate rings^{7,21}. Based on literature survey and our research, here we have synthesized and characterized two novel ligands and their mononuclear Cu(II) and Ni(II) complexes.

Materials and Methods

Chemicals

Metal salts used in the synthesis were commercially available pure samples from Merck. 2-furoic acid hydrazide, 4-pyridine carboxaldehyde and 2-thiophenecarboxaldehyde (Aldrich) were used as received. Methanol (Merck) used as solvent was of AR grade.

Characterisation techniques

The analysis of percentage of elements C, H, N and S in the ligands and complexes were carried out on Elementar Vario EL III CHNS analyzer at SAIF, Kochi. Electronic absorption spectra of the ligands and its copper and nickel complexes in the solution phase were recorded in the region of 200-900 nm on the Perkin Elmer Lambda UV-visible-NIR spectrophotometer. FT-IR spectra were recorded on a Bruker 360 FT-IR spectrophotometer using KBr pellet technique in the range 4000-400 cm^{-1} from St Joseph's College Devagiri, Kozhikode. ¹H NMR spectra of the ligands were recorded using Bruker AMX 400 FT-NMR Spectrometer using DMSO as solvent at Anthem Biosciences, Bengaluru. Molar conductivity measurements of complexes in acetonitrile and DMF (10^{-3} M) were measured at room temperature using direct reading digital conductivity meter (Systronics 302). The Electron paramagnetic resonance (EPR) spectra were recorded on JES- FA 200 spectrometer at SAIF, IIT Madras using diphenylpicrylhydrazine (DPPH) as the reference. EPR spectra were taken for the copper complexes. All the spectra were recorded in DMSO solution at both room temperature (RT) and liquid nitrogen temperature (LNT). Antimicrobial

studies were done by zone inhibition method on Miller Hilton agar plates against one gram positive bacteria *Escherichia coli*, one gram negative bacteria *Bacillus subtilis* and against the fungi, *Candida albicans*. DMSO was used as the solvent control. The standard used for the comparison of antibacterial activity was ampicillin and that for antifungal activity was flucanazole.

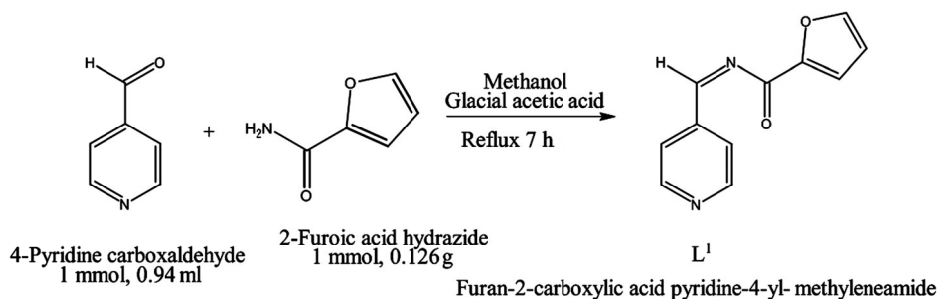
Preparation of Schiff bases

Furan-2-carboxylic acid pyridin-4-ylmethyleneamide (L¹)

1 mmol of 2-furoic acid hydrazide (0.126 g) was dissolved in 15 mL of methanol and to this 1 mmol of 4-pyridinecarboxaldehyde (0.94 mL) was added followed by two drops of glacial acetic acid. The reaction mixture was refluxed for 7 h followed by cooling to room temperature about 12 h. On slow evaporation, pale brown crystals of Furan-2-carboxylic acid pyridin-4-ylmethyleneamide (**L¹**) (Scheme 1) were separated out. The crystals formed were filtered, washed with methanol and dried over P₄O₁₀ under vacuo. **L¹** (C₁₁H₈N₂O₂): Yield, 73%; Colour, pale brown; Melting point, 182-185 °C; Anal. (%), Expt. (Calc.): C, 65.86 (65.99); H, 3.56 (3.98); N, 13.99 (13.97); Absorption: (λ_{max} , nm, acetonitrile): 303. IR: (KBr, cm^{-1}): 1244 [ν (C-O)], 1659 [ν (C=O)]; ¹H NMR (DMSO-*d*₆, δ in ppm): 8.4 (s, H-C=N), 7.733-8.6 (m, Ar-H).

Thiophene-2-carboxylic acid 1H-indol-2-ylmethyleneamide (L²)

1 mmol of indole-3-carboxaldehyde (0.145 g) was dissolved in 10 mL methanol and to this 1 mmol of 2-thiophenecarboxamide (0.127 g) was added along with two drops of glacial acetic acid. The mixture was refluxed for 10 h. It was cooled to room temperature about 12 h. On slow evaporation, pale pink coloured substance of thiophene-2-carboxylic acid 1H-indol-2-ylmethyleneamide (**L²**) (Scheme 2) were separated out. **L²** (C₁₄H₁₀N₂OS): Yield, 82%; Colour: pale pink; Melting point: 142-145 °C; Anal (%), Expt. (Calc.): C, 66.11 (66.38); H, 3.47 (3.58); N, 11.011 (11.05); S, 12.60 (12.68); Absorption: (λ_{max} , nm, acetonitrile): 249,



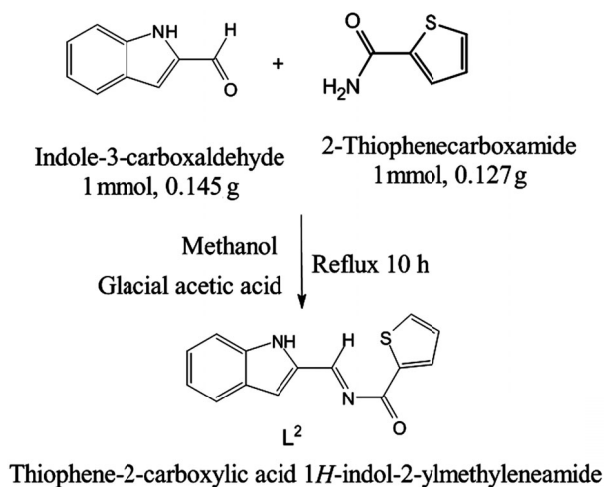
Scheme 1 — Synthesis of ligand **L¹**

279; IR: (KBr, cm^{-1}): 1633 [$\nu(\text{C}=\text{O})$], 1576 [$\nu(\text{C}=\text{N})$], 3166 [$\nu(\text{N}-\text{H})$], 756 [$\nu(\text{C}-\text{S})$], 949 [$\nu(\text{C}-\text{S}-\text{C})$]; ^1H NMR (DMSO, δ in ppm): 12.1 (s, $\text{H}-\text{C}=\text{N}$), 9.9 (s, $\text{N}-\text{H}$), 7.1-8.2 (Ar-H).

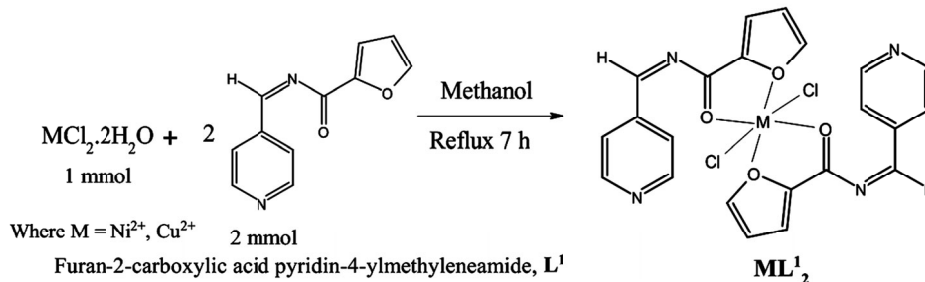
Preparation of complexes

Synthesis of copper and nickel complexes of L^1

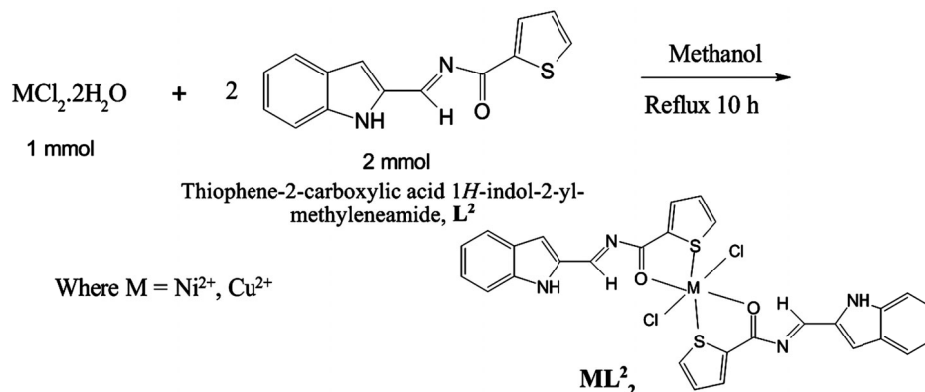
To a solution of 2 mmol of L^1 (0.200 g) in methanol, 1 mmol of metal chloride dissolved in methanol was added (Scheme 3). The reaction mixture was refluxed for 7 h. The resulting greenish yellow solution was



Scheme 2 — Synthesis of ligand L^2



Scheme 3 — Synthesis of ML_2^1



Scheme 4 — Synthesis of ML_2^2

allowed for slow evaporation at room temperature. The resulted greenish yellow precipitates were filtered, washed with methanol, recrystallized from methanol and dried under vacuo.

CuCl_2L^2 : Yield, 82%; Colour: Greenish yellow; Anal.(%) Expt. (Calc.): C, 46.64 (46.89); H, 3.46 (3.57); N, 9.68 (9.94); Absorption: (λ_{max} , nm, acetonitrile): 223, 293, 458; IR: (KBr, cm^{-1}): 1618 [$\nu(\text{C}=\text{O})$], 1551 [$\nu(\text{C}=\text{N})$], 1462 [$\nu(\text{C}=\text{C})$], 536 [$\nu(\text{Cu}-\text{O})$], 1220 [$\nu(\text{C}-\text{O})$], 3381 [$\nu(\text{H}_2\text{O})$]; Molar conductivity, 19.7 (DMF), 14.9 (acetonitrile)

$\text{NiCl}_2L^2 \cdot 2\text{H}_2\text{O}$: Yield, 82%; Color: Greenish yellow; Anal.(%) Expt. (Calc.): C, 47.52 (47.71); H, 3.54 (3.64); N, 10.01 (10.11); Absorption: (λ_{max} , nm, acetonitrile): 223, 290; IR: (KBr, cm^{-1}): 1618 [$\nu(\text{C}=\text{O})$], 1551 [$\nu(\text{C}=\text{N})$], 1462 [$\nu(\text{C}=\text{C})$], 536 [$\nu(\text{Ni}-\text{O})$], 1220 [$\nu(\text{C}-\text{O})$], 3321 [$\nu(\text{H}_2\text{O})$]; Molar conductivity, 19.5 (DMF), 15.2 (acetonitrile)

Synthesis of copper and nickel complex of L^2

1 mmol of metal chloride dissolved in methanol was added to methanolic solution of 2 mmol of L^2 (0.253 g). The mixture was refluxed for 10 h (Scheme 4). The resulting brownish red solution was allowed to stand at room temperature for slow evaporation. The separated brownish precipitates were filtered, washed and recrystallized from methanol and dried under vacuo.

$\text{CuCl}_2\text{L}^2_2 \cdot 2\text{H}_2\text{O}$: Yield, 70 %; Colour: brown; Anal.(%), Expt. (Calc.): C, 41.89 (42.09); H, 2.96 (3.02); N, 6.89 (7.01); S, 7.92 (8.02); Absorption: (λ_{max} , nm, acetonitrile): 243, 466; IR: (KBr, cm^{-1}): 1602 [$\nu(\text{C}=\text{O})$], 1576 [$\nu(\text{C}=\text{N})$], 1521 [$\nu(\text{C}=\text{C})$], 457 [$\nu(\text{Cu}-\text{CSC})$], 3357 [$\nu(\text{H}_2\text{O})$]; Molar conductivity, 16.5 (DMF), 14.6 (acetonitrile)

$\text{NiCl}_2\text{L}^2_2$: Yield, 72 %; Colour: pale green; Anal.(%), Expt. (Calc.): C, 53.79 (53.89); H, 2.87 (2.90); N, 8.95 (8.97); S, 10.24 (10.27); Absorption: (λ_{max} , nm, acetonitrile): 242, 292; IR: (KBr, cm^{-1}): 1612 [$\nu(\text{C}=\text{O})$], 1576 [$\nu(\text{C}=\text{N})$], 1521 [$\nu(\text{C}=\text{C})$], 3167 [$\nu(\text{N}-\text{H})$], 460 [$\nu(\text{Ni}-\text{CSC})$], 530 [$\nu(\text{Ni}-\text{O})$]; Molar conductivity, 17.1 (DMF), 15.4 (acetonitrile)

Results and Discussion

Copper(II) and nickel(II) complexes of ligands L^1 and L^2 were synthesized and characterised by different characterization techniques like elemental analysis, molar conductivity measurements, ^1H NMR, UV-visible absorption, and FT-IR. All the ligands and complexes were stable in room temperature and soluble in acetonitrile, DMF and DMSO. Molar conductivities of the complexes were recorded in 10^{-3} M solutions of DMF and acetonitrile. The molar conductivity values are in the range 14.6-19.7 ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) which indicate the non-electrolytic nature of complexes.

^1H NMR spectra of ligands

The proton NMR spectra of the ligands are shown in

Supplementary Data, Fig. S1. L^1 displayed a singlet at δ , 12.1 ppm which is assigned to azomethine proton. The peaks due to protons on furan and pyridine rings are in the range δ , 6.7 to 8.6 ppm. L^2 displayed a singlet at δ 9.9 ppm which is attributed to the indole NH and signal at δ , 12.1 ppm is ascribed to the azomethine proton. The resonance due to protons on thiophene and benzene rings are in the range δ , 7.1 to 8.2 ppm (Supplementary Data, Table S1).

IR spectra

The IR spectra of the ligands and complexes showed various significant bands in the region of 4000-400 cm^{-1} (Fig. 1), and their assignments were tentatively used to establish the mode of coordination as given in Supplementary Data, Table S2. A strong sharp band observed at 1244 cm^{-1} corresponds to the C-O group of L^1 (Fig. 1a) which is lowered to 1231 cm^{-1} in the copper complex (Fig. 1b). C=O band appeared at 1659 cm^{-1} in L^1 lowered to 1618 cm^{-1} in complexes. Coordination of L^1 to the Cu was further confirmed by the appearance of bands at 536 cm^{-1} corresponding to Cu-O bond. A strong sharp band at 1244 cm^{-1} corresponding to the C-O group of L^1 is lowered to 1220 cm^{-1} in complexes nickel (Fig. 1c). The band at 1659 cm^{-1} in L^1 corresponding to C=O was lowered to 1618 cm^{-1} in the Ni complexes. Coordination of L^1 to the metal was further confirmed by the appearance of bands at 536 cm^{-1} Ni-O. A sharp band observed at 3381 cm^{-1} in nickel complex of L^1 shows the presence of lattice water.

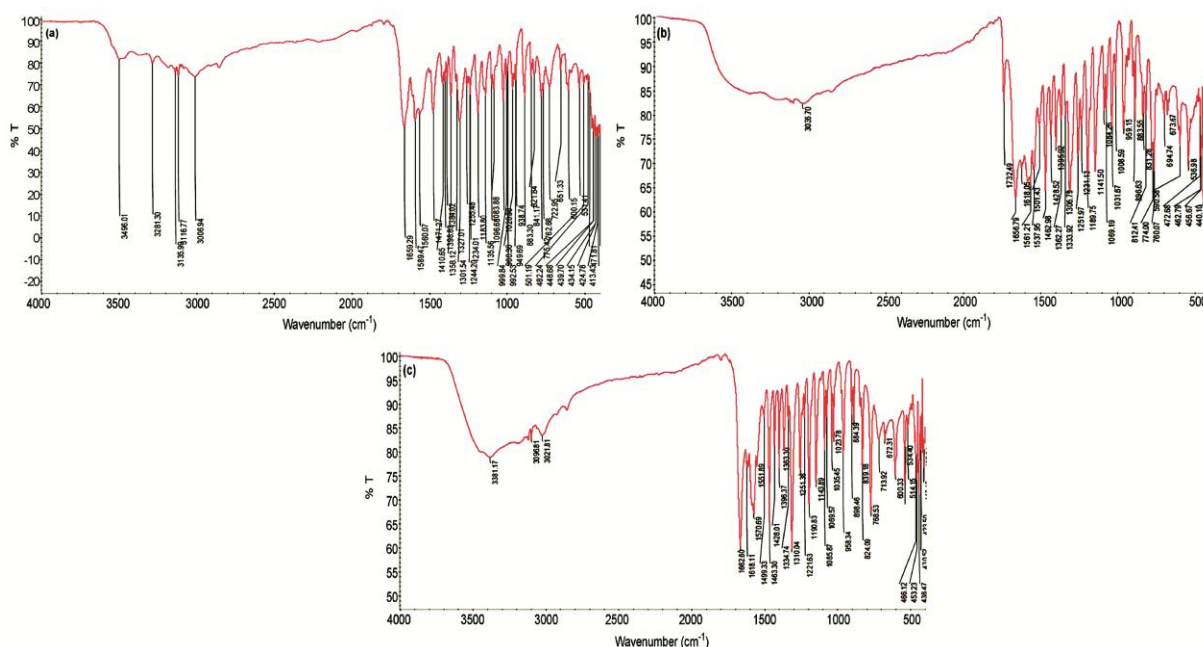


Fig. 1 — IR spectra of (a) ligand L^1 , (b) Cu(II)- L^1 and (c) Ni(II)- L^1 complexes

Fig. 2 shows the IR spectra of ligand L^2 and its Cu(II) and Ni(II) complexes. As shown in Fig. 2b, a strong sharp band observed at 1602 cm^{-1} for copper complexes of L^2 corresponds to the C=O group of the ligand coordinated to Cu. N-H stretching frequency in ligand and complexes remain unchanged in L^2 complexes. Coordination of ligand L^2 to the metal was further confirmed by the appearance of band at 536 cm^{-1} corresponding to Cu–O. A sharp band observed at 3357 cm^{-1} shows the presence of lattice water for copper complex of L^2 . A strong sharp band observed at 1612 cm^{-1} for nickel complexes of L^2 indicates that C=O group of the Ligand (Fig. 2c). N-H stretching frequency in ligand and complexes remain unchanged in L^2 complexes. Coordination of ligand L^2 to the metal was further confirmed by the appearance of bands at 530 cm^{-1} corresponding to Ni–O.

Electronic absorption spectra

The electronic spectra of the ligands were recorded in the range of 200-900 nm region in acetonitrile solution (10^{-5} M) and are shown in Fig. 3. In absorption spectrum of the ligand L^1 (Fig. 3a) band at 303 nm is

assigned to π - π^* transition and displayed bands for L^2 (Supplementary Data, Fig. S2a) at 249 and 273 nm are assigned to n - π^* and π - π^* transitions, respectively. For Cu(II) complex of L^1 , bands at 223, 293 and 458 nm are assigned to n - π^* , π - π^* and d-d transitions, respectively (Fig. 3b) and copper complex of L^2 shows bands at 243 and 466, which are assigned to π - π^* and d-d transitions, respectively (Fig. 3c). In the spectrum of Ni(II) complex of L^1 , bands at 223 and 290 nm are assigned to n - π^* and π - π^* transitions, respectively, and for nickel complex of L^2 bands at 242 and 292 nm are assigned to n - π^* and π - π^* transitions, respectively (Supplementary Data, Fig. S2b).

EPR spectral studies of copper complexes

EPR spectrum of copper complexes of L^1 was recorded in RT (300 K) as well as LNT (77 K) on X-band at 9.1 GHz frequency and the magnetic field of 3400 G in DMSO as solvent using DPPH as internal reference. In the complexes copper ion has oxidation state II and hence has d^1 electronic configuration. The spectrum at RT shows one intense band at high field region (Fig. 4). The EPR spectrum of the powder at

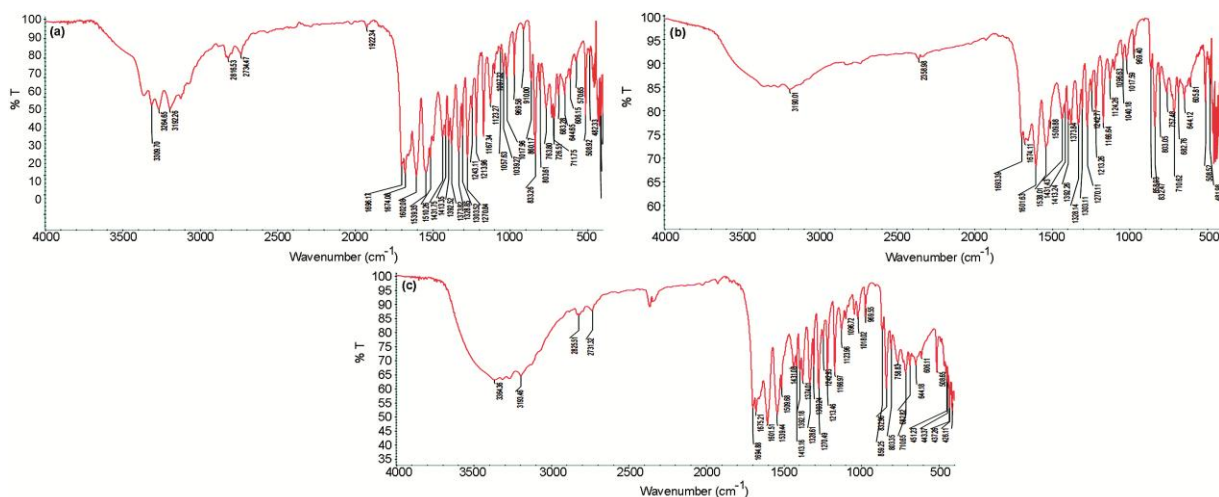


Fig. 2 — IR spectra of (a) ligand L^2 , (b) Cu(II)- L^2 and (c) Ni(II)- L^2 complexes

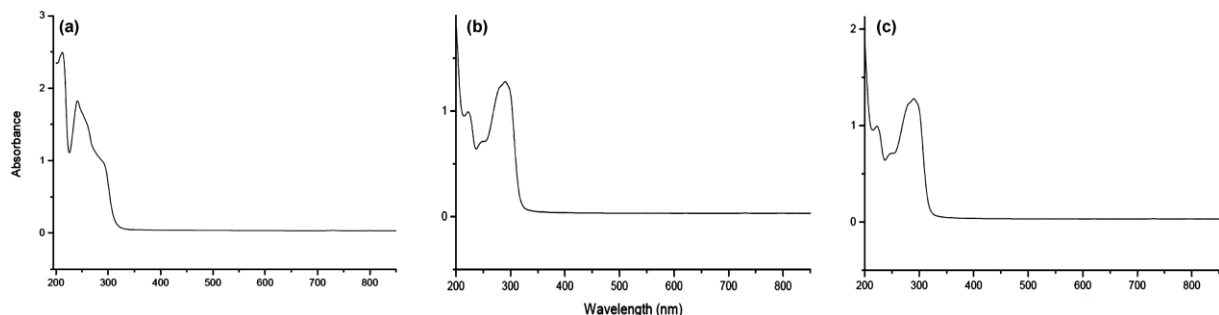
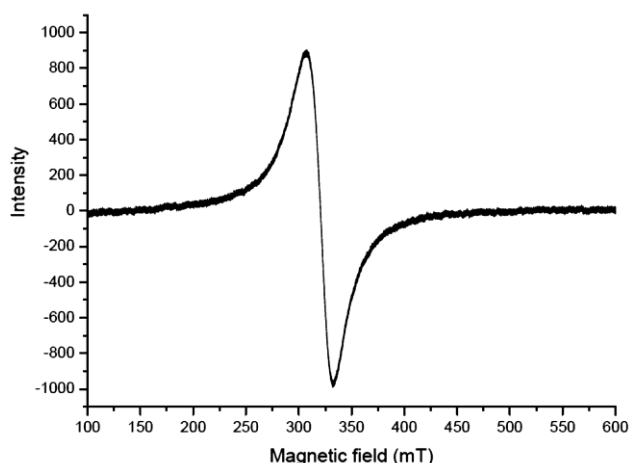


Fig. 3 — Absorption spectra of (a) ligand L^1 , (b) Cu(II)- L^1 complex and (c) Ni(II)- L^1 complex

Table 1 — Inhibitory activity of compounds and test organisms

Test compound	Conc. ($\mu\text{g}/25 \mu\text{L}$)	Zone of inhibition (mm)		
		Test organism		
		<i>Escherichia coli</i> MTCC 7410	<i>Bacillus subtilis</i> MTCC 121	<i>Candida albicans</i> MTCC 183
\mathbf{L}^1	10	-	-	-
	25	-	-	-
\mathbf{L}^2	10	-	-	-
	25	4.50 \pm 0.50	-	2.00 \pm 0.00
$\text{CuCl}_2\mathbf{L}^1_2 \cdot 2\text{H}_2\text{O}$	10	10.00 \pm 0.0	16.00 \pm 0.0	4.00 \pm 0.00
	25	12.00 \pm 0.0	18.00 \pm 0.0	6.00 \pm 0.00
$\text{CuCl}_2\mathbf{L}^2_2 \cdot 2\text{H}_2\text{O}$	10	13.00 \pm 0.0	13.00 \pm 0.0	4.00 \pm 0.00
	25	15.00 \pm 0.0	15.00 \pm 0.0	7.50 \pm 0.00
$\text{NiCl}_2\mathbf{L}^1_2 \cdot 2\text{H}_2\text{O}$	10	6.00 \pm 0.0	-	2.00 \pm 0.00
	25	8.00 \pm 0.0	-	2.00 \pm 0.00
$\text{NiCl}_2\mathbf{L}^2_2 \cdot 2\text{H}_2\text{O}$	10	6.00 \pm 0.0	-	2.00 \pm 0.00
	25	9.00 \pm 0.0	-	2.00 \pm 0.00
Standard Ampicillin ^{ref}	25	30.00 \pm 0.5	35.00 \pm 0.00	-
Standard Fluconazole ^{ref}	-	-	-	7.50 \pm 0.00

Fig. 4 — EPR spectrum of powder Cu(II)- \mathbf{L}^1 at room temperature

RT gave a $g_{\text{iso}} = 2.10$ ($A_{\text{iso}} = 320$). At LNT, the g_{\parallel} and g_{\perp} (avg) are found to be 2.25 and 2.07 ($A_{\perp} = 315$), respectively. $g_{\parallel} > g_{\perp} > 2.0023$ indicate that the unpaired electron is in $d_{x^2-y^2}$ of the Cu(II) ion. It is a characteristic of the axial symmetry with possibly a square planar geometry or a distorted octahedral³³.

Microbiology

The antibacterial activity of ligand, \mathbf{L}^2 and its complexes with Ni(II) and Cu(II), were tested against the one gram positive bacteria, *Bacillus subtilis* and against one Gram negative bacteria *Escherichia coli*. The antifungal activity of the ligands and its complexes with Ni(II) and Cu(II) were tested against fungi, *Candida albicans*. The standard used for antibacterial study was ampicillin and that for antifungal studies was

flucanazole. DMSO was used as solvent control. The values of zone inhibition were measured in millimeter. The zone of inhibition against standards and test samples are summarized in Table 1. The data reveal that the complexes have higher antimicrobial activities than the free ligand and it may be attributed to its higher stability constant³⁴. Among the test complexes copper complexes exhibited greater microbial inhibition than the nickel complexes.

Conclusions

The present work has focused on the synthesis, characterization and antimicrobial studies of two new ligands and their Cu(II) and Ni(II) complexes derived from furan-2-carboxylic acid pyridin-4-ylmethyleneamide (\mathbf{L}^1) and thiophene-2-carboxylic acid 1H-indol-2-ylmethyleneamide (\mathbf{L}^2). The ligands and complexes were characterized by CHNS analysis, ¹H NMR, UV-visible absorption, and FT-IR and EPR techniques. Molar conductivity measurements of the Cu(II) and Ni(II) complexes revealed their non-electrolytic nature in acetonitrile and DMF. ¹H NMR studies of the ligands correspond to the structure of the compound. FT-IR data showed the presence of lattice water for the copper complexes \mathbf{L}^1 and \mathbf{L}^2 , and for nickel complex of \mathbf{L}^1 . Lattice water is absent for nickel complex of \mathbf{L}^2 . FT-IR data confirmed the coordination of ligand to the metal ion. Absorption spectra of complexes were studied for their $n-\pi^*$ and $\pi-\pi^*$ transitions. EPR studies suggest the possibility of square planar geometry or distorted octahedral geometry. The antimicrobial study of the ligand \mathbf{L}^2 and its Cu(II) and

Ni(II) complexes showed microbial inhibition against the selected test microorganisms of bacteria and fungi. Among the test compounds copper complexes showed higher microbial inhibition activity.

Supplementary Data

Supplementary Data associated with this article are available in the electronic form at [http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A\(04\)538-544_SupplData.pdf](http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(04)538-544_SupplData.pdf).

Acknowledgement

The Department of Chemistry, CHRIST (Deemed to be University), Bangalore, is acknowledged for providing necessary research facilities. The authors thankfully acknowledge SAIF, CUSAT Cochin, SAIF, IIT Madras, Anthem Biosciences, Bengaluru and St Joseph's College, Kozhikode for all the analytical data.

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